BISMUTH

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A comprehensive review of the preparation, reactions, and physical properties of organobismuth compounds was published in 1982 [1]. In another paper the chemistry of the group VA heterobenzenes, arsabenzene (arsenin), stibabenzene (antimonin), and bismabenzene (bismin) was reviewed [2]. The Specialist Periodical Reports, published annually by the Chemical Society, reviewed organobismuth compounds in their volume on Organometallic Chemistry [3]. In a review article on Group VA elements, the chemistry of both inorganic and organic bismuth compounds investigated in 1980 was surveyed [4].

The bismuth atom in tertiary bismuthines is known to exhibit only weak donor properties, and relatively few coordination compounds of tertiary bismuthines are known. In order to overcome this difficulty Levason and coworkers have previously reported the preparation of tertiary bismuthines which also contained a tertiary phosphine, arsine, or stibine group. In such compounds the P, As, or Sb atom and the Bi atom both exhibited donor properties. Extending this concept, Levason and coworkers [5] have now reported the preparation of a number of tertiary bismuthines which contained oxygen (OMe), sulfur (SMe), or nitrogen (NMe_2) donor atoms. Presumably, a later paper will describe coordination compounds of these new ligands.

The previously known $(o\text{-}MeOC_6H_4)_3Bi$ was prepared by the Grignard reaction. The *o*-MeS and $o\text{-}Me_2N$ analogs were obtained from $BiCl_3$, BuLi, and $o\text{-}MeSC_6H_4Br$ or $o\text{-}Me_2NC_6H_4Br$, respectively. The amino compound (obtained only in poor yield) was light sensitive, both in the crystalline state and in solution. Three unsymmetrical tertiary bismuthines of the type $o\text{-}YC_6H_4BiPh_2$, where Y = MeO, MeS, or Me_2N, were obtained from Ph_2BiCl, BuLi, and the corresponding bromo compound $o\text{-}YC_6H_4Br$. The sulfur-containing bismuthine, $o\text{-}MeSC_6H_4BiPh_2$, could not be crystallized. The amine, $o\text{-}Me_2NC_6H_4BiPh_2$, was light sensitive, but less so than $(o\text{-}Me_2NC_6H_4)_3Bi$.

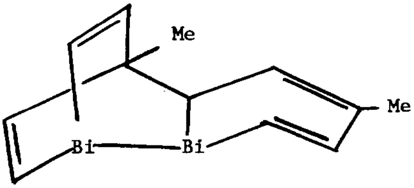
The Grignard reagent *o*-ClC_6H_4MgBr (obtained from *o*-ClC_6H_4Br) reacted with Ph_2BiCl to give *o*-$ClC_6H_4BiPh_2$. By the reaction between this compound and Ph_2SbNa, the stibine-bismuthine *o*-$Ph_2SbC_6H_4BiPh_2$ was obtained. With the preparation of this latter compound, the entire series *o*-$C_6H_4EPh_2(E'Ph_2)$, where E,E' = P, As, Sb, or Bi (except for E = E' = Bi) has now been prepared.

The PMR spectra of those bismuthines containing methyl groups were reported. PMR spectra of the known tolyl bismuthines, (*o*-$MeC_6H_4)_3Bi$ and (*p*-$MeC_6H_4)_3Bi$, were also listed. The mass spectra of all of the new bismuthines, as well as of (*o*-$MeC_6H_4)_3Bi$ and (*p*-$MeC_6H_4)_3Bi$, were given. A comparison of the mass spectra of the symmetrical and unsymmetrical bismuthines was of interest. Thus, with *o*-$MeOC_6H_4BiPh_2$, the molecular ion was not detected, and the base peak was Bi^+. By contrast (*o*-$MeOC_6H_4)_3Bi$ gave the molecular ion and the base peak was $[C_7H_7OBi]^+$. Similar effects were noted for the corresponding MeS and Me_2N compounds. The base peak for both (*o*-$MeC_6H_4)_3Bi$ and (*p*-$MeC_6H_4)_3Bi$ was Bi^+.

In the PMR spectra of Ph_3Bi and phenyl-substituted bismuth(III) compounds of the types Ph_2BiY and $PhBiY_2$, there is a paramagnetic shift (shift to lower field) of one of the phenyl proton signals. The extent of this shift is dependent on the electronegativity of the group or groups(Y) other than phenyl attached to bismuth and also on the number of such groups. This paramagnetic shift has been assigned by previous workers to the *ortho* phenyl protons. In order to substantiate this assumption Praeckel and Huber [6] have now prepared two organobismuth compounds containing phenyl groups in which an *ortho* phenyl proton has been substituted by a deuterium. Thus *o*-ClC_6H_4MgBr was solvolysed with CH_3CO_2D to yield *o*-ClC_6H_4D. The Grignard reagent from this compound was then treated with $BiCl_3$ to give (*o*-$DC_6H_4)_3Bi$. This compound was characterized by IR, Raman, and mass spectra and by elemental analyses. The PMR spectrum on integration showed that the paramagnetically shifted signal was only one-half as intense as the similar signal in Ph_3Bi. The chemical shift for this *o*-proton was $\delta = 7.71$ ppm; for the *m* + *p*-protons $\delta = 7.29$ ppm.

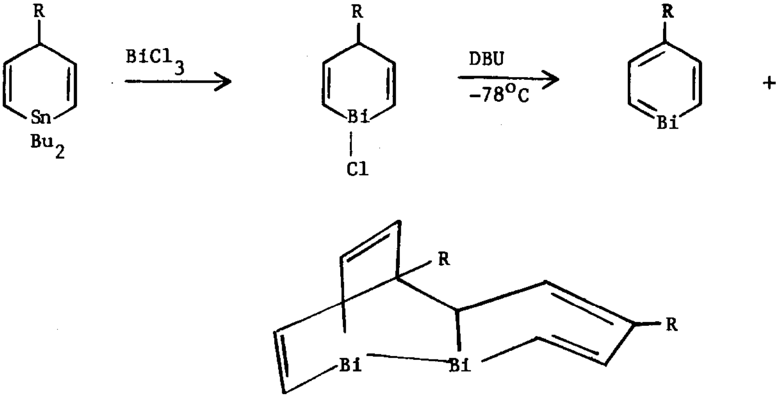
The (*o*-$DC_6H_4)_3Bi$ was than converted by reaction with $BiBr_3$ to (*o*-$DC_6H_4)_2BiBr$. The PMR spectrum of this compound showed the chemical shift of the *o*-proton to be $\delta = 8.25$ ppm, while the *m* + *p*-protons gave a value, $\delta = 6.95 - 7.70$. Integration gave a ratio of 1:3 for the *o vs m* + *p*-protons.

Antimonin and bismin, the antimony and bismuth analogs of pyridine, are extremely labile compounds. At -20°C the PMR spectrum of bismin indicates the presence of very weak low-field signals which have been assigned to monomeric bismin. The principal peaks in the spectrum, however, are due to dimeric bismin which contains a Bi-Bi bond and which has been assigned the structure A:



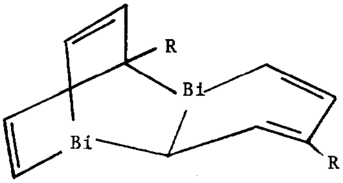
A

Ashe and coworkers [7] have suggested that monomeric bismin (and antimonin) might be stabilized by the addition of alkyl substituents to the heterocyclic ring carbons. When 2-methylantimonim proved to be less stable than antimonin, no attempt to prepare 2-methylbismin was made. However, both 4-methyl- and 4-*tert*-butylbismins were prepared by means of the following reaction sequence:



(where R = Me or *tert*-Bu and DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene)

When R = Me, a mixture of the monomer and dimer was obtained. These were in rapid thermal equilibrium since the relative intensity of the dimer PMR signals increased as the temperature was lowered and decreased with an increase in temperature. When R = *tert*-butyl, only the monomer was obtained. The authors have speculated on the reasons why a 4-alkyl substitutent has such a marked effect on increasing the stability of the monomeric form of bismin (and of antimonin). They concluded (by making use of the frontier molecular orbital approach) that the 4-position of the heterocyclic ring was the most reactive position for a radical-like attack involved in the dimerization mechanism and that the 4-alkyl group sterically inhibited such a radical-like attack. The authors also speculated on the reasons why the dimers possessed the head-to-head structure such as A rather than a head-to-tail structure B:



B

A rather rough calculation based on bond dissociation energies of Bi-Bi, Bi-C, and C-C bonds led the authors to conclude that A should be considerably more stable than B.

Since stable monomeric antimonins and bismins have now been prepared, it was possible to compare the ^{1}H and ^{13}C spectra of all of the group V heterobenzenes. The authors have discussed these spectra in considerable detail. Among the comparisons made were the ^{13}C-H coupling constants ($^{1}J_{CH}$) for the C_2, C_3, and C_4 carbon atoms of the ring. The authors concluded that the near identity of the $^{1}J_{CH}$ values for all of the heterobenzenes implied a hybridization close to sp^2 for all ring carbons in all of the compounds.

The reaction of the iron compounds $Cp(CO)_2FeEMe_2$(E = As, Sb, or Bi, Cp = cyclopentadienyl) with tertiary phosphines has led to the displacement of one CO group with the formation of compounds of the type $Cp(CO)(R_3P)FeEMe_2$ [8]. Only one bismuth compound was prepared, namely $Cp(CO)(Me_3P)FeBiMe_2$. The reactions were carried out in benzene solution, and in no case was more than one CO group replaced. The rate of the CO exchange reaction decreased in the order As > Sb > Bi. Since the iron atom was chiral the two methyl groups on the Group V element were diastereotopic and gave two different signals in the PMR spectrum.

In a long paper devoted to the possible use of organometallic compounds of the 3rd, 4th, and 5th row elements (Ge, As, Sn, Sb, Te, Pb, and Bi) as reagents in organic synthesis Kauffmann [9] mentions the synthesis of several new organobismuth compounds. For example the following reactions were carried out:

$$CH_2X_2 + 2\ Ph_2BiM \longrightarrow (Ph_2Bi)_2CH_2 + 2\ MX$$

$$(Ph_2Bi)_2CH_2 + RLi \longrightarrow Ph_2BiCH_2Li + Ph_2BiR$$

(where X = halogen, M = Li, Na, or K, and R = an alkyl group)

As an example of the use of an organobismuth compound in organic synthesis the preparation of 1,1-diphenylethene in 61% yield was described:

$$Ph_2BiCH_2Li \ + \ Ph_2CO \xrightarrow{HClO_4} Ph_2C{=}CH_2$$

If in the above reaction, instead of using perchloric acid, the reactants were passed through a short silica gel column, the yield of $Ph_2C{=}CH_2$ was increased to 91%. Bromohexane was obtained in 84% yield by means of the following reaction sequence:

$$Ph_2BiCl \ + \ C_6H_{13}Li \longrightarrow Ph_2BiC_6H_{13} \ + \ LiCl$$

$$Ph_2BiC_6H_{13} \ + \ Br_2 \longrightarrow C_6H_{13}Br \ + \ Ph_2BiBr$$

The author suggested that organometallic compounds of the main group elements undergo many reactions such as substitution or elimination that may prove useful in organic syntheses.

It is well known that triphenylbismuthine, unlike triphenylarsine or triphenylstibine, is completely cleaved to metallic bismuth by sodium metal in liquid ammonia. It was surprising, therefore, to find that triethylbismuthine reacted with sodium in liquid ammonia to give a dark red solution (presumably of Et_2BiNa) which underwent further reaction with 1,2-dichlorethane to yield tetraethyldibismuthine [10]:

$$Et_3Bi \ + \ 2\ Na \longrightarrow Et_2BiNa \ + \ EtNa$$

$$2\ Et_2BiNa \ + \ ClCH_2CH_2Cl \longrightarrow Et_2BiBiEt_2 \ + \ C_2H_4 \ + \ 2\ NaCl$$

The dibismuthine was obtained as a red oil which became almost black when the temperature was lowered to -30°C. At -196°C the color changed to yellow. Solutions of the compound in benzene were red, but in cyclohexane they were yellow. At 0°C the compound decomposed in a few days. The dibismuthine was characterized by elemental analysis and by its mass spectrum. A molecular ion of relative intensity 70 was found at 25 eV; the base peak was Et_3Bi^+. At 70 eV a molecular ion was also found but the base peak was Bi^+. The PMR spectrum gave an ABX_3 pattern due to the non-equivalence of the methylene protons. Both IR and UV data for the dibismuthine were also reported.

In addition to tetraethyldibismuthine, the preparation of tetramethyldibismuthine by a similar method has also been described [11]. In this synthesis sodium was added to a solution of trimethylbismuthine in liquid ammonia to produce a red solution of sodium dimethylbismuthide. This solution was treated with 1,2-dichloroethane, after which the ammonia was evaporated. The dibismuthine was extracted from the residue with pentane and recrystallized from this same solvent at -20°C.

Tetramethyldibismuthine was a viscous red oil at room temperature which solidified to a violet-blue crystalline solid at -12.5°C. At 25°C it decomposed to trimethylbismuthine and bismuth metal. The mass spectrum at 70 eV gave a molecular ion; the base peak was due to the Bi^+ ion. The ^1H and ^{13}C NMR spectra, and Raman spectra were reported. The reflectance spectrum of the blue crystals and the UV spectrum of a pentane solution were also reported. There is a marked difference between the two spectra. A similar difference has been found for some distibines.

It is interesting to note that the dibismuthine $(Me_3Si)_2BiBi(SiMe_3)_2$, which was also reported in 1982 [12], undergoes remarkable color changes on melting or dissolving in organic solvents.

Several methods for the preparation of diphenylbismuth carboxylates, Ph_2BiO_2CR, have been described by Huber and Bock [13]. An acetone solution of triphenylbismuthine and acetic acid, in a 1:1 molar ratio, was stirred for 30 days. The white precipate of $Bi(O)O_2CMe$ was removed by filtration and from the filtrate a small amount of Ph_2BiO_2CMe was obtained. When the ratio of Ph_3Bi to acetic acid was increased to 1:3, a difficultly soluble white product with the approximate composition $PhBi(O_2CMe)_2$ was obtained. When the reactants (Ph_3Bi and $MeCO_2H$) were used in a ratio of 1:2, a mixture of $PhBi(O_2CMe)_2$ and Ph_2BiO_2CMe was obtained. However, Ph_2BiO_2CMe was readily obtained in 59% yield from Ph_2BiCl and $MeCO_2Na$ in ethanol solution. The reaction was carried out by stirring the reactants for 20-30 hours. An even higher yield of Ph_2BiO_2CMe (77%) was obtained from Ph_2BiOEt and acetic acid. The Ph_2BiOEt was obtained from Ph_2BiCl and NaOEt. The NaCl was removed by filtration and the filtrate treated with acetic acid. In addition to Ph_2BiO_2CMe a number of other carboxylates Ph_2BiO_2CR (where R = Et, Pr, Me_2CH, *tert*-Bu, $MeCOCH_2CH_2$, and Ph) were prepared. The IR bands for the carboxylate groups and the symmetrical Bi-C band were listed. A polymeric structure with bridging bidentate carboxylate groups was suggested for the Ph_2BiO_2CR compounds.

An X-ray diffraction study of *p*-tolylbis(diethyldithiocarbamato)-thallium(III), $4\text{-}MeC_6H_4Tl(S_2CNEt_2)_2$, and of phenylbis(methylxanthogenato)-bismuth(III), $PhBi(S_2COMe)_2$, has been reported by Burschka [14]. In both compounds the sulfur-containing ligands are bidentate. Thus both compounds contain two four-membered rings. In the bismuth compound, however, the two ring are essentially coplanar, with the phenyl group perpendicular to the plane of the two rings. Thus in the bismuth compound the lone pair is stereochemically active. The bismuth atom is essentially octahedral with the lone pair *trans* to the phenyl group.

Lalitha and coworkers [15] have reported on the general inertia defect of a number of pyramidal molecules containing a Group VA element and tetrahedral molecules containing a Group IVA element. The inertia defect brings out the influence of vibration-rotation interaction on molecular structure. The five compounds Me_3E, where E was N, P, As, Sb, or Bi, were among the compounds for which the inertia defect was calculated. It has been found for pyramidal moleucles that the inertia defect was small and positive and increased with increasing mass of the molecules.

Compounds containing Ge-N, Sn-N, Pb-N, Sb-N, and Bi-N bonds have been prepared by the reaction between the silicon compound $Me_3SiN{=}PPh_3$ and Group IV or Group V organometallic halides [16]:

$$Ph_3EX_n \;+\; n\; Me_3SiN{=}PPh_3 \longrightarrow Ph_3E(N{=}PPh_3)_n \;+\; n\; Me_3SiX$$

(where E = Ge, Sn, or Pb and n = 1; E = Sb or Bi and n = 2; X = Cl or Br)

Only one bismuth compound was prepared, namely $Ph_3Bi(N{=}PPh_3)_2$, from Ph_3BiBr_2 and $Me_3SiN{=}PPh_3$. The crystalline product, m.p. 140-142°C, was obtained in 65% yield. The Bi-N bond was not cleaved by water or methanol.

Barton and coworkers have published a number of papers in which the use of organobismuth(V) compounds as reagents in organic synthesis was reported. One such reaction involved the use of triphenylbismuth carbonate for the phenylation of the α-carbon atom of the potassium enolate of a ketone. Usually more than one phenyl group was introduced. Thus acetophenone gave triphenylmethyl phenyl ketone. The authors have now extended the reaction to cyclohexanone and dibenzyl ketone [17]. The reaction of cyclohexanone with an eight-fold excess of potassium hydride and triphenylbismuth carbonate in THF solution gave 2,2,6,6-tetraphenylcyclohexanone. In an analogous manner dibenzyl ketone gave pentaphenylacetone. Hexaphenylacetone could not be detected in the reaction mixture, nor could it be prepared from pentaphenylacetone, potassium hydride, and triphenylbismuth carbonate in a separate experiment. The X-ray crystal structures of the two new polyphenylated ketones were given.

A second paper [18] from Barton's laboratory deals with the mechanism of *O*-phenylation or *C*-phenylation of phenols or enols by organobismuth(V) reagents of the type Ph_4BiY, where Y = $MeCO_2$, CF_3CO_2, $p\text{-}MeC_6H_4SO_3$, or CF_3SO_3. Three organic substrates, β-naphthol, 2-carboethoxycyclohexanone, and dimedone, were used. The reaction conditions employed were benzene alone, benzene in the presence of trichloroacetic acid, and benzene in the presence of *N-tert*-butyl-*N′,N″*-tetramethylguanidine. In the third case the phenol or enol anions were formed. Depending both on the reaction conditions and the choice of organobismuth(V) reagent, either *O*-phenylation or *C*-phenylation could be achieved. The authors speculated in considerable detail on the mechanism of these reactions.

The ability of the molybdenum(VI) compound, $(Et_2NCS_2)_2MoO_2$, to oxidize compounds of the type Ph_3E (where E = N, P, As, Sb, or Bi) to the corresponding oxides, Ph_3EO, has been studied [19]. A trace of oxidized product may have been obtained with Ph_3Bi. This conclusion was based on a spot test for $(Et_2NCS_2)_4Mo_2O_3$.

The use of triphenylbismuthine as a delayed action catalyst in propellant cure chemistry has been the subject of a study [20]. It has also been used in a catalyst mixture for controlling the cure rate of polyurethane resins [21]. Triphenylbismuth dibromide has been found not to be a catalyst for the cycloaddition of carbon dioxide to oxiranes, alone or in the presence of a Lewis base [22].

REFERENCES

1. L. D. Freedman and G. O. Doak, *Chem. Rev.,* 82 (1982) 15.
2. A. J. Ashe, III, *Top. Curr. Chem.,* 105 (1982) 125.
3. J. L. Wardell, *Organomet. Chem.* 10 (1982) 129.
4. M. F. A. Dove and D. B. Sowerby, *Coord. Chem. Rev.,* 40 (1982) 261.
5. W. Levason, B. Sheikh, and F. P. McCullough, *J. Coord. Chem.,* 12 (1982) 53.
6. U. Praeckel and F. Huber, *J. Organomet. Chem.,* 240 (1982) C45.
7. A. J. Ashe, III, T. R. Diephouse, and M. Y. El-Sheikh, *J. Amer. Chem. Soc.,* 104 (1982) 5693.
8. H.-A. Kaul, D. Greissinger, M. Luksza, and W. Malisch, *J. Organomet. Chem.,* 228 (1982) C29.
9. T. Kauffmann, *Angew. Chem., Int. Ed. Engl.,* 21 (1982) 410.
10. H. J. Breunig and D. Müller, *Angew. Chem., Int. Ed. Engl.,* 21 (1981) 439.
11. A. J. Ashe, III and E. G. Ludwig, Jr., *Organometallics,* 1 (1982) 1408.
12. G. Becker and M. Rössler, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.,* 37B (1982) 91.
13. F. Huber and S. Bock, *Z. Naturforsch., B: Anorg. Chem., Org. Chem.,* 37B (1982) 815.
14. C. Burschka, *Z. Anorg. Allg. Chem.,* 485 (1982) 217.
15. M. Lalitha, R. Srinivasamoorthy, and G. A. Savariraj, *Indian J. Pure Appl. Phys.* 19 (1981) 330.

16. K. Bajpai and R. C. Srivastava, *Synth. React. Inorg. Met.-Org. Chem.*, 12 (1982) 47.

17. D. H. R. Barton, M. T. B. Papoula, J. Guilhem, W. B. Motherwell, C. Pascard, and E. T. H. Dau, *J. Chem. Soc., Chem. Commun.*, (1982) 732.

18. D. H. R. Barton, B. Charpiot, and W. B. Motherwell, *Tetrahedron Lett.*, 23 (1982) 3365.

19. X. Lu and J. Sun, *Synth. React. Inorg. Met.-Org. Chem.*, 12 (1982) 427.

20. L. W. Haas and J. Sinclair, CPIA Publ. (1981) 407; *Chem. Abstr.* 97 (1982) 130013v.

21. W. H. Graham and G. I. Shepard, Can. CA 1,117,765; *Chem. Abstr.* 97 (1982) 25948f.

22. R. Nomura, M. Kimura, S. Teshima, A. Ninagawa, and H. Matsuda, *Bull. Chem. Soc. Jpn.*, 55 (1982) 3200.