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# Bismuth: annual survey covering the year 1992

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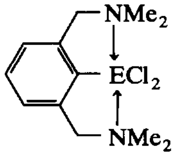
Several reviews dealing with organobismuth compounds appeared in 1992. Seppelt, who has contributed a number of papers on the structure and color of pentaarylorganobismuth compounds, has reviewed this subject in *Advances in Organometallic Chemistry* [1]. A Chinese publication has dealt with the use of organobismuth compounds as phenylating agents [2]. The use of organobismuth compounds in organic synthesis has been mentioned briefly in two 1992 reviews of organic synthesis by organometallics of the main group elements [3]. A few organobismuth compounds were briefly mentioned in a review on the structure and reactivity of arsenic compounds [4].

The potentially tridentate ligand $[2,6\text{-}(Me_2NCH_2)_2\text{-}C_6H_3]^-$ has proved to be useful for the stabilization of unusual oxidation states of various elements. Atwood and coworkers [5] have used this ligand to prepare compounds of Group 15 elements:



(where E was P, As, Sb, or Bi)

The bismuth compound was prepared from $2,6\text{-}(Me_2\text{-}NCH_2)_2C_6H_3Li$ and $BiCl_3$ in ether solution at −78°C. The colorless, microcrystalline solid was extracted with benzene. It was characterized by $^1H$ and $^{13}C$ NMR, and by high resolution mass spectrometry. Only the antimony compound gave crystals suitable for X-ray diffraction. The structure of this compound is described in the Antimony section.

Whitmire and coworkers [6] have reported the synthesis of two organobismuth alkoxides $Et_2BiOAr$ where Ar was Ph or $C_6F_5$. They were prepared by refluxing triethylbismuthine with an excess of the phenol, PhOH or $C_6F_5OH$, in toluene for 40 h. The mass spectra of the two products showed parent ions corresponding to the monomeric $Et_2BiOAr$, and fragments corresponding to $Et_2Bi$, EtBi, and Bi. Both compounds were readily soluble in organic solvents, and NMR data for $Et_2BiOC_6F_5$ indicated that the complexes were monomeric or rapidly exchanging oligomers in solution. The crystal and molecular structures of both compounds were determined by X-ray diffraction, and they were found to be isomorphous. They were composed of chiral helical chains with alternating Bi and O atoms. These lay about the crystallographic three-fold screw axes with $Et_2Bi$ and OAr groups situated on crystallographic two-fold axes. The geometry of the bismuth atom was trigonal-bipyramidal with the two ethyl groups and the stereochemically active electron lone pair occupying equatorial positions, and bridging aryloxy groups the axial positions. For the compound $(Et_2BiOC_6F_5)_\infty$ the O–Bi–O angle was 179.54°, the Bi–O–Bi angle was 113.57°, and the equatorial C–Bi–C angle was 80(2)°. Quite similar angles were found for $(Et_2BiOPh)_\infty$. Both compounds were extremely air and moisture sensitive, and satisfactory elemental analyses

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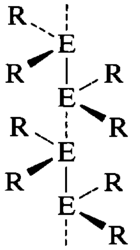
for either compound were not obtained. Satisfactory $^1H$ and $^{19}F$ NMR values for $Et_2BiOC_6F_5$ were reported, but clean spectral data for $Et_2BiOPh$ have not been obtained.

Whitmire and coworkers [7] have described the preparation and crystal structure of two new bismuth alkoxide dimers, $\{Bi[OCH(CF_3)_2]_3\ (THF)_2\}_2$ and $\{Bi(OC_6F_5)_3\ (C_7H_8)\}_2 \cdot 2C_7H_8$, where $C_7H_8$ was toluene. The second compound was obtained by refluxing three equivalents of $C_6F_5OH$ with triphenylbismuthine in toluene for 12 h.

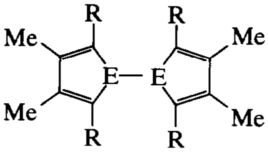
Calderrazzo and coworkers [8] were the first to prepare tetraphenyldibismuthine and to determine its crystal and molecular structure. The crystal was triclinic and the molecule possessed a staggered *trans* conformation. The C–Bi–Bi angles to the two *ipso*-carbon atoms were 91.6° and 90.9°. Whitmire and Cassidy [9] have now reported that tetraphenyldibismuthine, obtained as a by-product from the reaction of $Fe(CO)_5$ with $Ph_2BiNa$ in $NH_3$, gave crystals which grew as both monoclinic and tetragonal crystals from hexane solution. Both types of crystals were subjected to X-ray diffraction studies. In both cases the geometry of the bismuth atoms was pyramidal. For the monoclinic form, the average Bi–Bi–C angles (to the *ipso*-carbon atoms) was 93.6° and the average C–Bi–C angle was 93.3°. The corresponding average angles for the tetragonal form were 92.7° and 96.7°. As mentioned earlier by Calderazzo and coworkers, these results were in accord with a bismuth atom in which the lone pair of electrons possessed essentially *s*-character.

A number of distibines and dibismuthines are known, many of which show thermochromic behavior in that they give remarkable color changes when melted or when dissolved in an organic solvent. Structural determinations on distibines and dibismuthines have revealed that the thermochromic compounds possessed a stacked linear arrangement with short intermolecular pnictogen-pnictogen distances of the following type:



(where E was Sb or Bi)

There is considerable evidence that the solid phase colors of the thermochromic dipnictines were due to electronic interactions along the E–E · · · E–E chains. In all cases known to date, when a dibismuthine was thermochromic, its antimony analog was also thermochromic. However, since the van der Waals radius of bismuth (2.3 Å) is somewhat larger than that of antimony (2.2 Å), Spence and coworkers have argued that it might be possible to prepare thermochromic dibismuthines where the corresponding antimony analogs were not thermochromic [10]. Accordingly, they prepared the following four dipnictines and indeed found that the distibines were not thermochromic whereas the dibismuthines were:

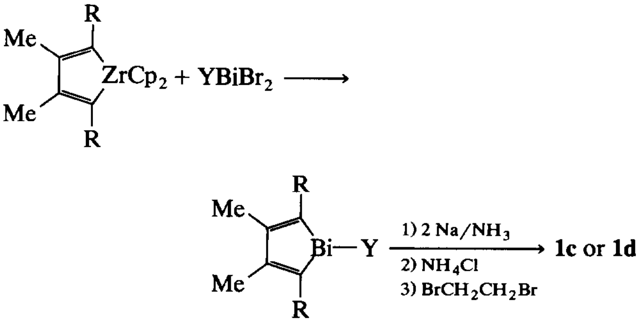


**1**

(**a**, E was Sb, R was Me; **b**, E was Sb, R was $Me_3Si$; **c**, E was Bi, R was Me; **d**, E was Bi, R was $Me_3Si$)

Compounds **1a** and **1b** were orange solids which melted to identically colored liquids and gave orange-yellow solutions. Compounds **1c** and **1d** were both deep green solids which melted reversibly to orange and red oils, respectively. Compound **1c** gave orange-yellow solutions; **1d** gave red solutions in hexane and benzene.

The preparation of the two dibismuthines was carried out in the following manner:

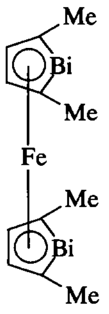


(where R was Me, Y was Ph; and where R was $Me_3Si$, Y was Br)

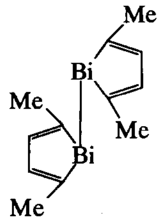
The two compounds 1-bromo-2,5-bis(trimethylsilyl)-3,4-dimethylbismole and 2,2′,5,5′-tetrakis(trimethylsilyl)-3,3′,4,4′-tetramethylbibismole (**1d**) were characterized by $^1H$ and $^{13}C$ NMR, IR spectroscopy, and also elemental analyses. The preparation of the distiboles has been described in the Antimony section.

Ashe and coworkers have previously shown that the inter-ring Sb---Sb bond distances in both 2,2′,5,5′-tetramethylbistibole and 2,2′,5,5′-tetramethyl-1,1′-distibaferrocene were well below the van de Waals distance and indicated some Sb · · · Sb bonding. The authors have now prepared 2,2′,5,5′-tetramethyl-1,1′-dibismaferrocene **2** and determined its molecular structure [11].

This was compared with the crystal and molecular structure of 2,2′,5,5′-tetramethylbibismole **3**.



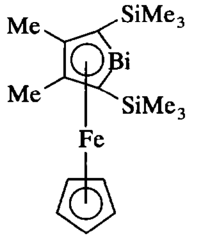
**2**



**3**

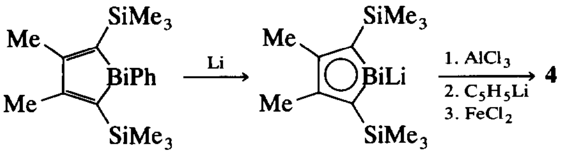
The preparation of **3** (but not its crystal structure) had been previously described in a preliminary communication [12]. The ferrocene compound **2** was synthesized starting with 1-phenyl-2,5-dimethylbismole. Treatment of the latter compound with lithium in THF resulted in cleavage of the phenyl group to give the lithium salt, 1-lithio-2,5-dimethylbismole. After removal of the phenyllithium with ammonium chloride, the THF solution of the lithium salt was added to a suspension of $FeCl_2$ to give the ferrocene compound **2**. It was characterized by elemental analyses, $^1H$ NMR (in both $CDCl_3$ and $C_6D_6$), $^{13}C$ NMR, and mass spectroscopy, as well as by X-ray diffraction. The crystal structure showed that the iron atom was $\pi$-bonded to the two eclipsed $\eta^5$-dimethylbismolyl rings. The two Bi atoms were displaced out of the ring planes away from the iron. The interannular separation of the Bi atoms (3.69 Å) was nearly 1 Å below the van der Waals distance which suggested a direct inter-ring Bi ⋯ Bi bond. An X-ray diffraction study of **3** showed a staggered *trans* conformation with the Bi atoms aligned in zigzag chains. The intramolecular Bi–Bi distances were 2.99 Å; the intermolecular Bi ⋯ Bi distances were 3.66 Å. It was suggested that the intermolecular Bi ⋯ Bi bonding was due to *p-p* overlap.

In continuation of their work on ferrocene type compounds derived from heteroatom aromatic rings, Ashe and coworkers [13] have described, in a preliminary communication, the preparation and the crystal and molecular structure of 2,5-bis(trimethylsilyl)-3,4-dimethyl-1-bismaferrocene (**4**):



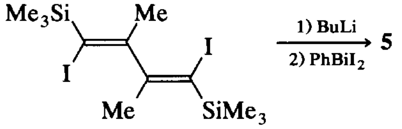
**4**

It was obtained from 2,5-bis(trimethylsilyl)-3,4-dimethyl-1-phenylbismole (**5**):



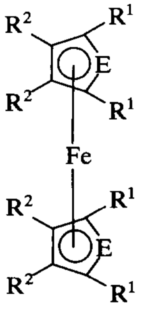
**5** **6**

The labile bismole **5** was not purified but was used directly for the preparation of **4**; **5** was prepared from a diiodobutadiene as follows:



The preparation of the diiodide via a zirconocene was also described. The crystal and molecular structure of **4** was determined by X-ray diffraction. Selected bond distances and bond angles were given. The data were consistent with a structure in which the bismolyl group served as an $\eta^5$-aromatic ligand to the iron atom. The four carbon atoms of this ring were parallel to the cyclopentadiene ring, but the bismuth atom was displaced 0.38 Å above the ring and away from the iron atom. The iron atom was slightly closer to the cyclopentadiene carbon atom (2.01 Å) than to the bismolyl ring carbon atoms (2.07 Å), while the Fe–Bi distance was 2.6 Å. The Bi–C bond distances (2.23, 2.24 Å) were slightly shorter than the sum of the covalent radii (2.29 Å) which was suggestive of some ring multiple bond character.

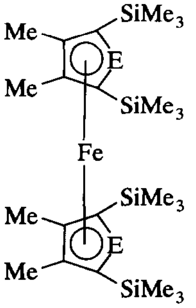
The molecular structure of the above bismaferrocene was compared with the structures of the following ferrocene derivatives containing Group 15 elements:



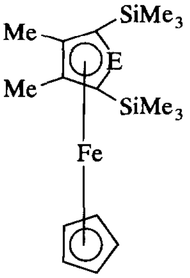
(where E was N, $R^1$ was tert-Bu and $R^2$ was H; where E was P, $R^1$ was H and $R^2$ was Me; where E was As, $R^1$ was Me and $R^2$ was H; where E was Sb, $R^1$ was Me and $R^2$ was H)

The E–C bond distances were all shorter than the sum of the covalent radii, consistent with some multiple bond character in all of the heterocyclic rings. The E–Fe bond distances increased essentially linearly from nitrogen to bismuth. When E was nitrogen, the heteroatom was in the plane of the ring, but the heteroatom was displaced from the ring with other Group 15 elements (P, 0.02; As, 0.07; Sb, 0.18; Bi, 0.39 Å). The C–C distances in all of the heterocyclic rings were essentially the same.

In another paper from Ashe's laboratory [14], the preparation and the crystal and molecular structures of the two antimony-containing ferrocene compounds **7** and **8** as well as the corresponding two bismuth compounds **9** and **4** were described.



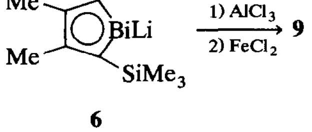
**7 and 9**



**8 and 4**

(**7** and **8**, E was Sb; **9** and **4**, E was Bi)

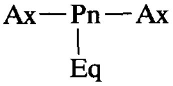
The preparation and the crystal and molecular structure of **4** were briefly described in the previous paper. Both bismaferrocenes were prepared from 2,5-bis(trimethylsilyl)-3,4-dimethyl-1-phenylbismole (**5**). Although this labile compound was not purified, the crude product was characterized by $^1H$ and $^{13}C$ NMR and by electron impact mass spectrometry as well as by elemental analyses. The phenyl group was then cleaved from the bismuth atom by lithium in THF to give the lithium bismacyclopentadienide **6**. The resulting solution was decanted from excess lithium and added to anhydrous aluminum chloride. The bismaferrocene **9** was obtained by adding this solution to iron(II) chloride in THF solution:



**6**

The product was recrystallized from methylene dichloride. It was characterized by $^1H$ and $^{13}C$ NMR, by electron impact mass spectrometry, and by elemental analyses. The PMR spectra of **7** and **9** were determined at 30 and −40°C. In both compounds two methyl singlets in a ratio of 3:1 were assigned to the $Me_3Si$ and ring Me groups, respectively. At the lower temperature the singlets were split into two sets of singlets, indicating that neither the two trimethylsilyl groups nor the two vicinal methyl groups were equivalent. At 30°C there must be rapid rotation on the NMR time scale. A barrier of $13.3 \pm 0.5$ kcal $mol^{-1}$ was calculated for the antimony compound and $13.1 \pm 0.5$ kcal $mol^{-1}$ for the bismuth compound. The rotation of the rings could be accomplished by either a clockwise or counterclockwise rotation of one ring around the other. Although experimental data do not allow a distinction to be made between these two modes of rotation, the authors believed that a counterclockwise rotation was more probable. The clockwise rotation would have resulted in all four trimethylsilyl groups eclipsing each other during the rotation, whereas in the counterclockwise rotation only two trimethylsilyl groups were eclipsed at one time.

Dixon, Arduengo, and coworkers [15] have written extensively on the mechanism of inversion of tricoordinate pyramidal Group 15 (pnictogen) compounds. They have found from *ab initio* calculations that compounds with electronegative substituents (*e.g.* $PHF_2$ or $PF_3$) undergo inversion through a T-shaped transition (or intermediate) state **10** (edge inversion) rather than by the classical trigonal planar structure (vertex inversion).

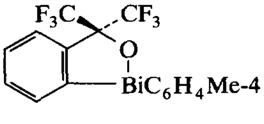


$$\mathrm{Ax{-}\underset{\displaystyle Eq}{\underset{|}{Pn}}{-}Ax}$$

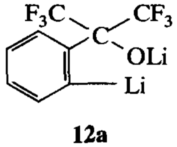
**10**

(where Pn was a pnictogen, Ax was axial, and Eq was equatorial)

Ammonia, phosphine, and $PH_2F$, however, undergo inversion by vertex inversion. The T-shaped transition state for edge inversion was found to be stabilized by σ-acceptors in the axial positions and by π-donors in the equatorial position. The barrier to inversion by the edge mechanism decreased with increasing pnictogen atomic number [16]. Akiba and coworkers [17] have now prepared several organobismuth(III) compounds in order to investigate their inversion by the edge mechanism. They first prepared compound **11** by the reaction of the dilithio compound **12a** with 4-tolyldichlorobismuthine.



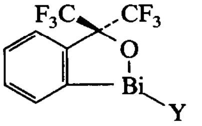
**11**



**12a**

Compound **11** was characterized by elemental analyses and $^1H$ and $^{19}F$ NMR spectroscopy. The $^{19}F$ NMR spectrum showed a pair of quartets at room temperature which coalesced when heated in DMSO-$d_6$ solution to 175°C. The energy for inversion was calculated to be 21.2 kcal $mol^{-1}$ at 175°C. There was no inversion when the compound was heated to 175°C in *o*-dichlorobenzene or benzonitrile.

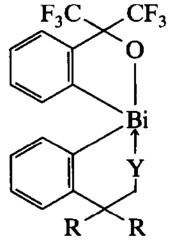
In addition to compound **11**, the authors prepared compounds **13a**, **b**, and **c**:



**13a, b, c**

(**13a**, Y was Cl; **13b**, Y was $MeCO_2$; **13c**, Y was $CF_3CO_2$)

Compound **13a**, although almost pure, did not give satisfactory elemental analyses; elemental analytical results (not reported) were satisfactory for compounds **13b** and **13c**. The $^{19}F$ NMR spectra of all three compounds in acetone-$d_6$ were singlets, even at −50°C. Since the inversion barrier of $Me_2PCl$ (40.4 kcal $mol^{-1}$) was known to be higher than that of $Me_3P$ (35.6 kcal $mol^{-1}$), indicative of vertex inversion for these compounds, the results for all four bismuth compounds, **11**, **13a**, **b**, **c**, were suggestive of edge inversion. The authors pointed out, however, that compounds **13a**, **b**, and **c** could possibly undergo inversion by an intermolecular process, and that compounds **13b** and **c** might also invert by an intramolecular process involving a 4-membered cyclic transition state by coordination of the carbonyl oxygen with bismuth. To further investigate the edge inversion process the authors prepared compounds **14a** and **b**:

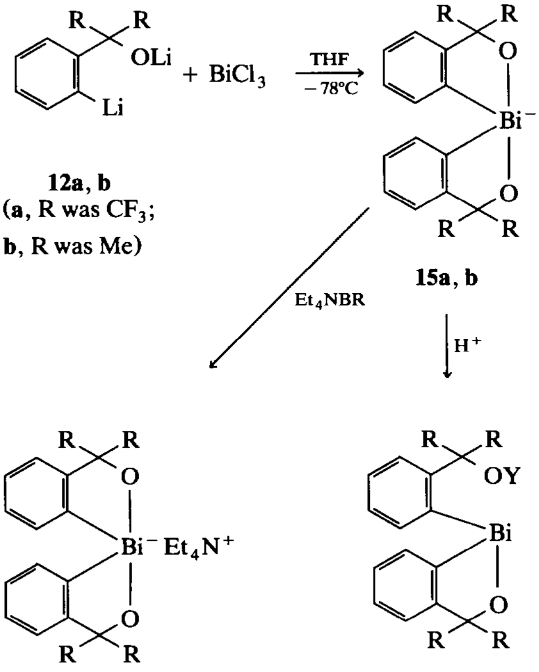


**14a and b**

(**14a**, Y was OMe and R was Me; **14b**, Y was $NMe_2$ and R was Me)

The compounds were prepared from **13a** and 2-$MeOCH_2C_6H_4Li$ or 2-$Me_2NCH_2C_6H_4Li$, respectively. Their structures were quite similar as determined by X-ray diffraction. The geometry of the Bi atom was essentially trigonal-bipyramidal with the two phenyl groups and the lone pair occupying equatorial positions. For **14a** the C–Bi–C angle was 94.4° and the O–Bi–O angle was 155.4°. For **14b** the N–Bi distance (2.63 Å) was considerably shorter than the sum of the van der Waals distances (3.74 Å). The $^{19}F$ spectra of both compounds showed a pair of quartets at room temperature in DMSO-$d_6$. Both compounds gave $^{19}F$ singlets when heated in DMSO-$d_6$. The coalescence temperature for **14a** was 125°C, and for **14b** was 55°C. The barrier for inversion ($\Delta G^{\ddagger}_{T_c}$) at the above temperatures was 18.6 and 15.4 kcal $mol^{-1}$, respectively. The latter values compared with 21.2 for **11** at 175°C. Thus, an oxygen or nitrogen atom in axial position markedly lowered the energy of activation for inversion. The coalescence temperature and the barrier for inversion were then determined in the following solvents: toluene-$d_8$, nitrobenzene, 2,6-lutidine, DMSO-$d_6$, and pyridine. The resulting values (°C, kcal $mol^{-1}$) were 125, 20.5; 170, 20.6; 170, 20.6; 55, 15.4; and 40, 40.6, respectively. These latter results were in accord with the conclusion that $\pi$ donors in the equatorial positions stabilized the transition state for edge inversion. The authors also pointed out that, even though **14a** and **b** possessed trigonal-bypyramidal geometry, the inversion could not be rationalized by Berry pseudorotation, since such a mechanism would involve placing the electron pair in the high energy apical position.

In continuation of previous work on heterocyclic bismuth compounds of the type 10-Bi-5 and 12-Bi-6, a new paper from Akiba's laboratory [18] has described the preparation of 10-Bi-4 compounds. These were obtained from $BiCl_3$ and two dilithio ligands (one of which, **12a**, had been used for preparing the 10-Bi-5 and 12-Bi-6 compounds):



**12a, b**
(**a**, R was $CF_3$;
**b**, R was Me)

**15a, b**

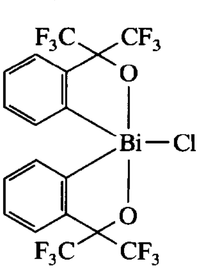
**16a, b**

**17a, b** (Y was H)

Compound **15a**, when chromatographed on $SiO_2$ or treated with acid, gave **17a** (Y = H). When **17a** was treated with $K_2CO_3$, the potassium salt corresponding to **15a** was obtained. When either the lithium salt (**15a**) or the potassium salt was treated with tetraethylammonium bromide, **16a** was obtained. This was stable to atmospheric moisture. Compound **16b**, however, was unstable to moisture and gave **17b** (Y = H), when an attempt was made to crystallize it from benzene.

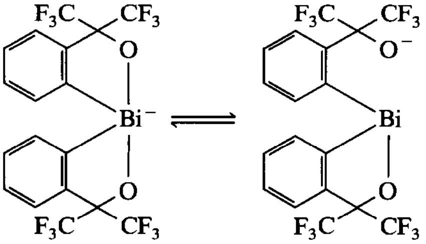
The crystal and molecular structure of **16a** was determined by X-ray diffraction. The geometry of the bismuth atom was that of a pseudotrigonal bipyramid, with the two Bi–C bonds and the bismuth lone pair occupying the equatorial positions. The Bi–O bond distances (2.273 and 2.306 Å) were longer than the sum of the covalent radii. Compound **15b** underwent reaction with MeI at room temperature in THF solution to give **17b** (Y = Me). Neither **15a** nor **16a** reacted with MeI, even when refluxed in THF solution.

When the potassium salt (corresponding to **15a**) was treated with sulfuryl chloride in $CH_2Cl_2$, the 10-Bi-5 compound **18** was obtained.



**18**

Compounds **16a**, **17a** and **b** (Y = H), **17b** (Y = Me), and **18** were characterized by $^1H$ NMR spectroscopy and (except for **17a**) by elemental analyses. Compounds **16a**, **17a** (Y = H) and **18** were also characterized by $^{19}F$ NMR spectroscopy. The $^{19}F$ NMR was of particular value in establishing the structure of those compounds containing $CF_3$ groups. Thus, the $^{19}F$ NMR spectra of **15a** and **16a** in acetone-$d_6$ showed a pair of quartets within the temperature range −50° to 50°C. By contrast, the $^{19}F$ NMR spectra of **17a** (Y = Me) (the preparation of which will be described in a later paper) gave two pairs of quartets. These results argued strongly against a ring-opening equilibrium:



Clegg and coworkers, after commenting on the paucity of data on the structures of organobismuth(III) halides, have reported on the crystal and molecular structures of a number of such compounds [19]. Dibromophenylbismuthine, crystallized from THF by solvent diffusion with hexane, contained a mole of THF of crystallization. The structure of this substance and of the other compounds described in this paper were determined by X-ray diffraction. The geometry of the bismuth atom was that of an almost ideal square pyramid with the phenyl group in apical position. Two bromines were in *cis* positions, with a bridging bromine from a neighboring molecule and the oxygen of the THF molecule occupying the other *cis*-positions. The molecule was polymeric with bridging Br–Bi–Br atoms connected in zig-zag chains. The Br–Bi–Br angle of the *trans* bromine atoms was 171.2°, and the O–Bi–Br angle (where the Br was non-bridging) was 177.4°. The Bi–Br distances were 2.684 (non-bridging bromine), 2.825 (bridging bromine) and 3.038 Å (bridging bromine from neighboring molecule). The Bi–O distance was quite long (2.67 Å) indicating a fairly weak bismuth–oxygen interaction. A similar compound, $PhBiI_2 \cdot THF$, was also prepared and its structure determined. It possessed a similar structure to the dibromide, although the two compounds were not isomorphous. In both the dibromide and the diiodide, the bismuth atoms lay almost in the basal plane of the square pyramid. When the diiodo compound was treated with $Et_4NI$ in THF, and the product crystallized from MeCN and $Et_2O$ by solvent diffusion, crystalline $[NEt_4]_2[Ph_2Bi_2I_6] \cdot Et_2O$ was obtained. The X-ray diffraction study of this compound revealed that each bismuth atom of the dianion possessed square-pyramidal geometry with apical phenyl groups. The basal plane contained four iodine atoms, with two bridging iodine atoms to form a Bi–I–Bi–I ring. The Bi atoms were 0.162 and 0.098 Å above the basal plane and the Bi–I–Bi–I ring was not planar, with the angles at the two iodine atoms being 77.3° and 78.3°, respectively. The two basal planes, each containing four iodine atoms, intersected at the two bridging atoms, with an angle of 105.2° between the two planes.

In addition to the dibromo and diiodo compounds reported above, two diphenylbromo compounds, $Ph_2BiBr \cdot THF$ and $[PPh_4]^+[Ph_2BiBr_2]^-$, were prepared and their crystal and molecular structures determined. The compound $Ph_2BiBr \cdot THF$ was monomolecular. The structure around the bismuth atom was described as an "equatorially vacant" trigonal bipyramid with the bromine and THF oxygen in apical positions and the two phenyl groups in equatorial positions. The Br–Bi–O angle was 173.5°, with the other listed angles in the molecule varying from 80.8° to 98.2°. Addition of $Ph_4PBr$ to the above bromide gave, after work-up and recrystallization from $CH_2Cl_2$-hexane, $[Ph_4P]^+[Ph_2BiBr_2]^-$. The anion was also an "equatorially vacant" trigonal bipyramid with the two bromines in apical positions with the Br–Bi–Br angle 177.3°. In addition to the structural descriptions above, the authors discussed at some length the primary Bi-X bonds and the secondary Bi ··· X bonds (where the X–Bi ··· X angle > 140°) and the influence of the secondary bond length on the primary bond length. The data for this discussion were taken from X-ray diffraction studies in the chemical literature and from the data reported in the present paper.

Although chiral tertiary bismuthines containing three different aryl groups have been prepared [20], the synthetic methods used for their preparation often led to complex mixtures, and the only chiral bismuthines obtained as pure compounds contained two or three bulky substituents. Suzuki and coworkers [21] have now described a general synthetic method for preparing chiral tertiary bismuthines containing only simple aryl groups, *e.g.* $(4\text{-}MeOC_6H_4)(4\text{-}ClC_6H_4)(4\text{-}MeC_6H_4)Bi$. The method utilized the tert-butylsulfonylphenyl group as one of the groups attached to bismuth. Use of this group prevented multiple iodination and dearylation leading to the formation of intractable mixtures. This group could then be selectively replaced by a simple aryl group to give the final product. The following synthesis was employed:

$$2\text{-}RC_6H_4Li + Ar_2BiCl \xrightarrow[-78°C]{Et_2O} 2\text{-}RC_6H_4BiAr_2$$

$$2\text{-}RC_6H_4BiAr_2 + I_2 \xrightarrow[RT]{Et_2O} 2\text{-}RC_6H_4Bi(Ar)I + ArI$$

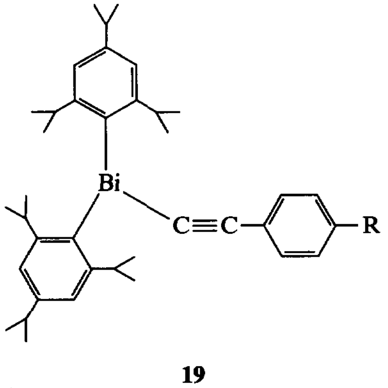
$$2\text{-}RC_6H_4Bi(Ar)I + Ar'MgBr \xrightarrow{THF} 2\text{-}RC_6H_4BiArAr' + MgBrI$$

(where R was tert-$BuSO_2$, Ar was $4\text{-}MeC_6H_4$, and Ar' was $4\text{-}ClC_6H_4$, $4\text{-}MeOC_6H_4$, or 1-naphthyl)

The three racemic mixtures $2\text{-}RC_6H_4BiArAr'$ were resolved on an analytical scale by means of optical HPLC columns, Chiracel OD or Chiralpak AS and AD.

Following the preparation of chiral tertiary bismuthines containing the 2-tert-butylsulfonylphenyl group, the authors attempted the exchange of this group by a simple aryl group. In preliminary experiments they found that when $RC_6H_4BiAr_2$ was treated with $4\text{-}ClC_6H_4Li$ or $4\text{-}MeOC_6H_4Li$ in THF at −78°C, the tert-butylsulfonylphenyl group was displaced preferentially to give di-4-tolyl(4-chlorophenyl)- or di-4-tolyl(4-methoxyphenyl)bismuthines in 87 and 95% yields, respectively. Following these results, the authors treated the racemic bismuthine $2\text{-}RC_6H_4Bi(Ar)C_6H_4\text{-}OMe\text{-}4$ with 4-chlorophenyllithium or 1-naphthyllithium to give $ArBi(4\text{-}MeOC_6H_4)(4\text{-}ClC_6H_4)$ or $ArBi(4\text{-}MeOC_6H_4)(C_{10}H_7)$ in 70 and 88% yields, respectively. These two bismuthines could not be resolved on the chiral columns. The authors stated that the isolation and characterization of optically pure enantiomeric bismuthines on a milligram scale is being attempted. The melting points and yields of the new bismuthines were given. They were characterized by elemental analyses and spectral data (results not given).

In another paper from Suzuki's laboratory [22], the preparation of several triarylbismuthines containing bulky substituents (mesityl, 2,4,6-triethylphenyl, 2,4,6-triisopropylphenyl, and 2,4,6-tri-tert-butylpheyl) was attempted. The preparation of the trimesityl and tris (2,4,6-triethylphenyl)bismuthines was readily accomplished from the corresponding Grignard reagents and bismuth trichloride. However, unlike the preparation of triphenylbismuthine by the Grignard reaction, it was necessary to reflux the reaction mixture in order to complete the reaction. The trimesitylbismuthine had been previously described in the chemical literature [23]. The reaction of the Grignard reagent from 1-bromo-2,4,6-triisopropylbenzene and bismuth trichloride at ambient temperature gave chlorobis(2,4,6-triisopropylphenyl)bismuthine in 90% yield. The main product obtained from the reaction of 2,4,6-tri-tert-butylphenyllithium and bismuth trichloride, after aqueous workup, was 1,3,5-tri-tert-butylbenzene. Chlorobis (2,4,6-triisopropylphenyl)bismuthine was remarkably stable to atmospheric moisture, compared with most diarylchlorobismuthines. It reacted with alkyl-, alkenyl-, or alkynyllithium reagents to yield the corresponding alkyl-, alkenyl-, or alkynylbis(2,4,6-triisopropylphenyl)-bismuthines. Thus, reaction with methyllithium gave methylbis(2,4,6-triisopropylphenyl)bismuthine. When this tertiary bismuthine was treated with sulfuryl chloride the bismuth-methyl bond was cleaved to yield methyl chloride and the chlorobismuthine. Reaction of the chlorobismuthine with 2-phenylethenyllithium gave (2-phenylethenyl)bis(2,4,6-triisopropylphenyl)bismuthine. Finally, the chlorobismuthine was treated with an ethynyllithium compound of the type $4\text{-}RC_6H_4C{\equiv}CLi$ (where R was H, Me, or Cl) to yield the corresponding arylethynylbis(2,4,6-triisopropylphenyl)bismuthine **19**:

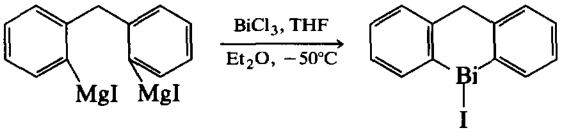


**19**

(where R was H, Me, or Cl)

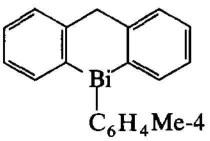
When **19** (R was Me) was treated with benzoyl chloride, the bismuth–ethynyl bond was cleaved to yield $PhCOC{\equiv}CC_6H_4Me\text{-}4$ and the starting chlorobismuthine. In another reaction, attempts were made to prepare bis(2,4,6-triisopropylphenyl)bismuthine by reduction of the corresponding chlorobismuthine with lithium aluminum hydride, sodium borohydride, or diisobutylaluminum hydride. A black inorganic material and 1,3,5-triisopropylbenzene were the only products. In another series of reactions, chlorodimesitylbismuthine was prepared by the redistribution reaction of trimesitylbismuthine and bismuth trichloride. The chlorobismuthine (without characterization) was converted into iododimesitylbismuthine by treatment with sodium iodide. Reaction of this iodobismuthine with methyllithium or with 2-phenylethynyllithium gave the corresponding methyldimesityl- or 2-phenylethynyldimesitylbismuthine, respectively. All of the new compounds (except for chlorodimesitylbismuthine) were characterized by elemental analyses, PMR, IR, and mass spectrometry. They were all crystalline solids with comparatively low melting points.

In a third paper from Suzuki's laboratory, the synthesis of a number of heterocyclic bismuth(III) compounds has been described [24]. 5-Iodo-5,10-dihydrodibenzo[*b,e*]bismin (**20**) was prepared from the Grignard reagent (obtained from activated magnesium, 2,2′-dichlorodiphenylmethane and potassium iodide) added to bismuth trichloride at −50°C.



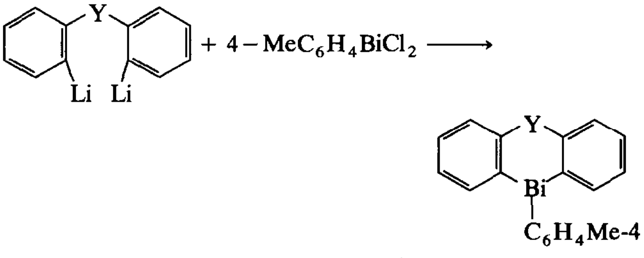
**20**

Treatment of this iodide with 4-tolyldichlorobismuthine in THF gave the corresponding tolylbismin **21** in 97% yield:



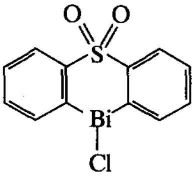
**21**

In addition to the above bismins, three heterocyclic compounds, **22**, **23**, and **24**, were obtained from the corresponding dilithio compounds and dichloro-4-tolylbismuthine:



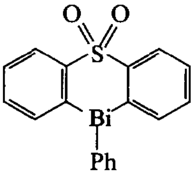
(**22**, Y was O; **23**; Y was S; **24**, Y was $SO_2$)

When benzene solutions of **21** and benzoyl chloride, in the presence of catalytic amounts of $(Ph_3P)_4Pd$, were refluxed, the only identifiable product was 4-methylbenzophenone, obtained in 80% yield. Similar results were obtained with **22** and **23**. However, when **24** was treated in this manner, the monochloride **25** was obtained in 86% isolated yield, together with 4-methylbenzophenone.



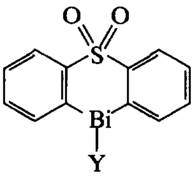
**25**

Compound **25** was a stable crystalline solid, unaffected by atmospheric moisture (in contrast to most other diarylchlorobismuthines). The authors suggested that transannular interaction between the bismuth and a sulfonyl oxygen stabilized the bismuth–chlorine bond. Compound **25** was also prepared from 2,2′-dilithiodiphenyl sulfone and bismuth trichloride, but only in 27% yield. When **25** was treated with phenyllithium, a mixture of triphenylbismuthine, diphenyl sulfone, and **26**



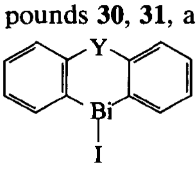
**26**

was obtained. However, if 4-tolylmagnesium bromide (rather than the lithium reagent) was used, compound **24** was obtained in 100% yield. In addition to compounds **24** and **26**, compounds **27**, **28** and **29** were obtained from **25** and the appropriate reagent:



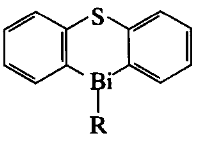
(**27**, Y was $4\text{-ClC}_6H_4C{\equiv}C$; **28**, Y was $Ph_2C{=}CH$; **29**, Y was Me)

Compound **27** was prepared from $4\text{-ClC}_6H_4C{\equiv}CLi$, **28** from $Ph_2C{=}CHMgBr$, and **29** from MeMgBr. Compounds **22**, **23**, and **24** reacted with iodine in ether solution at ambient temperature to yield the iodo compounds **30**, **31**, and **32**:



(**30**, Y was O; **31**, Y was S; **32**, Y was $SO_2$)

Compound **20**, the synthesis of which was described above, was also prepared from the Grignard reagent obtained from 2,2′-dichlorodiphenylmethane and bismuth trichloride in the presence of potassium iodide. Compounds **20** and **30** reacted with $4\text{-ClC}_6H_4C{\equiv}CLi$ to give unidentified polymeric substances. Compound **31**, however, gave the stable alkynyl product **33a**:



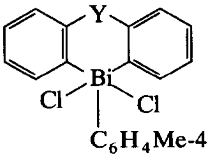
**33a**

(where R was $4\text{-ClC}_6H_4C{\equiv}C$)

In addition, two other stable crystalline compounds, **33b** (R was $Ph_2C{=}CH$) and **33c** (R was Me), were prepared in 58% and 35% yields, respectively.

The crystal and molecular structure of **27** was determined by X-ray diffraction. The most interesting feature was the short bismuth–sulfonyl oxygen distance (2.97 Å) compared with the van der Waals distance (3.72 Å). In addition, the Bi–O intermolecular distance (3.288 Å) was less than the van der Waals distance. These two effects obviously stabilized the heterocyclic compounds containing the sulfonyl group, but do not explain the stability of the compounds **33a**–**33c**. Another interesting but unexplained result was the bismuth–acetylene (Bi–C–C) angle of 160.4°, rather then the expected 180° angle.

In addition to the bismuth(III) heterocyclic compounds, the authors treated compounds **21**–**24** with sulfuryl chloride in hexane solution at ambient temperature to yield compounds **34**–**37**.



(**34**, Y was $CH_2$; **35**, Y was O; **36**, Y was S; **37**, Y was $SO_2$)

Compounds **34**–**36** were obtained in quantitative yields, but **37** was obtained only in 50% yield, accompanied by 36% of **25**. Compound **37** was also found to slowly decompose to give 4-chlorotoluene and **25** when stored at ambient temperature. The same decomposition occurred in 5 min when **37** was heated in dichloromethane. Finally, **37** reacted with the sodium salt of dibenzoyl methane at −50 to 0°C to give **25** and 2-(4-tolyl)-1,3-diphenylpropane-1,3-dione. All of the new compounds were characterized by elemental analyses and by $^1H$ NMR, IR, and mass spectroscopy.

In recent years metal oxide thin films have been intensely investigated as superconductors. Such films as Bi–Sr–Ca–Cu–O are among the most promising. The bismuth in such films has usually been produced by the decomposition of organobismuth compounds by the MOCVD (metalorganic chemical vapor deposition) method. The most commonly used organobismuth compound has been triphenylbismuthine [25–34]. In a few cases other organobismuth compounds have been used to form bismuth oxide films. A US patent [35] covers the use of bis(2-methyl-2-propenoato-*O*-)triphenylbismuth, $Ph_3Bi[O_2CC(Me){=}CH_2]_2$, for this purpose. Bismuth carboxylates and bismuth β-diketonates have also been used to prepare bismuth oxide films by the MOCVD method. The bismuth β-diketonates were best prepared by metathesis from triphenylbismuthine and the β-diketone [36]:

$$Ph_3Bi + 3R^1COCH_2COR^2 \longrightarrow Bi(R^1COCHCOR^2)_3 + 3PhH$$

(where $R^1$ and $R^2$ were groups wuch as $CF_3$, $CF_2CF_2CF_3$, $CMe_3$, or Ph)

Brooks and coworkers [37] have also investigated several β-diketonate complexes of bismuth. These were synthesized by heating three equivalents of the β-diketone with one molar equivalent of triphenylbismuthine in toluene solution. Four different β-diketones were used in these experiments, 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione [H(fod)], 1,1,1,5,5,5-hexafluoro-2,4-pentanedione [H(hfa)], 1,1,1-trifluoro-2,4-pentanedione [H(tfa)] and 2,2,6,6-tetramethyl-3,5-heptanedione [H(thd)]. Of these, H(fod) proved to give the most satisfactory product; by contrast H(thd) did not react with triphenylbismuthine, presumably due to the lower acidity of the enolate form of this ligand. In addition to the product obtained from three molar equivalents of H(fod), *i.e.* $Bi(fod)_3$, a product obtained from two molar equivalent of H(fod) and one molar equivalent of triphenylbismuthine was prepared. This material was presumed to be $PhBi(fod)_2$ since the ions $PhBi^+$ and $PhBi(fod)^+$ were among those identified in the mass spectrum of the product. The electron ionization mass spectrum of the product obtained from three molar equivalents of H(tfa) gave ions corresponding to $Ph_2Bi^+$, $PhBi(tfa)^+$ and $Ph_2Bi(tfa)^+$, and the PMR spectrum gave resonances in the phenyl region. It would thus appear that a mixed phenyl-tfa product was produced in this reaction.

Since the product obtained from three molar equivalents of H(fod) and one molar equivalent of triphenylbismuthine was the most promising, it was studied in greater detail. The crude reaction product was readily purified by vacuum sublimation. The resulting yellow solid (mp 88–90°C) was shown to possess the formula $Bi(fod)_3$ by elemental analysis. It was further studied by means of electron ionization and negative chemical ionization mass spectrometry, $^1$H NMR spectrometry, by gas chromatography/mass spectrometry, and by thermogravimetric analysis. The mass spectral, PMR, GC/MS, and thermogravimetric analyses all suggested that the crude product, before sublimation, contained an extra fod ligand which the authors suggested might be due to the existence of a tetrakis complex, HBi(fod)$_4$, or of a weakly associated complex, Bi(fod)$_3 \cdot$ H(fod).

The decomposition of the fod complex was studied in a MOCVD reactor; the unsublimed product was used for this purpose. The film consisted of 73% Bi, 15% C, and 12% O. Fluorine was not present as a major peak in the Auger spectrum of the film. The authors concluded that the Bi(fod)$_3$ complex was a suitable precursor for the preparation of bismuth-containing thin films by MOCVD.

X-ray contrast or radiopaque polymers have found extensive use as medical implants and for many other purposes. However, X-ray additives in current use are incompatible with most plastics. Bismuth compounds such as the trihalides have been used but are very moisture sensitive. Ignatious and coworkers [38] have studied triphenylbismuthine for this purpose. It was found to give radiopaque blends with a wide range of polymeric materials. Since it is moisture insensitive, has a low toxicity, and is heat stable, it is an attractive X-ray contrast additive. Organobismuth-containing polymers can be prepared by polymerizing styryldiphenylbismuthine with benzoyl peroxide. $\alpha$-Methylstyryldiphenylbismuthine was not homopolymerized by benzoyl peroxide but did copolymerize with methyl methacrylate or methyl acrylate. The copolymers had $T_g$ values varying from 10° to 112°C for polymers containing 0% to 26% bismuth monomers. It was found that the radiopacities of the polymers were proportional to the molar content of the radiopacifiers.

The preparation and properties of bismuth-containing polymers were described in much greater detail in another paper from Ignatious's laboratory [39]. Four tertiary bismuthines in which one of the substituents contained a vinyl grouping (and was thus susceptible to polymerization) were synthesized. Diphenyl(4-vinylphenyl)bismuthine was obtained from chlorodiphenylbismuthine and the Grignard reagent prepared from 4-bromostyrene. The product was obtained as a viscous yellow oil which could not be crystallized. It was characterized by PMR, mass spectroscopy and elemental analyses. However, HPLC studies revealed the presence of at least three different components in the product. (4-Isopropenylphenyl)diphenylbismuthine was prepared in a similar manner to the styryl compound and was also obtained in an impure state. However, tris(4-isopropenylphenyl)bismuthine was obtained as a crystalline solid. It was prepared from bismuth trichloride and the Grignard reagent obtained from 4-isopropenylphenyl bromide. It was characterized by its PMR spectrum. Only a single peak was obtained by HPLC. The fourth vinyl monomer prepared was 4-[dimethyl(vinyl)silyl]phenyldiphenylbismuthine. It was prepared by means of the following reactions:

$$1,4\text{-}C_6H_4Br_2 \xrightarrow[\text{2. }Me_2(CH_2{=}CH)SiCl]{\text{1. Mg,THF}}$$

$$4\text{-}[Me_2(CH_2{=}CH)Si]C_6H_4Br \xrightarrow[\text{2. }Ph_2BiCl]{\text{1. Mg,THF}}$$

$$4\text{-}[Me_2(CH_2{=}CH)Si]C_6H_4BiPh_2$$

The product was a viscous yellow oil characterized by PMR, mass spectra, and elemental analyses.

The first monomer, diphenyl(4-vinylphenyl)bismuthine, could be both homo- and copolymerized radically or anionically. The copolymerizations were performed with methyl methacrylate or with styrene. However, (4-isopropenylphenyl)diphenylbismuthine could only be copolymerized. The silicon-containing monomer could not be polymerized under any conditions.

The reaction of iron(III) compounds such as FeCl$_3$ or Fe(SCN)$_3$ with Ph$_3$P or Ph$_3$As leads to the formation of several different types of iron(III) complexes, depending on the solvent used for the reaction and also on the ratio between the iron(III) and the phosphine or arsine employed. Vancová and Ondrejkovicová [40] have now found that the reaction between iron(III) compounds and Ph$_3$Sb or Ph$_3$Bi took a quite different course in that one-third of the iron was reduced to produce an iron(III)–iron(II) complex with the concomitant oxidation of the Ph$_3$Sb or Ph$_3$Bi. Thus, from FeCl$_3$ and Ph$_3$Bi in a molar ratio of 1:0.5 in acetonitrile the complex [Fe(NCMe)$_6$][FeCl$_4$] and Ph$_3$BiCl$_2$ were formed. Similarly, [Fe(NCMe)$_6$][Fe(NCS)$_4$] was formed when Fe(NCS)$_3$ was used.

Cho and coworkers [41] have demonstrated that triarylbismuthines reacted with carbon monoxide in the presence of certain rhodium catalysts, [RhCl(CO)$_2$]$_2$ or RhCl$_3 \cdot$ 3H$_2$O, with the formation of diaryl ketones. Trace amounts of biaryls were also formed. When the reaction was carried out in methanol, the methyl ester, ArCO$_2$Me, was also formed. Thus, triphenylbismuthine (1 mmol) and RhCl$_3 \cdot$ 3H$_2$O (0.05 mmol) gave the following % yields of benzophenone, biphenyl, and methyl benzoate, respectively, in the following solvents: MeCN, 49, trace, 0; THF, 46, 1, 0; MeOH, 58, 0, 17. Under the same reaction conditions, but with the use of [RhCl(CO)$_2$]$_2$ as the catalyst, the % yields of benzophenone, biphenyl, and methyl benzoate in MeCN or MeOH, were 78, trace, 0; and 65, 0, 17. When the amount of catalyst, [RhCl(CO)$_2$]$_2$, was reduced from

0.05 mmol to 0.01 mmol, in both MeCN and MeOH, the yields of products were markedly decreased. In addition to triphenylbismuthine, the reaction was carried out with the following triarylbismuthines, (4-$YC_6H_4)_3Bi$, where Y was Me, OMe, and Cl. Thus, with 4-$(MeOC_6H_4)_3Bi$ and with $[RhCl(CO)_2]_2$ as the catalyst and MeCN as the solvent, the yields of (4-$MeC_6H_4)_2CO$ and (4-$MeC_6H_4)_2$ were 75% and 1%, respectively. The reactions were carried out at room temperature in carbon monoxide at 1 atm for 20 h. A mechanism for the reaction which involved the formation of an $Ar_3BiRh$ complex, followed by transfer of an aryl group from bismuth to rhodium, was suggested as the first two steps of the reaction. Thus, when the stronger base $Ph_3P$ (*i.e.* stronger than $Ph_3Bi$) was added to the reaction mixture (in MeCN with $RhCl_3 \cdot 3H_2O$ as the catalyst), the yield of benzophenone was reduced from 46 to 4%. Rhodium compounds, other than the two compounds mentioned above, *viz.* $Rh_2(OAc)_4$, $RhCl(PPh_3)_3$, and $RhCl(CO)PPh_3$, were only slightly effective as catalysts, while other metal salts such as $RuCl_3$, $IrCl_3$, and $PdCl_3$ were ineffective. Other Group 15 compounds, $Ph_3As$ and $Ph_3Sb$, did not undergo the same reaction as $Ph_3Bi$ with the effective rhodium catalysts. However, $Ph_2BiBiPh_2$ in place of $Ph_3Bi$ gave a 30% yield of benzophenone, with $[RhCl(CO)_2]_2$ as the catalyst. When a mixture of two triarylbismuthines, $Ph_3Bi$ (0.50 mmol) and (4-$MeC_6H_4)_3Bi$ (0.50 mmol) in MeCN with $[RhCl(CO)_2]_2$ as the catalyst was treated with carbon monoxide, all three possible ketones, $Ph_2CO$(0.26 mmol), (4-$MeC_6H_4)_2CO$ (0.24 mmol), and Ph(4-$MeC_6H_4)CO$ (0.38 mmol) were obtained.

The adsorption of the triphenyl derivatives of the Group 15 elements, N, P, As, Sb, and Bi, on thin layers of gold or copper has been studied by Steiner and coworkers [42]. The gold and copper slides were prepared by evaporation of about 2000 Å of metal onto silicon wafers, previously cleaned by immersing the slides in ethanol for 1 min under the influence of ultrasound, and then covered with a layer of about 50 Å of chromium for adhesion purposes. The slides were instantly immersed in a 1 mM solution of the Group 15 compound in ethanol or hexane for 6 h, removed and rinsed with ethanol, and finally dried in an argon stream. The adsorption was studied by reflection IR spectroscopy at grazing incidence, ellipsometry, contact angle measurements, and in two cases ($Ph_3Sb$ and $Ph_3Bi$) by X-ray photoelectron spectroscopy. As determined by IR spectroscopy, all of the compounds were adsorbed onto the gold or copper slides. On gold only $Ph_3Bi$ led to a surface layer significantly thicker than that expected for a monolayer. On copper, however, that was true for $Ph_3P$, and possibly for $Ph_3N$ and $Ph_3Bi$. After immersion of the slides in pure ethanol for 1 h, all of the compounds were desorbed from the copper slides, but not from the gold slides. In several days, however, all of the adsorbates had desorbed from the gold slides. At reduced pressure, all of the adsorbates except for $Ph_3Sb$ and $Ph_3Bi$ had desorbed within 30 min. The X-ray photoelectron spectroscopy of $Ph_3Bi$ on gold films showed an oxygen signal at 532.6 eV. This signal was not present on the gold slide before adsorption nor after immersing the gold slide in ethanol for 6 h. It was suggested that ill-defined oligomeric or polymeric oxidation products were formed from the adsorbed $Ph_3Bi$.

Naphthaleneytterbium, $C_{10}H_8Yb(THF)_2$, has been found to react with diphenylmercury or triphenylbismuthine to yield pentaphenyldiytterbium, $Ph_2Yb(THF)(\mu\text{-}Ph)_3Yb(THF)_3$ [43]. The reaction with triphenylbismuthine was slower than with diphenylmercury, and the yield was smaller.

Triphenylbismuthine has been suggested as a promising additive for making biomedical resins visible on X-ray images [44]. It was noted that the bismuthine possessed only a slight degree of cytotoxicity, both alone and in combination with self-cured poly(methylmethacrylate) (PMMA).

Because it is an effective curing agent, isophorone diisocyanate has been used in a number of hydroxyl-terminated propellants. Tan and Tan [45] have studied the reaction of isophorone diisocyanate with polyethylene glycol and with triphenylbismuthine or dibutyltin dilaurate as the catalyst. With triphenylbismuthine the reaction was zero order with respect to the isocyanate and second order with respect to the glycol. With dibutyltin dilaurate the reaction was second order with respect to both the isocyanate and the glycol. The use of both triphenylbismuthine and dibutyltin dilaurate showed an additive result. Reaction mechanisms were schematically proposed.

Masuda and coworkers have written extensively on the polymerization of acetylenic compounds. They have noted that silicon-containing polyacetylenes have shown unique properties, particularly high gas permeability. The present paper deals with the polymerization and properties of polymerized 1-(3-trimethylsilylphenyl)-1-propyne [46]. The polymerization was carried out by using $TaCl_5$ or $NbCl_5$ as the catalyst with a number of organometallic compounds as cocatalysts. Triphenylbismuthine was one of the organometallic compounds used as the cocatalyst.

The polymerization of various alkynes by alkoxides of molybdenum, tantalum, and niobium, as well as by molybdenum pentachloride, and the influence of cocatalysts ($Et_3Al$, $EtAlCl_2$, and $Ph_3Bi$) has been studied by Gal and coworkers [47]. The catalysis by $MoCl_5$-$Ph_3Bi$

(1 : 2) was less effective than by $MoCl_5$ alone. Catalysis by $Mo(OEt)_5$-$EtAlCl_2$ (1 : 2) was the most effective catalyst, followed closely by $Mo(OEt)_5$ itself.

Triethylbismuthine has been tested as a corrosion inhibitor for iron in acid solutions (1 N $HClO_4$, HCl, or $H_2SO_4$) [48]. Although less effective than $Et_3Sb$, the bismuthine was more persistent than $Et_3Sb$ in 1 N $HClO_4$. The protective film consisted of a layer of $[Et_3BiH]ClO_4$ at the outermost surface, an outer layer of ferrous oxide containing bismuth(III) oxide, and an inner layer of metallic bismuth deposited on the iron surface.

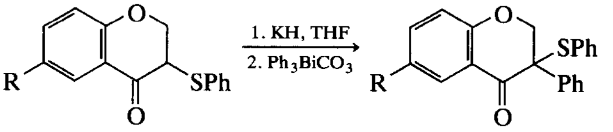
The semiconductors InAs and InAsBi have been prepared by vapor phase epitaxy [49]. The source of the bismuth was trimethylbismuthine.

Rate coefficients for the collisional relaxation of the first excited spin-orbit state of bismuth ($6p^3$, ${}^2D_{3/2}$) have been measured at 295 K for Ar, $CO_2$, $SF_6$, $H_2$, $D_2$, HF, and DF [50].The source for the excited bismuth atoms was the excimer laser photolysis of trimethylbismuthine at 193 nm, measured directly in emission.

A paper in the organoantimony section of these Annual Surveys is devoted to a comparison of $\sigma$- and $\pi$-bonded cyclopentadienyl compounds of elements of Groups 14 and 15 [51]. The authors stated that $(Me_5C_5)_2BiCl$ contained $\eta^5$-bonded pentamethylcyclopentadienyl ligands attached to the bismuth atom, and ascribed this result to a personal communication from J. Lorberth and S.H. Shin regarding work in preparation for publication.

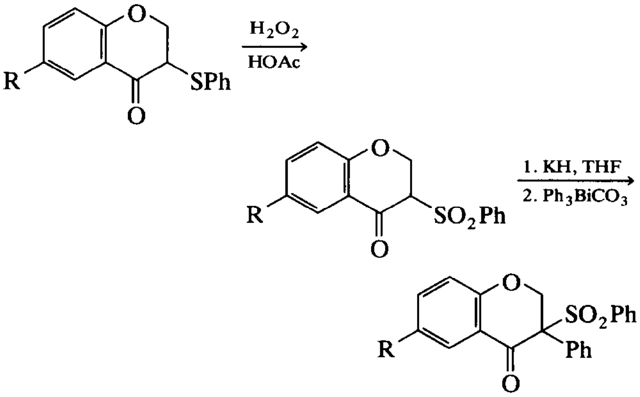
A number of $\pi$-bonded complexes between bismuth(III) halides and arenes have been prepared and their molecular and crystal structures studied. A new paper by Vezzosi and coworkers [52] has reported the 2 : 1 $\pi$-bonded complex formed from bismuth tribromide and [2.2]-paracyclophane. The crystalline product, prepared by mixing a dichloromethane solution of the hydrocarbon with a toluene solution of bismuth tribromide, was characterized by elemental analyses, UV, and IR spectroscopy. Thermogravimetric analysis and electrical resistivity measurements were also performed. The complex was thermally stable to 180°C and was more stable to air and to atmospheric moisture than other bismuth halide-arene complexes. The X-ray diffraction study of the complex showed a structure built up of polymeric linear chains of bismuth tribromide units with three short Bi–Br bonds, and two much longer Bi–Br bonds from adjacent $BiBr_3$ molecules. The geometry of the bismuth atom was a greatly distorted octahedron with a sixth position occupied by a centrosymmetric paracyclophane $\pi$-bonded molecule.

Organobismuth(V) compounds have received considerable attention as phenylating agents. Santhosh and Balasubramanian [53] have reported the use of triphenylbismuth carbonate for the preparation of isoflavanones and isoflavones. 3-Phenylthiochroman-4-ones were phenylated with triphenylbismuth carbonate to yield the corresponding phenyl derivative, but in only 20% yield:

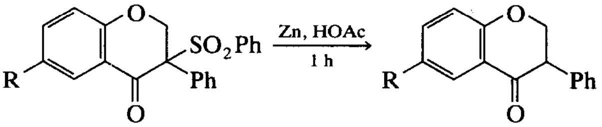


(where R was H, Me, Cl, and OMe)

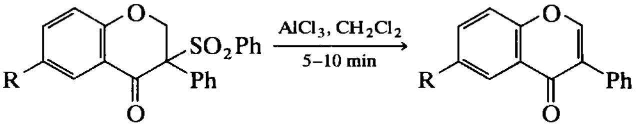
The authors were unable to convert the starting sulfide (R = H) into the sulfoxide with a variety of oxidizing agents. The sulfides, however could be converted into the corresponding sulfonyl derivatives, which were readily phenylated with triphenylbismuth carbonate in 80–88% yields:



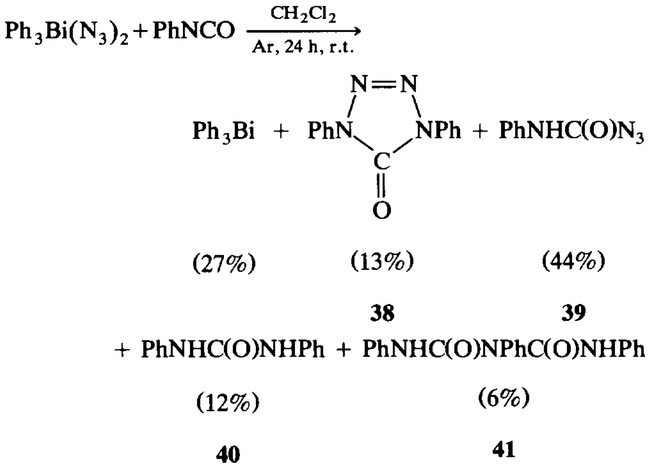
The phenylsulfonyl group was readily removed to yield the corresponding isoflavanones, by refluxing the phenylsulfonyl compounds with zinc in acetic acid for 1 h:



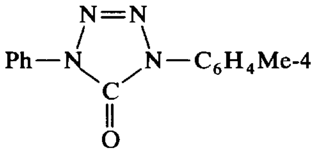
Treating the same starting materials with anhydrous aluminum chloride in dichloromethane for 5–10 min yielded the corresponding isoflavones:



The reactions of triarylbismuth diazides with a variety of unsaturated organic compounds have been investigated by Suzuki and coworkers [54]. The results were disappointing. Generally, under mild conditions, no reactions occurred, and under forcing conditions (*e.g.* in the presence of a Lewis acid or a transition metal catalyst) decomposition of the diazides usually resulted. However, they did react with isocyanates under mild conditions to give a variety of products. Thus, triphenylbismuth diazide reacted with phenylisocyanate in the following manner:



Similar results were obtained form triphenylbismuth diazide and 1-naphthylisocyanate, *i.e.* compounds corresponding to **39**, **40** and **41**, with 1-naphthyl rather than phenyl groups, were obtained. However, none of the 1-naphthyl compounds corresponding to **38** was detected. Tri-4-tolylbismuth diazide also reacted with phenylisocyanate to yield tri-4-tolylbismuthine and compound **42**, as well as compounds **39**, **40**, and **41**, in yields somewhat smaller than those obtained with triphenylbismuth diazide.



**42**

The course of the reaction of triphenylbismuth diazide with phenylisocyanate was followed by means of HPLC. It was found that compounds **39** and **40** were formed first and that the yields of triphenylbismuthine, and of compounds **38** and **41** gradually increased with time. Thus, interrupting the reaction after 20 min increased the yield of **39** from 44 to 58%. The reaction of triphenylbismuth diazide and phenylisocyanate in the presence of copper(II) acetate was also investigated. In addition to triphenylbismuthine, compounds **39** and **40** (but not **41**), were isolated. Compound **43**, $Ph_2NCON_3$, was also obtained in small yield (5%). A similar reaction between 3-tolylisocyanate and triphenylbismuth diazide gave compounds corresponding to **39** and **40**, with 3-tolyl rather than phenyl groups, as well as **44**, $(3\text{-}MeC_6H_4)PhNCON_3$. Copper(I) chloride, copper(II) chloride, and metallic copper were ineffective as catalysts. Refluxing triphenylbismuth diazide and phenylisocyanate in benzene for 30 min gave triphenylbismuthine, compounds **38** and **40**, as well as compound **43**, the latter in only 5% yield. When triphenylbismuth diazide was allowed to react with phenylisocyanate in the presence of boron trifluoride, compound **39** was obtained in almost quantitative yield. Tri-4-tolylbismuth diazide (0.6 molar equivalents) and phenylisocyanate (1 molar equivalent) gave $4\text{-}MeC_6H_4$ $NHCON_3$ in 54% yield. Triphenylbismuth diazide did not react with phenylisothiocyanate, even in the presence of boron trifluoride.

In an attempt to determine the mechanism of the reaction of triarylbismuth diazides with isocyanates, the authors mixed equimolar amounts of triphenylbismuth diazide and phenylisocyanate in benzene-$d_6$ and followed the course of the reaction by means of PMR. On the basis of their results a tentative mechanism was proposed. Triphenylbismuth diazide, tri-4-tolylbismuth diazide, and compounds **38**, **39**, **40**, **41** and **43** were characterized by PMR, IR, and mass spectrometry as well as by elemental analyses.

It has long been known that inorganic bismuth(V) compounds are extremely rare. Thus, $BiF_5$ is the only known bismuth(V) halide, and $BiH_5$ is unknown. By contrast, a number of stable pentaarylbismuth compounds have been prepared and their properties studied. In a theoretical paper, Schwerdtfeger and coworkers [55] have made extensive *ab initio* computations of vertical and horizontal trends in elemental-bond stabilities of a large number of inorganic compounds. Among their conclusions was that low valencies of compounds of the heavy elements (Au, Hg, Tl, Pb, and Bi) arose naturally as a consequence of lower M–X bond strengths with increasing atomic number. They suggested that the pentaarylbismuth compounds were thermodynamically unstable, and that their apparent stability at ambient temperature was probably kinetic.

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