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Preparation, Reactions, and Physical Properties of Organobismuth Compounds

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Contents

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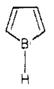
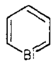
I. Introduction

A. Scope of Review

Over the course of years there have been a number of reviews on organobismuth compounds. The latest of these by Samaan[1] is in the well-known Houben-Weyl series and is in German. The volume is devoted to organoarsenic, -antimony, and -bismuth compounds and as with other volumes in this series is concerned mainly with the preparation and reactions of the relevant compounds. Another recent review, also in German, is by Wieber[2] in the equally well known Gmelin Handbuch series. This is a noncritical compilation of the preparation and properties of all known organobismuth compounds appearing in the nonpatent literature through 1975. Some patent literature is also covered. Prior to these two publications the coauthors of the present review published a monograph on organoarsenic, -antimony, and -bismuth compounds.[3] One chapter in this work was devoted to organobismuth compounds, and the present review is essentially an attempt to update that chapter. We also have reviewed progress in organobismuth chemistry on an annual basis since 1967 in the publication *Organometallic Chemistry Reviews, Section B*, later incorporated into *Journal of Organometallic Chemistry*. Heterocyclic bismuth compounds are reviewed in a monograph by F. G. Mann.[4] Two other comparatively recent works containing descriptions of organobismuth compounds are the noncritical compilations of Dub.[5,6] These works cover the literature for the periods 1937–1964 and 1965–1968, respectively, and give methods of synthesis, physical constants, and chemical reactions for all organobismuth (as well as organoarsenic and organoantimony) compounds prepared during the time period covered by these works. There are older monographs containing organobismuth compounds by Goddard[7] and by Krause and von Grosse.[8] Two older reviews and one more recent review devoted solely to organobismuth compounds are by Gilman and Yale,[9] by Lisowski,[10] and by Harrison.[11] Organobismuth compounds, of course, are discussed in texts devoted to organometallic chemistry. Among important ones are the volumes by Coates and Wade,[12a] Aylett,[13] Milne and Wright,[14] Crow and Cullen,[15] Rochow, Hurd, and Lewis,[16] and Kaufman.[17] There is a monograph in Russian on the organometallic chemistry of antimony and bismuth[18] which is not available to us. The *Specialist Periodical Reports* published by the Chemical Society, a series of annual reports of progress in various fields of chemistry, has a survey volume each year on organometallic chemistry which includes organobismuth compounds. The present review covers the literature as reported in *Chemical Abstracts* through 1980. A few more recent references have also been included. No attempt is made to list all of the organobismuth compounds made. Work reported since the publication of our book is reported in greater detail. Structure, spectra, and other physical properties of organobismuth compounds are emphasized.

TABLE I. Nomenclature of Organobismuth Compounds

group	example
$-BiH_2$	$MeBiH_2$, methylbismuthine
$=BiH$	Me_2BiH, dimethylbismuthine
$\equiv Bi$	Me_3Bi, trimethylbismuthine
$-BiX_2$	$CH_2{=}CHCH_2BiCl_2$, allyldichlorobismuthine
	$CH_2{=}CHCH_2Bi(OMe)_2$, allyldimethoxybismuthine
	EtBiO, ethyloxobismuthine
$=BiX$	$(CH_2{=}CHCH_2)_2BiCl$, diallylchlorobismuthine
	$(CH_2{=}CHCH_2)_2BiOMe$, diallylmethoxybismuthine
$=Bi-Bi=$	$Me_2BiBiMe_2$, tetramethyldibismuthine
$=Bi^-$	$Me_2Bi^-Na^+$, sodium dimethylbismuthide
$\equiv BiX_2$	Ph_3BiCl_2, triphenylbismuth dichloride
	$Ph_3Bi(OH)CN$, triphenylbismuth hydroxide cyanide
	$Ph_3Bi(Cl)OBi(Cl)Ph_3$, oxybis(triphenylbismuth) dichloride
$\equiv BiX$	Ph_4BiN_3, tetraphenylbismuth azide
	$[Ph_4Bi][ClO_4]$, tetraphenylbismuthonium perchlorate
$\equiv Bi=$	Ph_5Bi, pentaphenylbismuth
	 , bismole
	 , bismin

B. Nomenclature

Two systems are currently in use for naming organobismuth compounds, namely that used by *Chemical Abstracts*[19] and the IUPAC system.[20] These two systems differ considerably. The IUPAC system is generally followed in the present review with the following minor change. In the IUPAC system substituents are given in alphabetical order. Hence, one IUPAC name for $MeBiCl_2$ is dichloromethylbismuthine, whereas $CH_2{=}CHCH_2BiCl_2$ is allyldichlorobismuthine. Because in this review compounds are generally treated as a class, we have chosen to put the organic substituent first regardless of alphabetical order. In Table I the nomenclature used, based on the IUPAC system, is summarized. It should be noted that in the IUPAC system several names for the same compound are frequently allowed. Thus, Ph_2BiCl is named chlorodiphenylbismuthine, diphenylbismuth chloride, or chlorodiphenylbismuth. In Table I we have listed only one name for each compound. Names for heterocyclic bismuth compounds are based on the "Ring Index";[21] this system is also used by *Chemical Abstracts*.

II. Primary and Secondary Bismuthines

Only one primary and one secondary bismuthine are known with certainty, namely methyl- and dimethylbismuthine, $MeBiH_2$ and Me_2BiH.[22] These are prepared by reduction of methyldichloro- or dimethylchlorobismuthine, respectively (or the corresponding bromobismuthines), in dimethyl ether, with lithium aluminum hydride as the reducing agent. The reactions are carried out at low temperatures in a nitrogen atmosphere. Methylbismuthine is purified by vacuum distillation at low temperature. The boiling point by extrapolation is 72 °C at 760 torr. The boiling point of dimethylbismuthine by extrapolation is 103 °C at 760 torr. On warming to −45 °C methylbismuthine disproportionates to trimethylbismuthine and bismuthine. Dimethylbismuthine undergoes a similar disproportionation at −15 °C. Both compounds are stable, colorless liquids at −60 °C but at room temperatue they decompose to trimethylbismuthine, bismuth, and hydrogen. An attempt to prepare phenyl- and diphenylbismuthine by reduction of phenyldibromo- and diphenylbromobismuthines, respectively, with lithium aluminum hydride or sodium borohydride at low temperatures was unsuccessful.[23] Instead of the expected bismuthines, black polymeric substances (whose analyses correspond to the formula PhBi) are obtained. It has been claimed in a patent[24] that diphenyl- or dimethylbismuthine and titanium tetrachloride can be used to promote the polymerization of ethylene. Dimethylbismuthine and vanadium oxychloride are used in a similar manner in the preparation of polypropylene and polybutadiene. The source of the bismuthines is not mentioned.

III. Tertiary Bismuthines

A. Preparation

1. From Organometallic or Organosilicon Compounds

Tertiary bismuthines R_3Bi, where R is aliphatic or aromatic, are most frequently prepared by the reaction between a bismuth trihalide, either $BiCl_3$ or $BiBr_3$, and an organometallic compound. The most widely used organometallic compound for this purpose is the Grignard reagent:

$$BiX_3 + 3RMgX \rightarrow R_3Bi + 3MgX_2$$

The customary solvent is diethyl ether or tetrahydrofuran. When R is an aliphatic group the reaction is performed in an inert atmosphere since the trialkylbismuthines, particularly the lower members of the series, are spontaneously inflammable in air. The bismuth halides used in the reaction should be essentially completely soluble in ether. Commercially available bismuth trichloride and bismuth tribromide are usually partially or completely hydrolyzed due to exposure to atmospheric moisture. Such materials, which are insoluble in ether, are useless for the preparation of tertiary bismuthines by the Grignard reaction. The four tertiary bismuthines *m*- and $(p\text{-}FC_6H_4)_3Bi$ and *m*- and $(p\text{-}ClC_6H_4)_3Bi$ were prepared by pumping a refluxing $BiCl_3$/ether solution into an ether solution of the corresponding Grignard reagent.[25]

Trimethylbismuthine is the only trialkylbismuthine which can be distilled at atmospheric pressure from the reaction mixture after removal of the solvent.[9,26,27] Most other trialkylbismuthines can be distilled at reduced pressure and are purified in this manner. An example of the procedure used is the recent preparation of tri-*tert*-butylbismuthine.[28] With tertiary bismuthines which cannot be distilled, the reaction mixture is treated with water or aqueous ammonium chloride solution, and the bismuthine is extracted from the aqueous layer with ether or other organic solvent. This method has been widely used for the preparation of triarylbismuthines.

The yields of tertiary bismuthines by the Grignard reaction are usually excellent but may vary from about 20% to 90%. A wide variety of tertiary bismuthines containing such groups as alkyl, alkenyl, alkynyl, perfluoroalkyl, perfluoroalkenyl, cycloalkyl, phenyl, substituted phenyl, and naphthyl have been prepared. The only reported tertiary bismuthine containing three heterocyclic rings, namely tri-α-thienylbismuthine, is obtained by the Grignard reaction.[77] Two interesting bismuthines, tris(*o*-(dimethylarsino)phenyl)- and tris(3-(dimethylarsino)propyl)bismuthine, have utilized Grignard reagents in their synthesis.[29] These are liquids which have been used in studies of coordination compounds. Other tertiary bismuthines prepared by the Grignard reaction include tris((trimethylsilyl)methyl)bismuthine,[30] tribenzylbismuthine, and several substituted tribenzylbismuthines.[31]

The reaction of organobismuth chlorides $RBiCl_2$ and R_2BiCl with Grignard reagents to yield unsymmetrical bismuthines has been employed to only a limited extent. In addition to the earlier work of Gilman and Yablunky,[32] Norvick,[33] and Challenger[34] on this subject, a number of unsymmetrical triarylbismuthines have been more recently reported from Russian laboratories.[35,36] Only one unsymmetrical trialkylbismuthine, namely diethylpentylbismuthine, has been reported.[33] The compound is obtained, together with tripentyl- and triethylbismuthine, from pentyldichlorobismuthine and ethylmagnesium chloride, and it has not been adequately characterized. No mixed alkylarylbismuthines are known. A bismuthine containing a bismuth atom in a heterocyclic ring, namely 1-ethylbisminane, has been prepared from ethyldibromobismuthine and the di-Grignard reagent obtained from 1,5-dibromopentane.[37]

Organolithium compounds have not been used as extensively as Grignard reagents for the preparation of tertiary bismuthines, although in those cases where they have been used the yields are as satisfactory as with the Grignard reaction. Thus, triisopropenyl-, *cis*-tripropenyl-, and *trans*-tripropenylbismuthine are obtained in 62.5%, 73.5%, and 72.5% yields, respectively, by means of the corresponding organolithium compounds.[38] Levason and co-workers[39] have employed the lithium compounds obtained from *o*-bromodiphenylphosphine and *o*-bromodiphenylarsine to prepare (2-(diphenylphosphino)phenyl)- and (2-(diphenylarsino)phenyl)diphenylbismuthines. Wittig and Hellwinkel[40] have prepared 5-phenyl-5*H*-dibenzobismole from 2,2′-dilithiobiphenyl and diphenyliodobismuthine. The interesting bismuthine 1,4-phenylenebis(diphenylbismuthine) can be obtained from 1,4-phenylenedilithium and 2 mol of diphenylchlorobismuthine.[41] Tris(phenylcarboranyl)bismuthine is obtained from phenylcarboranyllithium and bismuth trichloride.[42] Tris(*p*-(dimethylamino)phenyl)bismuthine can be obtained from the corresponding lithium compound, but the yield is poor.[32] Quite recently, the interesting compound tris(pentachlorophenyl)bismuthine was obtained from pentachlorophenyllithium and bismuth trichloride.[43] A polymeric tertiary bismuthine has been obtained from poly(lithiostyrene) and diphenylchlorobismuthine.[44] The interesting cyclopentadienylmanganese compound tricymantrenylbismuthine has been obtained from the corresponding lithium compound and bismuth trichloride:[45]

$$3LiC_5H_4Mn(CO)_3 + BiCl_3 \rightarrow [(CO)_3MnC_5H_4]_3Bi + 3LiCl$$

$$C_5H_4 = \text{disubstituted cyclopentadiene}$$

Thermal decomposition of this compound is discussed in section III.B.2.

Tertiary bismuthines can be obtained from organoaluminum compounds. Thus, triethylbismuthine is prepared from triethylaluminum[46,47] or the sesquichloride $Et_3Al_2Cl_3$.[48] Several other trialkylbismuthines have also been obtained from the corresponding trialkylaluminum compounds.[46] Rather than use the dangerous trialkylaluminum compounds, it has been found, at least for the preparation of triethylbismuthine, that lithium tetraethylaluminate and bismuth trichloride give triethylbismuthine in excellent yield.[49]

Organosodium compounds have been used with considerable success in the preparation of mixed diarylalkynylbismuthines from diarylchlorobismuthines and sodium acetylides:[50]

$$Ar_2BiCl + NaC{\equiv}CR \rightarrow Ar_2BiC{\equiv}CR + NaCl$$

The compounds prepared in this manner are $Ph_2BiC{\equiv}CPh$, $(p\text{-}MeC_6H_4)_2BiC{\equiv}CH$, $(p\text{-}MeC_6H_4)_2BiC{\equiv}CPh$, and $(p\text{-}ClC_6H_4)_2BiC{\equiv}CPh$. The compound $(p\text{-}MeC_6H_4)_2BiC{\equiv}CH$ can also be prepared from $(p\text{-}MeC_6H_4)_2BiCl$ and the ethynyl Grignard reagent.

Two bismuthines containing cyclopentadienyl groups, $(C_5H_5)_3Bi$ and $(MeC_5H_4)_3Bi$, are obtained from the corresponding sodium cyclopentadienides and bismuth trichloride.[51] Both of those compounds are obtained in two different forms, a red crystalline σ-bonded form and a black π-bonded form. Three bismuthines containing ferrocenyl groups have been prepared from ferrocenylsilver compounds and either bismuth trichloride or tribromide.[52,53] These possess the formulas $(ClC_5H_4FeC_5H_4)_3Bi$, $(C_5H_5FeC_5H_3Cl)_3Bi$, and $(BrC_5H_4FeC_5H_4)_3Bi$. In addition to the ferrocenylbismuthines, a manganesecyclopentadienylbismuthine, $[(CO)_3MnC_5H_4]_3Bi$, has been prepared, again making use of a silver compound and bismuth trichloride.[54]

In addition to the various organometallic compounds mentioned above for the preparation of tertiary bismuthines, organomercury[55-57] and organozinc[58,59] compounds have been employed. Tertiary bismuthines have been obtained from organomercury compounds and either metallic bismuth[55,56] or bismuth tribromide.[57]

Closely related to the use of organometallic reagents in the synthesis of tertiary bismuthines is the use of organosilicon compounds by Müller and Dathe.[60-63] Thus, when bismuth hydroxide is warmed with hydrofluoric acid and ammonium fluoride in a platinum dish and this mixture then treated with phenyltrifluorosilane, triphenylbismuthine is obtained. In a similar manner the complex siloxy compound $PhSi(OCH_2CH_2)_3N$ and bismuth trioxide give triphenylbismuthine in 44% yield.[64,65]

2. *From Diazonium or Iodonium Salts*

The Nesmeyanov reaction involves the replacement of one or more halogens of a main-group metallic halide with one or more aryl groups by treating the metallic halide with a diazonium salt in an organic solvent in the presence of a powdered metal which acts as a reducing agent. Gilman and co-workers[66,67] first used this method to prepare organobismuth compounds. The diazonium salts used were the tetrachlorobismuthates $[ArN_2][BiCl_4]$, and copper was used as the metallic reducing agent. Unless aqueous ammonia or hydrazine was added to the reaction mixture, the products were aryldichloro- or diarylchlorobismuthines rather than triarylbismuthines. The yields by this reaction were poor. Later workers[68,69] obtained much larger yields of triarylbismuthines by using diazonium tetrachlorobismuthates and finely divided metallic bismuth. Although aqueous ammonia was used in the reaction workup, Nad and co-workers[69] demonstrated that, at least for the preparation of tris(p-bromophenyl)bismuthine, approximately the same yield of the desired tertiary bismuthine could be obtained by omitting the aqueous ammonia. Rather than use the diazonium tetrachlorobismuthates, Nesmeyanov and co-workers[70] obtained good yields of triarylbismuthines from the decomposition of diazonium tetrafluoroborates in acetone and in the presence of bismuth metal. Triarylbismuthines are also obtained from aryl azoformates[71] or from phenylhydrazine,[72] but both reactions are believed to involve the formation of diazonium salts and thus do not differ significantly from the previously described reactions.

In addition to diazonium salts, the decomposition of iodonium salts in the presence of bismuth trichloride and metallic bismuth leads to the formation of triarylbismuthines.[73,74] By the use of unsymmetrical iodonium salts it is possible to study the effect of structure on the cleavage of the iodonium salts:

$$3ArAr'ICl + 2Bi \xrightarrow{BiCl_3} Ar_3Bi + BiCl_3 + 3Ar'I$$

It is found that the bismuth atom is preferentially arylated by the more electronegative aryl group. Triphenylbismuthine can also be prepared from diphenylchloronium and diphenylbromonium salts by reactions similar to those used with iodonium salts.[75] The preparation of triarylbismuthines from diazonium and other onium salts was first reported in the period 1939–1962. Apparently there has not been any recent work on this method of synthesis.

3. *From Organic Halides*

The reaction between sodium– or potassium–bismuth alloys and alkyl or aryl halides leads to the formation of trialkyl- or triarylbismuthines, respectively. The first organobismuth compound, triethylbismuthine, was prepared by Löwig and Schweizer[76] in 1850 by the use of this method. The procedure was later extended by other workers[77-80] to the preparation of a number of triarylbismuthines. Although excellent yields have been obtained by this synthetic procedure, it has not been employed for many years.

Diphenyliodobismuthine reacts with alkali and alkaline earth metals (Li, Na, K, Ca, and Ba) in liquid ammonia to form deep red solutions of the corresponding diphenylbismuthides.[81] The reaction is carried out by addition of the metal to a liquid ammonia solution of diphenyliodobismuthine; the reverse addition of the bismuthine to a solution of sodium in liquid ammonia is not successful. The liquid ammonia solution of the diphenylbismuthide may then be used to prepare unsymmetrical tertiary bismuthines by the addition of an aryl halide. Thus, from sodium diphenylbismuthide and α-iodonaphthalene a 24.5% yield of diphenyl-α-naphthylbismuthine (together with triphenylbismuthine and naphthalene) is obtained. The yield of the unsymmetrical bismuthine is the same with the lithium or potassium bismuthide but is considerably smaller with the barium or calcium bismuthide. If the sodium diphenylbismuthide is prepared from diphenylchlorobismuthine or diphenylbromobismuthine, the subsequent yield of diphenyl-α-naphthylbismuthine is increased to 30.6% and 40.8%, respectively. (However, sodium diphenylbismuthide does not react with α-bromonaphthalene to yield diphenyl-α-naphthylbismuthine.) In addition to diphenyl-α-naphthylbismuthine, di-*p*-tolyl-α-naphthyl- and di-*p*-chlorophenyl-α-naphthylbismuthines can be prepared by this method. Diphenyl-β-naphthyl- and diphenyl-*p*-biphenylylbismuthines are obtained as oils which can be characterized by oxidation with chlorine to the dichlorides and subsequent conversion to the dibenzoates. Lithium diphenylbismuthide and *p*-bromophenol give a very small amount of a compound which may be diphenyl(*p*-hydroxyphenyl)bismuthine. Sodium diphenylbismuthide does not give the expected unsymmetrical bismuthines with *p*-bromodimethylaniline, *o*-iodobenzoic acid, *m*-bromobenzoic acid, or *p*-bromobenzoic acid.

Alkali or alkaline earth bismuthides have only been prepared by the interaction of diarylhalobismuthines and the alkali or alkaline earth metal in liquid ammonia. In contrast to triarylphosphines, -arsines, or -stibines, all three phenyl groups are cleaved from triphenylbismuthine by sodium in liquid ammonia.[81,82]

4. By the Reaction of Free Radicals with Bismuth

The existence of free radicals in the gaseous state was first demonstrated by Paneth and Hofeditz[83] in 1929. By heating tetramethyllead in a silica tube in a stream of an inert gas, metallic lead and methyl radicals are formed. Although these radicals have only a very short lifetime, if a mirror of some metal is located a short distance down the tube, the radicals will react with this metal to form organometallic compounds. Thus, by using a cold mirror of bismuth, the formation of trimethylbismuthine can be demonstrated. From tetraethyllead triethylbismuthine is obtained.[83-85] By use of heated bismuth mirrors, evidence can be obtained for the formation of tetramethyl- and tetraethyldibismuthine. The Paneth technique is of no value as a synthetic method for the synthesis of bismuthines. It has been utilized in a recent study of the radioactive decay of ^{224}Ra, by converting the decay products ^{212}Pb, ^{212}Bi, and ^{208}Tl to the corresponding methyl and ethyl compounds by methyl and ethyl radicals generated by the thermal decomposition of tetramethyl- or tetraethyllead.[86,87]

Bell and co-workers[88] have attempted the synthesis of tris(trifluoromethyl)bismuthine by the reaction of trifluoromethyl radicals and a heated bismuth mirror, but the amount of product obtained is too small to permit elemental analysis and the identity of the product rests only on IR data and the presence of fluoroform when the product is hydrolyzed. These difficulties in preparing tris(trifluoromethyl)bismuthine have now been overcome by a greatly improved method of generating trifluoromethyl radicals.[89] Hexafluoroethane at a pressure of 1 torr is converted to trifluoromethyl radicals by a glow discharge produced by a radiofrequency generator operating at 8.6 MHz. The resulting radicals react with bismuth triiodide over 100 h, and the products are trapped in two cold traps at −78 and −196 °C. The bismuthine is found in both traps and is purified by low-temperature distillation. Since tris(trifluoromethyl)bismuthine is thermally unstable at 100 °C, the authors[89] suggest that the previous report of the preparation of this compound is in error. The reaction has been extended to the preparation of a number of other organometallic compounds containing alkyl groups by the reaction of radiofrequency-generated free radicals with metals.[90] Among the compounds prepared by this method are $(CF_3)_4Sn$, Me_2Hg, Me_2Cd, Me_4Sn, Me_4Ge, $(CF_3)_3Bi$, and Me_3Bi. Reaction of the radiofrequency-generated radical SiF_3 with mercury gave $Hg(SiF_3)_2$. This new method of preparing organometallic compounds will probably find important applications in the future.

5. Miscellaneous Methods

It is possible to prepare unsymmetrical bismuthines by disproportionation reactions between trialkylbismuthines and perfluoroalkyl iodides. Thus, trimethylbismuthine and an excess of trifluoromethyl iodide, when heated in a sealed tube at 100 °C for 12 h, give a mixture of 82% Me_2BiCF_3 and 18% $MeBi(CF_3)_2$. There is no evidence for the formation of $(CF_3)_3Bi$.[26,91] This same type of reaction is used for the preparation of $Me_2BiC_2F_5$, $MeBi(C_2F_5)_2$, Et_2BiCF_3, $EtBi(CF_3)_2$, $Me_2BiC_3F_7$, and $MeBi(C_3F_7)_2$. A disproportionation reaction also occurs when tris(trifluoromethyl)phosphine reacts with trimethylbismuthine; dimethyl(trifluoromethyl)- and methylbis(trifluoromethyl)bismuthine are obtained.

In addition to the above disproportionation reactions, metal–metal exchange reactions occur between triarylbismuthines and alkyllithium or alkylsodium reagents:[92,93]

$$Ar_3Bi + 3BuLi \rightarrow 3ArLi + Bu_3Bi$$

The tributylbismuthine has not been isolated from the reaction mixture, and the procedure probably has no synthetic importance.

Another method for the preparation of trialkylbismuthines involves the electrolysis of organometallic compounds at a sacrificial bismuth anode. Triethylbismuthine can be prepared in yields as high as 95% by this method.[94-96] The organometallic compounds that have been used in this method are all compounds of aluminum or boron. Tris(2-cyanoethyl)bismuthine is prepared by the reduction of acrylonitrile in aqueous dipotassium phosphate solution by the use of a sacrificial bismuth cathode and a platinum anode in a cell equipped with a ceramic diaphragm.[97] Electrolysis of 3-iodopropionitrile in a similar manner to that employed with acrylonitrile gives a mixture of tris(2-cyanoethyl)bismuthine and iodobis(2-cyanoethyl)bismuthine. The preparation of organobismuth compounds (presumably tertiary bismuthines) by electrolysis with a tungsten cathode (and presumably a bismuth anode) is mentioned in a Russian patent. The organic compounds used in the electrolysis were of the type $RCH{=}CHX$, RCH_2Y, and $RCHYCH_2X$, where X was Cl or Br and Y was an electron-attracting group such as CN or CO_2H.[98]

An interesting preparation of triarylbismuthines involves the thermal elimination of sulfur dioxide from tris(arenesulfinato)bismuthines [$Bi(O_2SAr)_3$, where Ar = Ph or p-MeC_6H_4], bis(benzenesulfinato)phenylbismuthine [$PhBi(O_2SPh)_2$], and (benzenesulfinato)diphenylbismuthine [$Ph_2Bi(O_2SPh)$].[99] The reactions involved are as follows:

$$Bi(O_2SAr)_3 \xrightarrow{\Delta} 3SO_2 + Ar_3Bi$$

$$Ph_{3-n}Bi(O_2SPh)_n \xrightarrow{\Delta} nSO_2 + Ph_3Bi$$

$$n = 1 \text{ or } 2$$

The unsymmetrical tertiary bismuthine Me_2BiCp (Cp = cyclopentadienyl) has been prepared by the following method:[100]

$$Me_2BiN(Me)SiMe_3 + CpH \xrightarrow{Et_2O} Me_2BiCp + HN(Me)SiMe_3$$

Triarylbismuthines can be readily obtained by reduction of triarylbismuth dihalides. Hydrazine hydrate is the reagent of choice for this reduction,[101] but sodium hydrosulfite may also be used.[102] Since triarylbismuth dihalides are usually prepared by halogenation of triarylbismuthines, this method is not of synthetic importance. However, the method may be useful for the purification of triarylbismuthines. Thus, tri-*m*-tolylbismuthine, when prepared from the corresponding Grignard reagent, is difficult to obtain in pure form. It may be converted to the dichloride which, after recrystallization, can be reduced to the pure tertiary bismuthine.

B. Reactions

1. Oxidative Addition

Trialkylbismuthines generally react with halogens, even at low temperatures, with cleavage of a carbon-bismuth bond and the formation of a dialkylhalobismuthine:[58,59]

$$R_3Bi + X_2 \rightarrow R_2BiX + RX$$

An exception to this generalization involves the preparation of both *cis*- and *trans*-tripropenylbismuth dibromides:[38]

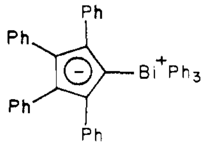
$$(MeCH{=}CH)_3Bi + Br_2 \xrightarrow{-55\ ^\circ C} (MeCH{=}CH)_3BiBr_2$$

It is interesting that the carbon-bismuth bonds in the propenyl compounds are more stable than the carbon-bismuth bonds in other aliphatic bismuthines. The carbon-bismuth bond is cleaved, however, in triisopropenylbismuthine when this compound is treated with bromine. In contrast to the alkyl compounds, most triarylbismuthines readily react with bromine or chlorine to yield the corresponding triarylbismuth dibromides or dichlorides. The reaction is usually carried out in an organic solvent such as petroleum ether,[78,103] chloroform,[63] carbon tetrachloride,[104] or toluene,[103] and the dichlorides or dibromides precipitate from solution in essentially quantitative yields. There is no evidence for the formation of a tetrabromide (Ar_3BiBr_4) as is the case with the addition of bromine to triarylarsines.[105] Triphenylbismuthine is fluorinated to triphenylbismuth difluoride by fluorine gas diluted with argon.[106] The reaction is carried out at room temperature in $CFCl_3$ solution. The oxidative halogenation of triarylbismuthines is not always successful, however. For example, Gilman and Yablunky[32] failed in the bromination and chlorination of trimesitylbismuthine. There was evidence of some nuclear chlorination accompanied by oxidative chlorination, but the product of bromination was apparently unstable and decomposed on standing. Tris(pentachlorophenyl)bismuthine is decomposed by chlorine or bromine to unidentified decomposition products.[43] No triarylbismuth diiodide is known. It is possible that triphenylbismuth diiodide is formed from triphenylbismuthine and iodine in ether solution at low temperatures, but the compound, if formed, decomposes into diphenyliodobismuthine when the mixture is warmed to room temperature.[107,108] The iodination has been studied by Beveridge and coworkers,[109] who have shown that a polyiodide is not formed from triphenylbismuthine and excess iodine in acetonitrile solution. The reaction of triphenylbismuthine and iodine vapor to form a brown-colored substance of unknown composition has been used as a sensitive test for the detection of triphenylbismuthine.[110,111]

Although oxidative halogenation with the halogens Br_2 or Cl_2 is the most common method of converting triarylbismuthines to the corresponding dibromides or dichlorides, a few other chlorinating agents can be employed. Sulfur dichloride, sulfur monochloride, sulfuryl chloride, thionyl chloride,[112,113] and iodine trichloride[114,115] will convert triphenylbismuthine to the dichloride. The yields are frequently less satisfactory than with direct chlorination. Tris(*p*-(dimethylamino)phenyl)bismuthine dichloride is obtained from the corresponding bismuthine by the use of a stoichiometric amount of phenyliodine dichloride in methylene chloride or chloroform at low temperatures.[116]

In addition to the halides Ar_3BiX_2 where X = F, Cl, or Br, several other compounds of the type Ar_3BiY_2 have been prepared by the oxidative addition of Y groups to a triarylbismuthine. Thus, triphenylbismuth diacetate is prepared from triphenylbismuthine and lead tetraacetate in carbon tetrachloride[103] or acetic acid[40] solution. Triphenylbismuth dibenzoate is obtained from triphenylbismuthine and benzoyl peroxide,[117] while triphenylbismuth dinitrate is obtained in a similar manner by the use of benzoyl nitrate.[108]

The conversion of triarylbismuthines to ylides has not been investigated to any extent. Diazotetraphenylcyclopentadiene and triphenylbismuthine react at 140 °C to give the following cyclopentadienide:[118]

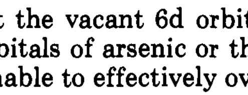


The ylide is deep blue in color and is so unstable that an analytically pure sample cannot be obtained. The UV spectrum of the bismuthonium cyclopentadienide in benzene or methanol solution closely resembles the spectrum of pyridinium tetraphenylcyclopentadienylide in the same solvents. Because of these results it is suggested[118] that the vacant 6d orbitals of bismuth, unlike the 4d orbitals of arsenic or the 5d orbitals of antimony, are unable to effectively overlap the 2p orbitals of the cyclopentadienide ring.

The imine $p\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}{=}\text{BiPh}_3$ is obtained when triphenylbismuthine reacts with Chloramine-T in acetonitrile solution:[119]

$$\text{Ph}_3\text{Bi} + p\text{-MeC}_6\text{H}_4\text{SO}_2\text{NClNa} \rightarrow p\text{-MeC}_6\text{H}_4\text{SO}_2\text{N}{=}\text{BiPh}_3 + \text{NaCl}$$

The interesting compound



is formed when triphenylbismuthine reacts with *N*-bromosuccinimide.[120] The one-electron oxidation of triphenylbismuthine (as well as the triphenyl compounds of other group 5A elements) by the radicals $(4\text{-RC}_6\text{H}_4)_3\text{N}^{+}\cdot$, where R is Br, Ph, Me, or MeO, has been studied by Koshechko and co-workers[121] and found to be first order in each reactant. The rate of the reaction depends strongly on both the nature of R and the group 5A element.

2. Reactions in Which a Carbon–Bismuth Bond Is Cleaved

Almost all reactions of trialkylbismuthines involve cleavage of the carbon–bismuth bond. Most trialkylbismuthines are oxidized in the air; the lower members are spontaneously inflammable. The controlled oxidation of triethylbismuthine has been studied at low temperatures, and the compound diethylethoxybismuthine (Et_2BiOEt) has been identified as the first product of the oxidation.[122] Further oxidation at higher temperatures yields a product which is probably EtBiO_2. In a more modern study, it has been shown that both trimethyl- and triethylbismuthine undergo autoxidation in benzene solution to give polymeric bismuth oxides of variable composition which contain an average of one or less than one alkyl group per metal atom. The oxidation reaction appears to be a radical chain reaction. Oxidizing agents other than oxygen, such as *tert*-butyl hydroperoxide, also cleave the carbon–bismuth bond of trialkylbismuthines.[123]

Halogens cleave trialkylbismuthines with the formation of dialkylhalobismuthines. A possible exception is the reported formation of *cis*- and *trans*-tripropenylbismuth dibromides from the corresponding tertiary bismuthines and bromine at −55 °C.[38] Mineral acids cleave all three alkyl groups of trialkylbismuthines; e.g., trimethylbismuthine and hydrochloric acid give bismuth trichloride and methane.[58] Sulfuric acid or nitric acid reacts explosively with trialkylbismuthines. Hydrogen sulfide, mercaptans, and selenols also cleave the carbon–bismuth bond.[124,125] Triethylbismuthine and H_2S in diethyl ether yield Bi_2S_3, but in ethanol–HNO_3 solution Et_3BiS is formed.[126,127] When triethylbismuthine and thiophenol are allowed to stand for 16 h Et_2BiSPh and ethane are formed.[128] When heated with sulfur in ethanol solution, triethylbismuthine yields Bi_2S_3.[126,127]

An ethereal solution of hydrazoic acid and trimethylbismuthine yield the azide Me_2BiN_3 according to the equation[129]

$$\text{Me}_3\text{Bi} + \text{HN}_3 \rightarrow \text{Me}_2\text{BiN}_3 + \text{MeH}$$

Trimethylbismuthine and thiocyanogen react in a somewhat similar manner:[130]

$$\text{Me}_3\text{Bi} + (\text{SCN})_2 \rightarrow \text{Me}_2\text{BiSCN} + \text{MeSCN}$$

When heated with alkyl iodides, one alkyl group is cleaved and a dialkylbismuth iodide is formed.[58,59] Trifluoromethyl iodide and perfluoroalkyl iodides react with trialkylbismuthines with exchange of alkyl groups.[26] Thus, trimethylbismuthine and trifluoromethyl iodide at 100 °C give a mixture of Me_2BiCF_3 and $\text{MeBi(CF}_3)_2$. The same bismuthine and $\text{C}_2\text{F}_5\text{I}$ give $\text{Me}_2\text{BiC}_2\text{F}_5$ and $\text{MeBi(C}_2\text{F}_5)_2$.

Reactive metals cleave the Bi–C bond of trialkylbismuthines. Thus, sodium and tribenzylbismuthine react to form metallic bismuth.[31] The Bi–C bond is also cleaved by metallic salts. Triethylbismuthine reacts with 1 mol of BiCl_3 in acetic acid[58] or 1 mol of HgCl_2 in ethanol[126,127] to yield Et_2BiCl. The reaction of tribenzylbismuthine and silver nitrate gives metallic silver and presumably involves cleavages of the Bi–C bond. Thallium(III) chloride and triisopropenylbismuthine in ether solution at −40 °C give diisopropenylthallium chloride.[38]

Organometallic hydrides of silicon, germanium, or tin react with triethylbismuthine with rupture of one or more C–Bi bonds and the formation of compounds with Bi–Si, Bi–Sn, or Bi–Ge bonds. Thus triethylgermane reacts as follows:[131]

$$n\text{Et}_3\text{GeH} + \text{Et}_3\text{Bi} \rightarrow n\text{EtH} + (\text{Et}_3\text{Ge})_n\text{BiEt}_{3-n}$$

$$n = 1, 2, \text{ or } 3$$

With Et_3SiH or Et_3SnH only compounds of the type $(\text{Et}_3\text{M})_3\text{Bi}$, where M = Si or Sn, have been obtained.[132,133] The reaction between pentafluorophenylgermanes and triethylbismuthine is more complicated.[134] Thus, $(\text{C}_6\text{F}_5)_3\text{GeH}$ and Et_3Bi give $(\text{C}_6\text{F}_5)_3\text{GeBiEt}_2$ at 90–100 °C but $[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{BiEt}$ at 170 °C. In both cases ethane is also obtained. Only 1 mol of ethane is evolved when $(\text{C}_6\text{F}_5)_2\text{GeH}_2$ and Et_3Bi are warmed slowly in the temperature range 60–105 °C, but at higher temperatures 2 mol of ethane is evolved with formation of a dimer $[(\text{C}_6\text{F}_5)_2\text{GeBi}]_2$ and an undistillable liquid once believed to be a polymer of $[(\text{C}_6\text{F}_5)_2\text{GeBiEt}]_2$. This compound was later shown by X-ray diffraction studies to contain three germanium and two bismuth atoms in each molecule.[135] Scheme I was postulated to explain its formation. The Ge–Bi bonds of $[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{BiEt}$ are cleaved by mercury:

$$3[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{BiEt} + 3\text{Hg} \rightarrow 3[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{Hg} + 2\text{Bi} + \text{Et}_3\text{Bi}$$

The electrolysis of triethylbismuthine at a lead anode results in the formation of tetraethyllead and metallic bismuth.[136]

One methyl group is cleaved from Me_3Bi when this compound is heated to 100 °C for 100 h with $\eta^5\text{-C}_5\text{H}_5(\text{CO})_3\text{MH}$ (M = Mo or W) in methylcyclohexane.[137] The reaction is as follows:

$$\mathrm{Cp(CO)_3MH + Me_3Bi \rightarrow MeH + Cp(CO)_3MBiMe_2}$$
$$\mathrm{Cp\ is\ }\eta^5\text{-}\mathrm{C_5H_5}$$

In contrast to trialkylbismuthines, triarylbismuthines are stable in the air but are oxidized with rupture of the C–Bi bond when treated with hydrogen peroxide,[138] N_2O_3, or a mixture of N_2O_3 and NO.[139] When heated in xylene solution for 24 h in a hydrogen atmosphere at a pressure of 60 atm and a temperature of 150 °C, only 6.9% of the triphenylbismuthine is reduced to form benzene, but under the same reaction conditions except at a temperature of 225 °C, 99.4% of the carbon–bismuth bonds are ruptured.[140] Tricymantrenylbismuthine, heated in an argon atmosphere in the temperature range 220–330 °C, decomposes to metallic bismuth and bicymantrenyl quantitatively according to the equation[45]

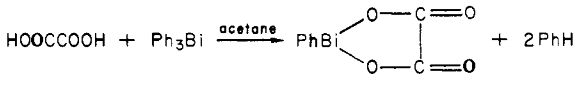
$$\mathrm{2[(CO)_3MnC_5H_4]_3Bi \xrightarrow{300\ ^\circ C} 2Bi + 3[(CO)_3MnC_5H_4]_2}$$
$$\mathrm{C_5H_4}\text{ is a disubstituted cyclopentadiene}$$

Unlike trialkylbismuthines, most triarylbismuthines undergo oxidative halogenation with chlorine or bromine, but the carbon–bismuth bond is cleaved by iodine.[107–109] Tris(pentachlorophenyl)bismuthine, however, is cleaved by chlorine or bromine to give unidentified products.[43] Strong mineral acids cleave all three carbon–bismuth bonds of triarylbismuthines with the formation of inorganic bismuth salts of the acid. From cryoscopic and conductometric studies, Paul and coworkers[141] have suggested that triphenylbismuthine undergoes solvolysis in disulfuric acid according to the equation

$$\mathrm{Ph_3Bi + 9H_2S_2O_7 \rightarrow Bi(HSO_4)_3 + 3PhOSO_2H_2^+ + 3HS_3O_{10}^- + 3H_2SO_4}$$

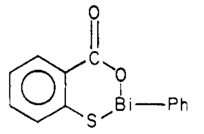
Triphenylstibine undergoes a similar type of solvolysis. In chlorosulfuric acid, however, triphenylstibine is converted to $Sb(SO_3Cl)_3$, whereas triphenylbismuthine does not dissolve.[142] Liquid hydrogen chloride and hydrogen bromide cleave all three phenyl groups of triphenylbismuthine.[148,149]

Aryl groups are also cleaved by organic acids. Formic acid cleaves all three phenyl groups of triphenylbismuthine at room temperature.[143] The products are bismuth formate, basic bismuth formates, and benzene. Acetic acid does not react at room temperature, but at 50 °C for 1 h a mixture of basic bismuth acetates is formed. With cinnamic acid at 150 °C or with benzoic acid at 100 °C, phenyldicinnamato- and phenyldibenzoatobismuthine are formed, respectively. The dicarboxylic acids oxalic, malonic, succinic, and maleic react with triphenylbismuthine with cleavage of two carbon–bismuth bonds and formation of five-, six-, or seven-membered ring compounds.[145] For example, oxalic acid reacts with triphenylbismuthine in refluxing acetone as follows:



Triphenylbismuthine reacts with chloroacetic acid to yield $Bi(O_2CCH_2Cl)_3$ in 90% yield.[144]

Phenols cleave all three phenyl groups from triphenylbismuthine when the reaction is carried out at elevated temperatures.[146,147] Hydrogen sulfide as well as thiophenols cleave one or more carbon–bismuth bonds of triphenylbismuthine. With H_2S in alcoholic ammonia, Bi_2S_3 and benzene are obtained. Thiophenol similarly cleaves all three phenyl groups when heated with triphenylbismuthine at 75–130 °C[150] or when refluxed in xylene solution for 15 h.[151] The product in both cases is $(PhS)_3Bi$. However, triphenylbismuthine and thiophenol, when refluxed in $CHCl_3$ solution for 2 h, give $PhBi(SPh)_2$.[151] 2-Mercaptobenzoic acid and triphenylbismuthine yield a compound which has been assigned the following cyclic structure on the basis of a bismuth analysis:



The cleavage of the carbon–bismuth bond by the mercaptocarboxylic acids mercaptoacetic, 2-mercaptopropionic, 3-mercaptopropionic, and 2-mercaptobenzoic has recently been reported by Praeckel and Huber.[152] The tertiary bismuthines employed were trimethyl- and triphenylbismuthines. In the case of trimethylbismuthine two methyl groups were cleaved from the bismuth with the formation of methane and an organobismuth compound. Thus, with mercaptoacetic acid the following reaction occurred:

$$\mathrm{Me_3Bi + HSCH_2COOH \xrightarrow{Me_2CO} 2MeH + MeBi(SCH_2CO_2)}$$

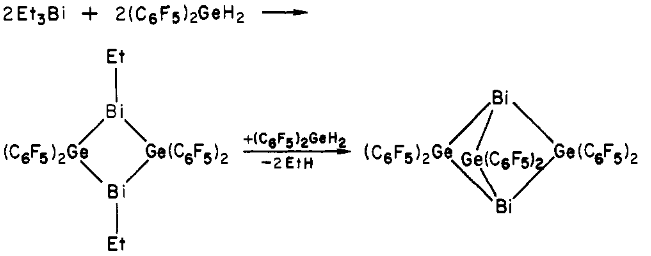
Similar compounds were obtained with 2- and 3-mercaptopropionic and 2-mercaptobenzoic acids. The reaction product obtained was independent of the concentration and molar ratio of the reactants. The solvent used in the reaction was acetone, and the reaction was carried out at room temperature. With triphenylbismuthine the product obtained depended on the concentrations employed and also apparently on the solvent. With the three aliphatic mercapto acids in chloroform solution and with 2-mercaptobenzoic acid in methanol solution, three carbon–bismuth bonds were cleaved with the formation of benzene and the bismuth compound. Thus, with mercaptoacetic acid (0.04 mol in 50 mL of $CHCl_3$) and triphenylbismuthine (0.02 mol in 50 mL of $CHCl_3$) the following reaction occurred:

$$\mathrm{Ph_3Bi + 2HSCH_2CO_2H \rightarrow Bi(SCH_2CO_2)(SCH_2CO_2H) + 3PhH}$$

Similar compounds were obtained from 2- and 3-mercaptopropionic acids and 2-mercaptobenzoic acid. The structure of these inorganic bismuth compounds could not be determined from the data available. With 3-mercaptopropionic acid or 2-mercaptobenzoic acid (0.01 mol in 80 mL of acetone) and triphenylbismuthine (0.01 mol in 40 mL of acetone), the compounds obtained were $PhBi(SCH_2CH_2CO_2)$ and $PhBi(o\text{-}SC_6H_4CO_2)$, respectively.

Metals, particularly alkali metals, readily cleave all three carbon–bismuth bonds of triarylbismuthines. Thus, Rossi and Bunnett[82] were unstable to obtain any evidence of cleavage of only one or two phenyl groups when triphenylbismuthine was treated with sodium in liquid ammonia. This is in contrast to triphenylarsine or triphenylstibine, where sodium diphenylarsenide or diphenylstibide is readily obtained. Metallic antimony

SCHEME I



and triphenylbismuthine at 300 °C give an 85% yield of triphenylstibine.[153] Metallic mercury and triphenylbismuthine react reversibly:[56,154]

$$2Ph_3Bi + 3Hg \rightleftharpoons 3Ph_2Hg + 2Bi$$

Thus, from diphenylmercury and bismuth metal a 41% yield of triphenylbismuthine is obtained when the reaction is carried out at 250 °C.

The reaction of inorganic metal or metalloid halides with triphenylbismuthine results in cleavage of one or more of the carbon–bismuth bonds, depending both on the reaction conditions and on the particular metal or metalloid halide used.[103,115,155–157] Thus, such chlorides as PCl_3, $AsCl_3$, $SbCl_3$, $TiCl_4$, $TlCl_3$, $SnCl_4$, $CuCl_2$, $SiCl_4$, or $HgCl_2$, when added to the bismuthine in ether solution, give diphenylchlorobismuthine as the principal bismuth-containing product. Except for titanium, copper, and possibly silicon, phenylation of the element of the elemental chloride occurs. A somewhat similar study has been carried out between metal or metalloid chlorides and triphenylbismuthine by refluxing in chloroform solution for 5–6 h. Under these reaction conditions diphenylchlorobismuthine, bismuth trichloride, traces of benzene, and often biphenyl are formed. Among the elemental chlorides causing cleavage are $SbCl_3$, $SnCl_4$, $AlCl_3$, $TlCl_3$, $SiCl_4$, $CuCl_2$, $TiCl_4$, $FeCl_3$, $HgCl_2$, and $ZnCl_2$.[115,156,157] There is no reaction, however, between triphenylbismuthine and $CdCl_2$, $PbCl_2$, $MnCl_2$, $NiCl_2$, or $CoCl_2$.[115] Another rather curious observation is that silver nitrate and triphenylbismuthine react in chloroform to yield $Ph_2Ag{\cdot}AgNO_3$ and bismuth trichloride.[115,158] Triphenylbismuthine and tungsten hexachloride are employed as catalysts for the metathesis of 2-heptene according to the equation[159]

$$2Me(CH_2)_3CH{=}CHMe \xrightarrow[WCl_6]{Ph_3Bi} MeCH{=}CHMe + Me(CH_2)_3CH{=}CH(CH_2)_3Me$$

The reaction is carried out at room temperature with 1,2,4-trichlorobenzene as a solvent. The other products of the reaction are biphenyl and small amounts of chlorobenzene. The reaction is believed to involve exchange of phenyl groups and chlorine between tungsten and bismuth with formation of $PhWCl_5$, Ph_2WCl_4, and presumably bismuth trichloride. The reaction of triphenylbismuthine with Chloramine-T in acid solutions results in the cleavage of the carbon–bismuth bonds.[160]

Acid chlorides (SO_2Cl_2, MeCOCl, SO_2Cl, etc.) cleave one phenyl group from triphenylbismuthine to give Ph_2BiCl.[112,155] Halogen halides and cyanogen halides behave in a similar manner.[57,107,108] Iodine chloride yields Ph_2BiCl and PhI; cyanogen bromide yields Ph_2BiCN and PhBr. Cyanogen iodide yields Ph_2BiCN and PhI.[161]

Triphenylbismuthine and trimethylamine hydrochloride heated together to 130 °C in a sealed tube yield benzene and bismuth trichloride, but with tri-α-naphthylbismuthine, under the same reaction conditions, some di-α-naphthylchlorobismuthine, as well as naphthalene and bismuth trichloride, is formed.[162]

The Bi–C bond of triphenylbismuthine is cleaved by SeO_2 in benzene–alcohol.[163] This is in contrast to Ar_3P, Ar_3As, and Ar_3Sb, which are oxidized by selenium dioxide. No bismuth compounds are isolated in the reaction, but phenylselenic acid is obtained in large yields. Apparently the phenyl groups of triphenylbismuthine are transferred to the selenium. Triarylbismuthines also react with liquid sulfur dioxide with cleavage of the C–Bi bond.[164] Thus, $PhBi(O_2SPh)_2$, which is readily prepared by other reactions, can be identified from its ^1H NMR spectrum as one of the products of the reaction. It is stated[164] that mono-, bis-, and tris(benzenesulfinato)bismuth compounds are formed, but no details of this reaction are given. Benzenesulfinic acid also cleaves one or two phenyl groups from triphenylbismuthine.[99] In boiling benzene–chloroform solution two phenyl groups are cleaved; in ether at room temperature, one phenyl group is cleaved:

$$Ph_3Bi + nPhSO_2H \rightarrow Ph_{3-n}Bi(O_2SPh)_n + nPhH$$

$$n = 1 \text{ or } 2$$

Mercury diarenesulfinates, however, cleave all three phenyl groups from triphenylbismuthine when the reaction is carried out in chloroform or methanol solution at room temperature:

$$Ph_3Bi + 3Hg(O_2SR)_2 \rightarrow Bi(O_2SR)_3 + 3PhHg(O_2SR)$$

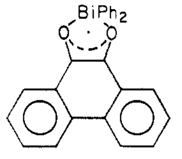
$$R = Ph \text{ or } p\text{-}MeC_6H_4$$

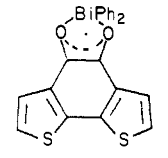
Triphenylbismuthine undergoes carbon–bismuth cleavage when irradiated with ultraviolet light.[165–167] The cleavage is homolytic. Metallic bismuth, benzene, and products produced by the phenylation of the solvents (pyridine and benzene) by the radicals formed in the photolysis reaction are isolated.[165] Biphenyl is also formed in substantial amounts. When the photolysis is carried out in benzene-d_6 as the solvent, the biphenyl that is isolated contains three fractions, viz., unlabeled PhPh and two labeled fractions, PhPh* and Ph*Ph* (where Ph* is a partially or completely deuterated phenyl group). The principal fraction (95.2%) is PhPh*.

Photolysis of triphenylbismuthine as well as triphenylarsine and triphenylstibine, all in isopentane at 300 K, has been studied by Smirnov and co-workers.[167] The irradiations were carried out directly in the resonator of the ESR spectrometer with UV light (λ = 250 nm). A radical photolysis mechanism was proposed to account for the results obtained. The rate of formation of the radical products increases noticeably and their photostability decreases in going from arsenic to bismuth.

Triphenylbismuthine is also decomposed by γ radiation from a cobalt source.[168,169] Metallic bismuth and biphenyl are among the products formed. In benzene solution phenylcyclohexadienes, hydrogen, and an unidentified white solid containing 60% bismuth are also formed. In chloroform, however, triphenylbismuth dichloride is produced. This is probably formed from chlorine radicals produced by radiolysis of the solvent.

When triphenylbismuthine is heated to 160 °C with either 9,10-phenanthraquinone or benzo[2,1-*b*:3,4-*b*′]-dithiophene-4,5-dione in the cavity of an ESR spectrometer, ESR signals are observed.[170] These signals are attributed to the following radicals:





All three phenyl groups of Ph_3Bi are cleaved when it is treated with palladium(II) acetate (or palladium(II) chloride) and an olefin such as 1-octene or ethyl acrylate.[171] In this reaction the olefin is phenylated and the palladium reduced to palladium metal. Biphenyl is also a product of the reaction. The reaction is believed to involve formation of a phenylpalladium compound which transfers its phenyl groups to the olefin:

$$Ph_3Bi + PdX_2 \rightarrow Ph_2BiX + PhPdX$$

$$CH_2{=}CHCO_2Et \xrightarrow{Pd(II),\ Ph_3Bi} Ph{-}Ph + PhCH{=}CHCO_2Et$$

Ph_3Sb and Ph_2Te react in a similar manner, but with Ph_3As only two phenyl groups as a maximum are transferred to the palladium.

3. *Coordination Compounds*

Trialkyl- and triarylbismuthines have found comparatively little use as donors to transition-metal atoms in coordination chemistry studies. This is due largely to the predominantly s character of the lone pair in the tertiary bismuthines. A recent study by Carty and co-workers,[172] in which the bond angles and bond distances in the compounds $[Cr(CO)_5EPh_3]$, where E = P, As, Sb, and Bi, have been determined by X-ray, has revealed that the Bi–Cr bond has far more s character than the corresponding E–Cr bond where E is P, As, or Sb. Thus, the C–Bi–C angle in Ph_3Bi is 94°, which increases to 98.7° when the bismuth atom is bonded to chromium. This indicates that the amount of s character decreases when the bismuth is bonded to the transition metal, but the Bi–Cr bond is still essentially s in character.

A somewhat different explanation for the weak donor capacity of tertiary bismuthines is advanced by Wuyts and co-workers.[173] These authors obtained $^{13}C-^{1}H$ coupling constants for ortho, meta, and para positions in the compounds Ph_3E, where E = P, As, Sb, or Bi. In the case of Ph_3P, Ph_3As, and Ph_3Sb, data were also obtained for a number of coordination compounds with transition metals. From these experimental values the Taft–Hammett substituent constant $\sigma_R°$ can be readily calculated by the relationship $\delta_p(^{13}C)-\delta_m(^{13}C) = -22.06\sigma_R°$. It was found that the $\sigma_R°$ values for Ph_3P, Ph_3As, and Ph_3Sb were extremely small, namely 0.00_8, -0.01_0, and -0.01_4, respectively, whereas the value for Ph_3Bi was -0.12_3. Since the value of $\sigma_R°$ has often been used as a measure of π-electron distribution, the large negative value for Ph_3Bi indicates, according to the authors, strong delocalization of p lone-pair electrons into the π framework of the ring. The authors then state that this "could then explain the low donor capacity of trivalent bismuth". In agreement with this conclusion they cite older X-ray data in which it had been reported that Ph_3Bi is a planar molecule (i.e., the Bi is sp^2 hybridized) and hence that the lone pair of electrons on bismuth occupies a p orbital. Since the older work on the structure of Ph_3Bi has been shown to be erroneous,[174] this explanation for the lack of donor capacity of trivalent bismuth compounds is certainly of doubtful value. Furthermore, it does not explain the weak donor capacity of trialkylbismuthines where any p electrons would not be delocalized.

Relatively few compounds are known in which a trialkylbismuthine acts as a donor to a transition metal. The nickel complex $Ni(CO)_3BiEt_3$, prepared from nickel tetracarbonyl and triethylbismuthine, and the two molybdenum complexes $Mo(CO)_5BiEt_3$ and *cis*-$Mo(CO)_4(BiEt_3)_2$, prepared in a similar manner from molybdenum hexacarbonyl, have been reported by Benlian and Bigorne,[175] but the compounds were difficult to prepare. Trialkylarsines and -stibines react with the carbene complex $(CO)_5CrC(OMe)Me$ with displacement of a carbonyl group and formation of the complexes $(R_3E)(CO)_4CrC(OMe)Me$, where E = As or Sb. By contrast the tertiary bismuthines R_3Bi, where R = Me, Et, or cyclohexyl, give the complexes $(CO)_5CrBiR_3$. These same complexes are also formed when the same tertiary bismuthines react with $(CO)_5Cr(THF)$.[176]

Recently, the photoinduced substitution of CO groups by group 5 ligands R_3E, where E = P, As, Sb, or Bi, has been studied by Talay and Rehder.[177] Thus, $BiEt_3$ reacts with $[Et_4N][V(CO)_6]$ to form $[Et_4N][V(CO)_5BiEt_3]$. With $[\eta^5\text{-}CpV(CO)_4]$, where Cp = the cyclopentadienyl group, two compounds $[\eta^5\text{-}CpV(CO)_3BiEt_3]$ and *cis*-$[\eta^5\text{-}V(CO)_2(BiEt_3)_2]$ are obtained. From ^{51}V NMR chemical shift values on the various compounds formed with group 5 ligands, the following sequence of ligand strengths has been given: $Et_3Bi < R_3As < R_3P < R_3Sb$.

Tri-*tert*-butylbismuthine, prepared from the corresponding Grignard reagent and $BiCl_3$, forms the coordination compound $(Me_3C)_3BiNi(CO)_3$ with nickel tetracarbonyl.[28] This compound possesses C_{3v} symmetry. The bismuthine reacts also with $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$, with displacement of one carbon monoxide molecule and formation of the complexes $(Me_3C)_3BiM(CO)_5$, where M = Cr, Mo, or W. These complexes possess C_{4v} symmetry. In addition to tri-*tert*-butylbismuthine, the corresponding tin and germanium compounds $(Me_3Sn)_3Bi$ and $(Me_3Ge)_3Bi$ are also found to yield similar complexes with $Ni(CO)_4$, $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$. All of the compounds are unstable, but the three compounds $(Me_3C)_3BiM(CO)_5$ (M = Cr, Mo or W) are obtained in crystalline form and possess definite melting points. Two of the nickel compounds are obtained only as oils.

Triarylbismuthines are used more extensively than trialkylbismuthines as donors to transition metals, but the number of compounds prepared is still quite limited as compared with triarylphosphines, -arsines, and -stibines. Triphenylbismuthine does not form coordination compounds with mercuric chloride or cupric chloride. Rather diphenylchlorobismuthine and phenylmercuric chloride or cuprous chloride are formed, respectively.[155] With silver nitrate the silver complex $AgNO_3{\cdot}2AgPh$ is obtained.[155] By contrast Stilp[178] has reported that tri-*o*-tolylbismuthine, tri-*p*-tolylbismuthine, tri-*m*-xylylbismuthine, and tri-α-

naphthylbismuthine all form coordination complexes with mercuric chloride. However, Deganello and coworkers,[179] without referring to Stilp's work, report that not only triphenylbismuthine but also tri-*o*-tolyl- and tri-*p*-tolylbismuthines react with mercuric chloride at 0 °C to form the corresponding diarylchlorobismuthines and the arylmercury chloride.

A few coordination compounds of triarylbismuthines with transition metals have been isolated and characterized. The silver compound $Ph_3Bi\cdot AgClO_4$, prepared by mixing the two components in ether solution, has been reported,[180] but other than a perchlorate ion absorption peak in the IR spectrum at 1095 cm^{-1}, no physical properties of this compound are given. It has been pointed out that the coordination could involve either the bismuth atom or the π-electron system of the phenyl rings acting as the donor to the silver, but no attempt was made to decide between those two possibilities. A thermodynamic study of complex formation between the triaryl compounds of group 5A elements, N, P, As, Sb, and Bi, and silver perchlorate in Me_2SO has recently been carried out.[181] Stability constants, determined potentiometrically with silver electrodes, and enthalpy changes, determined calorimetrically, established quantitatively the following order of stability of the Ph_3E complexes coordinated with Ag^+: $N \ll P < As > Sb > Bi$. While Ar_3P, Ar_3As, and Ar_3Sb formed mono, bis, and tris complexes, only a mono compound was found for triphenylbismuthine.

The pyrophoric compound $(Ph_3Bi)_2Fe(CO)_4$ is obtained by the sluggish reaction between iron pentacarbonyl and Ph_3Bi.[182] The reaction is carried out in ether solution and requires 8 days for completion. It has been reported that triphenylbismuthine does not react with either nickel tetracarbonyl[178,183] or $[Rh(CO)_2Cl]_2$.[184] However, several nickel coordination compounds are known, prepared by Levason and co-workers[185] from the interesting quadridentate ligand tris(*o*-(dimethylarsino)phenyl)bismuthine, $(o\text{-}Me_2AsC_6H_4)_3Bi$. Thus, nickel halides NiX_2 (X = Cl, Br, or I), sodium tetraphenylborate, and the ligand form the complexes $[NiLX][BPh_4]$, where L = the (arsinophenyl)bismuthine. The ^1H NMR spectra of these compounds suggest that the nickel is square-pyramidal, with three As–Ni bonds and one Bi–Ni bond. Another complex prepared is $[Ni_2L_3][ClO_4]_4$, but this complex does not contain a Bi–Ni bond.

In addition to tris(*o*-(dimethylarsino)phenyl)bismuthine, Levason and co-workers[29] have also prepared tris(3-(dimethylarsino)propyl)bismuthine, which forms two nickel complexes $[NiL(OH)_2][ClO_4]_2$ and $[NiL(OH)_2][BF_4]_2$. Both of these complexes have trigonal-bipyramidal geometry around the nickel. In addition to nickel, cobalt forms a complex $[CoLBr][BPh_4]$ where L is the bismuthine $(o\text{-}Me_2AsC_6H_4)_3Bi$. Another coordination compound of cobalt is $Co(MeCSCHCSMe)_2\cdot BiPh_3$, prepared from bis(dithioacetylacetonato)cobalt(II) and triphenylbismuthine.[186] It is a crystalline compound which gives excellent elemental analyses. One iridium complex of triphenylbismuthine, namely $[Ph_3BiIr(Ph_3P)_2CO]ClO_4$, is known.[187] It is prepared from $(Ph_3P)_2Ir(CO)OClO_3$ and Ph_3Bi. Two complexes of niobium, $NbCl_5\cdot BiPh_3$ and $2NbCl_5\cdot BiPh_3$, are known.[188] The former is formed from the reactants in hexane or cyclohexane solution, whereas the latter complex is obtained in benzene solution. No physical properties of these complexes are listed.

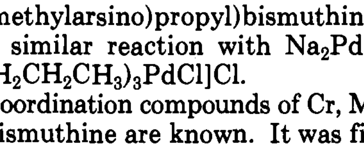
No coordination compounds of platinum or palladium and tertiary bismuthines are known. When tris(*o*-(dimethylarsino)phenyl)bismuthine reacts with sodium tetrachloropalladate(II) in 1-butanol solution, metallic bismuth is formed, although there is evidence for the intermediate formation of a complex with a Bi–Pd bond.[189] The following reaction sequence is suggested to explain the results:

$$Na_2PdCl_4 + (o\text{-}Me_2AsC_6H_4)_3Bi \xrightarrow{BuOH} [(o\text{-}Me_2AsC_6H_4)_3Bi\cdot PdCl]Cl \xrightarrow{\text{rapidly}} [(o\text{-}Me_2AsC_6H_4)_3PdCl]Cl + Bi$$

Tris(3-(dimethylarsino)propyl)bismuthine appears to undergo a similar reaction with Na_2PdCl_4 to yield $[(Me_2AsCH_2CH_2CH_3)_3PdCl]Cl$.

Several coordination compounds of Cr, Mo, or W and triphenylbismuthine are known. It was first reported that molybdenum hexacarbonyl reacts with Ph_3Bi with displacement of only one carbon monoxide moiety.[175] This is in contrast to Ph_3Sb which forms both $(CO)_5MoSbPh_3$ and *cis*-$(CO)_4Mo(SbPh_3)_2$. The bismuth compound was not isolated and was characterized only by its IR spectrum in solution. Crystalline complexes, $Ph_3BiM(CO)_5$, where M = Cr, Mo, or W, were later prepared, however, from the corresponding group 6B hexacarbonyls and Ph_3Bi by UV irradiation of the reactants in benzene solution.[190] The complexes are air stable and possess definite melting points, but decompose rapidly in solution. The molybdenum complex is the least stable, and the previously reported[175] IR spectrum of this compound in solution is the spectrum of decomposition products.

One coordination compound of uranium and triphenylbismuthine is known.[191] This possesses the structure



It is prepared by the reaction between Ph_3Bi and $UCl_5\cdot Cl_2C{=}CClCOCl$. The complex is a pale green solid which decomposes on heating and appears to be a 1:1 electrolyte in nitromethane solution.

A study of donor–acceptor complexes between oxygen and tri- and tetraphenyl compounds of groups 5A and 4A has been made by Razuvaev and co-workers.[192,193] The compounds studied were of the type Ph_4E where E is C, Si, Ge, Sn, or Pb, and Ph_3E, where E is N, P, As, Sb, or Bi. The luminescence spectra of these compounds in *n*-hexane solution was first obtained at 77 K. The solutions were then alternately frozen and unfrozen while being evacuated at 10^{-4} torr, after which the spectra were again obtained. There was a marked increase in the intensity of the spectrum during this procedure which was reversed by the addition of oxygen. The results suggested the reversible formation of a complex between oxygen and the group 4 or group 5 compound. The bimolecular quenching obeyed the Stern–Volmer equation:

$$I_p/I_p^{O_2} = 1 + K_q[O_2]$$

where K_q is the quenching constant. With the group 5 compounds, values for the constant decreased markedly in going from Ph_3N to Ph_3P and then increased slowly in the sequence $Ph_3P < Ph_3As < Ph_3Sb < Ph_3Bi$. The variation in K_q for the last four compounds was attributed to the amount of d_π–p_π interaction between the heteroatom and the phenyl rings. This interaction was absent in Ph_3N and decreased in the sequence P > As > Sb > Bi.

In a discussion of the effect of various solvents on complex formation between a ligand and a metal ion, Ahrland[194] has pointed out that dimethyl sulfoxide is an excellent solvent for phosphines, arsines, stibines, and bismuthines and for their complexes with various metal ions. By thermodynamic measurements in dimethyl sulfoxide the relative affinities of donor ligands with Cu(I), Ag(I), and Hg(II) is in the order N << P > As > Sb > Bi.

C. Physical Properties

1. Spectra

The IR spectra of Me_3Bi, Me_2BiCF_3, and $MeBi(CF_3)_2$ have been determined between 700 and 4000 cm^{-1}.[26] With two exceptions all bands are assigned to C–H or C–F vibrations; weak bands in the 1253–1262- and 907–915-cm^{-1} regions are tentatively assigned to the first overtones of the asymmetric and symmetric Bi–C stretching frequencies, respectively. The IR spectra of the following tertiary bismuthines in the 700–4000-cm^{-1} region are also listed: $Me_2BiC_2F_5$, $MeBi(C_2F_5)_2$, $Me_2BiC_3F_7$, $MeBi(C_3F_7)_2$, Et_2BiCF_3, and $EtBi(CF_3)_2$. No assignments of bands associated with any Bi–C mode are given.[26] Limited IR data for $(CF_2{=}CF)_3Bi$[195] and the cis and trans isomers of $(MeCH{=}CH)_3Bi$[38] are reported, but no Bi–C modes are given. The Raman spectrum of Me_3Bi has been reported by Pai.[196] Extraordinary precautions were taken to obtain pure samples of this spontaneously inflammable and photosensitive liquid. Two very strong broad lines at 460 and 171 cm^{-1} are the only lines found in the low-frequency region of the spectrum. Pai concludes from his data that the molecule is pyramidal (C_{3v} symmetry), with the bismuth at the apex of the pyramid. If the molecule is pyramidal, there should be two stretching modes and two bending modes, all of which are Raman active. These four lines are indeed found in the Raman spectra of Me_3N, Me_3P, and Me_3As, but only two strong lines are found in the low-frequency portion of the spectra of Me_3Bi and Me_3Sb. The reason for this observation is discussed in considerable detail by Rosenbaum and co-workers,[197] by Kohlrausch,[198] and by Maslowsky.[199] Rosenbaum and co-workers conclude that the line at 460 cm^{-1} represents the two bending modes and the line at 171 cm^{-1} represents the two stretching modes for Me_3Bi. Two similar lines occur at 513 and 188 cm^{-1} for Me_3Sb.[200] Such degeneracy will occur as the mass of the central atom becomes very large and as the angle between the edge of the pyramid and its symmetry axis approaches 54° 44′. In Me_3Bi this angle is 57°, and in Me_3Sb, 58°. The existence of only two lines in the spectra of these two compounds, then, is a consequence of this accidental degeneracy leading to a superposition of two pairs of lines. Maslowsky[199] offers a similar explanation but also suggests that the intensities of the missing bands may be too low to be detected. He terms such nonplanar molecules, the vibrational spectra of which appear to be governed by planar selection rules, "pseudoplanar". Another tertiary bismuthine containing the methyl–bismuth bond is Me_2BiCp, where Cp = the cyclopentadienyl group.[100] The compound is too unstable to allow a Raman spectrum to be obtained, but an IR spectrum is reported. A single strong peak at 450 cm^{-1} is assigned to a degenerate ν_s/ν_{as} mode. The cyclopentadienyl portion of the spectrum resembles the spectrum of cyclopentadiene itself, and, therefore, this group is believed to be σ bonded to the bismuth atom.

Force constants of the Bi–C bond have been calculated from Pai's Raman data.[197,201,202] Thus Siebert[202] calculates values of 1.82×10^5 and 0.120×10^5 dyn/cm for the stretching and bending force constants, respectively.

Plots of the rocking (δ_{CH_3}) frequency and the symmetrical deformation (γ_{CH_3}) frequency of the methyl group against the parameter log ($\chi_X\gamma_{CX}{}^2$), where χ is the electronegativity of a group 5A, 6A, or 7A element (X) and γ_{CX} is the bond length of the C–X bond, give two straight lines.[203] The coordinates for Me_3Bi agree well with those for other group 5, 6, and 7 elements.

The Raman spectrum of Et_3Bi has been reported by Jackson and Nielsen[204] and assignments of various frequencies made. The irradiation was carried out with intense 4358-Å mercury light at low temperatures so that photochemical decomposition was negligible. A barely resolved triplet of three strong absorption lines is observed at ~440, ~450, and ~460 cm^{-1} and assigned to Bi–C stretching frequencies. Except for these three absorption lines, the spectrum is almost identical with that of tetramethyllead. Very weak lines at ~124, ~160, and 213 cm^{-1} are assigned to C–Bi–C bending, Bi–C–C torsion, and Bi–C–C bending frequencies, respectively. Maslowsky,[199] in his review article on vibrational spectra of the group 5 elements, comments on the Raman spectra of Et_3Bi. He assumes, as in the case of Me_3Bi, that the symmetric and asymmetric stretching frequencies are degenerate and that they occur at 450 cm^{-1}. The IR and Raman spectra of $(Me_3C)_3Bi$ have also been reported.[28] In the IR spectrum no bands below 748 cm^{-1} are reported, and no assignments of bands to any Bi–C modes are made. In the Raman spectrum a band at 487 cm^{-1} is assigned to ν_{Bi-C_3}; two bands at 221 and 120 cm^{-1} are assigned to $\delta_{CC_3} + \delta_{BiC_3}$.

Tri(cyclopentadienyl)bismuthine is known to occur in two different crystalline forms, an orange-red form obtained from sodium cyclopentadienide and $BiCl_3$ at low temperatures and a black form obtained when the orange-red form is allowed to stand at 15–20 °C.[51] Crystallization of the black form from hexane at −78 °C again yields the orange-red form. The IR spectra of both modifications are known. The occurrence of a single band in the far IR at 188 cm^{-1} for the orange-red modification but two bands at 238 and 182 cm^{-1} for the black modification has led to the suggestion[205] that the black modification contains only Bi–C π bonds whereas the orange-red modification exists as a rapid equilibrium mixture of a π-bonded and a σ-bonded form.

The pioneering investigations of Whiffen[206] on the vibrational spectra of halobenzenes laid the foundation for the interpretation of the vibrational spectra of heavy elements attached to an aromatic ring. According to Whiffen there are six X-sensitive bands (where X is the heavy element), designated q, r, t, y, u, and x. The q, r, and t bands contain contributions from phenyl–X stretching modes as well as phenyl ring modes. Similarly the y, u, and x bands contain contributions from phenyl–X bending modes. Recent workers who have studied the vibrational spectra of Ph_3Bi have used Whiffen's nomenclature to assign the various frequencies observed. Shobatake and co-workers[207] have reported the IR and Raman spectra of Ph_3Bi, both in benzene solution and as Nujol mulls (as well as similar data for Ph_3P, Ph_3As, and Ph_3Sb). They also performed an approximate coordinate analysis, and they assigned frequencies to the y, t, x, and u X-sensitive modes. In benzene solution the t-vibration, which is the principal phenyl–heavy element stretching vibration, is assigned to strong bands at 237 and 220 cm^{-1} in the IR spectrum and to a medium-polarized band at 237 cm^{-1} and a depolarized band (shoulder) at 219 cm^{-1} in the Raman spectrum. The u vibration, the principal phenyl–heavy element bending mode, is assigned to a medium band at 157 cm^{-1} in the IR spectrum and a broad depolarized band at 155 cm^{-1} in the Raman spectrum. In the solid state the IR and Raman spectra are more complicated, and conclusions as to the structure of Ph_3Bi are deduced from the solution spectra. An independent vibrational spectral investigation by Parrett[208] assigns frequencies to the q, r, t, y, u, and x X-sensitive vibrations. In apparent agreement with Shobatake and co-workers, Parrett assigns the t-vibration to modes at 235 and 225 cm^{-1} in the IR spectrum and to modes at 236 and 223 cm^{-1} in the Raman spectrum. The u vibration, however, is assigned to a medium band at 216 cm^{-1} and a shoulder at 199 cm^{-1} in the IR spectrum and a strong band at 210 cm^{-1} and a shoulder at 201 cm^{-1} in the Raman spectrum. Assignments for the y vibration are similar in the two investigations, but assignments for the x vibration differ.

Shobatake and co-workers[207] conclude, on the basis of their spectral data, that triphenylbismuthine possesses either C_3 or C_{3v} symmetry. These two point groups cannot be distinguished by means of the observed spectral data, although they favor C_{3v} symmetry. A comparison of the stretching and bending modes (t and u) with those calculated on the basis of C_{3v} symmetry gave excellent agreement between observed and calculated values. Thus, four C_{3v} symmetry vibrational modes should occur, at 218, 240, 159 and 150 cm^{-1}. In the Raman spectrum bands are observed at 219, 237, and 155 cm^{-1}, and in the IR spectrum at 220, 237, and 157 cm^{-1}. The authors[207] have also calculated Urey–Bradley force constants (stretching, bending, and repulsive) with values of 1.37, 0.24, and 0.40 mdyn/Å, respectively. The stretching force constants for the compounds Ph_3P, Ph_3As, and Ph_3Sb are 1.90, 1.82, and 1.65 mdyn/Å, and it is seen that there is a progressive decrease in this force constant in descending the periodic table. The authors point out that this is a consequence of the weakening of the Ph–E bond and weakening of repulsions between the phenyl rings in going from phosphorus to bismuth. There have been several other papers on the vibrational spectra of Ph_3Bi,[209–214] but the papers by Shobatake and co-workers[207] and by Parrett,[208] as well as the review paper by Maslowsky,[199] are by far the most comprehensive and informative.

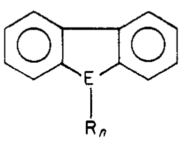
The Raman and IR spectra of the *m*- and (p-$XC_6H_4)_3E$ compounds, where E = P, As, Sb, or Bi and X = F or Cl, have been determined by De Ketelaere and Van der Kelen.[215] Assignments for all observed frequencies are made using the numbering system proposed by Varšanyi for substituted benzene derivatives.[216] Since four group 5A elements are used, the various modes that are X sensitive to the element are easily seen. On the other hand, the *p*-F, *p*-Cl, *m*-F, and *m*-Cl bands are remarkably insensitive to the nature of either X or E. The IR spectrum of $(C_6F_5)_3Bi$ has been reported in the range 4000–700 cm^{-1}, but no assignment of bands has been made.[217] The IR spectrum of 1,4-phenylenebis(diphenylbismuthine) has been reported and assignments of the bands have been suggested.[41]

The only trialkylbismuthine whose UV spectrum is reported is Me_3Bi.[218] It exhibits broad absorption in the far-UV region with a maximum at 211.5 nm (ϵ 1.65 $\times 10^4$ L mol^{-1} cm^{-1}) and shoulders at 222.5 (ϵ 1.4 $\times 10^4$) and 260.0 nm (ϵ 2.4 $\times 10^3$).

The UV spectrum of triphenylbismuthine has been reported by several authors.[209,210,219] Triphenylphosphine, -arsine, and -stibine all show a maximum near 250 nm and strong end absorption. By contrast triphenylbismuthine does not show a maximum near 250 nm, but does show two inflection points, one at 248 nm and another at 280 nm.[210,219] Jaffé[219] has suggested that the peaks near 250 nm arise from electron transitions that are delocalized over the entire molecule, i.e., the three phenyl groups are conjugated with one another, while the shoulder at 280 nm represents an $n \rightarrow \pi^*$ transition. Rao and co-workers[210] assign bands at 248, 255, and 281.5 nm for Ph_3As, Ph_3Sb, and Ph_3Bi to the B band of benzenee ($\pi \rightarrow \pi^*$ transition) and the band at 248 nm for triphenylbismuthine to the dissociation process. Other authors believe that they have detected weak bands at 281.7 nm for Ph_3P[220] and at 261, 267, and 273 nm for Ph_3As[221] which are $\pi \rightarrow \pi^*$ transitions and that the intense bands at 260 nm and 248 nm, respectively, are either $n \rightarrow \pi^*$ or charge-transfer transitions. Borisova and Petrov,[222] who are in agreement with the assignments made by Rao and co-workers,[210] have written a theoretical paper on the electronic structures of the group 5A triphenyl compounds. The simple Hückel MO treatment, the Pople–Sentry method, and a method involving the d orbitals of the central atoms are employed. They conclude that with these compounds both the chemical and the optical properties must be interpreted by two different electronic effects acting in opposite directions. These effects are the electron-donating properties of the lone pair on the central atom vs. the negative inductive σ effect. The latter involves the electron-accepting properties of the empty d orbitals. In their MO treatment the lowest unoccupied level is of a pure π type. However, the inclusion of d orbitals removes the degeneracy of this level. The magnitude of the splitting is proportional to the increase in the d component. Within the series the splitting is most pronounced for Ph_3P, the least is for Ph_3Bi, in accord with the greatest overlap of d orbitals for phosphorus and the least for bismuth. These results are, of course, in accord with the chemical properties of the series Ph_3P to Ph_3Bi.

In two recent papers by Rogozhin and co-workers,[223,224] the assignment of bands in the electronic spectra of group 5 triaryl derivatives made by the earlier workers is disputed. These Russian authors studied the electronic spectra of a number of triaryl compounds of groups 3A, 4A, and 5A as a function of temperature. Whereas there was little effect on either the intensity or position of the long-wavelength bands in the group 4A compounds as the temperature was lowered from 295 to 77 K, there was a marked increase in extinction coefficients and a strong bathrochromic shift of the long-wavelength band for all triaryl compounds of the group 5A elements. The authors believe that these results negate the assignments of Shaw and co-workers[220] and of Jaffé[219] that the bands at 260 nm for Ph_3P and at 280 nm for Ph_3Bi are $n \rightarrow \pi^*$ transitions. Instead these bands should be assigned to πl, π^* transitions for two different conformations of the molecules. Furthermore, they suggest that their temperature-dependent spectral findings are caused by a pyramidal form of the molecule which exists at 295 K and a more nearly planar form which exists at 77 K. These conclusions are strengthened by the findings reported in the earlier paper[223] of differences in the electronic spectra at different concentrations in solution and also by the magnitude of the S,T splitting. The bismuth compounds studied in these investigations are Ph_3Bi, $(2,4,6\text{-}Me_3C_6H_2)_3Bi$, and $(\alpha\text{-}C_{10}H_7)_3Bi$.

The latest paper[225] from the Russian group concerns the electronic spectra of fluorene-type compounds (where E is a group 4A or group 5A element or an oxygen or sulfur atom, R is Me, Et, or Ph, and n is 0, 1, or 2):



For the bismuth compound included in this study, R = Ph and n = 1. Two transitions were found in the long-wavelength portion of the spectrum, the shorter of which was more sensitive to the nature of the heteroatom. The intensities of the fluorescence and phosphorescence bands are listed for all of the compounds investigated.

In a paper devoted principally to the crystal structure of $(p\text{-}MeC_6H_4)_3Sb$, Sobolev and co-workers[226] comment on the progressive decrease in the C–E–C angles (E = N, P, As, Sb, and Bi), the increase in the covalent radii of the heteroatom, and the hypsochromic shift in the long-wavelength band of the UV spectra (N, 297 nm; P, 261 nm; As, 248 nm; Sb, 256 nm; and Bi, 248 nm) of the triaryl derivatives of the group 5A elements and conclude that all three of these factors indicate a decrease in the $p_\pi\text{–}d_\pi$ overlap and an increase in the s character of the lone pair in going from nitrogen to bismuth. The UV spectrum of 1,4-phenylenebis(diphenylbismuthine) is remarkably similar to the spectrum of triphenylbismuthine itself.[41]

The ^1H NMR spectrum of trimethylbismuthine was first reported by Allred and co-workers in two papers dealing with the electronegativities of various elements.[227,228] The spectrum was measured at several concentrations in isopentane solution with water as an external standard. There appears to be a linear relationship between the chemical shift and the electronegativity of the central atom in organometallic compounds. Somewhat later, Kostyanovskii and co-workers[229] reported on the ^1H NMR spectrum of trimethylbismuthine. In CCl_4 solution the δ value is 1.08 ppm (Me_4Si as the standard). These authors also report a linear dependence of the δ_{Me} value with the electronegativity of the central atom in going from Me_3N to Me_3Bi, expressed by the equation $\chi = 1.03\delta + 0.797$, where χ = the electronegativity of the central atom. The ^1H NMR spectrum of Me_2BiCp (Cp is cyclopentadienyl) has also been reported.[100] The δ_{Me} value is 0.85 ppm and the δ_{Cp} value is 5.98 ppm. Chemical shifts of two diazo-substituted methyl-containing tertiary bismuthines are reported by Krommes and Lorberth.[230] The δ value for the Me_2Bi protons of $(Me_2Bi)_2CN_2$ is 1.00 and of $Me_2BiC(N_2)CO_2Et$ is 0.92. The only other reported ^1H NMR spectrum of a trialkylbismuthine is of $(Me_3C)_3Bi$, which gives a value of δ = 1.8.[28]

The ^1H NMR spectrum of triphenylbismuthine in CCl_4 solution gives δ values for the ortho and meta hydrogens of 7.7 and 7.4 ppm, respectively (the values were actually reported in τ units).[231] Also reported are the chemical shifts for the aryl protons in a number of substituted triphenylbismuthines, namely p-Me, p-OMe, p-Cl, p-Br, $p\text{-}SO_2NH_2$, o-Me, m-Me, and a dimethyl compound, presumably $2,4\text{-}Me_2$. The δ values (actually τ values) did not differ significantly from those reported for triphenylbismuthine, and for p-Br, $p\text{-}SO_2NH_2$, o-Me, m-Me, and $2,4\text{-}Me_2$, only one phenyl signal is reported. Also reported are the δ_{Me} values for those compounds containing methyl groups. The δ value for the phenyl para hydrogen of Ph_3Bi in $CHCl_3$ solution is 7.39 ppm.[232] The δ values for the protons ortho and meta to the bismuth atom in $(p\text{-}MeC_6H_4)_3Bi$ in dimethyl sulfoxide solution are 7.60 and 7.18, respectively.[164] The δ values for the protons ortho and meta to the bismuth atom in $(p\text{-}FC_6H_4)_3Bi$ are 7.64 and 7.00, respectively.[25] Because of the fluorine atom this compound gives an AA′XX′ spectral pattern for the ring protons.

The only ^{19}F NMR spectrum for a fluorine-substituted aliphatic bismuthine is for $(CF_3)_3Bi$ where the chemical shift is reported as −45.9 ppm (downfield from CF_3CO_2H).[89] The ^{19}F NMR spectrum of $(C_6F_5)_3Bi$ gives δ values of 118.4, 149.7, and 158.8 for the o-, p-, and m-F substituents, respectively.[217] The reference standard is not given, but it is presumably $CFCl_3$, and the shifts are presumably upfield. Chemical shifts for the ^{19}F NMR spectra of $(p\text{-}FC_6H_4)_3Bi$ in CCl_4 and in benzene solution and for $(m\text{-}FC_6H_4)_3Bi$ in CCl_4, benzene, and acetone solutions are reported by De Ketelaere and co-workers.[25] The δ values, referred to $CFCl_3$, are all negative (lower frequency, upfield shift). Thus the δ value for $(p\text{-}FC_6H_4)_3Bi$ is −113 and for $(m\text{-}FC_6H_4)_3Bi$ is −111.8, both measured in CCl_4 solution. The ^{19}F–H coupling constants for protons ortho and meta to the fluorine varied between 5.6 and 9.1 Hz.

Nesmeyanov and co-workers[35] have reported the ^{19}F spectra of m- and $(p\text{-}FC_6H_4)_3Bi$ and of m- and $p\text{-}FC_6H_4BiPh_2$ in cyclohexane, $CHCl_3$, and pyridine solution and of $p\text{-}FC_6H_4BiPh_2$ in anisole and phenol solution. The ^{19}F chemical shifts are reported relative to fluorobenzene. There are only slight differences in chemical shifts in all of the solvents under investigation. From the slight differences of chemical shifts for $(m\text{-}FC_6H_4)_3Bi$ and $(p\text{-}FC_6H_4)_3Bi$ in cyclohexane, chloroform, and pyridine, it is concluded that Bi (as well as Sb) does not coordinate to the molecules of strongly coordinating solvents (pyridine) despite the presence of vacant d orbitals in these elements. The extremely small differences in the chemical shifts of $p\text{-}FC_6H_4BiPh_2$ in cyclohexane, anisole, and phenol suggest that Bi (as well as Sb) is a poor proton-accepting atom. The poor donor ability of the triaryl derivatives of Sb and Bi is attributed to the strong s character of the lone pair in these compounds. A comparison of the ^{19}F chemical shifts of *m*- and $(p\text{-}FC_6H_4)_3Bi$ with the shifts for *m*- and $p\text{-}FC_6H_4BiPh_2$ (as well as for the corresponding Sb compounds) leads to the conclusion that both the $m\text{-}FC_6H_4$ and $p\text{-}FC_6H_4$ groups are slightly electron withdrawing as compared with phenyl groups. That this effect is mainly inductive in nature is shown by the use of Taft σ_I and $\sigma_R{}^\circ$ constants for the ^{19}F chemical shifts. The small $\sigma_R{}^\circ$ values for the Ph_2Sb and Ph_2Bi groups and the negative signs for substituent constants indicate the absence of any noticeable electron-withdrawing effect due to d_π–p_π interaction between π orbitals of the rings and vacant d orbitals of the two metals. The study was later extended by Pombrik and coauthors[36,233] by studying the ^{19}F chemical shifts of compounds of the type $p\text{-}FC_6H_4EAr_2$, where E is Bi, Sb, N, or CH and Ar is phenyl or a substituted phenyl. The ^{19}F chemical shifts of the compounds where E is Sb, Bi or CH correlate well with the polar constants ($\Sigma\sigma^\circ$ and $\Sigma\sigma$) of the various substituents on the phenyl rings (e.g., $p\text{-}NMe_2$, *p*-OMe, *p*-Me, *p*-Cl, *m*-Cl, *p*-F, 3,4-Cl_2, and 3,4,5-Cl_3). This suggests that the electronic effects are predominately inductive in nature, in contrast to the compounds where E is N, where there is a significant resonance effect. The slopes of the lines (ρ) for the chemical shift correlations vs. $E\sigma^\circ$ for the substituents where E is CH and E is Bi are essentially identical; i.e., there is no increase in electron transmission in bismuth-bridged systems as compared with carbon-bridged systems.

Only a few ^{13}C NMR studies of tertiary bismuthines are reported. The δ value for the methyl carbons in the diazo compound $Me_2BiC(N_2)CO_2Et$ occurs at 11.93, and for the other carbon attached to bismuth it is 26.3.[230] These are apparently the only ^{13}C NMR values reported to date for an aliphatic tertiary bismuthine. The δ values are for Me_4Si as the standard. The δ values for the ortho, meta, and para carbons of Ph_3Bi are reported as 10.1, 0.3, and 3.0 ppm.[232] These values are referred to benzene as the standard and are downfield with respect to the carbons of benzene. A chemical shift value for the carbon attached to bismuth could not be found in this study. A later paper[173] reports δ values of 138.33, 131.26, and 128.52 (downfield from Me_4Si) for the ortho, meta, and para carbons and a value of −0.12 for the carbon attached to bismuth. It is suggested that this negative value shows an electron release by p_π–p_π conjugation from the bismuth (as well as for As and Sb) toward the phenyl ring.

The NQR spectrum of triphenylbismuthine has also been reported.[234] Since the bismuth atom has a spin of $^9/_2$, the NQR spectrum should consist of four lines; all of these are observed as follows (MHz): $\nu_1 = 29.785$, $\nu_2 = 55.214$, $\nu_3 = 83.516$, and $\nu_4 = 111.438$, where ν_1 corresponds to the transition $\pm^1/_2 \leftrightarrow \pm^3/_2$, ν_2 to the transition $\pm^3/_2 \leftrightarrow \pm^5/_2$, etc. The quadrupole coupling constant eQq_{zz} is 669.06 ± 0.13 MHz. This rather large value reveals that the bismuth bonds have significant s character since pure p bonds would lead to a vanishing field gradient q_{zz}. The authors then calculate from the data that the bismuth bonds possess approximately 8–9% s character. There is a fairly large asymmetry of the field gradient ($\eta = \sim 9\%$) which the authors[234] suggest is due to bond strains for a bulky molecule such as Ph_3Bi in the crystalline state. For pure C_{3v} symmetry this parameter should be zero.

Two other papers dealing with the NQR spectra of triarylbismuthines have appeared. Petrov and coworkers[235] report on the resonance frequencies, the quadrupole coupling constants eQq_{zz}, and the asymmetry parameters (η, %) of triphenylbismuthine and a series of substituted triphenylbismuthines. The experiments were carried out at 77 K and at room temperature. The compounds studied in addition to Ph_3Bi were the *o*-Me, *p*-Me, *m*-Me, *p*-Cl, and *p*-Br derivatives. The NQR resonance frequencies do not differ significantly from each other, the quadrupole coupling constants are similar, and the asymmetry parameters vary only between 4.0 and 8.75%. From these results the authors conclude that the planar structure of Ph_3Bi is unchanged in these substituted triphenylbismuthines. The assumption, however, that Ph_3Bi is planar is based on earlier and incorrect X-ray diffraction data (cf. section IIIC2). Finally, Van der Kelen and De Ketelaere[236] report on the NQR spectra of Ph_3Bi and three substituted phenyl derivatives, *p*-F, *p*-Cl, and *m*-Cl. A number of similarly substituted triarylphosphines, -arsines, and -stibines are also included in this study, and chlorine resonances as well as those for the central atoms, Bi, As, and Sb, are given. It was hoped that the NQR frequencies would yield information about the polarity of the C–E bonds in the molecules $(m\text{-}XC_6H_4)_3E$ and $(p\text{-}XC_6H_4)_3E$ (where X is F or Cl, E is ^{75}As, $^{121}Sb/^{123}Sb$, or ^{209}Bi) and that the ^{35}Cl frequencies might shed light on simultaneous inductive and mesomeric electron shifts and thus the extent of p_π–d_π bonding in the C–E bond. The results, however, were hardly definitive. It is concluded that the ionic character of the C–Cl bond increases in the *m*- and *p*-Cl-substituted triaryl derivatives in the sequence $P \simeq As < Sb < Bi$, an order which more or less parallels the order of decreasing electronegativity. Hammett meta and para σ values for the E group in the compounds *m*- and $(p\text{-}XC_6H_4)_3E$ were calculated from the data on the basis that ^{35}Cl NQR values are a measure of Hammett σ values. The values of *m*-E, where E is P, As, Sb, or Bi, are 0.15, 0.09, −0.01, and −0.19, respectively; the values of *p*-E are 0.29, 0.29, 0.02, and −0.06, respectively.

There are relatively few papers on the mass spectra of aliphatic tertiary bismuthines. In a short article on the fragmentation of trimethyl derivatives of the group 5A elements, nitrogen to bismuth, Kostyanovskii and Yakshin[237] list, in tabular form, the percentages of the various fragments relative to Me_3E^+ as 100%. Thus, with Me_3Bi these percentages are as follows: $Me_2BiCH_2^+$, 2.5%; Me_2Bi^+, 190%; $MeBi^+$, 156%; Bi^+, 230%; CH_2Bi^+, 18%. Fragmentation pathways, confirmed by metstable peaks, are suggested for Me_3P, Me_3As, and Me_3Sb, but not for Me_3Bi. Metastable peaks for the transitions $Me_3Bi^+ \rightarrow Me_2Bi^+$ and $Me_2Bi^+ \rightarrow Bi^+$ are found, however. A second paper[238] from the same laboratory gives the relative intensities of the ion fragments (as diagrams) for the compounds Me_3Bi, Et_3Bi, and Pr_3Bi. Thus, for Me_3Bi the base peak is Bi^+, and other fragments are (with approximate relative intensities) $MeBi^+$, 85%; Me_2Bi^+, 70%; and Me_3Bi^+, 50%. These values are reported at 30 eV. Metastable peaks are reported for the transitions $Me_3Bi^+ \rightarrow Me_2Bi^+$, $Me_3Bi^+ \rightarrow MeBi^+$, $Me_2Bi^+ \rightarrow MeBi^+$, and $MeBi^+ \rightarrow Bi^+$. The spectrum of Pr_3Bi is recorded at 12 and 30 eV. At 12 eV the base peak is the molecular ion, and other fragments are reported as Pr_2Bi^+, 95%; $PrBiH^+$, 40%; and Bi^+, 90%. No metastable peaks are reported for any of these transitions. For this same compound at 30 eV the base peak is Bi^+ and fragments are reported as $PrBi^+$, 15%; $PrBiH^+$, 40%; Pr_2Bi^+, 35%; and Pr_3Bi^+, 10%. There is a metstable peak for the transition $PrBi^+ \rightarrow Bi^+$. The authors comment on the fact that in Me_3N the base peak is $Me_2NCH_2^+$ (α cleavage) whereas this peak is small for Me_3P and essentially absent for Me_3As, Me_3Sb, and Me_3Bi. This result they attribute to an increase in the configurational stability of the element and a decrease in the ability to stabilize the ion $Me_2ECH_2^+$. The authors also comment that the main fragmentation path for ethyl derivatives of P, As, Sb, and Bi consists of elimination of ethylene via a four-membered transition state. While their data suggest that this is the case with Et_3P, Et_3As, and Et_3Sb, there is only a very small peak at m/e 268 in the mass spectrum of Et_3Bi corresponding to the loss of C_2H_4, while there is a large peak at m/e 267 corresponding to the loss of an ethyl group. There is a peak, however, at m/e 239 corresponding to the loss of C_2H_4 from Et_2Bi^+, and a metastable peak for the loss of C_2H_4 and H_2 from $EtBiH^+$ to give Bi^+. Another paper[239] on the mass spectra of ethyl derivatives of group 5A elements from the same laboratory includes the mass spectrum of Et_3Bi, but does not add new information on this compound.

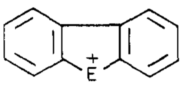
The mass spectrum of $(CF_3)_3Bi$ is reported by Morrison and Lagow.[89] The base peak is Bi^+ and the molecular ion is 6.8% of the base peak. Metastable peaks are found corresponding to the following transitions:

$$Bi(CF_3)_3^+ \rightarrow Bi(CF_3)_2^+ + CF_3$$

$$Bi(CF_3)_2^+ \rightarrow BiF_2^+ + C_2F_4$$

$$BiCF_3^+ \rightarrow Bi^+ + CF_3$$

Although several authors have reported peaks in the mass spectrum of triphenylbismuthine,[240-243] the first detailed report on the mass spectrum of this compound is by Bowie and Nussey.[244] These authors report that the base peak at 70 eV is Bi^+, and the relative abundance of some other ions are $M - C_{12}H_{10}$, 91%; M − Ph, 6%; M − (Ph + Bi), 4%; M^+, 0.1%. Loss of $C_{12}H_{10}$ from the molecular ion, loss of $C_{12}H_{10}$ from Ph_2Bi^+, and loss of Ph from $PhBi^+$ are supported by metastable peaks. The negative ion spectrum of Ph_3Bi is also reported. Here the base peak is M − Ph and other peaks as percentage of the base peak are [M − (Ph· + Ph·)], 25%; [M − (Ph· + Ph· + H_2)], 4%; [M − Ph· − H_2], 2%; and $M^{-}\cdot$, 1%. There is a difference in the mass spectrum of Ph_3Bi as compared with Ph_3P, Ph_3As, and Ph_3Sb, in that with the latter three compounds the ion Ph_2E^+ loses two hydrogen atoms to form the fragment



This process does not occur with Ph_3Bi. This difference was first pointed out by Zeeh and Thomson.[242] In the negative ion spectrum of Ph_3Bi, however, there is a peak corresponding to the transition [M − Ph· − H_2]. This peak constitutes only 2% of the base peak, whereas in Ph_3P, Ph_3As, and Ph_3Sb, this peak constitutes 68%, 25%, and 8% of the base peak, respectively. The mass spectrum of Ph_3Bi is also reported by Hellwinkel and co-workers.[245] Only four peaks for fragments containing bismuth are reported. The base peak is Bi^+ (47.6% of the total ion current); other peaks are $PhBi^+$, 41%; Ph_2Bi^+, 1.1%; Ph_3Bi^+, 0.5%. Some of the postulated transitions are supported by metastable peaks. The mass spectrum of Ph_3Bi is also reported by Spalding[246] who, in contrast to all of the previous workers, reports the base peak (at 70 eV) as $PhBi^+$. He incorrectly states that this result is in agreement with the earlier work of Bowie and Nussey.[244] The relative values of the various fragments (as percentage of the total ion current) are Ph_3Bi^+, trace; Ph_2Bi^+, 0.8; $PhBi^+$, 86.8; Bi^+, 12.4. Spalding also reports on the mass spectra of *o*-, *m*-, and (p-$MeC_6H_4)_3E$ compounds, where E = P, As, Sb, and Bi. As in the case of Ph_3Bi he reports the base peak of all three tolyl compounds to be the $MeC_6H_4Bi^+$ ion. For the ortho, meta, and para compounds the values (as percentage of the total ion current) are 46.4, 56.2, and 60.3, respectively. Corresponding values for the Bi^+ ion are 17.3, 40.3, and 38.4 and for the ion $(MeC_6H_4)_2Bi^+$ they are 18.8, 2.7, and 1.0. The molecular ion constitutes 6.3% of the total ion current for (o-$MeC_6H_4)_3Bi$, but only traces of the corresponding ions are found for the meta and para isomers. Another type of ion found for the three tolyl compounds is $C_7H_6Bi^+$ which constitutes 1.9%, 0.5%, and 0.3% of the total ion current for the ortho, meta, and para isomers, respectively. The $C_6H_4E^+$ ion is not found for Ph_3Bi, but is reported for Ph_3P, Ph_3As, and Ph_3Sb. Another ion, $C_{14}H_{13}Bi^+$, constitutes 9.3% of the total ion current for (o-$MeC_6H_4)_3Bi$, but is only 0.3% for (m-$MeC_6H_4)_3Bi$ and is absent for the para isomer. The proposed fragmentation pathways of the three tolylbismuthines are supported by metastable peaks in most cases. Principal peaks in the mass spectrum of tri-*p*-tolylbismuthine are reported by Deacon and Fallon who, in agreement with Spalding, report the base peak to be p-$MeC_6H_4Bi^+$. These same authors report principal peaks in the mass spectrum of (p-$ClC_6H_4)_3Bi$, namely (p-$ClC_6H_4)_2Bi^+$, p-$ClC_6H_4Bi^+$, and Bi^+, with the last the base peak.

The only other mass spectrum of an aromatic tertiary bismuthine reported is that of 5-phenyl-5*H*-dibenzobismole, reported by Hellwinkel and coauthors.[125] The base peak of the mass spectrum of this compound is [M − Bi]$^+$. The molecular ion is 3.7% of the total ion current, and only two other bismuth-containing fragments are reported, namely [M − Ph]$^+$ and Bi^+. The fragmentation pattern is supported by metastable peaks for several of the pathways suggested.

The X-ray photoelectron spectra (XPS) of a series of phenyl compounds of P, As, Sb, and Bi are reported by Hoste and co-workers.[247] This relatively new technique measures the binding energy E_b of inner electrons as given by

$$E_b = E_{X\text{-ray}} - E_{kin} - \phi_{sp}$$

(where E_{kin} is the kinetic energy of the ejected electron, $E_{X\text{-ray}}$ is the energy of the X-radiation, and ϕ_{sp} is the work function of the spectrometer material). Stec and coauthors[248] had earlier determined the binding energy shifts of 3p and 3d electrons in a series of organic and inorganic arsenic compounds, and the work was later extended to inorganic antimony and bismuth compounds.[249] Hoste and coauthors[247] report the binding energy of the bismuth $5d_{5/2}$ electrons for the two triarylbismuthines, Ph_3Bi and $(p\text{-}MeC_6H_4)_3Bi$, as 25.57 and 25.80 eV, respectively.

2. Molecular Structure by Diffraction Methods

There have been only a few X-ray diffraction studies of tertiary aromatic bismuthines and no corresponding studies of aliphatic bismuthines. There has been, however, an electron diffraction determination of the structure of trimethylbismuthine in the gas phase.[250] The Bi–C distance is 2.267 Å, significantly longer than the Pb–C distance (2.238 Å) in tetramethyllead. Since bismuth is to the right of lead in the periodic table, the expectation would have been that the Bi–C bond would have been slightly shorter than the Pb–C bond. Some calculated bond angles are C–Bi–C 96.7 ± 1.0° and Bi–C–H 107.6 ± 1°.

The first reported X-ray diffraction study of triphenylbismuthine was by Wetzel[251] in 1942. He reported that there was a planar distribution of Bi–C bonds with the plane of the benzene rings inclined at 60° to (010). This early work of Wetzel involved only two-dimensional X-ray diffraction. However, since the results were consistent with the observation that triphenylbismuthine does not possess a dipole moment (cf. section IIIC3), Wetzel's values have been widely quoted in tables of structural parameters, and incorrect conclusions as to the hybridization of the bismuth atom have been reached.[235] Somewhat later, Iveronova and Roitburd[252] reported cell and space group data for triphenylbismuthine. The question of the structure of triphenylbismuthine has been finally settled by the excellent work of Hawley and co-workers. In a preliminary paper[253] the authors point out that there is an inconsistency in Wetzel's reported results, namely, that a projection of the crystal structure is inconsistent with the short *b* axis; i.e., in a diagram of the 5.8-Å projection there are overlapping benzene rings. Hawley and co-workers then report preliminary data for the crystal structure of triphenylbismuthine, assigning it space group *C*2/*c*. They also point out that Iveronova and Roitburd's cell is incorrect for space group *C*2/*c* or *Cc*. In the later full paper[174] they report a three-dimensional crystal structure for triphenylbismuthine. It is monoclinic, space group *C*2/*c*, with eight molecules in the unit cell. Although the molecule is pyramidal, it does not possess overall symmetry due to unequal rotations of the phenyl groups about the Bi–C bonds. The mean Bi–C distance is 2.24 ± 0.02 Å, fairly close (fortuitously) to the distance given by Wetzel and quoted in various tables of crystal structure. The average C–Bi–C bond angle is 94°, which suggests that there is little 6s–6p hybridization.

The crystal structures of two other triarylbismuthines have been recently reported. Trimesitylbismuthine has an average Bi–C bond length of 2.29 Å and a C–Bi–C bond angle of 102°.[254] In the compound $[(CO)_3MnC_5H_4]_3Bi$, where C_5H_4 is a disubstituted cyclopentadiene, the cyclopentadiene rings are planar, and the bismuth atom is only 0.26 Å out of the ring planes.[255]

3. Dipole Moments, Kerr Constants, and Related Physical Properties

There has been only one reported dipole moment for a tertiary alkyl bismuthine, namely tris(perfluorovinyl)bismuthine, with a reported value of 3.99 D.[256] This value is higher than for the corresponding phosphorus, arsenic, and antimony compound, the order being Bi > Sb > As > P. There is no obvious explanation for this phenomenon. The dipole moment of triphenylbismuthine was first reported to be zero in benzene solution, and this compound accordingly was assigned a planar structure.[257] Aroney and co-workers[258] likewise found a dipole moment of zero for triphenylbismuthine, and this value was also given by Smyth.[259] In view of the first X-ray diffraction study, wherein triphenylbismuthine was reported (erroneously) to be planar with C–Bi–C angles of 120° (cf. section IIIC2), these dipole moment results were not unexpected. However, when later X-ray work clearly demonstrated that triphenylbismuthine is pyramidal, it became necessary to explain the dipole moment results. With this in mind Hayes and co-workers[260] determined the dipole moment of tris(*p*-chlorophenyl)bismuthine in benzene solution and obtained a value of 2.6 D. From this dipole moment result and the known dipole moment of chlorobenzene (1.59 D), a C–Bi–C angle of 93° can be calculated for this compound. Since it has been shown by NQR studies[235] that there is little change in configuration about the bismuth atom in triphenylbismuthine and its *p*-chloro and *p*-bromo analogues, this calculation strongly suggests that the zero dipole moment of triphenylbismuthine is due to the fact that each Ph–Bi group is effectively nonpolar. In a similar study Romm and co-workers[261] found that the dipole moment of triphenylbismuthine is essentially zero in the three solvents benzene, cyclohexane, or octane, while tri-*p*-tolylbismuthine possesses a dipole moment of 0.62 D in benzene solution and tris(*p*-bromophenyl)bismuthine a dipole moment of 2.52 D in the same solvent. Arguing from these data, these authors suggest that the zero dipole moment of triphenylbismuthine is due to the mutual compensation of the resultant moments of the three Ph–Bi bonds vs. the moment of the lone pair. In an even more recent paper, Claeys and co-workers[262] report a dipole moment of 0.47 D for triphenylbismuthine. This value is not corrected for atomic polarization as had been done by Aroney and co-workers.[258] Had this correction been applied, Claeys and co-workers would indeed have found a zero dipole moment for this compound. The authors also report values of 2.37, 2.59, and 0.66 D for tris(*p*-fluorophenyl)-, tris(*p*-chlorophenyl)- and tri-*p*-tolylbismuthine, respectively. These values compare with theoretical values of 2.40, 2.60, and 0.60 D, calculated by assuming a C–Bi–C angle of 93°. Dipole moments for two other tertiary aromatic bismuthines, tris(*m*-fluorophenyl)- and tris(*m*-chlorophenyl)bismuthine, were found experimentally to have values of 2.53 and 2.61 D, respectively. From these experimental values and again assuming a C–Bi–C angle of 93°, several conformational parameters for these two molecules were calculated. The dipole moment of tricyclopentadienylbismuthine has been found to be 1.17 D, consistent with the pyramidal structure deduced from the IR spectrum.[51] The dipole moment of 1,4-phenylenebis(diphenylbismuthine) is zero in benzene solution.[41]

In addition to dipole moment studies, Aroney and co-workers[258] report molar Kerr constants for the Ph_3E compounds in benzene solution, where E is P, As, Sb, or Bi. The value for triphenylbismuthine is 7.1×10^{-12}. From the dipole moment and the Kerr constant, an angle of 51 ± 3° is calculated for ϕ, the angle of rotation of the phenyl groups from a conformation ($\phi = 0$) in which the planes of the phenyl groups intersect along the lines of action of the resultant moments. Results in this paper were based on the belief that triphenylbismuthine was a planar molecule. In a later paper[260] a value of $\phi = 44 \pm 1°$ was calculated for tris(*p*-chlorophenyl)bismuthine in benzene solution. The value of ϕ for triphenylbismuthine was believed to be close to 45° in solution; this result was based on an experimental Kerr constant of $(7 \pm 8) \times 10^{-12}$. This value of ϕ differs from the value of 66.5° calculated by Bothorel[263,264] from Rayleigh scattering in cyclohexane.

4. Thermochemical Measurements

There have been several investigations of the heat of combustion of tertiary bismuthines. The earlier investigations employed static bomb calorimeters and are less reliable than the later investigations employing rotating bomb calorimetry. Long and Sackman[265] first determined the heat of formation ($\Delta H_f°$) of liquid trimethylbismuthine. After corrections for the presence of free bismuth metal and carbon in the combustion products, a value for $\Delta H_f°$ of 37.5 kcal/mol at 25 °C was found. From this result a value for the heat of formation of the gaseous species of 45.8 kcal/mol was calculated. By subtracting from this value the heat of formation of three methyl radicals and the heat of atomization of bismuth, a mean dissociation energy (bond energy) for the Bi–C bond of 33.7 kcal/mol was calculated. This value should be contrasted with a value of 44.0 kcal/mol for the bond dissociation energy of the first Bi–C bond obtained from kinetic studies.[266] This result is in line with the general observation that the bond dissociation energy of the first metal–carbon bond is larger than the mean value in organometallic compounds in which the valence of the metal is 2, 3, or 4. The heat of combustion of triethylbismuthine was determined by Lautsch and co-workers,[267,268] again using a static bomb calorimeter, and a value of 23.8 kcal/mol was calculated for the bond energy of the Bi–C bond. The large difference between this value and that of Long and Sackman for the Bi–C bond energy in trimethylbismuthine is surprising and suggests that one or both values are in error. The thermodynamic functions, entropy, heat capacity, free energy function, and enthalpy of trimethylbismuthine have been calculated in 100° steps from 289.15 to 1000 K by use of the rigid rotator–harmonic oscillator approximation,[269] making use of the molecular geometry data of Beagley and McAloon[250] determined by electron diffraction.

The bond energy of the C–Bi bond in trimethylbismuthine is given as 44 kcal/mol in a Russian publication[270] not available to the authors. Birr,[271] who also used a static bomb calorimeter, has determined the heat of combustion of triphenylbismuthine. The bond energy of the Bi–C bond was calculated as 46.8 kcal/mol. Skinner,[272] however, has pointed out errors in Birr's calculations and has recalculated the bond energy and assigned a value of 42.2 kcal/mol. Using slightly different values for the heat of sublimation of bismuth and the heat of formation of methyl radicals, Skinner has also recalculated the bond energy of the Bi–C bond in trimethylbismuthine; his value is 34.1 kcal/mol. The higher bond energy in the phenyl compound compared with the methyl compound was attributed to π bonding between the metal and the benzene rings.

The latest determination of the bond energy of the Bi–C bond in triphenylbismuthine is that of Steele,[273] who used a rotating bomb calorimeter. The author questions the values of the bond energies obtained with static bomb calorimeters for all the compounds of the type Ph_3E, where E is N, P, As, Sb and Bi. His value for the mean gas-phase bond dissociation energy $\langle D \rangle$ (Ph–Bi) was 193.9 ± 10.8 kJ/mol (46.2 kcal/mol). A plot of the mean bond dissociation energy against the period number for the group 5A triphenyl compounds shows a smooth decrease in descending the periodic table from N to Bi, with the exception of triphenylstibine, the value of which Steele believes to be in error. Derived values for the standard molar energy of combustion $\Delta E_c°$, standard molar enthalpy of combustion $\Delta H_c°$, and standard molar enthalpy of formation $\Delta H_f°$ for triphenylbismuthine are 9992.3 ± 5.0, 10003.5 ± 5.0, and 489.7 ± 5.2 kJ/mol, respectively.

5. Other Physical Measurements

All of the unsubstituted trialkylbismuthines are liquids at room temperature. Only trimethylbismuthine can be distilled at atmospheric pressure without decomposition. A few trialkylbismuthines of higher molecular weight, e.g., tribenzylbismuthine (mp 64.5–65.5 °C), substituted tribenzylbismuthines,[31] and all triarylbismuthines, are solids at room temperature. Triphenylbismuthine can be distilled at reduced pressure (bp 242 °C (14 mm), 208 °C (0.07 mm));[274] the pure substance obtained in this manner has been used to determine the atomic weight of bismuth.[274-276] Tertiary bismuthines are not associated. Thus, triphenylbismuthine gives a normal molecular weight cryoscopically in benzene solution.[114,277] Tri-*p*-tolylbismuthine and tri-α-naphthylbismuthine also give normal molecular weights by the same method. Other tertiary bismuthines which give normal molecular weights (cryoscopically in benzene) are tris(*o*-chlorobenzyl)bismuthine,[31] tricyclopentadienylbismuthine,[51] and a series of alkynylbismuthines containing the $Ar_2BiC{\equiv}C$ grouping.[50] The Trouton constant values for the trialkylbismuthines are all normal, indicating that these compounds also are nonassociated.

The vapor pressure of trimethylbismuthine was first determined by Bamford and co-workers[278] in 1946. Their measurements covered the range −10 to +97 °C, and they obtained an extrapolated boiling point of 107.1 °C at 760 torr, a latent heat of vaporization of 8308 cal/mol, and a freezing point of −85.8 °C. Long and

Sackman[279] also measured the vapor pressure of trimethylbismuthine. The temperature range was −25 to +15 °C, and they calculated a normal boiling point of 109.3 °C. Their reported freezing point, however, was −107.7 °C, a value which differs considerably from that of Bamford and co-workers. A third report on the vapor pressure of trimethylbismuthine is that of Amberger.[22] His measurements covered the range −58 to +107 °C, and he calculated a normal boiling point of 108.8 °C and an enthalpy of vaporization of 8.3768 kcal/mol at 107 °C. Vapor pressure measurements on trivinylbismuthine lead to an extrapolated normal boiling point of 158.1 °C.[280,281]

The polarographic half-wave potential of triphenylbismuthine in glyme solution with 10^{-3} M Ag|AgClO$_4$ as the reference electrode has been found to be 3.1 V.[282] The reaction involved is

$$Ph_3Bi + 2e^- \rightarrow Ph_2Bi^- + Ph^-$$

Half-wave potentials for the corresponding phosphorus, arsenic, and antimony compounds are 3.5, 3.4, and 3.3 V, respectively. The protonic basicity (pK_b) of triphenylbismuthine (as well as its nitrogen, phosphorus, arsenic, and antimony analogues) has been measured by a potentiometric method in glacial acetic acid solution.[283] The reaction involved is

$$Ph_3E{\cdot}HOAc \rightleftharpoons Ph_3EH^+ + OAc^-$$

(where E is N, P, As, Sb, or Bi). The pK_b values for the triphenyl compounds of the above elements are 9.20, 10.60, 8.57, 8.76, and 8.81, respectively. The specific conductance of the compounds Ph$_3$E, where E is As, Sb, or Bi, in fluorosulfuric acid has been measured by Paul and co-workers.[284] By comparison of the concentration of these weak bases with that concentration of a fully ionized reference base which gives the same conductance, the degree of ionization could be determined. From these data, values of 10^2K_b for triphenylarsine, -stibine, and -bismuthine are 45.80, 15.86, and 7.88, respectively. As expected, the tertiary bismuthine $(C_6Cl_5)_3Bi$ is a nonelectrolyte in nitromethane solution.[43]

In a series of papers Smith and Andrews have reported the heat capacities of various organic compounds and have reached certain conclusions as to bond energies from the resulting data. In one of these papers, the authors[285] have determined the molal heat capacities of the compounds Ph$_3$E, where E is N, P, As, Sb, or Bi, over a considerable temperature range. While there is a general trend for the heat capacities to increase with increasing atomic weight, there is but little difference between triphenylstibine and triphenylbismuthine. The authors conclude that their data indicate a weakening of the bonding force between the phenyl group and the central atom as the mass of the latter increases.

Forward and co-workers[286] measured the density and surface tension of triphenylbismuthine over a considerable temperature range and found that the parachor (average value = 650.4) and the Kleeman–MacLeod constant ($C = \gamma/(D - d)^4$, where γ = surface tension, D = density of the solid, and d = density of the liquid) do not vary over the temperature range studied. From these results they conclude that triphenylbismuthine is not associated. The atomc parachor of bismuth was calculated to be 80.4 or 85.5, depending upon the value selected for the parachor constant for the phenyl group. The authors also investigated phase equilibria between triphenylbismuthine and each of the compounds triphenylmethane, triphenylamine, triphenylstibine, and tetraphenyltin.

The diamagnetic susceptibility of triphenylbismuthine has been determined by Pascal[287] and by Parab and Desai.[288,289] The latter authors also determined the diamagnetic susceptibility of tri-*p*-tolyl- and tri-*m*-xylylbismuthines and have calculated an average susceptibility of the trivalent bismuth atom of -36.98×10^{-6} cgs units. By comparing their results with those obtained with organoantimony compounds they conclude that the Bi–C bond is more ionic than the Sb–C bond. A gas–liquid chromatographic study of the primary alcohols ROH (where R is Et, Pr, Bu, or $CHF_2(CF_2)_3CH_2$) over squalene containing Ph$_3$P, Ph$_3$As, Ph$_3$Sb, or Ph$_3$Bi has shown that the H-bond strength between the alcohols and the group 5 compound decreased in the order P > As > Sb > Bi.[290] This order was supported by NMR data for complexes formed between the triphenyl compounds and the phenol $2,6\text{-}(Me_3C)_2C_6H_3OH$.

Empirical force-field calculations have been employed for studying the interconversion between various conformers of triaryl compounds that can occur when one or more aryl rings "flip" (i.e., rotate about the bond to the central atom and pass through a plane perpendicular to that formed by the three carbon atoms attached to the central atom).[291] The compounds employed in this study are Ar$_3$B, Ar$_3$N, Ar$_3$P, Ar$_3$As, Ar$_3$Bi, Ar$_3$CH, Ar$_3$SiH, and Ar$_3$GeH, where Ar is mesityl. Four mechanisms are considered for the interconversion, namely a zero-, one-, two-, or three-ring flip. Calculated energies of the idealized transition states point to a two-ring flip mechanism as the pathway of lowest energy over a wide range of structures. The activation energy predicted for trimesitylbismuthine is 3–5 kcal/mol.

Triarylamines and triarylphosphines are known to be efficient quenchers of the triplet state of carbonyl compounds. Although the results are mainly due to physical quenching, in some cases chemical reaction can be detected. The process is believed to involve the exiplex $[R^1R^2COEPh_3]$ (where E is N or P) according to

$$R^1R^2CO + Ph_3E \rightarrow [R^1R^2COEPh_3] \rightarrow R^1R^2CO + Ph_3E$$

The reaction has now been extended to the use of the three triphenyl compounds Ph$_3$As, Ph$_3$Sb, and Ph$_3$Bi.[292] The carbonyl compound used is butyrophenone, the solvent benzene or carbon tetrachloride.

The photolyses of butyrophenone–Ph$_3$Bi mixtures in benzene lead to the precipitation of metallic bismuth. In carbon tetrachloride, a white photosensitive material, believed to be Ph$_2$BiCl, is found. The analytical results, however, are somewhat at variance with this structure. Chlorobenzene is also formed in the photolysis. In order to determine if the group 5A triphenyl compounds also affect singlet quenching as well as triplet quenching, the reaction was extended to the quenching of fluorenone fluorescence.[293] The results were somewhat similar. It is concluded that the rate of quenching is influenced by the availability of the lone pair on the group 5A element and that the solvent effects are small.

IV. Halobismuthines, Dihalobismuthines, and Related Compounds

A. Preparation

1. By Redistribution Reactions

Halo- and dihalobismuthines containing either alkyl or aryl groups have been described in the literature. The chloro-, dichloro-, bromo-, and dibromobismuthines are best prepared by the reaction of a tertiary bismuthine with bismuth trichloride or bismuth tribromide. The monochloro and monobromo compounds are formed in good yields when 1 mol of bismuth trichloride or tribromide is added to 2 mol of a solution of the tertiary bismuthine in an organic solvent such as ether, petroleum ether, benzene, chloroform, acetic acid, or acetone:

$$2R_3Bi + BiX_3 \rightarrow 3R_2BiX$$

R is alkyl or aryl and X is Cl or Br

If the molar ratio of tertiary bismuthine to bismuth trihalide is reversed, dichloro- or dibromobismuthines are obtained:

$$R_3Bi + 2BiX_3 \rightarrow 3RBiX_2$$

These redistribution reactions have been carried out at room temperature in most cases, but higher temperatures have been used occasionally. Compounds prepared by these reactions include methyldichlorobismuthine,[22,58] methyldibromobismuthine,[22,58] ethyldichlorobismuthine,[58] isobutyldibromobismuthine,[59] isoamyldibromobismuthine,[59] phenyldichlorobismuthine,[294] phenyldibromobismuthine,[57,77,294,295] diphenylchlorobismuthine,[32,44,103,107,155,295–298] diphenylbromobismuthine,[32,78,112,295] *o*-tolyldibromobismuthine,[32] di-*p*-tolylchlorobismuthine,[32,57,112] α-naphthyldibromobismuthine,[32,57,107] di-α-naphthylchlorobismuthine,[57] di-*p*-biphenylylchlorobismuthine,[104] *p*-fluorophenyldibromobismuthine,[233] bis(*p*-fluorophenyl)bromobismuthine,[233] bis(*p*-chlorophenyl)chlorobismuthine,[32] bis(*p*-chlorophenyl)bromobismuthine,[155] bis(*p*-bromophenyl)chlorobismuthine,[50] bis(*p*-methoxyphenyl)chlorobismuthine,[50] bis(*p*-(dimethylamino)phenyl)chlorobismuthine,[50] and bis(*p*-(dimethylamino)phenyl)bromobismuthine.[233] The interaction of triphenylbismuthine and ^{210}Bi-labeled bismuth trichloride in alcohol or alcohol–benzene has been employed for the preparation of ^{210}Bi-labeled diphenylchlorobismuthine.[299] The use of redistribution reactions for the preparation of iodobismuthines, diiodobismuthines, and compounds of the type RBiXY (where R is an alkyl or aryl group, X is a halide, and Y is another anionic group) is claimed in the patent literature.[300] The following examples are cited:

$$2(HC{\equiv}C)_3Bi + BiI_3 \rightarrow 3(HC{\equiv}C)_2BiI$$

$$(HC{\equiv}C)_3Bi + 2BiI_3 \rightarrow 3HC{\equiv}CBiI_2$$

$$BuBiCl_2 + BuBi(OPh)_2 \rightarrow 2BuBi(OPh)Cl$$

$$PhBiBr_2 + PhBi(SPh)_2 \rightarrow 2PhBi(SPh)Br$$

$$PhCH_2BiCl_2 + PhCH_2Bi(CN)_2 \rightarrow 2PhCH_2Bi(CN)Cl$$

The synthesis of halo- and dihalobismuthines is also mentioned in a short review on redistribution reactions of arsenic, antimony, and bismuth.[301]

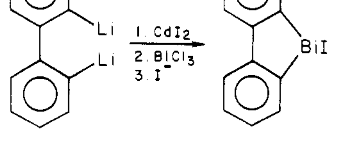
2. By Metathetical Reactions of Halo- or Dihalobismuthines

Iodo- and diiodobismuthines are easily prepared by the reaction of the corresponding chloro-, bromo-, dichloro-, or dibromobismuthines with sodium or potassium iodide.[32,126,127,302] Compounds of the R_2BiY and $RBiY_2$ types (where Y is an anionic group other than halogen) can also be obtained by metathetical reactions. These reactions are discussed in sections IVB2 and IVB3.

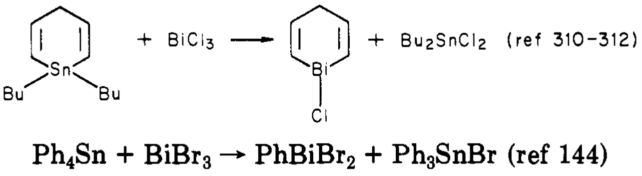
3. From Organometallic Reagents

As previously noted (section IIIA1), 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. For example, methyldibromobismuthine[303] and ethyldibromobismuthine[37] have been obtained in low yields by the addition of the corresponding Grignard reagent to an ether solution of bismuth tribromide, and the patent literature[304] mentions the formation of bis(2-methoxy-4-vinylphenyl)chlorobismuthine by the addition of 2 mol of Grignard reagent to 1 mol of bismuth trichloride in tetrahydrofuran. There is also a report of the preparation of phenyldichlorobismuthine by the action of phenylmagnesium bromide on an excess of bismuth trichloride.[305] The melting point of the dichloro compound obtained in this manner is said to be 72–74 °C, a value much lower than the melting points of other aryldichlorobismuthines and, in fact, rather close to the melting point of triphenylbismuthine (77–78 °C). Accordingly, the purity of the phenyldichlorobismuthine prepared by the Grignard reaction should be regarded as uncertain.

Organometallic compounds other than Grignard reagents have also been used for the preparation of halo- and dihalobismuthines. Thus, the interaction of dimethylzinc and bismuth tribromide yields methyldibromobismuthine,[58] while organolead compounds have been employed to obtain diphenylbromobismuthine,[306] vinyldichlorobismuthine,[307] and probably diethylchlorobismuthine[306] (although this spontaneously inflammable substance was not analyzed). A heterocyclic iodobismuthine has been prepared via an organocadmium intermediate:[309]



The conversion of organotin compounds to halo- or dihalostibines has also been observed:



$$Ph_4Sn + BiBr_3 \rightarrow PhBiBr_2 + Ph_3SnBr \text{ (ref 144)}$$

$$Ph_2SnEt_2 + 2BiBr_3 \rightarrow 2PhBiBr_2 + Et_2SnBr_2 \text{ (ref 144)}$$

4. Miscellaneous Methods

The cleavage of tertiary bismuthines by a variety of inorganic and organic reagents often leads to the formation of halobismuthines, dihalobismuthines, or related compounds (cf. section IIIB2). Substances of these types may also be formed by various reactions of triarylbismuth dihalides and related compounds (cf. section VB1). The formation of halo- and dihalobismuthines as intermediates in the preparation of tertiary bismuthines from diazonium salts has been mentioned in section IIIA2. The decomposition of tetraphenylbismuth tribromide at room temperature has been shown to yield diphenylbromobismuthine (cf. section VIB).

It has been found possible to prepare dihalobismuthines by the reaction of a halobismuthine with a halogen or halogen halide. Thus, phenyldibromobismuthine has been obtained by the reaction of either diphenylbromobismuthine[34,294] or diphenyliodobismuthine[298] with bromine. There is conductometric evidence that phenyldibromobismuthine may also be formed by the interaction of diphenylbromobismuthine and iodine monobromide,[109] while treatment of diphenylbromobismuthine with iodine monochloride yields phenylchlorobromobismuthine, PhBiClBr.[107,298]

Dichlorobismuthines have been prepared by the disproportionation of chlorobismuthines in chloroform or tetrahydrofuran at room temperature or in liquid ammonia:[50]

$$2(p\text{-BrC}_6\text{H}_4)_2\text{BiCl} \rightarrow p\text{-BrC}_6\text{H}_4\text{BiCl}_2 + (p\text{-BrC}_6\text{H}_4)_3\text{Bi}$$

$$2(p\text{-MeOC}_6\text{H}_4)_2\text{BiCl} \rightarrow p\text{-MeOC}_6\text{H}_4\text{BiCl}_2 + (p\text{-MeOC}_6\text{H}_4)_3\text{Bi}$$

$$2(p\text{-Me}_2\text{NC}_6\text{H}_4)_2\text{BiCl} \rightarrow p\text{-Me}_2\text{NC}_6\text{H}_4\text{BiCl}_2 + (p\text{-Me}_2\text{NC}_6\text{H}_4)_3\text{Bi}$$

(*p*-Chlorophenyl)dibromobismuthine can be obtained by an analogous reaction.[155] Disproportionation also occurs on the treatment of diphenylchlorobismuthine with a sodium dialkyldithiocarbamate:[313]

$$2\text{Ph}_2\text{BiCl} + 2\text{NaS}_2\text{CNR}_2 \rightarrow \text{PhBi(S}_2\text{CNR}_2)_2 + \text{Ph}_3\text{Bi} + 2\text{NaCl}$$

R is Me or Et

In a similar manner, the interaction of diphenylacetatobismuthine and sodium 1-oxopyridine-2-thiolate results in the formation of triphenylbismuthine and a compound containing two bismuth–sulfur bonds.[314,315] The structure of the latter substance is discussed in section IVC.

Ethyldichlorobismuthine and diethylchlorobismuthine have been prepared via the cleavage of the Ge–Bi bond with hydrogen chloride:[134]

$$[(\text{C}_6\text{F}_5)_3\text{Ge}]_2\text{BiEt} + 2\text{HCl} \rightarrow \text{EtBiCl}_2 + 2(\text{C}_6\text{F}_5)_3\text{GeH}$$

$$(\text{C}_6\text{F}_5)_3\text{GeBiEt}_2 + \text{HCl} \rightarrow \text{Et}_2\text{BiCl} + (\text{C}_6\text{F}_5)_3\text{GeH}$$

The electrochemical synthesis of dimethylbromobismuthine, diethylbromobismuthine, and bis(2-cyanoethyl)iodobismuthine at a bismuth cathode has been described in the Russian literature.[97] Methyldibromobismuthine has been prepared in low yield by the copper-catalyzed reaction of bismuth metal and methyl bromide at 250 °C.[316] (Trifluoromethyl)diiodobismuthine and bis(trifluoromethyl)iodobismuthine are probably formed in trace amounts by heating bismuth metal with trifluoroiodomethane at 245 °C for 65 h.[26] Alkyldiiodobismuthines can be prepared by heating a trialkylbismuthine with an alkyl iodide.[58,59] Phenyldibromobismuthine has been obtained in quantitative yield by the interaction of bromine vapor and a polymeric substance of empirical formula PhBi[23] (see section II).

The reaction of diazomethane with bismuth trichloride in ether or benzene does not yield the expected (chloromethyl)dichlorobismuthine but instead gives an oxobismuthine presumably formed from traces of water inadvertently introduced:[317,318]

$$\text{CH}_2\text{N}_2 + \text{BiCl}_3 \rightarrow [\text{ClCH}_2\text{BiCl}_2] \xrightarrow{\text{H}_2\text{O}} \text{ClCH}_2\text{BiO}$$

When a hydrochloric acid solution of this substance is evaporated in vacuo, an impure sample of (chloromethyl)dichlorobismuthine is obtained. Attempts to purify this material by recrystallization have been unsuccessful.

A mixture of ^{210}Bi-labeled substances, including diphenyliodobismuthine and phenyldiiodobismuthine, is obtained as the result of β disintegration of ^{210}Pb-labeled triphenyllead iodide.[319]

B. Reactions

1. General

Halobismuthines, dihalobismuthines, and related compounds are, in general, very reactive compounds and are decomposed by moisture, alcohols, and ammonia.[9,298] There are, however, a few ortho-substituted diarylchloro- and aryldichlorobismuthines that appear to be unaffected by water and can be recrystallized from alcohol.[67] Dialkylhalobismuthines are extremely sensitive substances. They are spontaneously inflammable in air and may decompose on standing even when precautions are taken to exclude water and oxygen. The diaryl compounds should also be handled with caution, since some of them are known to be powerful sternutators.[320] Thus, diphenylchlorobismuthine, -bromobismuthine, and -cyanobismuthine are probably more powerful than the chemical warfare agent diphenylchloroarsine. The diphenylacyloxybismuthines $\text{Ph}_2\text{BiO}_2\text{CR}$, where R is BrCH_2, ICH_2, or Et, are barely tolerable at a concentration of 1 part in 2.5×10^7 parts of air, and they are said to produce unpleasant aftereffects.

The iodobismuthines appear to be much less reactive than the corresponding bromo or chloro compounds. Thus, the preparation of diphenylchlorobismuthine and -bromobismuthine must be carried out under strictly anhydrous conditions, while one method for recrystallizing diphenyliodobismuthine involves pouring an alcoholic solution of the compound into boiling water.[302] Treatment of the iodo compound with liquid ammonia for 3 h yields 21% triphenylbismuthine, but 65% of the iodo compound can be recovered unchanged.[81] In contrast, a similar experiment with diphenylbromobismuthine results in considerable decomposition to inorganic bismuth. No triphenylbismuthine is obtained, and only 38.2% of the diphenylbromobismuthine can be recovered.

It has been stated[155,321] that the reaction of halo- or dihalobismuthines with fluoride ion, alcoholic ammonia, or other bases may yield tertiary bismuthines and inorganic bismuth compounds. In many cases, however, the interaction of halo- or dihalobismuthines with nucleophiles results in metathesis (cf. section IVB2).

The diphenylhalobismuthines and -pseudohalobismuthines Ph_2BiX, where X is Cl, Br, CN, SCN, or N_3, have been found to be stable at room temperature.[322] The selenocyanato compound $Ph_2BiSeCN$ decomposes slowly at room temperature but can be kept for several days in a refrigerator. All of these compounds are insoluble in nonpolar organic solvents but are somewhat soluble in polar solvents such as acetone and ethanol. Dimethylazidobismuthine, Me_2BiN_3, is insoluble in tetrahydrofuran, ethanol, pyridine, and other common organic solvents.[129] It dissolves with decomposition in inorganic acids, but it is not explosive and only slightly light sensitive. At about 150 °C, it decomposes and turns gray.

The diphenylxanthatobismuthines of the type Ph_2BiS_2COR, where R is Me, Et, Pr, Bu, Me_2CH, or Me_2CHCH_2, decompose slowly in organic solvents at room temperature according to the equation[323]

$$2Ph_2BiS_2COR \rightarrow Ph_3Bi + PhBi(S_2COR)_2$$

The decomposition can be monitored by means of ^1H NMR spectroscopy.

2. Replacement of the Halogen in Halo- and Dihalobismuthines by Other Anionic Groups

Halo- and dihalobismuthines undergo a variety of metathetical reactions with lithium, sodium, potassium, ammonium, silver, and lead salts. These reactions are useful for preparing iodo- and diiodobismuthines[32,126,127,302] as well as compounds of the R_2BiY and $RBiY_2$ types, where Y is an anionic group other than halogen:

$$Ph_2BiCl + MY \rightarrow Ph_2BiY + MCl \quad \text{(ref 322, 324)}$$

M = Na or K; Y = N_3, CN, SCN, or SeCN

$$Ph_2BiBr + KCN \rightarrow Ph_2BiCN + KBr \quad \text{(ref 321)}$$

$$2Ph_2BiBr + Pb(SCN)_2 \rightarrow 2Ph_2BiSCN + PbBr_2 \quad \text{(ref 321)}$$

$$EtBiI_2 + 2AgONO_2 \rightarrow EtBi(ONO_2)_2 + 2AgI \quad \text{(ref 127)}$$

$$MeBiBr_2 + 2NaOR \rightarrow MeBi(OR)_2 + 2NaBr \quad \text{(ref 325, 326)}$$

R = Me, Et, or Me_2CH

$$PhBiBr_2 + 2NaOEt \rightarrow PhBi(OEt)_2 + 2NaBr \quad \text{(ref 327)}$$

$$Et_2BiBr + NaOEt \rightarrow Et_2BiOEt + NaBr \quad \text{(ref 122)}$$

$$Ph_2BiBr + NaOR \rightarrow Ph_2BiOR + NaBr \quad \text{(ref 328)}$$

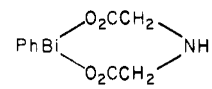
R = Me, Et, Me_2CH, or Ph

$$MeBiBr_2 + 2NaOSiMe_3 \rightarrow MeBi(OSiMe_3)_2 + 2NaBr \quad \text{(ref 329)}$$

$$Me_2BiBr + NaOSiMe_3 \rightarrow Me_2BiOSiMe_3 + NaBr \quad \text{(ref 329)}$$

$$Ph_2BiBr + NaOSiMe_3 \rightarrow Ph_2BiOSiMe_3 + NaBr \quad \text{(ref 329)}$$

$$PhBiCl_2 + (NaO_2CCH_2)_2NH \rightarrow$$



+ 2NaCl (ref 330)

$$Ph_2BiCl + NH_4O_2CC(Me){=}CH_2 \rightarrow Ph_2BiO_2CC(Me){=}CH_2 + NH_4Cl \quad \text{(ref 331)}$$

$$MeBiBr_2 + 2LiN(Me)SiMe_3 \rightarrow MeBi[N(Me)SiMe_3]_2 + 2LiBr \quad \text{(ref 27)}$$

$$Me_2BiBr + LiN(Me)SiMe_3 \rightarrow Me_2BiN(Me)SiMe_3 + LiBr \quad \text{(ref 27, 230)}$$

$$Ph_2BiCl + NaSC_6H_4F\text{-}p \rightarrow Ph_2BiSC_6H_4F\text{-}p + NaCl \quad \text{(ref 36)}$$

$$Ph_2BiBr + NaSR \rightarrow Ph_2BiSR + NaBr \quad \text{(ref 332, 333)}$$

R = Et, Me_3C, $PhCH_2$, m-FC_6H_4, p-FC_6H_4, p-ClC_6H_4, or Ac

$$2Ph_2BiBr + NaS(CH_2)_nSNa \rightarrow Ph_2BiS(CH_2)_nSBiPh_2 + 2NaBr \quad \text{(ref 333)}$$

n = 2 or 3

$$MeBiBr_2 + 2NaS_2CNR_2 \rightarrow MeBi(S_2CNR_2)_2 + 2NaBr \quad \text{(ref 334)}$$

R_2N = Me_2N, Et_2N, or 1-piperidyl

$$PhBiBr_2 + 2NaS_2CNR_2 \rightarrow PhBi(S_2CNR_2)_2 + 2NaBr \quad \text{(ref 313, 334)}$$

R_2N = Me_2N, Et_2N, or 1-piperidyl

$$Ph_2BiBr + NaS_2COR \rightarrow Ph_2BiS_2COR + NaBr \quad \text{(ref 323)}$$

R = Me, Et, Pr, Bu, Me_2CH, or Me_2CHCH_2

The reaction of sodium 1-oxopyridine-2-thiolate with either phenyldiiodobismuthine or diphenylacetatobismuthine has been found to yield phenylbis(1-oxopyridine-2-thiolato)bismuthine.[314,315] The structure of this compound is discussed in section IVC. An arylthiobismuthine has been obtained by the interaction of a halobismuthine and a free thiol:[151]

$$Ph_2BiCl + HSPh \rightarrow Ph_2BiSPh + HCl$$

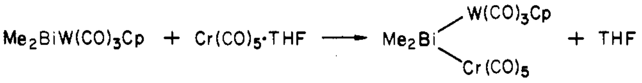
There are several reports of the conversion of halobismuthines and dihalobismuthines to hydroxybismuthines and oxobismuthines, respectively. Thus, Marquardt[58] reported that the hydrolysis of the zinc bromide double salt of dimethylbromobismuthine yields dimethylhydroxybismuthine, Me_2BiOH. The latter substance is a spontaneously inflammable solid that yields methane on treatment with hydrochloric acid and reacts with methyl iodide to form methyldiiodobismuthine. Diphenylhydroxybismuthine, Ph_2BiOH, is probably formed by the reaction of diphenyliodobismuthine with alcoholic sodium hydroxide[80] or the reaction of diphenylbromobismuthine with alcoholic ammonia,[78] but the hydroxy compound appears to be very unstable and has not been adequately characterized. Treatment of an alcoholic solution of the zinc bromide double salt of methyldibromobismuthine with ammonia yields an amorphous solid that is said[58] to be methyloxobismuthine, MeBiO. This substance appears to be amphoteric; i.e., it is insoluble in water or aqueous ammonia but soluble in both dilute sodium hydroxide and dilute nitric acid. It is very easily oxidized by air, and it reacts with hydrogen sulfide in ethanol to give a substance formulated as MeBiS.[59] Ethyldiiodobismuthine has been reported[126,127] to react with potassium hydroxide in aqueous ethanol to give ethyloxobismuthine, EtBiO, which is spontaneously inflammable. Lecoq[335] claimed that phenyldichlorobismuthine (prepared by the Grignard reaction as described in section IVA3) reacts instantly with water to yield a white, granular precipitate of phenyloxobismuthine, PhBiO. This substance is said to be soluble in alcohol and alkalies and to give a normal molecular weight. A white solid—described[23] as $(PhBiO)_n$—has been obtained by the oxidation of a black, presumably polymeric, substance, $(PhBi)_n$. The latter material was prepared by the reduction of phenyldibromobismuthine or diphenylbromobismuthine with lithium borohydride or lithium aluminum hydride (see section II). The possible conversion of (chloromethyl)dichlorobismuthine to the corresponding oxobismuthine has been mentioned in section IVA4. A compound containing the bismuth–rhenium bond has been obtained by the following metathetical reaction:[336]

$$Ph_2BiCl + NaRe(CO)_5 \rightarrow Ph_2BiRe(CO)_5 + NaCl$$

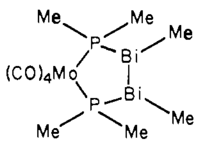
The reaction of equimolar quantities of dimethylbromobismuthine and a salt of the type $NaM(CO)_3Cp$ (where M is Cr, Mo, or W and Cp is η^5-cyclopentadienyl) is more complicated and yields mixtures of trimethylbismuthine, $MeBi[M(CO)_3Cp]_2$, and $BrBi[M(CO)_3Cp]_2$.[137] These products are the result of various substitution and redistribution processes. The use of excess transition metal anion favors the formation of the dimethyl derivatives $Me_2BiM(CO)_3Cp$, but these substances are more readily obtained by means of the following type of reaction:

$$Me_3Bi + Cp(CO)_3MH \rightarrow Me_2BiM(CO)_3Cp + MeH$$

The compounds thus prepared exhibit pronounced lability in solution. The tungsten derivative in tetrahydrofuran adds chromium pentacarbonyl:



The interaction of methyldichlorobismuthine and the dilithium salt *cis*-$Mo(CO)_4(Me_2PLi)_2$ has been found to yield the following unusual type of coordination compound:[337]



The stoichiometry of this reaction has not been elucidated.

Treatment of a diphenylhalobismuthine with the pyridine complex $HCo(DH)_2{\cdot}Py$, where DH_2 is dimethylglyoxime, leads to the formation of the bimetallic compound $Ph_2BiCo(DH)_2{\cdot}Py$.[338] This material is stable toward oxygen, soluble in several common organic solvents, and resistant to alkali, but it is decomposed by strong acids. The bismuth–cobalt bond can be cleaved by oxidation with bromine or reduction with sodium borohydride.

3. Metathetical Reactions of Alkoxy- and Dialkoxybismuthines

Methyldiethoxybismuthine reacts with a number of thiols to form compounds containing two bismuth–sulfur bonds:[325,326]

$$MeBi(OEt)_2 + 2RSH \rightarrow MeBi(SR)_2 + 2EtOH$$

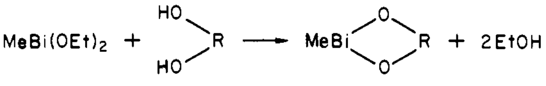
R = Et, Me_2CH, Me_3C, $HOCH_2CH_2$, Ph, $PhCH_2$, *p*-MeC_6H_4, cyclohexyl, or 2-benzothiazolyl

Other methyldialkoxybismuthines react in a similar manner:[326]

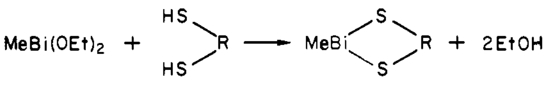
$$MeBi(OR')_2 + 2RSH \rightarrow MeBi(SR)_2 + 2R'OH$$

R' = Me or Me_2CH; R = Me_2CH, Me_3C, *p*-MeC_6H_4, or cyclohexyl

Methyldiethoxybismuthine undergoes exchange reactions with vicinal diols or dithiols to give heterocyclic compounds:[325]



R = CH_2CH_2, CH_2CHMe, CMe_2CMe_2, CHPhCHPh, or *o*-C_6H_4)

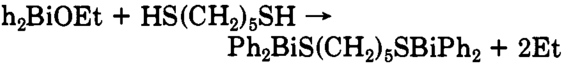


R = CH_2CH_2 or 4-Me-1,2-C_6H_3

Phenyldiethoxybismuthine also reacts with thiols and 1,2-ethanedithiol:[327]

$$PhBi(OEt)_2 + 2RSH \rightarrow PhBi(SR)_2 + 2EtOH$$

R = Et, Ph, $PhCH_2$, or $HOCH_2CH_2$



In an analogous manner, the interaction of diphenylethoxybismuthine and a thiol or dithiol results in displacement of the ethoxy group:[328]

$$Ph_2BiOEt + RSH \rightarrow Ph_2BiSR + EtOH$$

R = Me_2CH, Me_3C, cyclohexyl, or *p*-MeC_6H_4

$$2Ph_2BiOEt + HS(CH_2)_5SH \rightarrow Ph_2BiS(CH_2)_5SBiPh_2 + 2EtOH$$

4. Reduction

Diarylhalobismuthines in liquid ammonia react with 2 equiv of lithium, sodium, potassium, calcium, or barium to form deep red, highly reactive compounds of the type Ar_2BiM (where M is Li, Na, or K) or $(Ar_2Bi)_2M'$ (where M' is Ca or Ba).[81,339,340] The use of only 1 equiv of metal results in a deep-green solution, which changes to red when more metal is added. It has been suggested that the green color is due to a diarylbismuth radical[81] or possibly to a tetraaryldibismuthine, $Ar_2BiBiAr_2$,[12b] but there is little real evidence for either type of structure. The diarylbismuthides disproportionate slowly to the corresponding tertiary bismuthines and inorganic bismuth, but they are stable enough to react with aryl halides to form unsymmetrical tertiary bismuthines (cf. section IIIA3).

The electrolytic reduction of diphenylchlorobismuthine in anhydrous glyme (1,2-dimethoxyethane) has also been investigated.[282,341] When the electrolysis is conducted at −1.2 V, one electron is involved in the reduction and a pale yellow solution is obtained. This result has been attributed to the formation of tetraphenyldibismuthine by the rapid coupling of diphenylbismuth radicals:

$$Ph_2BiCl + e^- \rightarrow Ph_2Bi\cdot + Cl^-$$

$$2Ph_2Bi\cdot \rightarrow Ph_2BiBiPh_2$$

Further reduction of the solution gives rise to a green solution, which presumably contains the diphenylbismuthide ion:

$$Ph_2BiBiPh_2 + 2e^- \rightarrow 2Ph_2Bi^-$$

This anion is unstable and deposits bismuth metal.

It is interesting that all attempts to isolate tetraphenyldibismuthine have failed; however, the corresponding arsenic and antimony compounds are well-known. Thus, the dibismuthine could not be prepared by the reaction of diphenyliodobismuthine with silver, mercury, zinc, copper bronze, or sodium hypophosphite.[302] In the case of the first two metals, black precipitates are formed. Sodium hypophosphite at room temperature does not seem to react at all with an alcoholic solution of the iodobismuthine, but on warming a black product is formed. None of these black materials have been identified. The apparent instability of the dibismuthine may be associated with the fact that the Bi–Bi bond strength is only 25 kcal/mol, while the As–As and Sb–Sb bond strengths are 32.1 and 30.2 kcal/mol, respectively.[342] Dessy and co-workers[341] have stated that reductive cleavage of the metal–metal bond requires less cathodic potentials as one goes from arsenic to antimony to bismuth. Tetramethyldibismuthine, $Me_2BiBiMe_2$, may have been prepared by the reaction between methyl radicals and a heated bismuth mirror, but not enough material was obtained for analysis.[85]

The polarographic reduction of diphenyliodobismuthine in aqueous alcohol produces a single wave with a diffusion current that is directly proportional to the concentration of the iodobismuthine.[343] The observed half-wave potential is a function of the pH; when the solution is 1 N in hydrochloric acid, the potential at 25 °C is −0.166 V (relative to the saturated calomel electrode).[344]

Diarylhalobismuthines and aryldihalobismuthines can be reduced to triarylbismuthines by means of hydrazine hydrate.[67,81,101] The chloro and bromo derivatives react rapidly to give high yields of the tertiary bismuthines. In contrast, the interaction of diphenyliodobismuthine and hydrazine hydrate under similar conditions is slow and gives only a 61.2% yield of triphenylbismuthine after 8 h. In some cases, such as bis(*o*-carbomethoxyphenyl)chlorobismuthine, the reaction with hydrazine is complicated by secondary reactions.[67]

The reduction of methyldichlorobismuthine or dimethylchlorobismuthine with lithium aluminum hydride at low temperatures yields methylbismuthine and dimethylbismuthine, respectively,[22] while the reduction of phenyldibromobismuthine or diphenylchlorobismuthine under similar conditions yields polymeric substances of empirical formula PhBi.[23] These reactions have been discussed in section II.

5. Coordination Chemistry

Okawara and co-workers[295] have described the preparation of pyridine adducts of phenyldihalobismuthines by two different methods. One method consists simply of the addition of pyridine to the dibromobismuthine:

$$PhBiBr_2 + 2Py \rightarrow PhBiBr_2{\cdot}2Py$$

$$Py = \text{pyridine}$$

The other method involves the cleavage of a phenyl group from a diphenylhalobismuthine:

$$2Ph_2BiX + 2Py \rightarrow PhBiX_2{\cdot}2Py + Ph_3Bi$$

$$X = Cl \text{ or } Br$$

The reaction of phenyldihalobismuthines with 1,10-phenanthroline (Phen) or 2,2′-bipyridine (bpy) has been found to yield adducts of the type $PhBiX_2{\cdot}L$, where X is Cl, Br, or I and L is Phen or bpy.[294,345] Attempts to prepare adducts of diphenylhalobismuthines and these ligands, however, have been unsuccessful. In the presence of hydrogen bromide, the interaction of phenyldibromobismuthine and bpy yields a dipyridinium salt:

$$PhBiBr_2 + bpy + HBr \rightarrow [bpyH][PhBiBr_3]$$

Molecular weight determinations show that the $PhBiX_2{\cdot}L$ adducts mentioned above are monomeric in dichloromethane, and electrical conductivity measurements indicate that they are only slightly dissociated in nitromethane. The UV absorption bands of the dibromo- and diiodobismuthine adducts in the solid state and in dichloromethane occur at lower wavelengths than those found for the free dihalobismuthines under the same conditions. These results are compatible with the conclusion that the adducts do not decompose to the starting materials in solution. The presence of coordinated bpy or Phen in the adducts is clearly shown by their IR spectra. It has been concluded[294] that both bpy and Phen are acting as bidentate (and presumably chelating) ligands in these adducts. It has also been suggested that complex formation leads to breaking of the bismuth–halogen bridges assumed to exist in the uncomplexed phenyldihalobismuthines (cf. section IVC).

Faraglia[346] has made a study of the preparation and properties of several tetraphenylarsonium salts containing the anionic species $Ph_2BiX_2^-$ (where X is Cl, Br, I, or SCN) and $PhBiX_3^-$ (where X is Cl, Br, or I). One tetramethylammonium salt, viz., $[Me_4N][Ph_2BiCl_2]$, was also included. Most of these compounds were prepared by mixing equimolar quantities of a tetraphenylarsonium halide and a diphenylhalobismuthine (or a phenyldihalobismuthine) in a nonaqueous solvent:

$$Ph_4AsX + Ph_2BiX \rightarrow [Ph_4As][Ph_2BiX_2]$$

$$Ph_4AsX + PhBiX_2 \rightarrow [Ph_4As][PhBiX_3]$$

In two cases the salts were obtained by acid cleavage of phenyl groups from triphenylbismuthine:

$$Ph_4AsCl + Ph_3Bi + HCl \rightarrow [Ph_4As][Ph_2BiCl_2]$$

$$Ph_4AsCl + Ph_3Bi + 2HCl \rightarrow [Ph_4As][PhBiCl_3]$$

One compound was prepared by metathesis:

$$[Ph_4As][Ph_2BiCl_2] + 2NaSCN \rightarrow [Ph_4As][Ph_2Bi(SCN)_2] + 2NaCl$$

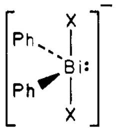
The molar conductivities of all of these salts in acetone are in the 105–125 ohm^{-1} cm^2 mol^{-1} range, while the values for tetraphenylarsonium chloride, bromide, and thiocyanate at the same concentration (1×10^{-3} M) are about 150 ohm^{-1} cm^2 mol^{-1}. Osmometric measurements of the anionic bismuth compounds in acetone yield i values between 1.62 and 1.96 at a concentration of 2.5×10^{-3} M. In dichloromethane, however, the molar conductivities and the i values are considerably lower. In contrast to the results obtained with the anionic bismuth compounds, the uncomplexed halo- and dihalobismuthines are nonelectrolytes in acetone or dichloromethane and give normal molecular weights in both solvents (cf. section IVC). Faraglia also compared the UV absorption spectra of diphenylchloro-, diphenylbromo- and phenyldibromobismuthine in dichloromethane with the spectra of the corresponding anionic complexes. With the diphenylhalobismuthines, complex formation causes a shift of λ_{max} to lower wavelengths. A bathochromic shift is observed, however, when phenyldibromobismuthine is converted to tetraphenylarsonium phenyltribromobismuthate(III).

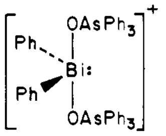
More recently, Allman, Goel, and Prasad[347] have investigated the tetraethylammonium salts $[Et_4N][Ph_2BiX_2]$, where X is Cl, Br, CN, SCN, or N_3. The chloro and bromo compounds are formed by the interaction of the appropriate tetraethylammonium halide and diphenylhalobismuthine in acetone. The pseudohalo compounds are obtained by the following type of metathetical reaction:

$$[Et_4N][Ph_2BiCl_2] + 2NaX \rightarrow [Et_4N][Ph_2BiX_2] + 2NaCl$$

$$X = CN, SCN, \text{ or } N_3$$

The perchlorate of the cationic species $[Ph_2Bi(OAsPh_3)_2]^+$ was also studied. This substance is prepared by mixing equimolar amounts of diphenylchlorobismuthine and silver perchlorate in ethanol, removing the precipitated silver chloride by filtration, and then adding 2 equiv of triphenylarsine oxide to the filtrate. All of the complexes prepared for this study are white crystalline solids. They are stable at room temperature and are unaffected by atmospheric moisture. They are insoluble in nonpolar solvents but are soluble in polar solvents such as acetone or ethanol. Their electrical conductances in acetone are consistent with their formulation as 1:1 electrolytes. Each $Ph_2BiX_2^-$ or $[Ph_2Bi(OAsPh_3)_2]^+$ ion presumably possesses a stereochemically active lone pair. Although IR and Raman studies have not unequivocally established the geometry of these ions, the data obtained are consistent with the structures:





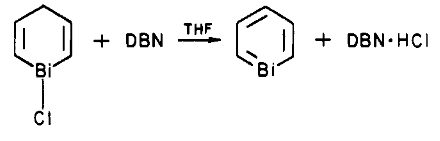
6. Other Reactions

The reaction of mercuric chloride with diphenylchlorobismuthine leads to cleavage of the carbon–bismuth bonds.[348] When an aqueous alcoholic solution of the two compounds is boiled for 90 min, an almost quantitative yield of phenylmercuric chloride is obtained:

$$Ph_2BiCl + HgCl_2 + H_2O \rightarrow PhHgCl + BiOCl + PhH + HCl$$

In alkaline medium the reaction yields some triphenylbismuthine and a little phenylmercuric chloride. No diphenylmercury is formed as a reaction product in any case.

Treatment of the chlorobismuthine 1 with 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) in tetrahydrofuran results in the exothermic loss of hydrogen chloride and yields a solution which appears to contain bismin (bismabenzene).[310–312] Although attempts to isolate this substance have failed, a 1:1 adduct of bismin and hexafluoro-2-butyne can be obtained by addition of the latter compound to the THF solution after precipitation of the DBN hydrochloride. The adduct is a bicyclic compound, presumably formed by a Diels–Alder reaction:



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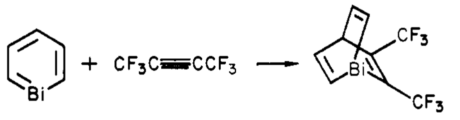
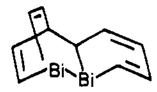


At low temperatures (<−10 °C), bismin in THF solution appears to exist in the form of a Diels–Alder dimer:



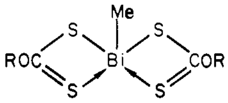
As the solution is warmed, the intensity of the ^{1}H NMR peaks attributed to the dimer diminishes, and at −10 °C the spectrum is consistent with that expected for bismin itself.

Methyldialkoxybismuthines react with freshly distilled carbon disulfide to give xanthates:[326]

$$MeBi(OR)_2 + 2CS_2 \rightarrow MeBi(S_2COR)_2$$

$$R = Me, Et, \text{ or } Me_2CH$$

The sulfur atoms in these compounds may be coordinated to the bismuth in the following manner (see section IVC):



Bismuth-containing diazo compounds can be prepared by the reaction of [methyl(trimethylsilyl)amino]dimethylbismuthine with diazomethane,[230] ethyl diazoacetate,[230] or (diazomethyl)dimethylarsine:[349]

$$2Me_2BiN(Me)SiMe_3 + CH_2N_2 \rightarrow (Me_2Bi)_2CN_2 + 2Me_3SiNHMe$$

$$Me_2BiN(Me)SiMe_3 + CH(N_2)CO_2Et \rightarrow Me_2BiC(N_2)CO_2Et + Me_3SiNHMe$$

$$Me_2BiN(Me)SiMe_3 + Me_2AsCHN_2 \rightarrow (Me_2Bi)(Me_2As)CN_2 + Me_3SiNHMe$$

The aminobismuthine also reacts with cyclopentadiene:[350]

$$Me_2BiN(Me)SiMe_3 + CpH \rightarrow Me_2BiCp + Me_3SiNHMe$$

Bismuth–carbon bonds can be formed by the thermal elimination of sulfur dioxide from (arenesulfinato)bismuth(III) compounds.[99] For example, bis(benzenesulfinato)phenylbismuthine and (benzenesulfinato)diphenylbismuthine undergo the following type of reaction:

$$Ph_{3-n}Bi(O_2SPh)_n \rightarrow nSO_2 + Ph_3Bi$$
$$n = 1 \text{ or } 2$$

The oxidation of diethylethoxybismuthine with pure oxygen at 14–17 °C yields ethylene, a solid of empirical formula $Et_{1.2}BiO_{1.8}$, and a liquid consisting of a mixture of ethyl alcohol, diethyl ether, and diethyl peroxide.[122]

Phenyldiethoxybismuthine is very moisture sensitive and decomposes at room temperature in the solid state or in solution.[327] It is stable, however, at −70 °C. When heated to boiling in absolute ethanol for about 30 min, it undergoes the following type of disproportionation:

$$3PhBi(OEt)_2 \rightarrow Ph_3Bi + 2Bi(OEt)_3$$

The fate of the carbon–bismuth bonds in diphenylchlorobismuthine has been examined when the bismuth atoms undergo n,γ reactions in a nuclear reactor.[351] In this investigation the samples were irradiated for 1 h in sealed ampules, allowed to decay for 3–4 days, and then analyzed by column chromatography. Some triphenylbismuthine was detected, but over 50% of the activity appeared in the inorganic bismuth fraction.

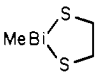
Compounds labeled with ^{210}Bi have been used in a study of the thin-layer chromatographic separation of bismuth trichloride, phenyldichlorobismuthine, triphenylbismuthine, and triphenylbismuth dichloride.[352] The solvent employed was a mixture of benzene, ethanol, acetic acid, and water in the ratio of 40:11:3.5:1.

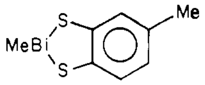
Unsymmetrical tertiary bismuthines can be prepared by the reaction of organomagnesium, -lithium, or -sodium reagents with halo- or dihalobismuthines. These reactions have been discussed in section IIIA1. Triphenylbismuthine (and not an unsymmetrical tertiary bismuthine) is obtained, however, when a mixture of a diphenylhalobismuthine, α-bromonaphthalene, and sodium is heated with benzene for 20 h.[57] Triphenylbismuthine (in addition to phenylmercuric bromide and di-α-naphthylmercury) is also formed by the interaction of diphenylmercury and α-naphthyldibromobismuthine in cold ether.[57]

C. Structure and Physical Properties

Although halo- and dihalobismuthines were first described in 1854,[127] relatively little is known about their structure or physical properties. They are crystalline solids and generally have melting points above 100 °C, although one report[305] of doubtful validity lists the melting point of phenyldichlorobismuthine as 72–74 °C (cf. section IVA3). Most of these substances are white or yellow, but dicyclopentadienylchlorobismuthine[51] is described as orange-red. Molecular weight and electrical conductance measurements show that halobismuthines and dihalobismuthines exist as monomeric, molecular species in either acetone or dichloromethane.[322,346] There is evidence from vibrational[322] and electronic[294] spectroscopy, however, that these compounds may be associated in the solid state via intermolecular halogen bridging (vide infra). Their high melting points and relatively low solubilities in organic solvents have been attributed to association of this type.

Diphenylphenoxybismuthine and the alkoxybismuthines Ph_2BiOR (where R is Me, Et, or Me_2CH) give normal molecular weights by cryoscopic measurements in benzene, and their mass spectra provide no evidence of association.[328] Mass spectral data also indicate that the thio compounds Ph_2BiSR[328,333] (where R is Et, Me_2CH, Me_3C, cyclohexyl, $PhCH_2$, p-ClC_6H_4, p-MeC_6H_4, or Ac), $PhBi(SR)_2$[327] (where R is Et, Ph, $PhCH_2$, or $HOCH_2CH_2$), and $MeBi(SR)_2$[325,326] (where R is Et, Me_2CH, Me_3C, cyclohexyl, Ph, $PhCH_2$, p-MeC_6H_4, or $HOCH_2CH_2$) are monomeric. Similarly, normal molecular weights have been obtained from the mass spectra of the following heterocyclic derivatives:[325]





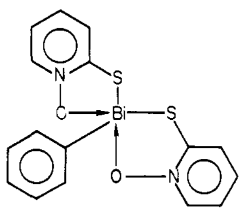
It has been suggested, however, that the dialkoxybismuthines $MeBi(OR)_2$[326] (where R is Me, Et, or Me_2CH) and several related heterocyclic compounds[325] are polymeric. Unfortunately, their slight solubility in organic solvents other than alcohols has prevented the measurement of their molecular weights by cryoscopic methods, and the peaks in their mass spectra probably originate from decomposition products.

Goel and Prasad[322] have made a detailed study of the IR and Raman spectra of six compounds of the Ph_2BiX type, where X is Cl, Br, CN, SCN, SeCN, or N_3. The Raman spectra of acetone solutions of the chloro-, bromo-, thiocyanato-, and azidobismuthines are satisfactorily explained by assuming that these compounds have discrete molecular structures of C_s symmetry. All four spectra exhibit a strong, polarized band at 204 cm^{-1} (due to the symmetric Bi–Ph stretching frequency) and a weak, depolarized band at about 215 cm^{-1} (due to the antisymmetric Bi–Ph stretching frequency). There is another strong, polarized band for the chloro-, bromo-, thiocyanato-, and azidobismuthines at 270, 170, 237, and 336 cm^{-1}, respectively. This band is assigned to the Bi–X stretching frequency. Marked differences are found between the solution spectra and the corresponding (IR or Raman) spectra in the solid state. Thus, no IR or Raman band attributable to the Bi–Cl or Bi–SCN stretching frequency is observed with the solid chloro- or thiocyanatobismuthine. The failure to observe these frequencies is explicable if one assumes intermolecular association in these compounds. Abnormally low Bi–Br, Bi–CN, and Bi–N_3 stretching frequencies found in the solid-state spectra of the bromo-, cyano-, and azidobismuthines also suggest some type of association via the anionic groups. The Raman spectrum of diphenylselenocyanatobismuthine has not been determined because this compound is decomposed by the laser beam. Although the IR spectrum of this substance is compatible with a monomeric structure containing the Bi–Se bond, the possibility of an associated structure in the solid state has not been ruled out.

The ultraviolet absorption spectra of of phenyldibromobismuthine, diphenylchlorobismuthine, and diphenylbromobismuthine in dichloromethane exhibit maxima at 341 (ϵ 2.8 × 10^3), 316 (ϵ 2.2 × 10^3), and 325 nm (ϵ 2.3 × 10^3), respectively.[346] In the solid state the maximum for phenyldibromobismuthine shifts to a higher wavelength (about 380 nm).[294] This shift has been attributed to the presence of bromine bridges in the solid state and consequent weakening of the Bi–Br bond.

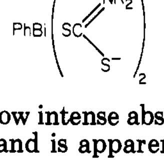
An investigation of the IR and Raman spectra of azidodimethylbismuthine, Me_2BiN_3, has led to the conclusion that this compound has a nonionic, monomeric structure.[129] The mass spectrum exhibits a weak molecular ion and relatively strong peaks corresponding to Me_2Bi^+, $MeBi^+$, and Bi^+; no peaks above M + 1 have been observed.

X-ray diffraction data have been used to determine the crystal and molecular structure of phenylbis(1-oxopyridine-2-thiolato)bismuthine:[314]



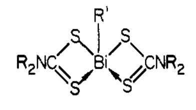
The coordination about the bismuth atom is approximately octahedral, with a pair of electrons presumably occupying one coordination site. The bismuth atom and the sulfur and oxygen atoms are almost exactly in the same plane. The plane of the phenyl group is nearly perpendicular (85.1°) to this plane. The C–Bi bond distance is 2.26(2) Å, not significantly different from the corresponding distance in triphenylbismuthine.[174] The IR spectrum of the thiolato compound exhibits a peak at 442 cm^{-1} (Bi–C stretching) and peaks at 330 and 350 cm^{-1} (both attributed to Bi–O stretching). The two Bi–O bands are believed to be consistent with the cis configuration of the oxygen atoms.

A few papers have been published that contain information about the physical properties of bis(dialkyldithiocarbamato)bismuthines of the type $MeBi(S_2CNR_2)_2$ and $PhBi(S_2CNR_2)_2$, where R_2N is Me_2N, Et_2N, or 1-piperidyl. Kupchik and Theisen[313] found that the molecular weights of phenylbis(dimethyldithiocarbamato)- and phenylbis(diethyldithiocarbamato)bismuthine in benzene, chlorobenzene, or camphor are somewhat higher than theoretical for a monomeric structure, but these authors do not suggest that the compounds are associated. The IR spectra of the two substances contain a strong band near 1500 cm^{-1} that is attributed to the stretching frequency of the partial C=N bond of the following type of canonical form:



$$PhBi\left(SC\overset{+}{=}NR_2 \, , \, S^-\right)_2$$

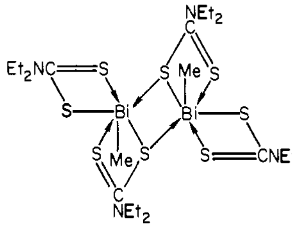
Their UV spectra show intense absorption near 260 nm (ϵ 6 × 10^4). This band is apparently not caused primarily by the phenyl group but by the dialkyldithiocarbamato moiety, since tris(diethyldithiocarbamato)bismuthine also absorbs at 260 nm (ϵ 7 × 10^4). Wieber and Basel[334] have investigated the mass and ^1H NMR spectra of all six compounds. The mass spectrum of methylbis(dimethyldithiocarbamato)bismuthine exhibits a peak for the molecular ion, while the spectra of the other two methyl compounds contain M − 15 peaks. All six mass spectra show $MeBi^+$ or $PhBi^+$ fragments and an intense peak corresponding to Bi^+. The ^1H NMR signal of the methyl group attached to bismuth appears at lower field (by about 0.5 ppm) than the corresponding signal observed with compounds of the $MeBi(SR)_2$ type,[326] where R is an alkyl, cycloalkyl, or aryl group. A similar deshielding effect is observed with the phenylbis(dialkyldithiocarbamato)bismuthines. These ^1H NMR results are attributed to the strong chelating ability of the dialkyldithiocarbamato groups that leads to the following type of structure:



R' = Me or Ph

Wieber and Baudis[326] have obtained similar ^1H NMR results with compounds of the $MeBi(S_2COR)_2$ type (where R is Me, Et, or Me_2CH) and have suggested analogous chelated structures.

More recently, Burschka and Wieber[353] have reported that methylbis(dithiocarbamato)bismuthine gives a normal cryoscopic molecular weight in benzene solution but forms dimeric units in the crystalline state. The dimers are held together by intermolecular bismuth–sulfur interactions:



The coordination around each bismuth atom is that of a slightly distorted pentagonal pyramid. The five bismuth–sulfur bonds are directed to the corners of the base of the pyramid, and the methyl group bonded to the bismuth is at the apex. The free electron pair on the bismuth is presumably directly opposite this methyl group. The intermolecular Bi–S bonds are unusually long but are, nevertheless, significantly shorter than the sum of the van der Waals radii. The C–Bi distances are 2.21 (4) Å and 2.27 (3) Å. These values are not significantly different from the C–Bi distances found in triphenylbismuthine[174] and phenylbis(1-oxopyridine-2-thiolato)bismuthine.[314]

An X-ray crystallographic determination of the structure of the xanthatobismuthine $Ph_2BiS_2COCHMe_2$ has been described in another recent paper from Wieber's laboratory.[323] One noteworthy observation is that the thioxo sulfur atom appears to be within the coordination sphere of the bismuth atom of a neighboring molecule; i.e., the xanthato group functions in the crystal as a bidentate ligand. This arrangement makes it possible to regard the coordination around each bismuth atom as that of a distorted trigonal bipyramid in which the apical positions are occupied by sulfur atoms and two equatorial positions are occupied by the carbon atoms of the two phenyl groups bonded to the bismuth. A pair of nonbonding bismuth electrons presumably occupies the third equatorial position. The C–Bi bond distances, 2.26 (1) and 2.24 (1) Å, are not significantly different from the corresponding distances in triphenylbismuthine or the other compounds discussed in this section.

Compounds of the type $ArBiX_2$ (where Ar is Ph, o-MeC_6H_4, m-MeC_6H_4, or p-MeC_6H_4 and X is Cl, Br, or O_2SPh) have been found to give apparent first-order ^1H NMR spectra at 60 MHz.[164,327] For example, the spectrum of phenyldichlorobismuthine in dimethyl sulfoxide exhibits a well-defined doublet at τ 1.00 and two well-defined triplets at τ 2.08 and 2.62. The three signals can be assigned to the ortho, meta, and para protons, respectively. Solutions in acetonitrile and other donor solvents give similar spectra, in which the separation between the meta and para signals is greater than that obtained with benzyl alcohol in the presence of the powerful shift reagent, tris(dipivalomethanato)europium. The ^1H NMR spectra of compounds of the Ar_2BiX type have also been investigated; the resolution of the aromatic proton signals is much poorer than that observed with the $ArBiX_2$ compounds.

In addition to the data already discussed in this section, the literature contains a number of other observation about the structure and physical properties of halobismuthines, dihalobismuthines, and related compounds. Thus, the following information has been reported: the IR spectra of dicyclopentadienylchlorobismuthine,[51] phenyldibromobismuthine,[294] dimethylthiocyanatobismuthine,[130] dimethyl(trimethylsiloxy)bismuthine,[329] diphenyl(trimethylsiloxy)bismuthine,[329] methylbis(trimethylsiloxy)bismuthine,[329] diphenyl(benzenesulfinato)bismuthine,[99] phenylbis(benzenesulfinato)bismuthine,[99] and phenylbis(p-toluenesulfinato)bismuthine;[243] the ^1H NMR spectra of 1-chloro-1,4-dihydrobismin,[310] dimethyl(trimethylsiloxy)bismuthine,[329] diphenyl(trimethylsiloxy)bismuthine,[329] methylbis(trimethylsiloxy)bismuthine,[329] dimethyl[methyl(trimethylsilyl)amino]bismuthine,[27] methylbis[methyl(trimethylsilyl)amino]bismuthine,[27] diphenylphenoxybismuthine,[328] several diphenylalkoxybismuthines[328] and methyldialkoxybismuthines,[326] and 2-methyl-1,3,2-benzodioxabismole;[325] the ^1H NMR spectra of a number of thio compounds of the types Ph_2BiSR,[328,333] $PhBi(SR)_2$,[327] and $MeBi(SR)_2$[325,326] (where R is an alkyl, aryl, or similar group); the ^{19}F NMR spectra of the meta[332] and para[36,332] isomers of diphenyl(fluorophenylthio)bismuthine; and the ^1H NMR spectra of the xanthatobismuthines Ph_2BiS_2COR (where R is Me, Et, Pr, Bu, Me_2CH, or Me_2CHCH_2).[323]

V. Tertiary Bismuth Dihalides and Related Compounds

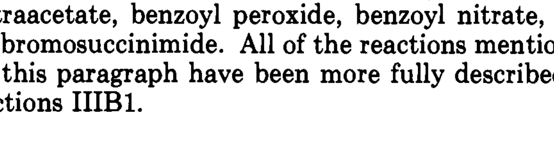
A. Preparation

1. By Oxidative Addition Reactions

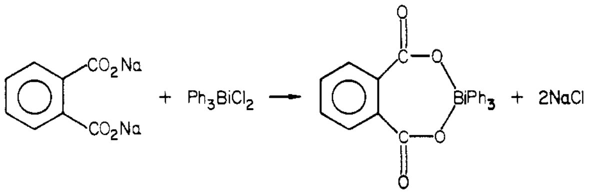
Triarylbismuth dichlorides and dibromides are usually prepared by the addition of a stoichiometric quantity of the halogen to a cold solution of the triarylbismuthine in an organic solvent. Trialkylbismuthines are cleaved by chlorine or bromine even at 0 °C, but it has been reported that the cis and trans isomers of tripropenylbismuthine are converted on treatment with bromine at −55 °C to the corresponding tripropenylbismuth dibromides. Recently, fluorine diluted with argon has been used for the preparation of triphenylbismuth difluoride from triphenylbismuthine. No tertiary bismuth diiodide has ever been isolated. Triphenylbismuth diiodide is probably formed at low temperatures by the interaction of triphenylbismuthine and iodine in ether or acetonitrile, but it decomposes on warming to give diphenyliodobismuthine and iodobenzene. The oxidation of triphenylbismuthine to pentavalent triphenylbismuth derivatives has also been accomplished by means of lead tetraacetate, benzoyl peroxide, benzoyl nitrate, and N-bromosuccinimide. All of the reactions mentioned in this paragraph have been more fully described in sections IIIB1.

2. By Metathetical Reactions of Triarylbismuth Dichlorides and Dibromides

Triarylbismuth dichlorides and dibromides undergo metathetical reactions with silver salts to give a variety of other triarylbismuth compounds of the type Ar_3BiY_2, where Y is an anionic group. These reactions have proved useful for the preparation of triphenylbismuth difluoride,[354] dicyanate,[117,354,355] dinitrate,[78,102,354,356,357] dihydroxide,[158] oxide,[355] diacetate,[354] bis(fluoroacetate),[354] bis(difluoroacetate),[354] bis(trifluoroacetate),[354,355] bis(chloroacetate),[354] bis(dichloroacetate),[354] bis(trichloroacetate),[354] bis(bromoacetate),[354] bis(cyanoacetate),[354] and dibenzoate[117] as well as several other triarylbismuth difluorides,[358] dinitrates,[78,79,102,104,356,357,359] and dibenzoates.[81] A bis(succinimide) derivative has been prepared in a similar manner:[120]



Sodium, potassium, and lead salts also undergo metathetical reactions with triarylbismuth dichlorides and dibromides. Thus, lead acetate has been used to prepare triarylbismuth diacetates,[102] while sodium or potassium salts have been used to prepare triphenylbismuth difluoride,[321] diazide,[158,360] dicyanide,[360] carbonate,[78,361,362] oxalate,[361] chromate,[361] bis(benzenethiolate),[363] and a number of dicarboxylates.[363] The interaction of triphenylbismuth dichloride and disodium phthalate is said to yield a heterocyclic derivative of bismuth:[363]



A number of triphenylbismuth dicarboxylates have been prepared by the following type of reaction:[364]

$$Ph_3BiBr_2 + 2RSCH_2CO_2H + 2Et_3N \rightarrow Ph_3Bi(O_2CCH_2SR)_2 + 2Et_3NH^+Br^-$$

$$R = Me, Et, Pr, Me_2CH, Bu, Ph, \text{ or } PhCH_2$$

Triphenylbismuth dibenzoate,[232] dipropionate,[232] and bis(phenoxyacetate)[364] can be obtained in a similar manner. Triphenylbismuth molybdate has been prepared from a quaternary ammonium salt:[365]

$$Ph_3BiBr_2 + (Bu_4N)_2MoO_4 \rightarrow Ph_3BiMoO_4 + 2Bu_4NBr$$

An attempt in 1966 to prepare triphenylbismuth diperchlorate by the interaction of triphenylbismuth dichloride (in acetone) and silver perchlorate (in absolute alcohol) was found to yield tetraphenylbismuthonium perchlorate.[366] The mechanism of this remarkable reaction has not been elucidated. A similar rearrangement was noted in 1973 when triphenylbismuth dichloride was allowed to react with silver tetrafluoroborate in acetylacetone or methyl ethyl ketone; i.e., tetraphenylbismuthonium tetrafluoroborate was formed.[367] In pure acetone, however, both silver perchlorate and silver tetrafluoroborate react with triphenylbismuth dichloride to yield acetonyltriphenylbismuthonium derivatives:[368]

$$Ph_3BiCl_2 + 2AgX + Me_2CO \rightarrow [Ph_3BiCH_2COMe]X + 2AgCl + HX$$

$$X = ClO_4 \text{ or } BF_4$$

Treatment of a benzene solution of triphenylbismuth dichloride with an *aqueous* solution of silver perchlorate yields still another type of organobismuth compound, namely the dihydrate of oxybis(triphenylbismuth) diperchlorate, $[Ph_3Bi(H_2O)OBi(H_2O)Ph_3][ClO_4]_2$.[355] (The anhydrous diperchlorate is obtained by drying the dihydrate in vacuo for about a week or by recrystallizing the dihydrate from absolute ethanol and anhydrous diethyl ether.) The interaction of triphenylbismuth dichloride and silver tetrafluoroborate under similar conditions, however, does not yield oxybis(triphenylbismuth) ditetrafluoroborate; surprisingly, the main product is triphenylbismuth difluoride. Oxybis(triphenylbismuth) dinitrate can be prepared by the reaction of an acetone solution of triphenylbismuth dichloride with an aqueous solution of silver nitrate. The reaction of triphenylbismuth dichloride with silver cyanate or trifluoroacetate under similar conditions, however, does not give the oxy compounds; triphenylbismuth dicyanate or bis(trifluoroacetate) is obtained instead. The two oxy compounds can be prepared by the following type of metathetical reaction:

$$(Ph_3BiCl)_2O + 2AgX \rightarrow (Ph_3BiX)_2O + 2AgCl$$

$$X = NCO \text{ or } O_2CCF_3$$

(Preparation of the oxybis(triphenylbismuth) dichloride required for these reactions is described later in this section.) The oxydiacetate cannot be obtained via a similar reaction with silver acetate; the main product has been found to be impure triphenylbismuthine.

Many years ago Challenger and co-workers reported the preparation of compounds of the type $Ph_3Bi(OH)X$, where X is Cl,[114,158] Br,[114] or CN.[158] They[158] also mentioned triphenylbismuth hydroxide azide but gave no information about its preparation. The hydroxide chlorides and hydroxide bromides were obtained by several methods: by passing moist ammonia gas into a chloroform solution of the triphenylbismuth dihalide; by warming a solution of the dihalide in moist ether with sodium; and by dissolving triphenylbismuth sulfate in ammonia and treating the solution with hydrochloric acid. The hydroxide cyanide was prepared by treatment of triphenylbismuth dichloride or dihydroxide with aqueous potassium cyanide and recrystallization of the crude product from a mixture of petroleum ether and chloroform. The preparation of triarylbismuth hydroxide chlorides and hydroxide bromides has also been mentioned in a few publications[102,115] from other laboratories.

Goel and Prasad[355,360] believe, however, that the existence of compounds of the type $Ar_3Bi(OH)X$ is open to question. Their studies indicate that the reaction between equimolar amounts of triphenylbismuth dichloride or dibromide and alcoholic sodium or potassium hydroxide yields an oxybis(triphenylbismuth) dihalide.[355] The interaction of triphenylbismuth difluoride and an alkali hydroxide under similar conditions, however, gives triphenylbismuthine and some uncharacterized material. According to Goel and Prasad[360] the product obtained by the reaction of triphenylbismuth dichloride with aqueous potassium cyanide is triphenylbismuth dicyanide (*not* triphenylbismuth hydroxide cyanide). The diazide can be prepared by an analogous reaction. The resistance of the dicyanide and diazide to hydrolysis seems remarkable.

Metathetical reactions of triarylbismuth dihalides and related compounds have been used for the preparation of various coordination complexes. The preparation and properties of these complexes is described in section VB4.

3. *Miscellaneous Methods*

Triphenylbismuth selenate[361] and a number of triphenylbismuth dicarboxylates[114,331,363] have been prepared by treatment of triphenylbismuth carbonate with the appropriate acid. The interaction of the carbonate and concentrated hydrochloric acid yields triphenylbismuth dichloride,[144] but this reaction has no synthetic value since the carbonate is prepared from the dichloride or dibromide. Triphenylbismuth sulfate[112,114,361] has been prepared by dissolving the dichloride in cold, concentrated sulfuric acid, drawing air through the solution to remove hydrogen chloride, and then pouring the mixture on ice. Tri-*o*-tolylbismuth dichloride has been sulfonated to mono-, di-, and trisulfo derivatives of tri-*o*-tolylbismuth sulfate.[102,359] The trisulfo derivative has been converted to a tris(hydroxy-2-tolyl)bismuth hydroxide chloride. The methyl groups of tri-*o*-tolyl- and tri-*p*-tolylbismuth dichlorides can be oxidized to carboxy groups with potassium permanganate or chromic acid. The carboxy compounds in turn can be esterified by dissolving them in methanol saturated with hydrogen chloride or by treating them with dimethyl sulfate in alkaline solution. Both the oxidation and esterification reactions give low yields.

The nitration of triarylbismuth dinitrates has been carried out successfully at relatively low temperatures. Thus, triphenylbismuth dinitrate on treatment with fuming nitric acid at 0 °C yields a mixture of tris(nitrophenyl)bismuth dinitrates.[369] The orientation of the nitro groups is approximately 86% meta, 12% ortho, and 2% para. In other work[108] dinitro, tetranitro, and hexanitro derivatives of triphenylbismuth dinitrate have been reported; no information about the structure of these compounds has been given. Trinitro derivatives of tri-*o*-tolyl-, tri-*p*-tolyl- and tris(*p*-carbomethoxyphenyl)bismuth dinitrates have also been prepared by nitration.[102,356]

Triphenylbismuth dibromide has been converted to triphenylbismuth dinitrate by treatment with nitric acid,[370] while a number of triarylbismuth dinitrates have been converted to dichlorides by treatment with hydrogen chloride.[78,102,108,356] The reaction of aqueous triphenylbismuth dihydroxide with sodium chloride is said to yield triphenylbismuth dichloride and triphenylbismuth hydroxide chloride.[158] Treatment of triphenylbismuth hydroxide chloride with hydrobromic acid yields a mixture of the dichloride and dibromide.[298] Triphenylbismuthine oxide has been prepared by the reaction:[360]

$$Ph_3Bi(CN)_2 + HgO \rightarrow Ph_3BiO + Hg(CN)_2$$

Triphenylbismuth difluoride has been obtained by the decomposition of a pentacoordinate cationic bismuth complex in dichloromethane solution:[371]

$$[Ph_3Bi(OAsPh_3)_2](BF_4)_2 \rightarrow Ph_3BiF_2 + 2Ph_3AsOBF_3$$

Two quaternary bismuth compounds have been converted to triphenylbismuth dihalides:

$$Ph_4BiBr_3 \xrightarrow{5\ ^\circ C} Ph_3BiBr_2 + PhBr \quad \text{(ref 119)}$$

$$Ph_4BiOSiPh_3 + 2HCl \rightarrow Ph_3BiCl_2 + Ph_3SiOH + PhH \quad \text{(ref 372)}$$

The radiolysis of a chloroform solution of triphenylbismuthine by means of γ-radiation from a ^{60}Co source results in the formation of triphenylbismuth dichloride.[168,169]

B. Reactions

1. General

Except for the metathetical reactions discussed in section VA2, tertiary dihalides and related compounds undergo relatively few reactions that do not involve cleavage of the carbon–bismuth bond. The thermal stability of the dihalides is in the order difluorides > dichlorides > dibromides > diiodides.[321] Two types of decomposition appear to occur:

$$(1) \quad Ar_3BiX_2 \rightarrow Ar_2BiX + ArX$$

$$(2) \quad 2Ar_3BiX_2 \rightarrow Ar_3Bi + ArBiX_2 + 2ArX$$

At higher temperatures the triarylbismuthines formed in the second type of decomposition may react as follows:

$$2Ar_3Bi \rightarrow 3Ar\text{–}Ar + 2Bi$$

As previously mentioned (section VA1), triphenylbismuth diiodide is not stable at room temperature but decomposes spontaneously to diphenyliodobismuthine and iodobenzene. Triarylbismuth dibromides are more stable but apparently undergo a similar type of decomposition on heating. Thus, triphenylbismuth dibromide on boiling with benzene gives a good yield of diphenylbromobismuthine; if the dibromide is heated alone at 100 °C for a few minutes, it decomposes to a yellow, viscous material that apparently contains bromobenzene.[34] Similarly, tri-α-naphthylbismuth dibromide on being heated at 100 °C for 0.5 h yields α-bromonaphthalene, tri-α-naphthylbismuthine, α-naphthyldibromobismuthine, and inorganic bismuth (which was isolated as the oxybromide).[57] Triphenylbismuth dichloride decomposes only slowly in boiling benzene;[107,321] the pure dichloride melts at 141 °C and decomposes at 150 °C.[321] Triphenylbismuth difluoride is stable up to 200 °C.[321] At 250–260 °C it decomposes rapidly to form fluorobenzene, triphenylbismuthine, biphenyl, and, presumably, inorganic bismuth.

Like the dihalides, other compounds of the Ar_3BiY_2 type also may be thermally unstable. Thus, triphenylbismuth diazide decomposes slowly at room temperature and rapidly at 100 °C to diphenylazidobismuthine and phenyl azide:[158,360]

$$Ph_3Bi(N_3)_2 \rightarrow Ph_2BiN_3 + PhN_3$$

The diphenylazidobismuthine is said to decompose subsequently to yield triphenylbismuthine, but the stoichiometry of this reaction has not been elucidated. Triphenylbismuth dicyanide is stable at room temperature but decomposes on heating. At 140 °C, complete cleavage of the Ph–Bi and Bi–CN bonds occurs, and the evolution of cyanogen is observed. Both the diazide and dicyanide are insoluble in petroleum ether but soluble in other common organic solvents. In solution, however, the dicyanide decomposes in several hours to yield cyanodiphenylbismuthine and benzonitrile.

Triphenylbismuth dihydroxide decomposes violently at 100–120 °C and deflagrates when heated with a flame.[158] In water or in organic solvents it decomposes even in the cold to yield bismuth hydroxide and triphenylbismuthine. Triphenylbismuthine oxide[355] appears to be stable in the solid state at room temperature, but decomposes slowly in benzene solution.

Attempts to prepare triarylbismuth dithiocyanates or diselenocyanates via metathetical reactions of triarylbismuth dihalides have yielded diarylthiocyanatobismuthines[321] or diarylselenocyanatobismuthines,[373] respectively. From this result it has been concluded that the dithiocyanates and diselenocyanates must be extremely unstable compounds.

It seems likely that the cyanide iodide $Ph_3Bi(CN)I$ is also unstable. Thus, an attempt to prepare this substance has resulted in the formation of diphenylcyanobismuthine and iodobenzene:[161]

$$Ph_3Bi + ICN \rightarrow Ph_2BiCN + PhI$$

2. Reduction

The reduction of triarylbismuth dihalides to the corresponding triarylbismuthines has been carefully studied.[101-103] Hydrazine hydrate is often the reagent of choice for this reation. Another good procedure involves solution of the dihalide in acetone and treatment of the cooled mixture with concentrated, aqueous sodium hydrosulfite. This method has been used in the preparation of two tris(nitroaryl)bismuthines.[102] It has also proved useful in obtaining pure tri-*m*-tolylbismuthine. When this compound is prepared by the Grignard reaction, it is contaminated with traces of toluene and *m*-bromotoluene that are difficult to remove. The crude compound can, however, be converted easily into tri-*m*-tolylbismuth dichloride, which can be purified by recrystallization and then reduced with sodium hydrosulfite to pure tri-*m*-tolylbismuthine.

Gilman and Yablunky[81] have reported that liquid ammonia itself reduces triphenylbismuth dichloride to triphenylbismuthine in about 10% yields. Treatment of the dichloride in liquid ammonia with 4 equiv of sodium produces a deep red solution, the color of which can be discharged by the addition of α-iodonaphthalene. The resulting solution yields 71% naphthalene and 12.3% triphenylbismuthine.

Attempts to prepare the pentavalent hydride Ph_3BiH_2 by the reduction of triphenylbismuth dichloride with either lithium borohydride or lithium aluminum hydride have been unsuccessful.[374] The only organic product isolated was triphenylbismuthine. The interaction of triphenylbismuth dichloride and a sodium dialkyldithiocarbamate also yields triphenylbismuthine:[313]

$$Ph_3BiCl_2 + 2NaS_2CNR_2 \rightarrow Ph_3Bi + (R_2NCS_2)_2 + 2NaCl$$

The electrolytic reduction of triphenylbismuth dibromide has been found to be a one-step, two-electron process that involves loss of bromine as bromide ion:[282]

$$Ph_3BiBr_2 + 2e^- \rightarrow Ph_3Bi + 2Br^-$$

The formation of triarylbismuthines by the decomposition of triarylbismuth dihalides or related compounds has often been observed (cf. section VB1).

Oxybis(triphenylbismuth) dichloride, in the presence of an excess of potassium carbonate or sodium bicarbonate, has been found to be a mild but effective reagent for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively.[375] The reagent is easily prepared by the alkaline hydrolysis of triphenylbismuth dichloride (cf. section VA2):

$$2Ph_3BiCl_2 + 2OH^- \rightarrow (Ph_3BiCl)_2O + 2Cl^- + H_2O$$

The oxidations are conveniently carried out in dichloromethane in which the reagent is readily soluble. It is particularly useful for the oxidation of allylic alcohols (to the corresponding aldehydes), and it can also be employed for the cleavage of 1,2-glycols. The aldehydes or ketones formed in these reactions are easily separated from the triphenylbismuthine produced by reduction of the reagent.

In a second paper,[362] it was noted that oxybis(triphenylbismuth) dichloride suffers a loss of oxidizing power if the carbonate or bicarbonate used in the above reactions is replaced by pyridine or collidine. Further investigation led to the conclusion that triphenylbismuth carbonate is actually the active oxidant. This substance is easily obtained by a metathetical reaction carried out in aqueous acetone (cf. section VA2):

$$Ph_3BiCl_2 + K_2CO_3 \rightarrow Ph_3BiCO_3 + 2KCl$$

It turns out to be a useful heterogeneous oxidant for a number of functional groups. Thus, alcohols are oxidized to aldehydes or ketones, hydrazones to diazo compounds, and hydrazines to azo compounds. Thiols are oxidized to disulfides, but the rate is much slower. Aniline, dimethylaniline, pyrrolidine, and 3-pyrrolidinocholesta-2,5-diene appear to be unaffected by the oxidant. Completely homogeneous oxidation conditions can be realized by employing triphenylbismuth dicarboxylates of the type $Ph_3Bi(O_2CR)_2$, where R is Me, CF_3, or Ph, in the presence of relatively strong bases such as tetramethylguanidine or 1,5-diazobicyclo[5.4.0]undec-5-ene. These bases also accelerate the oxidation of cinnamyl alcohol by triphenylbismuth carbonate.

Two later papers[376,377] have reported that, in some cases, cleavage of a carbon–bismuth bond may accompany the oxidation of organic substrates with the pentavalent bismuth reagents discussed in the above two paragraphs. In some reactions, the aryl group thus cleaved may be transferred to nitrogen or carbon. This new arylation process appears to have a number of synthetically useful applications.

3. With Organometallic Reagents

In 1952 Wittig and Clauss[119] prepared the first quinquenary bismuth compound by the interaction of triphenylbismuth dichloride and phenyllithium at −75 °C. At room temperature, however, this reaction yields decomposition products such as triphenylbismuthine. In 1969 two other quinquenary bismuth compounds were prepared by the low-temperature reaction of triphenylbismuth dichloride with aryllithium compounds. All of this work is discussed in more detail in section VII.

Many years earlier Challenger and co-workers[34,114] attempted to prepare tetraarylbismuth halides by the interaction of triarylbismuth dihalides and Grignard reagents. The desired products, however, were never isolated. In the case of the reaction between triphenylbismuth dibromide and phenylmagnesium bromide, the only compounds obtained were triphenylbismuthine, diphenylbromobismuthine, phenyldibromobismuthine, and bromobenzene. It was noted by Challenger[34] that an intense but short-lived purple color developed during the course of these Grignard reactions. The purple color can probably be attributed to the transitory presence of a pentaarylbismuth compound. Thus, both pentaphenylbismuth and triphenylbis(*p*-chlorophenyl)bismuth are now known to be purple and quite unstable (cf. section VIIB). Gilman and Yablunky[378] showed that the evanescent purple color first observed by Challenger could be made the basis of a sensitive test for arylmagnesium halides and aryllithium compounds. No color is given by any alkylmetallic compound or by relatively unreactive arylmetallic compounds such as tetraphenyllead. Steric factors, either in the triarylbismuth dihalide or the reactive organometallic reagent, decrease the intensity of the purple color or may even prevent its formation. For example, tri-*o*-tolylbismuth dichloride gives a weak purple color with phenylmagnesium bromide or with *p*-tolylmagnesium bromide, and it gives a negative test with α-naphthylmagnesium bromide. Both trimesitylbismuth dichloride and tri-α-naphthylbismuth dibromide give negative tests with Grignard reagents. Not surprisingly, diarylhalobismuthines and aryldihalobismuthines also fail to give the color test on treatment with reactive organometallic compounds.

4. Coordination Chemistry

Beaumont, Goel, and Prasad[371] have reported that treatment of anhydrous oxybis(triphenylbismuth) diperchlorate with oxygen-donor bases results in the formation of pentacoordinate cationic complexes of the type $[(Ph_3BiL)_2O](ClO_4)_2$, where L is dimethyl sulfoxide (Me_2SO), pyridine *N*-oxide (PyO), Ph_3PO, or Ph_3AsO.

Pentacoordinate complexes can also be prepared from triphenylbismuth dichloride by the following type of reaction:

$$Ph_3BiCl_2 + 2L + 2AgY \rightarrow (Ph_3BiL_2)Y_2 + 2AgCl$$

$$L = Me_2SO,\ PyO,\ Ph_3PO,\ \text{or}\ Ph_3AsO;\ Y = ClO_4,\ BF_4,\ \text{or}\ PF_6$$

An unstable dinitrate, $[Ph_3Bi(OAsPh_3)_2](NO_3)_2$, can be obtained in a similar manner. Except for this compound, all the complexes are stable in the solid state at room temperature for at least several months. In dichloromethane the complex $[Ph_3Bi(OAsPh_3)_2](BF_4)_2$ decomposes to yield triphenylbismuth difluoride:

$$[Ph_3Bi(OAsPh_3)_2](BF_4)_2 \rightarrow Ph_3BiF_2 + 2Ph_3AsOBF_3$$

The IR spectra of the complexes clearly show the presence of ionic perchlorate, tetrafluoroborate, hexafluorophosphate, or nitrate groups as well as cations of the type $Ph_3BiL_2^{2+}$ or $[(Ph_3BiL)_2O]^{2+}$ in which the ligands L are bonded to the bismuth through their oxygen atoms. It has been concluded that the bismuth atoms in these complexes possess a trigonal-bipyramidal configuration with the phenyl groups occupying equatorial positions. All of the complexes behave as 1:2 electrolytes in nitromethane. In dichloromethane, however, the molar conductance values for the oxybis complexes in which L is Me_2SO or PyO are lower than anticipated for 1:2 electrolytes. The decrease in conductivity may result from the following type of equilibrium reaction:

$$[(Ph_3BiL)_2O]^{2+} + 2ClO_4^- \rightleftarrows [Ph_3Bi(OClO_3)]_2O + 2L$$

In accordance with this hypothesis, the conductance of dichloromethane solutions of these Me_2SO and PyO complexes increases markedly upon addition of excess ligand.

Faraglia and co-workers[379,380] have used metathetical reactions of triphenylbismuth dihalides to prepare the compounds $Ph_3Bi(Ox)X$, where Ox is the oxinate (8-quinolinolate) group and X is Cl or Br:

$$Ph_3BiX_2 + NaOx \rightarrow Ph_3Bi(Ox)X + NaX$$

Preparation of the bromide by another procedure has been described in an East German patent:[381]

$$Ph_3Bi(NR_2)Br + HOx \rightarrow Ph_3Bi(Ox)Br + R_2NH$$

$$R_2NH = \text{succinimide}$$

Osmometry in benzene and conductivity measurements in methanol show that the organobismuth oxinates exist in solution as essentially monomeric, undissociated species. The electronic spectra of the complexes in the solid state exhibit absorption bands centered around 360 nm, which are characteristic of a chelating oxinate group. The IR spectra are consistent with the presence of such a chelate, and they also suggest the presence of bismuth–halogen bonds. The solid complexes thus appear to contain bismuth atoms bonded to the oxygen and nitrogen atoms of the oxinate group and to the halogen atom; i.e., the bismuth is hexacoordinate and presumably octahedral. In methanol solution, however, the Bi–N bond is cleaved, and the complexes exist as monomeric, undissociated species in which the bismuth atom is bonded to the oxinate group only through the oxygen atom.

A compound containing the anionic species $[Ph_3Bi(MoO_4)_2]^{2-}$ can be prepared by either of the following reactions:[365]

$$Ph_3BiBr_2 + 2(Bu_4N)_2MoO_4 \rightarrow [Bu_4N]_2[Ph_3Bi(MoO_4)_2] + 2Bu_4NBr$$

$$Ph_3BiMoO_4 + (Bu_4N)_2MoO_4 \rightarrow [Bu_4N]_2[Ph_3Bi(MoO_4)_2]$$

Conductivity data indicate that this substance is a 2:1 electrolyte in acetonitrile. The ^{17}O NMR spectrum shows a resonance at δ 267, a value typical for a bridging oxygen, and the ^{13}C NMR spectrum indicates only one type of phenyl group. It has been concluded that the spectroscopic data support a structure involving trigonal-bipyramidal geometry at bismuth, with phenyl groups occupying equatorial sites and unidentate tetrahedral molybdate groups occupying the axial sites.

5. Other Reactions

The reaction of triphenylbismuth dichloride with mercuric chloride in aqueous alcohol leads to cleavage of the carbon–bismuth bonds and to a nearly quantitative yield of phenylmercuric chloride.[348] The following stoichiometry has been suggested:

$$Ph_3BiCl_2 + HgCl_2 + H_2O \rightarrow PhHgCl + BiOCl + 2PhH + Cl_2$$

In alkaline medium the interaction of triphenylbismuth dichloride and mercuric oxide yields triphenylbismuthine. Treatment of triphenylbismuth dicyanide with mercuric oxide results in the metathetical reaction:[360]

$$Ph_3Bi(CN)_2 + HgO \rightarrow Ph_3BiO + Hg(CN)_2$$

Attempts to prepare triphenylbismuth dicyanate by oxidation of triphenylbismuth dicyanide with manganese dioxide or by treatment of triphenylbismuth diazide with carbon monoxide have been unsuccessful. The dicyanate has, however, been prepared by the metathetical reaction of triphenylbismuth dichloride and silver cyanate (cf. section VA2).

Attempts to cleave the ether linkage in tris(*p*-methoxyphenyl)bismuth dibromide with hydriodic acid or aluminum chloride have resulted either in extensive decomposition or in recovery of the unchanged starting material.[102] The bromination of tri-*o*-tolyl- or tri-*p*-tolylbismuth dibromide in the presence of UV light causes cleavage of the carbon–bismuth bond and the formation of bismuth bromide and *o*-bromo- or *p*-bromobenzyl bromide.

Nefedov and co-workers[382,383] have studied the rate of ^{210}Bi exchange between labeled triphenylbismuthine and triphenylbismuth dichloride. They found that the exchange is first order with respect to each compound and that the activation energy is 15.9 kcal/mol.

It has been reported[384–387] that organic compounds of ^{210}Po are formed as the result of the β decay of ^{210}Bi incorporated in triarylbismuth dihalides (which were prepared by utilizing the β decay of ^{210}Pb in tetraaryllead compounds). The ^{210}Po compounds have been isolated by means of paper or thin-layer chromatography and have been tenatively identified as diarylpolonium dichlorides, triarylpolonium chlorides, or, in one case, the diarylpolonium $(p\text{-}MeC_6H_4)_2Po$.

The bismuth in triphenylbismuth dichloride has been converted in part to ^{210}Bi by means of neutron irradiation.[388-390] The decay of the ^{210}Bi in triphenylbismuth dichloride to ^{206}Tl and α particles has also been observed.[389]

Keck and Klar[116] have reported that tris(*p*-(dimethylamino)phenyl)bismuth dichloride reacts with antimony pentachloride or aluminum chloride to form salts of the type $[Ar_3Bi][SbCl_6]_2$ or $[Ar_3Bi][AlCl_4]_2$ in which the bismuth atom has an oxidation state of +5 and a coordination number of 3. The authors were, however, unable to purify these substances.

The interaction of triphenylbismuth dichloride and a palladium(II) salt in the presence of an excess of 1-octene or ethyl acrylate results in the cleavage of all three C–Bi bonds and the formation of biphenyl as well as phenylated derivatives of the olefinic compound.[171] The phenylation reactions appear to involve the intermediate formation of phenylpalladium compounds.

The hydrolysis of triphenylbismuth diacetate in dichloromethane yields metallic bismuth plus a complex mixture of organic compounds.[113] Mass spectrometric examination indicates that this mixture contains diphenylacetatobismuthine, phenyl acetate, chlorobenzene, and biphenyl. There is no evidence for the formation of triphenylbismuth dihydroxide.

The use of triphenylbismuth dihalides as analytical reagents has been discussed in a paper on the extraction of halide ion by a variety of organic and organometallic compounds.[391]

C. Structure and Physical Properties

Tertiary bismuth dihalides are beautifully crystalline, nonhygroscopic solids, most of which are soluble in benzene, chloroform, dioxane, or acetone, slightly soluble in alcohol or ether, and insoluble in water. The melting (or decomposition) points of most of these substances are between 100 and 200 °C. Tri-*m*-tolylbismuth dibromide[102,392] and *cis*-tripropenylbismuth dibromide,[38] however, melt below 100 °C, while a few triarylbismuth dihalides[102,359] do not melt or decompose below 250 °C. The solubilities and melting points of compounds of the type Ar_3BiY_2 (where Y is an anionic group other than halide) seem to be similar to those of the dihalides, but triphenylbismuth dihydroxide[158] is said to be soluble in water and to decompose in organic solvents. Triphenylbismuthine oxide[355] is moderately soluble in benzene and slightly soluble in acetonitrile but is insoluble in chloroform or ether; it is reduced to triphenylbismuthine by alcohol or acetone. Oxybis(triphenylbismuth) derivatives of the type $(Ph_3BiY)_2O$, where Y is Cl, Br, $OClO_3$, ONO_2, NCO, or O_2CCF_3, are soluble in dichloromethane, ethanol, or acetonitrile. With the exception of the diperchlorate and the dinitrate, they are also soluble in chloroform or acetone. The diperchlorate is not appreciably soluble in either of these two solvents, while the dinitrate is moderately soluble in chloroform and very sparingly soluble in acetone.

Triarylbismuth dihalides and related compounds appear to have nonionic, five-coordinated structures in which there is a trigonal-bipyramidal arrangement of bonds around the bismuth atom. Thus, an X-ray investigation of triphenylbismuth dichloride has shown that the bismuth atom and the three carbon atoms to which it is bonded are coplanar and the two Bi–Cl bonds are approximately perpendicular to this plane.[393] The C–Bi–C bond angles range from 113° to 130°, while the C–Bi–Cl angles are between 84° and 95°. The average C–Bi distance of 2.12 Å is comparable to that found in triphenylbismuthine, and the average Bi–Cl distance (2.57 Å) is only slightly shorter than those found in the $BiCl_5^{2-}$ ion. The X-ray study shows the presence of two crystallographically independent molecules of triphenylbismuth dichloride. Although their configurations and conformations are similar, the two molecules as a whole possess no symmetry because of the asymmetric orientation of the phenyl groups. Two crystallographically different bismuth sites are also indicated by a NQR investigation of triphenylbismuth dichloride.[394] The same study suggests that triphenylbismuth dibromide is probably isostructural with the dichloride. A comparison of the bromine resonances in the dibromide with those for the analogous antimony and arsenic compounds shows a decrease in frequency with increasing atomic number of the central atom. This decrease is attributed to an increase in ionic character of the metal–bromine bond in going from arsenic to antimony to bismuth.

Oxybis(triphenylbismuth) diperchlorate, $[Ph_3Bi(OClO_3)]_2O$, has also been shown by X-ray methods to be a derivative of pentacoordinated bismuth.[395] Each metal atom is in a somewhat distorted trigonal-bipyramidal environment with the bridging oxygen at one apex and a perchlorato group at the other. The O–Bi–O angles (163.7–173.5°) are nonlinear, presumably because of intramolecular overcrowding. The three phenyl carbon atoms bonded to each bismuth atom are in a plane slightly below the bismuth (with respect to the bridging oxygen) so that the mean (bridging) O–Bi–C angle is 97.1°. The Bi–O–Bi angle, 142.4 (7)°, is much larger than tetrahedral as a consequence of π bonding or steric interactions between the phenyl groups in the two halves of the molecule. The (perchlorato) O–Bi distance, 2.65 (1) Å, is extremely long for a covalent bond and suggests that the bonding is intermediate in character between a formal covalent bond and an ionic interaction. Other bond lengths and angles in this molecule are in accord with expected values.

Goel and Prasad[354] have examined the molecular weights, electrical conductances, and IR spectra (in the 4000–200-cm^{-1} region) of 14 compounds of the type Ph_3BiY_2 (where Y is F, Cl, Br, ONO_2, NCO, O_2CMe, O_2CCH_2F, O_2CCHF_2, O_2CCF_3, O_2CCH_2Cl, O_2CCHCl_2, O_2CCCl_3, O_2CCH_2Br, or O_2CCH_2CN). In agreement with earlier work on the dichloride[114,277] and the difluoride,[396] all of these compounds gave normal molecular weights in benzene, and conductivity data show that these substances behave as molecular species in nitromethane or acetonitrile.[109] The IR spectra, which indicate that the anionic groups are covalently bound to the bismuth, provide further support for the nonionic, monomeric nature of the compounds. The difluoride exhibits a very strong band at 412 cm^{-1}, which can be assigned to Bi–F stretching. Since only one Bi–F band is observed, the F–Bi–F group is probably linear, and it may be presumed that the fluorine atoms occupy the axial positions of a trigonal-bipyramidal molecule. A very strong, broad band at 240 cm^{-1} is present in the spectrum of the dichloride and can be assigned to Bi–Cl stretching. All the bands observed in the spectrum of the dibromide can be attributed to the triphenylbismuth group, and it was concluded by Goel and Prasad that the Bi–Br stretching frequency occurs below 200 cm^{-1}. (Earlier workers[213] who had studied the IR spectrum of the dibromide had noted strong, sharp bands at 219 and 242 cm^{-1} and had assigned them to Bi–Br vibrations.) The spectrum of the dinitrate exhibits bands that are characteristic of covalently bound nitrate groups. Although bands associated with O–C–N asymmetric stretching and O–C–N bending are observed in the spectrum of the dicyanate, the mode of bonding of the cyanate group to the bismuth atom cannot be ascertained from the IR results. Asymmetric and symmetric carboxylate stretching frequencies are noted in the spectra of the diacetate, bis(cyanoacetate), and the bis(haloacetates). The separation between the asymmetric and symmetric frequencies in these compounds indicates that the anionic groups are present as unidentate ligands. In brief, all the evidence obtained in this investigation supports the conclusion that these organobismuth compounds have nonionic five-coordinate structures.

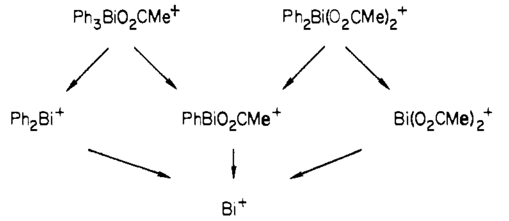
In another paper, Goel and Prasad[360] reported molecular weight and conductance measurements that show that triphenylbismuth diazide and triphenylbismuth dicyanide exist in acetone solution as nonionic, monomeric species. IR and laser Raman spectra indicate that both compounds have trigonal-bipyramidal structures analogous to that previously established for triphenylbismuth dichloride by X-ray diffraction studies. More recently, Goel and Prasad[397] compared the IR and Raman spectra of the compounds Ph_3BiY_2, where Y is F, Cl, Br, ONO_2, NCO, or O_2CMe. Again the data are in accord with a trigonal-bipyramidal skeleton.

Goel and Prasad[355,397] have used vibrational spectroscopy and conductance measurements to study the structural characteristics of of triphenylbismuthine oxide and six oxybis(triphenylbismuth) derivatives of the type $(Ph_3BiY)_2O$, where Y is Cl, Br, ONO_2, NCO, O_2CCF_3, or $OClO_3$. A dihydrate of the diperchlorate was also included in this investigation. The IR spectrum of this dihydrate suggests that the compound has an ionic structure containing the $[Ph_3Bi(OH_2)]_2O^{2+}$ cation. The IR spectra of all the other oxybis derivatives indicate that these substances are nonionic compounds in the solid state and that the anionic groups act as monodentate ligands. The IR spectrum of triphenylbismuthine oxide exhibits a strong band at 625 cm^{-1} that can be attributed to the Bi–O–Bi asymmetric stretch. Similar bands are observed in the IR spectra of the oxybis compounds. These results suggest that the oxide has a five-coordinate polymeric structure involving -Bi–O–Bi- units. The relatively low solubility of this compound in organic solvents is consistent with this formulation. The far-IR and Raman spectra of triphenylbismuthine oxide and the oxybis(triphenylbismuth) dihalides have also been examined. In each of these spectra there is a band in the 340-cm^{-1} region that can be assigned to the symmetric Bi–O–Bi stretching mode. The conductance measurements demonstrate that both the hydrated and the anhydrous diperchlorates behave as 1:2 electrolytes in acetonitrile and that all the other compounds are not significantly ionized. In dichloromethane, however, even the diperchlorates appear to be un-ionized.

Jensen[357] found that the molar polarization of triphenylbismuth dichloride in benzene is independent of temperature and, accordingly, concluded that the compound has no dipole moment. An older report[398] that the dichloride has a dipole moment of 1.17 D is almost certainly in error, presumably caused by the extraordinarily large (about 30 cm^3/mol) atomic polarization of the compound. Jensen's result is consistent with the conclusion that the geometry of the dichloride in benzene solution is similar to that found in the solid state.

Triphenylbismuth molybdate has been shown by osmometry in chloroform to have a molecular weight of 6700 and is, therefore, polymeric.[365] The ^{17}O and ^{13}C NMR spectra of this substance appear to be consistent with a structure in which Ph_3Bi units are linked together by bridging MoO_4 groups in such a way that each molybdenum is bonded tetrahedrally to two terminal oxygens and to two Mo–O–Bi bridging oxygens and each bismuth is in a trigonal-bipyramidal environment with three equatorial phenyl groups and two axial molybdate oxygens.

The mass spectrum of triphenylbismuth diacetate does not exhibit a molecular ion, but there are nine peaks corresponding to the following bismuth-containing fragments: $Ph_3BiO_2CMe^+$, $Ph_2Bi(O_2CMe)_2{}^+$, Ph_2Bi^+, $PhBiO_2CMe^+$, $Bi(O_2CMe)_2{}^+$, $PhBiOH^+$, $PhBi^+$, BiO_2CMe^+, and Bi^+ (which is the base peak).[113] The fragmentations noted below are supported by the presence of the appropriate metastable ions in the spectrum:



The diamagnetic susceptibilities of several triarylbismuth dihalides have been determined by Parab and Desai.[288,289] The average molar susceptibility of the bismuth in these compounds was found to be −30.48 × 10^{-6} cgs unit. Comparison of this value with the corresponding value (−15.50 × 10^{-6} cgs unit) for pentavalent antimony led these authors to conclude that the Bi–C bond is more ionic than the Sb–C bond.

In addition to the data already discussed in this section, the literature contains a number of other observations about the structure and physical properties of tertiary bismuth dihalides and related compounds. Thus, the following information has been reported: the ^{13}C[106] and ^{19}F[106,396] NMR spectra of triphenylbismuth difluoride; the UV and ^1H NMR spectra of tris(*p*-(dimethylamino)phenyl)bismuth dichloride;[399] the ^1H NMR and ^{13}C NMR spectra of triphenylbismuth dibromide;[232] the X-ray photoelectron spectra of triphenylbismuth dichloride and oxide;[247] the IR, ^1H NMR, and ^{13}C NMR spectra of a number of triphenylbismuth dicarboxylates;[232,364] the IR and ^1H NMR spectra of triphenylbismuth bis(succinimide);[120] the dipole moment of triphenylbismuth dinitrate;[357] and the optic axial angles of triphenylbismuth dichloride as a function of wavelength and temperature.[400,401]

VI. Quaternary Bismuth Compounds

A. Preparation

1. From Quinquenary Bismuth Compounds

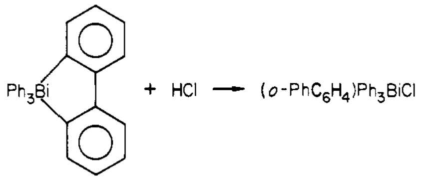
In spite of numerous attempts by earlier investigators,[34,57-59,114,155,402-404] it was not until 1952 that the first quaternary bismuth compound was prepared. In that year Wittig and Clauss[119] found that the reaction of pentaphenylbismuth with bromine, hydrogen chloride, or triphenylboron results in cleavage of one carbon–bismuth bond and the formation of a quaternary bismuth compound. Thus, the treatment of pentaphenylbismuth in ether at −70 °C with 1 mol of bromine gives the highly unstable, colorless, crystalline tetraphenylbismuth bromide:

$$\mathrm{Ph_5Bi + Br_2 \rightarrow Ph_4BiBr + PhBr}$$

If 2 mol of bromine is used, one obtains an orange tribromide that can be isolated at −30 °C. Tetraphenylbismuth chloride can be prepared by the treatment of pentaphenylbismuth at −70 °C with the stoichiometric quantity of dry hydrogen chloride in ether:

$$\mathrm{Ph_5Bi + HCl \rightarrow Ph_4BiCl + PhH}$$

In a similar way, hydrogen chloride removes a *p*-chlorophenyl group from triphenylbis(*p*-chlorophenyl)bismuth and cleaves the heterocyclic ring of 5,5-dihydro-5,5,5-triphenyl-5*H*-dibenzobismole:[405]



Hydrogen tetrafluoroborate[406] and triphenylsilanol[372] also convert quinquenary bismuth compounds to quaternary bismuth derivatives:

$$\mathrm{Ph_5Bi + HBF_4 \rightarrow [Ph_4Bi][BF_4] + PhH}$$

$$\mathrm{Ph_5Bi + Ph_3SiOH \rightarrow Ph_4BiOSiPh_3 + PhH}$$

The interaction of pentaphenylbismuth and triphenylboron results in a transfer of a phenyl group from bismuth to boron:[119] The possible formation of tet-

$$\mathrm{Ph_5Bi + Ph_3B \rightarrow [Ph_4Bi][Ph_4B]}$$

raphenylbismuth hydroxide as an intermediate in the hydrolysis of pentaphenylbismuth is mentioned in section VIIB.

2. By Metathesis

Although solid tetraphenylbismuth chloride decomposes in a few minutes at room temperature, it is reasonably stable in water for several days at 20 °C. Treatment of an aqueous solution of the chloride with sodium[119] (or potassium[367]) nitrate, sodium perchlorate,[119] sodium tetraphenylborate,[119] potassium cyanate,[367] or potassium thiocyanate[367] yields the corresponding tetraphenylbismuth compounds. In a similar way, the compounds $\mathrm{Ph_4BiX}$, where X is $\mathrm{BF_4}$, $\mathrm{PF_6}$, $\mathrm{ClO_4}$, $\mathrm{CCl_3CO_2}$, or $\mathrm{NO_3}$, can be obtained by the metathetical reaction of tetraphenylbismuth chloride in cold acetone or methanol with the appropriate silver salt.[367] The reaction of the chloride with sodium azide or potassium selenocyanate gives tetraphenylbismuth azide or selenocyanate, both of which decompose rapidly at room temperature. The metathetical reaction of tetraphenylbismuthonium perchlorate in absolute alcohol with sodium tetraphenylborate[366] or potassium thiocyanate[367] yields tetraphenylbismuthonium tetraphenylborate or tetraphenylbismuth thiocyanate, but attempts to prepare other tetraphenylbismuth compounds from the perchlorate have been unsuccessful. Tetraphenylbismuth octahydrotriborate, $\mathrm{[Ph_4Bi][B_3H_8]}$, has been obtained as a colorless precipitate by the interaction of tetraphenylbismuth nitrate and ammonium octahydrotriborate in water.[407]

Metathetical reactions have also been used for preparing quaternary bismuth compounds other than the tetraphenylbismuth derivatives discussed in the above paragraph. Thus, triphenyl(*p*-chlorophenyl)bismuth chloride has been converted to the tetraphenylborate, and triphenyl(*o*-biphenylyl)bismuth chloride has been converted to both the nitrate and the tetraphenylborate:[405]

$$(p\text{-}\mathrm{ClC_6H_4)Ph_3BiCl + NaBPh_4 \xrightarrow{EtOH} [(}p\text{-}\mathrm{ClC_6H_4)Ph_3Bi][BPh_4] + NaCl}$$

$$(o\text{-}\mathrm{PhC_6H_4)Ph_3BiCl + NaNO_3 \xrightarrow{H_2O} (}o\text{-}\mathrm{PhC_6H_4)Ph_3BiONO_2 + NaCl}$$

$$(o\text{-}\mathrm{PhC_6H_4)Ph_3BiCl + NaBPh_4 \xrightarrow{EtOH} [(}o\text{-}\mathrm{PhC_6H_4)Ph_3Bi][BPh_4] + NaCl}$$

A tetraalkylbismuthonium tetraphenylborate has been obtained in a similar way:[408]

$$\mathrm{[MeEt_3Bi][Et_3AlCl] + NaBPh_4 \xrightarrow{PhMe} [MeEt_3Bi][BPh_4] + Et_3Al + NaCl}$$

3. From Tertiary Dihalobismuth Compounds

The formation of tetraphenylbismuthonium perchlorate by the interaction of triphenylbismuth dichloride (in acetone) and silver perchlorate (in absolute ethanol) was first observed in 1966.[366] This reaction is remarkable since metathesis between triarylbismuth dihalides and other silver salts had often been employed previously without any rearrangement being noted. It is also of interest because it offers a relatively simple route to the preparation of the tetraphenylbismuth group. In 1971 Goel and Prasad[368] reported that in acetone both silver perchlorate and silver tetrafluoroborate react with triphenylbismuth dichloride to yield acetonyltriphenylbismuthonium derivatives:

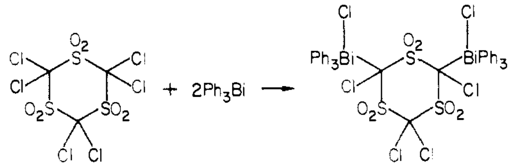
$$\mathrm{Ph_3BiCl_2 + 2AgX + Me_2CO \rightarrow [Ph_3BiCH_2COMe]X + 2AgCl + HX}$$

$$\mathrm{X = ClO_4 \text{ or } BF_4}$$

Strangely enough, tetraphenylbismuthonium perchlorate (or tetraphenylbismuthonium tetrafluoroborate) is the only bismuth-containing species obtained when the above reaction is carried out in acetylacetone or methyl ethyl ketone.[376] It has also been found that the reaction of an aqueous solution of silver perchlorate with a benzene solution of triphenylbismuth dichloride yields a dihydrate of oxybis(triphenylbismuth) diperchlorate, $[Ph_3Bi(H_2O)OBi(H_2O)Ph_3][ClO_4]_2$.[355] This type of compound has been discussed in section VA2.

4. Miscellaneous Methods

As previously mentioned (section IIIB4), tertiary bismuthines are almost devoid of nucleophilic or donor character, and numerous attempts at the direct quaternization of these compounds have been unsuccessful. In sharp contrast to these many failures, it has been reported[409] that hexachloro-*s*-trithiane 1,1,3,3,5,5-hexaoxide reacts with an ethereal solution of triphenylbismuthine to form a diquaternary compound:



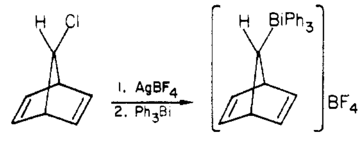
The compound is described as a colorless, amorphous substance, mp 110–112 °C after recrystallization from a mixture of ether and alcohol. No other information about its chemical and physical properties is available.

A tetraalkylbismuth compound has been prepared by the reaction of an adduct of triethylbismuthine and triethylaluminum with methyl chloride at 50 °C:[408]

$$Et_3BiAlEt_3 + MeCl \rightarrow [MeEt_3Bi][Et_3AlCl]$$

This work was reported at an international symposium in 1967, but details have not yet been published.

The formation of a quaternary bismuth compound by the interaction of the 7-norbornadienyl cation and triphenylbismuthine has been observed by ^{1}H NMR.[410] The required cation was generated by treatment of 7-norbornadienyl chloride in liquid sulfur dioxide with silver tetrafluoroborate at −70 °C:

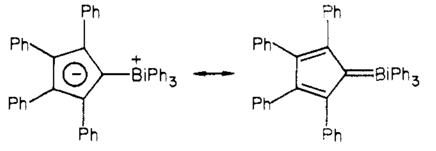


The ^{210}Bi-labeled tetramethylbismuth cation is probably formed during the β decay of ^{210}Pb-labeled tetramethyllead in the gas phase:[411]

$$Me_4{}^{210}Pb \rightarrow \beta + Me_4{}^{210}Bi^+$$

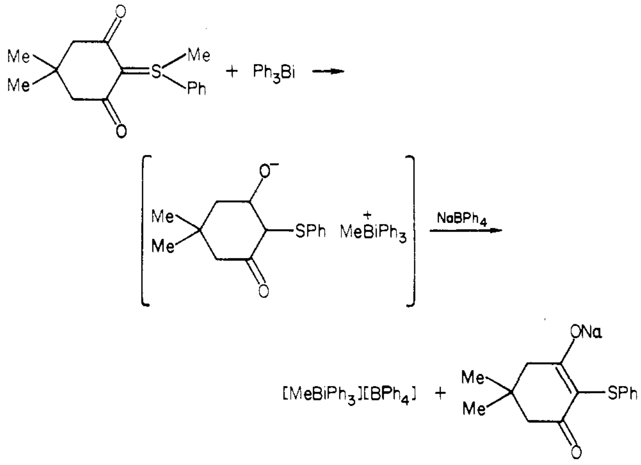
The intermediate cation quickly undergoes further reactions which lead to 100% of the daughter ^{210}Bi being deposited on the walls of the containing vessel.

A bismuth ylide has been prepared by heating a mixture of triphenylbismuthine and diazotetraphenylcyclopentadiene to 140 °C.[118] Under these conditions the tetraphenylcyclopentadiene moiety (presumably generated as a carbene) reacts with the lone pair of electrons on the bismuth atom and forms triphenylbismuthonium tetraphenylcyclopentadienylide:



The above compound appears to be a very unstable substance, and an analytically pure sample has not been obtained. Attempts to convert the ylide to a picrate or perchlorate has resulted in decomposition.

It has been suggested[412] that the methyltriphenylbismuth cation is formed by heating triphenylbismuthine and a carbonyl-stabilized sulfonium ylide in the presence of sodium tetraphenylborate:



The postulated methyltriphenylbismuthonium tetraphenylborate has not been isolated, but acidification of the reaction mixture does give 2-phenylthiodimedone.

B. Reactions

Except for the metathetical reactions discussed above (section VIA2) and for the interaction of tetraphenylbismuth chloride and phenyllithium to form pentaphenylbismuth (section VIIA), relatively little is known about the chemical properties of quaternary bismuth compounds. It has been noted[119] that these substances are less stable than the corresponding phosphorus, arsenic, and antimony analogues. Thus, both tetraphenylbismuth chloride and bromide decompose rapidly in the solid state at room temperature:

$$Ph_4BiX \rightarrow Ph_3Bi + PhX$$

$$X = Cl \text{ or } Br$$

The cyanide and nitrite have not been isolated but apparently undergo a similar type of decomposition. The tribromide is stable at −30 °C for several hours, but gradually decomposes at 5 °C into triphenylbismuth dibromide and bromobenzene:

$$Ph_4BiBr_3 \rightarrow Ph_3BiBr_2 + PhBr$$

When quickly warmed to room temperature, the tribromide undergoes an exothermic reaction that gives diphenylbromobismuthine:

$$Ph_4BiBr_3 \rightarrow Ph_2BiBr + 2PhBr$$

Beaumont and Goel[367] have stated that all the tetraphenylbismuth compounds studied by them eventually decompose at room temperature. The perchlorate, tetrafluoroborate, and hexafluorophosphate, however, do not show any noticeable decomposition after a week, although the perchlorate is known to explode on being heated strongly. The nitrate, trichloroacetate, cyanate, and thiocyanate are less stable, and their decomposition is noticeable within a day; of these four compounds the trichloroacetate appears to be least stable, but even it can be kept at room temperature for a few hours. The cyanate and thiocyanate decompose in benzene, alcohol, or acetone to give triphenylbismuthine as the sole bismuth-containing product. Both the azide and selenocyanate decompose rapidly at room temperature to give triphenylbismuthine. Amberger and Gut[407] have reported that tetraphenylbismuth octahydrotriborate decomposes to triphenylbismuthine during attempted recrystallization from alcohol–ether or methanol–water.

The treatment of tetraphenylbismuthonium tetrafluoroborate with alcoholic sodium hydroxide has been found to give an 82% yield of triphenylbismuthine.[406] The reaction is complete in a few minutes at room temperature. In aqueous sodium hydroxide, however, the decomposition is rather slow, and after a month about 60% of the starting material can be recovered.

A study has been made of the interaction of tetraphenylbismuthonium tetrafluoroborate with the electron donors tetramethyl-*p*-phenylenediamine (TMPD) and triphenylphosphine.[413] In both cases reactions occur rapidly at room temperature in acetone under the influence of diffuse light. The reaction with TMPD gives triphenylbismuthine, benzene, and the radical cation $TMPD^{+\cdot}$ (which can be detected by ESR). The tetraphenylbismuthonium cation apparently accepts an electron and is thus reduced to the corresponding radical. An analogous process appears to be involved during the photochemical interaction of tetraphenylbismuthonium tetrafluoroborate and triphenylphosphine, a reaction that leads to the formation of tetraphenylphosphonium tetrafluoroborate (in 90% yield), benzene (in 10% yield), and triphenylbismuthine. A thermal reaction between tetraphenylbismuthonium tetrafluoroborate and triphenylphosphine in refluxing acetone has also been observed. This reaction requires several days to give a 50% yield of tetraphenylphosphonium tetrafluoroborate; triphenylbismuthine can also be isolated from this reaction mixture.

Treatment of tetraphenylbismuth triphenylsilanolate with an ethanolic solution of hydrogen chloride results in the reaction:[372]

$$Ph_4BiOSiPh_3 + 2HCl \rightarrow Ph_3BiCl_2 + Ph_3SiOH + PhH$$

C. Structure and Physical Properties

Challenger[414] assumed as long ago as 1913 that quaternary bismuth compounds would contain positively charged, tetrahedrally coordinated bismuth, and it has become customary to refer to these substances as "bismuthonium" salts. In 1973 the first unambiguous determination of the structure of a quaternary bismuth compound was effected by an X-ray diffraction study of a single crystal of tetraphenylbismuthonium perchlorate.[415] The compound was indeed found to consist of tetrahedral Ph_4Bi^+ and ClO_4^- ions and thus agreed with an earlier IR study[366] that suggested the presence of ionic perchlorate in this substance. Beaumont and Goel[367] have studied the structure of the perchlorate and of six other tetraphenylbismuth compounds (Ph_4BiX, where X is BF_4, PF_6, NO_3, CCl_3CO_2, NCO, or NCS) by means of IR and laser Raman spectroscopy and by molecular weight and conductance measurements. The vibrational spectra of the perchlorate, tetrafluoroborate, and hexafluorophosphate clearly show the presence of the free anion and are consistent with a tetrahedral BiC_4 skeleton for the cation. Furthermore, these three bismuth compounds behave as 1:1 electrolytes in acetonitrile or nitromethane. Tetraphenylbismuth nitrate and thiocyanate are also 1:1 electrolytes in these solvents. Their IR spectra, however, indicate that the anionic groups are present as monodentate ligands, and their Raman spectra suggest a trigonal-bipyramidal skeleton, with the four phenyl groups occupying one axial and three equatorial positions and the anionic group at the remaining axial position. Tetraphenylbismuth trichloroacetate and cyanate are weak electrolytes in both acetonitrile and nitromethane, and they exhibit vibrational spectra that leave little doubt that these compounds are also nonionic derivatives of five-coordinate bismuth. Molecular weight determinations in benzene give normal values for the nitrate and the trichloroacetate and hence confirm the nonionic constitution of these substances. Molecular weight data for the cyanate and thiocyanate are not available, since these compounds decompose in benzene, alcohol, or acetone. The acetonyltriphenylbismuth derivatives $[Ph_3BiCH_2COMe]X$, where X is ClO_4 or BF_4, appear to be true "bismuthonium" salts.[368] Both compounds are white crystalline solids that are soluble in polar organic solvents but very slightly soluble in benzene. The ^1H NMR spectra exhibit a phenyl multiplet (δ 7.60) and two singlets. One singlet occurs at δ 5.50 for the perchlorate and at δ 5.33 for the tetrafluoroborate; the other singlet occurs at δ 2.37. The δ 5.50 or 5.33 peak is assigned to the methylene protons and the 2.37 peak to the methyl protons. The equivalent conductances in acetonitrile show that the compounds behave as 1:1 electrolytes in this solvent, and the IR spectra are also consistent with the proposed structures.

Triphenylbismuthonium tetraphenylcyclopentadienylide (like the corresponding pyridinium ylide) is dark blue-purple, while the corresponding phosphonium, arsonium, and stibonium ylides are yellow.[118,416] In benzene solution the bismuth compound exhibits UV absorption maxima at 280, 345, and 596 nm; in methanol the compound is red-purple and has maxima at 240, 335, and 528 nm. These maxima are almost the same as those shown by the pyridinium ylide in benzene and methanol. It has been suggested that the diffuse 6d orbitals of bismuth (unlike the 4d orbitals of arsenic or the 5d orbitals of antimony) cannot effectively overlap the 2p orbitals of the anionic ring and that the linkage between the bismuth atom and the anionic ring is, accordingly, almost entirely a single (dipolar) bond.

The polarographic half-wave potential of tetraphenylbismuthonium perchlorate (dissolved in anhydrous glyme) has been found to be 3.1 V with respect to a 10^{-3} M $Ag/AgClO_4$ reference electrode.[282]

VII. Quinquenary Bismuth Compounds

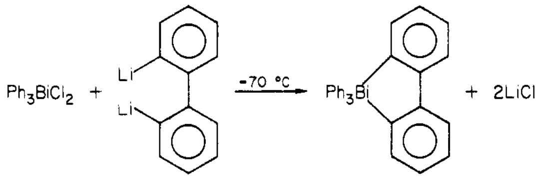
A. Preparation

Only a few compounds containing five carbon–bismuth bonds are known. The first compound of this type was obtained by Wittig and Clauss[119] in 81% yield by means of the reaction:

$$Ph_3BiCl_2 + 2PhLi \xrightarrow{-75\ ^\circ C} Ph_5Bi + 2LiCl$$

Triphenylbis(*p*-chlorophenyl)bismuth and 5,5-dihydro-5,5,5-triphenyl-5*H*-dibenzobismole were later prepared by analogous reactions:[405]

$$\mathrm{Ph_3BiCl_2} + 2p\text{-}\mathrm{ClC_6H_4Li} \xrightarrow{-70\ ^\circ\mathrm{C}} (p\text{-}\mathrm{ClC_6H_4})_2\mathrm{BiPh_3} + 2\mathrm{LiCl}$$



An attempt to obtain pentakis(p-chlorophenyl)bismuth by a similar procedure, however, yielded a red solution, from which only tris(p-chlorophenyl)bismuthine was isolated.

In the first paper describing pentaphenylbismuth it was noted that this substance can be prepared by the interaction of tetraphenylbismuth chloride and phenyllithium:

$$\mathrm{Ph_4BiCl} + \mathrm{PhLi} \xrightarrow{-70\ ^\circ\mathrm{C}} \mathrm{Ph_5Bi} + \mathrm{LiCl}$$

This reaction has at present no synthetic utility since tetraphenylbismuth chloride has been prepared only by the treatment of pentaphenylbismuth with hydrogen chloride. Another method that has been used for preparing pentaphenylbismuth involves the interaction of phenyllithium and the N-triphenylbismuth derivative of p-toluenesulfonamide:[40]

$$p\text{-}\mathrm{MeC_6H_4SO_2N{=}BiPh_3} + 2\mathrm{PhLi} \xrightarrow{-60\,^\circ\mathrm{C}} \mathrm{Ph_5Bi} + p\text{-}\mathrm{MeC_6H_4SO_2NLi_2}$$

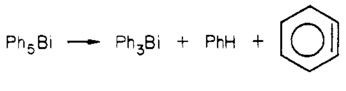
The yield of pentaphenylbismuth thus obtained is only 18–26%.

B. Reactions

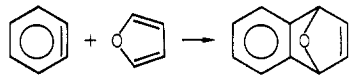
Pentaphenylbismuth is much less stable than its phosphorus, arsenic, and antimony analogues.[119,372] Nevertheless, it can be recrystallized (under nitrogen) from aqueous tetrahydrofuran to yield the pure substance as deep-purple crystals, mp 90–100 °C. The exact melting point observed depends on the rate of heating[417] and undoubtedly involves decomposition. At room temperature pentaphenylbismuth is stable for several days under nitrogen, while in air it decomposes in a short time to a yellow-brown material of unknown composition. When heated between 100 and 105 °C in a nitrogen atmosphere, pentaphenylbismuth decomposes exothermally with the evolution of a gas. The products of this decomposition include benzene, biphenyl, and triphenylbismuthine.

Triphenylbis(p-chlorophenyl)bismuth is also purple and unstable.[405] It decomposes at 70–80 °C, but the products of its decomposition have not been elucidated.

The decomposition of pentaphenylbismuth in several solvents has been recently investigated.[372,418] In dry pyridine at room temperature, it decomposes in 1 to 2 min in a manner consistent with the equation:



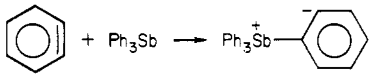
Thus, the decomposition mixture contains triphenylbismuthine in almost quantitative yield, somewhat more than a 100% yield of benzene, and tarry products presumably formed from the intermediate benzyne. The decomposition of pentaphenylbismuth requires about 10 min in chloroform or carbon tetrachloride, but the products are similar to those obtained in dry pyridine. The formation of benzyne during the decomposition in carbon tetrachloride can be demonstrated by running the reaction in the presence of furan and isolating a Diels–Alder addition product from the reaction mixture:



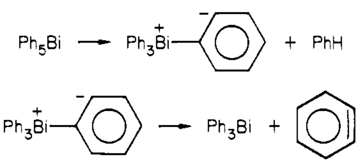
The benzyne can also be trapped with *tert*-butyl alcohol (which yields *tert*-butyl phenyl ether) or phenol (which yields diphenyl ether). The decomposition of pentaphenylbismuth in moist pyridine yields triphenylbismuthine, benzene, phenol, and diphenyl ether. At first[372] these products were explained by a mechanism involving tetraphenylbismuth hydroxide as an intermediate:

$$\mathrm{Ph_5Bi} + \mathrm{H_2O} \longrightarrow [\mathrm{Ph_4BiOH}] + \mathrm{PhH} \longrightarrow \mathrm{Ph_3Bi} + \mathrm{PhOH}$$

In a more recent paper,[418] however, it was suggested that the decomposition of pentaphenylbismuth in moist pyridine produces benzyne, part of which reacts with the water to yield phenol and part of which reacts with the phenol thus formed to yield diphenyl ether. When the decomposition of pentaphenylbismuth is carried out in carbon tetrachloride in the presence of triphenylstibine, a dipolar substance is obtained that is believed to be an addition product of the stibine and benzyne:



The formation of a similar (but very unstable) dipolar bismuth compound may occur in the first step of the decomposition of pentaphenylbismuth, and this dipolar compound may then yield benzyne:



The reaction of a pentaarylbismuth compound with bromine, hydrogen chloride, hydrogen tetrafluoroborate, triphenylsilanol, or triphenylboron results in cleavage of one carbon–bismuth bond and has already been discussed under quaternary bismuth compounds (section VIA). In contrast to these results, isopropyl alcohol quantitatively reduces pentaphenylbismuth to triphenylbismuthine:[372]

$$\mathrm{Ph_5Bi} + \mathrm{Me_2CHOH} \rightarrow \mathrm{Ph_3Bi} + \mathrm{Me_2CO} + 2\mathrm{PhH}$$

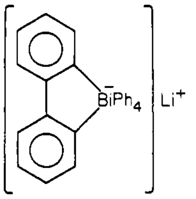
The reaction of pentaphenylbismuth with *tert*-butyl alcohol, phenol, or water is more complicated and has been discussed in the previous paragraph.

Pentaphenylbismuth has recently been shown to be a useful reagent for the specific ortho phenylation of certain phenols under very mild conditions.[377] Thus, addition of the bismuth compound to 2-naphthol in benzene or dichloromethane at room temperature leads to immediate discharge of the characteristic purple color of the reagent, the presumed formation of intermediate $\mathrm{Ph_4BiOAr}$ (where Ar is 2-naphthyl), and the isolation of a 61% yield of 1-phenyl-2-naphthol. 1-Naphthol similarly gives 2-phenyl-1-naphthol. The interaction of pentaphenylbismuth and a 2,6-dimethylphenol, however, gives a satisfactory yield of a 6-phenyl-2,6-dimethylcyclohexa-2,4-dienone. Under similar conditions, 2,4-dimethylphenol yields both 2,4-dimethyl-6-phenylphenol and a 2,6-diphenylcyclohexa-2,4-dienone. 4-Nitrophenol reacts via reductive elimination of the 4-$O_2NC_6H_4OBiPh_4$ intermediate and formation of 4-nitrophenyl phenyl ether. Benzyl alcohol and cholestanol are oxidized by pentaphenylbismuth to give modest yields of the corresponding carbonyl compounds. Oxidation of 2-phenylethanol is followed by phenylation of the resulting aldehyde to give a 14% yield of triphenylacetaldehyde. 2-Nitropropane is phenylated to 2-phenyl-2-nitropropane. Thiophenols are converted to the mixed diaryl sulfides PhSAr. It has been concluded that the phenylation reactions of pentaphenylbismuth do not involve free phenyl radicals since quenching by triethylsilane has not been observed.

There is considerable evidence that pentaarylbismuth compounds can be converted into hexaarylbismuthate complexes. Thus, if a suspension of pentaphenylbismuth in ether at −70 °C is treated with an excess of phenyllithium, a gradual color change from purple to yellow is observed.[417] This color change can be reversed by warming the mixture to room temperature. If the mixture is again cooled to −70 °C and allowed to stand for 14 h at this temperature, one obtains a yellow crystalline substance that reacts exothermally with methanol to regenerate pentaphenylbismuth. Although this yellow substance has not been analyzed, it is probably lithium hexaphenylbismuthate, formed by the following reversible reaction:

$$\mathrm{Ph_5Bi + PhLi \rightleftarrows [Ph_6Bi]Li}$$

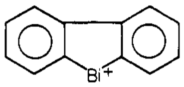
It has also been found that the reaction of butyllithium with pentaphenylbismuth produces phenyllithium, presumably via a bismuthate complex.[419] Similarly, the product of the interaction of tritium-labeled phenyllithium and unlabeled pentaphenylbismuth in tetrahydrofuran is probably lithium hexaphenylbismuthate, since hydrolysis of the reaction mixture gives labeled pentaphenylbismuth. Treatment of an ether solution of 5,5-dihydro-5,5,5-triphenyl-5*H*-dibenzobismole (which is an orange compound) with an excess of phenyllithium at −70 °C yields a lemon-yellow precipitate, which reverts at room temperature to an orange solution.[405] The precipitate is presumably an "ate-complex" of the structure:



Nefedov and co-workers[420] have investigated the chemical changes accompanying β decay in ^{210}Bi-tagged pentaphenylbismuth. The tagged compound was obtained by the interaction of phenyllithium and triphenylbismuth dichloride, which had been prepared from neutron-irradiated bismuth. After the radioactive pentaphenylbismuth is allowed to stand for a period equal to five half-lives of ^{210}Bi, a mixture of various phenylpolonium compounds is obtained.

C. Spectra

The mass spectrum of pentaphenylbismuth exhibits five bismuth-containing fragments but no molecular ion.[245] The most intense peak is for the Bi^+ ion, and there is a somewhat weaker peak for $PhBi^+$. There are also weak peaks for Ph_3Bi^+, Ph_2Bi^+, and $(Ph_2Bi - 2H)^+$, the last of which has been attributed to the heterocyclic species:



This ion is presumably formed by some sort of "ortho coupling" reaction, but the exact pathway has not been elucidated.

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