

BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1984 *

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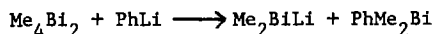
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The annual survey of organometallic compounds [1], and the *Annual Reports on the Progress of Chemistry* [2], both published by the Royal Society of Chemistry, included short sections on organobismuth compounds. An excellent report on the synthesis of chiral organobismuthines was the subject of a doctoral thesis [3]. Several organobismuth compounds were mentioned in a review devoted to the use of Group V compounds as ligands in coordination chemistry [4]. Three perfluoroorganobismuth compounds were described in a monograph devoted to perfluoroorgano compounds of the main group elements [5]. Heterocyclic rings containing bismuth atoms were included in the first volume of an eight volume work devoted to heterocyclic chemistry [6]. In a monograph entitled *Organometallic Compounds and Living Organisms* a few organobismuth compounds were included [7]. The antifungal activity of a series of organobismuth compounds has been studied by Burrell and coworkers [8]. The most effective compound tested was $[\text{Et}_4\text{N}][\text{Ph}_2\text{BiCl}_2]$. It was considerably less fungitoxic, however, than the commercial fungicide, benomyl.

Although tetramethyldibismuthine has been previously prepared from Me_2BiBr and 1,2-dichloroethane in liquid ammonia, Wieber and Sauer [9] have now reported that the dibismuthine was readily obtained in 78% yield by the action of sodium on Me_2BiBr in liquid ammonia. The pure compound, mp -17°C , was extremely air and moisture sensitive. It was characterized by PMR and ^{13}C spectroscopy and by elemental analysis. It decomposed on standing in air at 0°C , more rapidly in solution. *In vacuo* at -20° it decomposed to Me_3Bi and bismuth. It reacted with bromine to give MeBr and BiBr_3 . Under carefully controlled conditions Me_4Bi_2 reacted with oxygen to form $\text{Me}_2\text{BiOBiMe}_2$ and with

*Previous review see R.B. King and J.P. Oliver (Eds.), *J. Organomet. Chem. Library*, 17(1985)353-364.

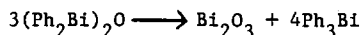
sulfur to form $\text{Me}_2\text{BiSBiMe}_2$. The PMR and mass spectra of these two compounds were reported. It reacted with PhLi in the following manner:



The tertiary bismuthine could be prepared in larger yield from Me_2BiBr and PhLi . The PMR and mass spectra of this tertiary bismuthine were reported. The Me_2BiBr used in these reactions was obtained in 96% yield from Me_3Bi and BiBr_3 .

Although several previous attempts to prepare tetraphenyldibismuthine have been unsuccessful, Calderazzo and coworkers [10] have prepared this compound by the reduction of Ph_2BiCl or Ph_2BiI with sodium in liquid ammonia. The yield from the iodide was considerably better than from the chloride. The compound could be crystallized from hot absolute ethanol. Although it was unstable in solution, it could be kept indefinitely under nitrogen at -30°C . The orange crystals turned yellow (reversibly) when cooled to liquid nitrogen temperature. An X-ray diffraction study showed that the compound was monomolecular with one molecule per unit cell. The two C-Bi-C angles were 91.6° and 90.9° suggesting that the lone pair on bismuth had essentially *s* character. By ESR measurements, both in toluene solution and in the solid state, it was concluded that no homolytic cleavage of the Bi-Bi bond occurred.

Molecular oxygen reacted rapidly with the dibismuthine but no pure product could be obtained, presumably due to the following redistribution reaction:

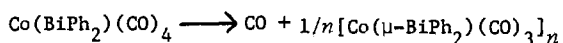


With S_8 the compound $(\text{Ph}_2\text{Bi})_2\text{S}$ could be obtained, but only in small yields. With iodine the dibismuthine gave Ph_2BiI . With *p*-benzoquinone the compound $p\text{-Ph}_2\text{BiOC}_6\text{H}_4\text{OBiPh}_2$ was obtained. Diazomethane reacted as follows:

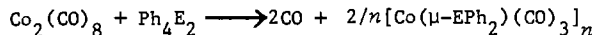


The reaction of Ph_4Bi_2 with $\text{Co}_2(\text{CO})_8$ led to the formation of $\text{Co}(\text{BiPh}_2)(\text{CO})_4$ [11]. This was a low-melting solid which could not be isolated in a pure state but which underwent a reaction with Ph_3P with the evolution of one mole of CO to form the crystalline compound $\text{Co}(\text{BiPh}_2)(\text{CO})_3(\text{Ph}_3\text{P})$. The crystal structure of this compound was determined and found to contain a distorted trigonal-bipyramidal cobalt atom with three CO groups in equatorial positions. The geometry of the bismuth atom was pyramidal. The lone pair on the bismuth atom possessed considerable *s* character. The authors were unable to convert

the tetracarbonyl compound to the μ -bridged complex, even by ultra-violet radiation:



By contrast, Ph_4P_2 , Ph_4As_2 , and Ph_4Sb_2 all reacted with $\text{Co}_2(\text{CO})_8$ with evolution of one mole of CO per cobalt atom:

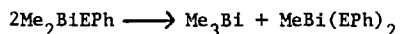


(where E = P, As, or Sb)

The compound where E was P did not react with Ph_3P , but the compounds where E was As or Sb reacted with Ph_3P to give the compounds $\text{Co}(\text{EPh}_2)(\text{CO})_3(\text{Ph}_3\text{P})$ (where E = As or Sb), similar to the compounds obtained from Ph_4Bi_2 .

The difference in reactivity of Ph_4Bi_2 with $\text{Co}_2(\text{CO})_8$, as compared with the analogous P, As, and Sb compounds, was explained as due to the low availability of the second lone pair on bismuth for bonding, *i.e.* for forming the $\mu\text{-BiPh}_2$ complex.

Wieber and Sauer [12] have reported the preparation of compounds of the type Me_2BiEPh , where E was S, Se, or Te, by the reaction of tetramethyldibismuthine with the corresponding disulfides, diselenides, or ditellurides Ph_2E_2 . The two compounds Me_2BiSPh and Me_2BiSePh were stable at -30°C , but the telluride decomposed slowly at this temperature. At ambient temperature all three compounds decomposed as follows:



The rate of decomposition was in the order $\text{S} < \text{Se} < \text{Te}$. The compounds were characterized by elemental analyses, PMR, and mass spectral determinations.

The interesting sulfur diimides, $\text{R}_2\text{EN}=\text{S}=\text{NER}_2$, where E was P, As, Sb, or Bi and R was an alkyl group, have been prepared by the reaction between K_2SN_2 and R_2EX (X = Cl or Br) [13]. Thus, *tert*- BuBiBr_2 reacted with K_2SN_2 in acetonitrile at -40°C to give the yellow, crystalline bismuth compound, which slowly decomposed at room temperature. The compound was characterized only by its mass spectrum. A peak corresponding to the molecular ion was not found, but a peak for the ion $\text{SN}_2\text{Bi}_2(\text{Bu-}i>tert)3$ was present to the extent of 3% of the base peak.

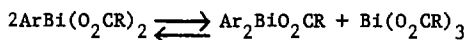
Deacon and coworkers [14] have found that one or two aryl groups were cleaved from triarylbismuthines when they were treated with acetic or trifluoroacetic acid in ether solution in the absence of oxygen:



(where Ar = Ph, *p*-MeC₆H₄, *p*-MeOC₆H₄, *p*-EtOC₆H₄ or C₆F₅ and *n* = 1 or 2)

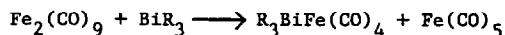
Trimethylbismuthine was also cleaved by acetic acid to yield MeBi(OAc)₂. The products formed in the reactions of the triarylbismuthines depended both on the nature of the Ar group and on the acid used. Thus, triphenylbismuthine and acetic acid gave only PhBi(OAc)₂ whereas the same bismuthine and trifluoroacetic acid gave either PhBi(O₂CCF₃)₂ or Ph₂BiO₂CCF₃, depending upon the ratio of bismuthine to acid used. Both (*p*-MeOC₆H₄)₃Bi and (*p*-EtOC₆H₄)₃Bi gave mixtures of the diaryl and monaryl compounds when treated with trifluoroacetic acid. With (C₆F₅)₃Bi and CF₃CO₂H only one C₆F₅ group was displaced, even under forcing conditions.

Because both the mono- and dicarboxylates were readily hydrolyzed, considerable difficulty was encountered in obtaining analytically pure samples. For this reason many of the compounds were characterized by their PMR spectra. It was found that successive replacement of the aryl groups by carboxylate groups led to a downfield shift of aromatic resonances which was of sufficient magnitude to allow a clear differentiation between the mono- and diarylbismuth carboxylates. Both IR and mass spectral data were reported. It was also found that arylbismuth dicarboxylates underwent disproportionation in dimethylsulfoxide solution:



Triphenylbismuthine was not obtained even after long standing. By contrast di-*p*-tolylbismuth trifluoroacetate gave tri-*p*-tolylbismuthine after 30 hours. Several other arylbismuth carboxylates were also found to undergo disproportionation.

Breunig and Graf^ë [15] have described the preparation of several iron-bismuth complexes of the type (CO)₄FeBiR₃, where R was Et, Pr, or Bu. They were prepared by means of the following reaction:



The complexes were brown liquids, soluble in hydrocarbons, stable in solution, and much less reactive in air than the free bismuthines. The

mass spectra, as well as the PMR and IR spectra, were reported. In the mass spectra a fairly intense signal for the molecular ion was found. The pattern and the positions of the IR carbonyl bands were similar to those of the corresponding phosphorus, arsenic, and antimony compounds. The PMR spectra differed considerably from the spectra of the corresponding free bismuthines. Because the bismuth lone pair was coordinated to the iron atoms, the protons of the α -methylene groups were strongly deshielded and were greatly shifted to lower fields. Attempts to prepare similar iron complexes using Me_3Bi or Ph_3Bi did not give the desired compounds but rather led to the formation of $\text{Fe}_3(\text{CO})_{12}$.

In addition to the iron bismuthine complexes, compounds of the type $\text{Bu}_3\text{BiM}(\text{CO})_5$, where M was Cr, Mo, or W, were prepared. These were obtained by irradiation of the corresponding hexacarbonyls in tetrahydrofuran followed by the addition of one equivalent of Bu_3Bi to the irradiated solution. The resulting compounds were yellow, light-sensitive liquids. The mass spectra of these compounds, in a similar manner to the iron complexes, gave fairly intense signals for the molecular ions.

The mass spectra of seventeen symmetrical triarylbismuthines Ar_3Bi (where Ar was phenyl or monosubstituted phenyl, 1-naphthyl, or mesityl), five unsymmetrical triarylbismuthines $\text{Ar}_2\text{Ar}'\text{Bi}$, two unsymmetrical bismuthines $\text{ArAr}'\text{Ar}''\text{Bi}$, and two bromodiarylbismuthines $\text{ArAr}'\text{BiBr}$, have been reported by Gielen and coworkers [16]. With the symmetrical compounds, the base peak was usually either Bi^+ , ArBi^+ , or Ar_2BiH^+ . With a few compounds fragment ions with higher masses were seen. Thus, with $(m\text{-FC}_6\text{H}_4)_3\text{Bi}$, the base peak was the ion $(m\text{-FC}_6\text{H}_4)_3\text{Bi}_2^+$ at 70eV, but $m\text{-FC}_6\text{H}_4\text{Bi}^+$ at 12 eV. The base peak for trimesitylbismuthine was the ion $2,4,6\text{-Me}_3\text{C}_6\text{H}_2\text{Bi-H}^+$. The authors suggested that the presence of ions of the type Ar_2Bi_2^+ may occur either by formation and fragmentation of collision ions (e.g. $\text{Ar}_2\text{Bi}^+ + \text{Ar}_2\text{Bi}^+$) or by thermal processes preceding the evaporation of the samples. They also noted that the results obtained sometimes varied with time, and thus one spectrum might be different from another spectrum of the same compound.

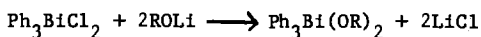
In a paper devoted to the separation and analysis of organometallic compounds of groups IVA and VA by means of high-performance liquid chromatography, optimal conditions for the separation of triphenyl and pentaphenyl derivatives of P, Sb, and Bi were given [17]. Retention times, using columns of either Silochrome C-80 or Silasorb 600 with either *n*-hexane or *n*-hexane with 3% ethyl ether, as eluents, were given in tabular form. It was noted that there was an increase in retention time in going from triphenylphosphine to triphenylbismuthine.

In addition to phenyl compounds, several ferrocenyl and cymanthrenyl compounds of Sb and Bi were studied. The bismuth compounds were FC_3Bi , Ct_3Bi , and Ct_2PhBi , where FC = the ferrocenyl group and Ct = the cymanthrenyl group. It was noted that there was a sharp decrease in retention time in going from Ct_3Bi to Ct_2PhBi .

Triphenylphosphine has been widely used as a ligand in the rhodium catalysed hydroformylation of olefins. Carlock [18] has compared the compounds Ph_3E (E = N, P, As, Sb, and Bi) for their effectiveness in this reaction. The olefin used was 1-dodecene. The most effective of these compounds was Ph_3P , which gave a conversion of 1-dodecene to tridecanal and 2-methyldodecanal of 86.9%. Ph_3Bi failed to promote the hydroformylation reaction. The polymerization of bromophenylacetylene by MoCl_5 or WCl_6 , either alone or in the presence of one of several organometallic compounds as cocatalysts, has been studied by Yamagata and coworkers [19]. One of the cocatalysts was Ph_3Bi . This was effective with MoCl_5 but much less effective with WCl_6 . Trimethylbismuthine has been used as a polymerization catalyst for the preparation of poly(chlorophenylacetylene) [20].

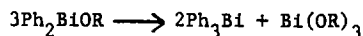
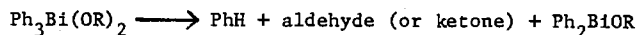
In a paper devoted to the reaction of L-cysteine with compounds of As(III), Sb(III) and Bi(III), no identifiable products were found when $[\text{Me}_4\text{N}][\text{PhBiCl}_3]$ was treated with L-cysteine [21].

The reaction between lithium alkoxides and dichlorotriphenylbismuth proceeded according to the following equation [22]:



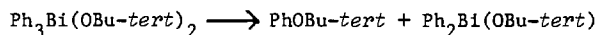
(where R = isopropyl, butyl, *sec*-butyl, *tert*-butyl, or cyclohexyl)

The yield of lithium chloride was quantitative; the dialkoxy compounds were thermally unstable and were not isolated. They decomposed according to the following equations (where R was a primary or secondary alkyl group):



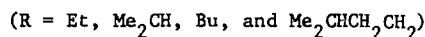
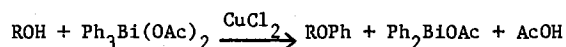
The ketones formed (when R was a secondary alkyl group) were isolated in only 0.41 - 0.71% yields, while the aldehyde formed from BuOLi could not be obtained. These results were attributed to loss of aldehyde or ketone by condensation reactions catalyzed by the lithium alkoxide. It was believed that these condensations occurred to a greater extent with the aldehyde than with the ketones. The alkoxides Bi(OR)_3 were not isolated but were converted to the corres-

ponding alcohols by hydrolysis. Where R was the *tert*-butyl group, the decomposition of the compound $\text{Ph}_3\text{Bi}(\text{O}i\text{-tert})_2$ proceeded in the following manner:



This reaction occurred by a radical mechanism as shown by ESR techniques in which 2-methyl-2-nitrosopropane was used as a spin trap.

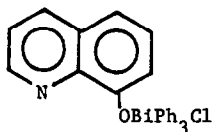
The oxidation of primary and secondary alcohols to the corresponding aldehydes or ketones by $\text{Ph}_3\text{Bi}(\text{OAc})_2$ is a well-known reaction. Dodonov and coworkers [23] have found, however, that if the reaction was carried out in the presence of copper salts (CuCl_2 , CuCl , or $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$) phenylation of the alcohols occurred to yield the corresponding ethers:



The yields were found to depend on the amount of copper salt used, with the largest yield being obtained with only a small amount of copper.

Barton and coworkers have previously shown that pentacovalent bismuth compounds of the type Ph_4BiX (X = carboxylate or sulfonate group) arylate enols or enolate anions in a regioselective manner. Under neutral or acid conditions O-arylation occurs, but under basic conditions the reaction leads to C-arylation. The present paper [24] involved the attempted isolation of intermediates in these reactions and a determination of the structure of such intermediates.

The reaction of Ph_3BiCl_2 with 8-hydroxyquinoline under basic conditions resulted in the formation of an orange crystalline compound possessing the following structure:



The crystal structure of this compound was determined by X-ray diffraction and found to involve a trigonal-bipyramidal bismuth atom with the Cl and O atoms in axial positions. The crystal structure of tetraphenylbismuth tosylate was also determined. It was found that the bismuth tetrahedron was considerably flattened so that the config-

uration of the bismuth atom tended towards that of a distorted trigonal bipyramid. The authors were unable to prepare crystals of the covalent tetraphenyltrifluoroacetatobismuth that were suitable for X-ray diffraction. However, they did obtain crystals of the interesting compound $[\text{Ph}_4\text{Bi}][\text{Ph}_2\text{Bi}(\text{OCOCE}_3)_2]$ and determined its structure. The anion was a distorted trigonal bipyramid with the two trifluoroacetato groups in axial positions and the lone pair presumably in an equatorial position. The O-Bi-O angle was 172° . The tetraphenylbismuthonium cation was a distorted tetrahedron.

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