BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1980 *

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With the exception of the Annual Survey covering the year 1979, there have been no reviews in 1980 devoted only to organobismuth compounds. Organobismuth compound were mentioned, however, in a new edition of a monograph on organometallic compounds [1] and also in the annual survey of organometallic chemistry [2] published by The Chemical Society.

In an interesting paper on mixed aryl-alkyl bismuthines, Steinseifer and Kauffmann [3] have described the preparation of three new compounds of the type Ph_2BiR, where R = Me, Bu, or Hex. They were prepared by the following type of reaction in near theoretical yields:

$$Ph_2BiCl + RLi \longrightarrow Ph_2BiR + LiCl$$

The syntheses were carried out in ether at low temperature (0°C to -70°C), but the resulting bismuthines could be distilled *in vacuo* almost without decomposition. A dibismuthine, $Ph_2BiCH_2BiPh_2$, was prepared as follows:

$$2\ Ph_2BiNa + CH_2Cl_2 \longrightarrow Ph_2BiCH_2BiPh_2 + 2\ NaCl$$

This dibismuthine could be converted to the lithiomethyl group:

$$Ph_2BiCH_2BiPh_2 + PhLi \xrightarrow{-70^{\circ}C} Ph_2BiCH_2Li + Ph_3Bi$$

The lithiomethyl compound reacted as follows:

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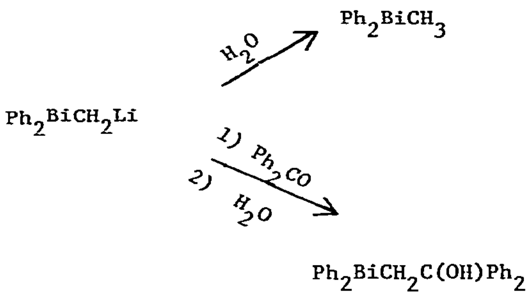
*Previous review see J. Organometal. Chem., 203 (1980) 359 - 365.

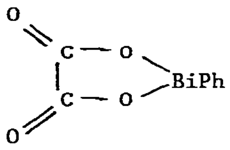


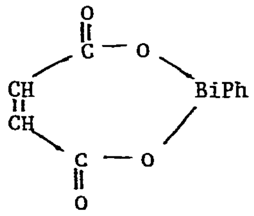
A carbon-bismuth bond of the alkyl-aryl bismuthines was cleaved at low temperatures by chlorine or bromine. Thus, chlorination of butyldiphenylbismuthine at 0°C proceeded as follows:

$$Ph_2BiBu + Cl_2 \xrightarrow{0^oC} BuCl(84\%) + PhCl(14\%)$$

The new bismuth compounds were characterized by PMR and mass spectra, and by elemental analyses.

Triphenylbismuthine reacted with the following dicarboxylic acids, oxalic, succinic, malonic, and maleic acids, with cleavage of two phenyl groups from the bismuthine and the formation of compounds containing five, six, or seven membered rings [4]. The reactions were carried out in refluxing acetone. The compounds obtained from oxalic and maleic acids, for example, possessed the following structures:





They were characterized by mass spectra and IR spectra but not by elemental analyses.

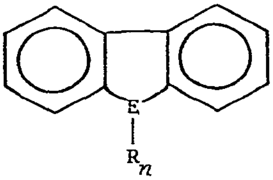
A study of the one electron oxidation of triphenyl derivatives of the Group V elements (N, P, As, Sb, and Bi) by radical cations of the type $(4\text{-}RC_6H_4)_3N^{\cdot +}$ (where R was Br, Ph, Me, or MeO) has shown that the reaction was first order in each reactant and that the rate was dependent on both R and on the Group V element [5].

Ahrland [6] has discussed the difference between protonic solvents and proton free solvents as to their effect on complex formation between a metal ion and a ligand. Among the ligands discussed were Group V compounds, amines, phosphines, arsines, stibines, and bismuthines. The relative affinity of such donor ligands in dimethyl sulfoxide to react with acceptor ions such as Cu(I), Ag(I), and Hg(II) were in the order N<<P>As>Sb>Bi.

The crystal structure of trimesitylbismuthine by X-ray diffraction has been determined in a study of the crystal structures of several Group V organometallic compound [7]. The three C-Bi-C angles were 95.2°, 105.4°, and 107.4°, and the three Bi-C bond distances were 2.25Å, 2.301Å, and 2.309Å. The crystal structure of trimesitylbismuthine was also reported in another paper from the same laboratory [8].

The crystal structure of tris(cymantrenyl)bismuthine, $[(CO)_3MnC_5H_5]_3Bi$, where C_5H_5 is cyclopentadienyl, has also been determined [9]. The cyclopentadiene rings were planar, and the bismuth atom was 0.26Å out of the ring planes.

In continuation of previous work on the electronic spectra of aryl compounds of the type ArE_n, where E was an element of groups II-VI, Davydov, Rodionov, and coworkers [10] have now examined the UV spectra as well as the fluoresence and phosphoresence spectra of a number of fluorene-type compounds:



(where E = C, Si, Ge, or Sn, R = Me, Ph, Ph, or Et, respectively, and n = 2; E = N, P, Sb, or Bi, R = Me, Ph, Ph, or Ph, respectively, and n = 1; E = O or S, and n = o).

The results were similar to those found for the acyclic compounds, but with these fluorene-type compounds there was a marked increase in the lifetime of the phosphorescent state as compared with the acyclic compounds, a fact which the authors suggested was associated with the coplanarity of the dibenzoheterocyclic skeleton and the predominantly $\pi\pi^*$ nature of the lowest electronic transition.

The use of photoelectron spectra (XPS) for determining the binding energy E_b of the inner electrons of a series of organic and inorganic antimony and bismuth compounds has been described by Hoste and coworkers [11]. The binding energy is given by the equation:

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

(where E_{kin} is the kinetic energy of the ejected electron, $E_{X\text{-}ray}$ is the energy of the X-radiation, and ϕ_{sp} is the work function of the spectrometer material)

The reported binding energy of the bismuth $5d_{5/2}$ electrons for Ph_3Bi and $(p\text{-}MeC_6H_4)_3Bi$ were 25.57 and 25.80 eV, respectively.

The photochemical deactivation of the electronically excited states of molecules of tetraphenyl compounds of Group IVA and triphenyl compounds of Group VA has been found to depend on the atomic number of the element, the state of aggregation, and on the excitation conditions [12]. Photodissociation efficiency in the gas phase and in liquid solutions increased sharply with increase in atomic number. With aromatic derivatives of Group VA elements a two-quantum photoionization process in solid solution at low temperatures was the predominant primary process for photochemical deactivation of electronically excited states of nitrogen compounds, but this two-stage process decreased markedly with increasing atomic number.

Wieber and coworkers [13] described the preparation and properties of a series of xanthates of the type $Ph_2BiSC(S)OR$, where R was Me, Et, Pr, Me_2CH, Bu, or Me_2CHCH_2. The compounds were prepared by metathesis between the required sodium xanthate and dibromophenylbismuthine. The solvent in each case was the alcohol corresponding to the R group in the xanthate. When chloroform was used as the solvent, disproportionation occurred and the products were triphenylbismuthine and the monophenyl xanthate:

$$2\,Ph_2BiSC(S)OR \longrightarrow Ph_3Bi + PhBi(SC(S)OR)_2$$

The same disproportionation occurred when the diphenyl compounds were allowed to stand for some time at room temperature. PMR spectra of all of the compounds were reported. An X-ray diffraction study of the isopropyl compound, $Ph_2BiSC(S)OCHMe_2$, was also reported.

A number of silyldiazoalkanes of the type $Me_3Si(Me_nE)CN_2$ (where E was Si, Ge, Sn, or Pb and n = 3, or E was As, Sb, or Bi and $n = 2$) have been prepared by several different routes [14]. The organobismuth compound $Me_3Si(Me_2Bi)CN_2$ was prepared as follows:

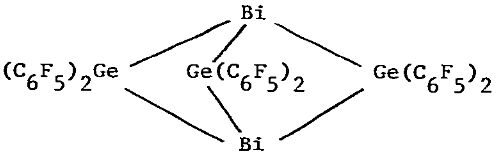
$$Me_3SiCHN_2 + Me_2BiN(Me)SiMe_3 \longrightarrow Me_3Si(Me_2Bi)CN_2 + HN(Me)SiMe_3$$

The bismuth compound was sensitive to light, air, and heat; and satisfactory spectral data were not obtained.

A German patent has described the use of two organobismuth compounds, dibutylbismuth octanoate and triphenylbismuth didecanoate, as catalysts (together with primary or secondary amines) for the copolymerization of polyols with polyisocyanates [15].

In another patent the use of organobismuth compounds as catalysts for the polymerization (or copolymerization with other monomers) of dicyclopentadiene was described [16]. A tungsten or molybdenum halide or oxyhalide was used in addition to the organobismuth compound. The reaction involved ring opening of the dicylopentadiene. An example was given of the copolymer obtained from dicyclopentadiene and 1-pentene by the use of triphenylbismuthine and tungsten hexachloride.

It has previously been reported [17] that the reaction of triethylbismuthine and $(C_6F_5)_2GeH_2$ gave an orange crystalline product for which the formula $[(C_6F_5)_2GeBiEt]_2$ was suggested. This structure was proposed on the basis of elemental analyses, molecular weight, and IR spectral data. The reaction of the compound with bromine to yield $BiBr_3$, $(C_6F_5)_2GeBr_2$, and EtBr was also consistent with the suggested structure. However, when the compound was allowed to react with dry HCl, only $(C_6F_5)_2Ge(H)Cl$ and bismuth metal were obtained; no compound containing an ethyl group was found. In the light of this latter finding the structure of the compound was reexamined by means of X-ray diffraction and the previously suggested structure was shown to be in error [18,19]. The compound did not contain any ethyl groups but possessed instead the following structure:



The elemental analyses and molecular weights calculated for the two structures differed significantly and in general were considerably closer to the structure originally proposed, namely $[(C_6F_5)_2GeBiEt]_2$. The authors suggested that these results were due to impurities present in their original sample. The authors also noted that a band in the IR spectrum of the compound occurring at 630 cm^{-1}, which they originally assigned to a Bi–C stretching mode, was present in their purified sample and hence cannot be due to a Bi–C mode. No assignment of this band was made.

In a paper devoted principally to tetraphenylphosphonium and tetraphenylarsonium salts of the type $[Ph_4P]Y$ and $[Ph_4As]Y$, where Y was a monovalent anion, one organobismuth compound, $[Ph_4Bi]ClO_4$, was listed [20]. The paper concerned the type of crystal structure assumed by most onium compounds of this type.

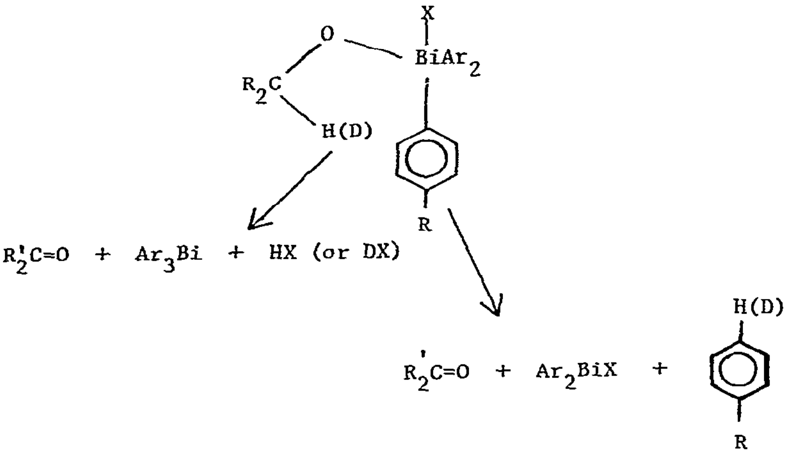
Two organobismuth compounds containing the Bi–O–Mo linkage have been described by Klemperer and Liu [21]. The first of these; $[Bu_4N]_2[Ph_3Bi(MoO_4)_2]\cdot 3H_2O$, was obtained by two different methods. By one method Ph_3BiBr_2 in CH_2Cl_2 was allowed to react with an impure sample of $[Bu_4N]_2MoO_4$. By the second method $[Bu_4N]_2MoO_4$ was added to the compound $(Ph_3BiMoO_4)_x$ (described below) in CH_2Cl_2. The second compound, $(Ph_3BiMoO_4)_x$, was also prepared by two different methods. The structure of the first compound was elucidated by means of ^{13}C and ^{17}O NMR data. The bismuth was believed to be a trigonal bipyramid with three equatorial phenyl groups and two unidentate tetrahedral oxoanions in axial positions. The second compound was also believed to contain a trigonal bipyramidal bismuth atom.

Barton and coworkers have previously reported on the use of organobismuth compounds containing pentavalent bismuth as selective oxidizing agents in organic syntheses. Triphenylbismuth carbonate was of particular value in this regard. The authors have now reported that this reagent did not oxidize the thiocarbonyl group in xanthates, dialkylaminothiocarbamates and di-*tert*-butyl thioketone [22]. By contrast, the thio groups of a complex thioamide was oxidized to a disulfide.

The authors have also shown previously that the oxidative cleavage of glycols gave essentially quantitative yields of a triarylbismuthine according to the following equation:

$$R_2C(OH)C(OH)R_2 + Ar_3BiY_2 \longrightarrow 2\ R_2CO + Ar_3Bi + 2\ HY$$

By contrast the oxidation of an allylic alcohol such as (–)-carveol gave (–)-carvone in 80% yield but triphenylbismuthine in only 50% yield. This fact suggested that a different mechanism was involved in the oxidation of allylic alcohols. This has now been shown to be the case. The reaction of (–)-carveol with triphenylbismuth diacetate was monitored by PMR spectra, and it was shown that an aromatic singlet at δ7.24 developed as the reaction proceeded. This strongly suggested the formation of benzene. The authors then oxidized (–)-carveol in tetralin solution with tri-*p*-tolylbismuth dibenzoate and were able to isolate toluene as a product of the reaction. They then prepared (–)-deuteriocarveol by the reduction of (–)-carvone and showed by mass spectral analysis that monodeuteriotoluene was produced in the reaction. Finally, the authors oxidized (–)-deuteriocarveol with tris(*p*-methoxyphenyl)bismuth carbonate and demonstrated that *p*-deuterioanisole was produced in the reaction. On the basis of these results, the authors suggested the following two competitive pathways for the oxidation of an allylic alcohol by a pentavalent organobismuth reagent:

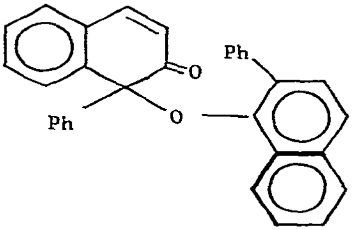


The authors were unable to trap free radicals in these reactions by the addition of nitrosobenzene or nitrosomesitylene, even in molecular excess.

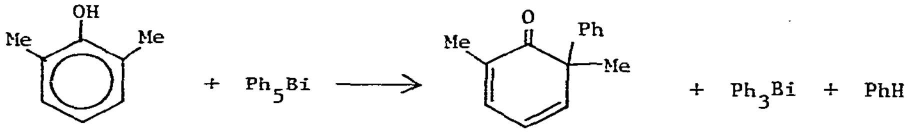
The above cleavage of an aryl group was then used in several organic syntheses. Phenylhydroxylamine on treatment with triphenylbismuth carbonate gave 22% nitrosobenzene and 64% diphenyl nitroxide. In a similar reaction phenylhydroxylamine and tri-*p*-tolylbismuth carbonate gave 50% phenyl-*p*-tolyl nitroxide. In both these reactions the aryl group was transferred to nitrogen. That the aryl group could also be tranferred to carbon was shown by the oxidative arylation of quinine where treatment of quinine with triphenylbismuth carbonate gave a 34% yield of the corresponding ketone quininone as an isolable intermediate. The final product, obtained in 75% yield, was a mixture of two diastereomeric α-phenylated ketones. When tri-*p*-tolylbismuth carbonate was used, the analogous diastereomeric α-tolyl ketones were obtained in 90% yields. β-Naphthol and triphenylbismuth carbonate, in the presence of tetramethylguanidine, gave a 76% yield of 1-phenyl-2-naphthol. Other arylation reactions were also cited.

Since organobismuth compounds of the type Ar_3BiY_2, where Y was an anionic group such as CO_3, $PhCO_2$, or $MeCO_2$, were shown in the previous paper to be arylating agents in some reactions the arylating properties of pentaphenylbismuth were then investigated [23].

As pointed out in the above paragraph, 2-naphthol and triphenylbismuth carbonate gave 1-phenyl-2-naphthol in excellent yield. The authors then attempted to introduce a second phenyl group into 1-phenyl-2-naphthol with triphenylbismuth carbonate and obtained the following dimer as a yellow crystalline product in 91% yield:

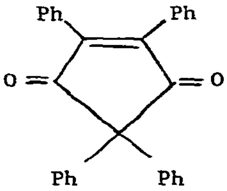


The reaction of 2,6-dimethylphenol with the carbonate gave 2,2',6,6'-tetramethylbiphenoquinone in 92% yield. When 2-naphthol was allowed to react with pentaphenylbismuth in dichloromethane or benzene, the product was 1-phenyl-2-naphthol in 61% yield. 1-Naphthol similarly gave 2-phenyl-1-naphthol in 41% yield. By contrast, 1-naphthol and triphenylbismuth carbonate gave an intractable mixture of products. The reaction of 2,6-dimethylphenol with pentaphenylbismuth gave 6-phenyl-2,6-dimethylcyclohexa-2,4-dienone, as follows:



The yield was 72%. Similarly, 4-*tert*-butyl-2,6-dimethylphenol gave 4-*tert*-butyl-6-phenyl-2,6-dimethylcyclohexa-2,4-dienone; 2,3,5,6-tetramethylphenol gave 6-phenyl-2,3,5,6-tetramethyl-2,4-dienone; 2,4-dimethylphenol gave a mixture of 2,4-dimethyl-6-phenylphenol and a compound said to be 2,4-dimethyl-2,6-diphenylcyclohexa-2,4-dienone; 4-nitrophenol gave 4-nitrophenyl phenyl ether. Estradiol gave three products, all phenylated in the 4-position, while estrone gave two 4-phenylated products. The authors point out that the formation of these 6-phenylcyclohexa-2,4-dienones provides a route to a group of compounds otherwise difficult to obtain.

In addition to the above phenols, a number of other compounds were phenylated with pentaphenylbismuth. The authors also point out that pentaphenylbismuth and triphenylbismuth carbonate do not always give similar results. Phloroglucinol gave a complex mixture of products with pentaphenylbismuth, but triphenylbismuth carbonate gave the following ene-dione in 60% yield:



Arylthiols and triphenylbismuth carbonate gave the corresponding disulfides whereas pentaphenylbismuth gave mixed diaryl sulfides. Thus *o*-tolylthiophenol and triphenylbismuth carbonate gave di-*o*-tolyl disulfide in 90% yield while pentaphenylbismuth gave phenyl *o*-tolyl sulfide in 47% yield.

The authors also pointed out that a relatively acidic proton must be present on the organic substrate in order that pentaphenylbismuth can act as a phenylating agent. Thus, the potassium enolate of cholestanone gave only a small amount of phenylated product with pentaphenylbismuth. The acidic proton requirement is not necessary with triphenylbismuth carbonate. Thus, the sodium salt of acetanilide and triphenylbismuth carbonate gave *N*,*N*-diphenylacetamide in 90% yield. The authors concluded that phenylation reactions of pentaphenylbismuth did not involve free phenyl radicals since quenching by triethylsilane was not observed.

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