BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1976*

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There were no books or critical review articles published in 1976 concerned only with organobismuth compounds. However, organobismuth compounds have been mentioned in several recent review articles on organometallic compounds [1-4]. In a review article on Group V pentaalkyls and alkylidene trialkyls, Schmidbaur [5] mentioned the fact that no compounds of the type R_5Bi or $R_3Bi{=}CR_2$ (R = alkyl) have been prepared and that it is unlikely such compounds can ever be isolated. A recent report in Czech on the nomenclature of organoarsenic, -antimony and -bismuth compounds based on the recently published IUPAC Information Bulletin, *Nomenclature of Organic Chemistry Section D*, has been puslished [6].

Wieber and Baudis [7] have prepared the compound $MeBi(OEt)_2$ by the following metathetical reaction:

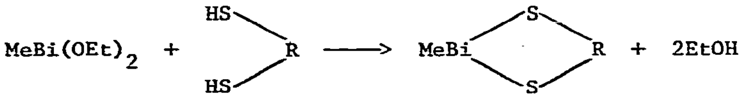
$$MeBiBr_2 + 2NaOEt \longrightarrow MeBi(OEt)_2 + 2NaBr$$

The product was unstable at room temperature but could be kept in ethanol solution at -20°. It reacted with a variety of thiols:

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

(where R was Et, Ph, $PhCH_2$, $HOCH_2CH_2$, or 3-benzothiazolyl)

With dithiols, ring compounds were formed:



(where R was CH_2CH_2 or 4-Me-1,2-C_6H_3)

Vicinal diols reacted in a similar manner to give heterocyclic compounds:

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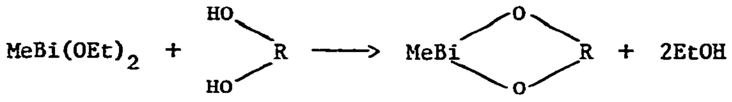
* Bismuth, Annual Survey covering the year 1975 see J. Organometal. Chem., 130(1977)405-410.



$$\mathrm{MeBi(OEt)_2} + \mathrm{(HO)_2R} \longrightarrow \mathrm{MeBi(O)_2R} + \mathrm{2EtOH}$$

(where R was CH_2CH_2, CH_2CHMe, CMe_2CMe_2, CHPhCHPh, or *o*-C_6H_4)

The mass and PMR spectra of the new compounds were reported.

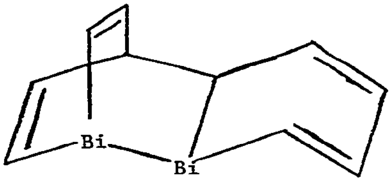
In a second paper Wieber and Baudis [8] have described the preparation of the phenyl compound $PhBi(OEt)_2$ from dibromophenylbismuthine and sodium ethylate. Like the methyl compound, $MeBi(OEt)_2$, it was unstable at room temperature. With thiols it yielded the compounds $PhBi(SR)_2$ and with dithiols it gave ring compounds. The diethoxy compound disproportionated on heating:

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

The triethoxybismuth also reacted with thiols to give compounds of the type $Bi(SR)_3$. PMR spectra for the new compounds were reported.

It has been reported that neither Ph_3Sb nor Ph_3Bi undergo reaction with bis(acetylacetonatotricarbonylrhenium) [9].

Although the heterocyclic compounds phosphabenzene, arsabenzene, and stibabenzene (phosphorin, arsenin, and antimonin) have been isolated and characterized, bismabenzene (bismuthin) is known only as a Diels-Alder addition product. Ashe [10] has now demonstrated the existence of bismabenzene as well as its dimer by PMR studies. When a solution of 1,4-dihydro-1-chlorobismabenzene in THF-d_8 was treated at −78° with 1,5-diazabicyclo[5.4.0]undec-5-ene, the hydrochloride of this base was precipitated and the PMR of the filtrate showed the presence of a dimer of bismabenzene:



When the solution was warmed the intensity of the peaks diminished and at −10° the spectrum was interpreted as that of the previously unknown bismabenzene. The positions of the α-protons in the different Group V compounds (in τ units) were as follows: pyridine, 1.9; phosphabenzene, 1.4; arsabenzene, 0.7; stibabenzene, −0.7; and bismabenzene, −3.25. Preparation of the dimer was also carried out using 1,4-dihydro-1-chlorobismabenzene-3,5-d_2. The PMR spectrum of the resulting dimer of bismabenzene was greatly simplified.

Soluble Bi^{+3} salts of the organic acid $Me_3CCH_2CHMeCH_2COOH$ have been prepared by refluxing triphenylbismuthine and the above acid in acetone solution [11]. The bismuth salt was used to prepare luster compounds of blue and green.

It is known that tris(*o*-dimethylarsinophenyl)bismuthine reacts with nickel(II) salts to form a complex. It has now been found [12] that with palladium(II) salts the C-Bi bond was broken. Thus $[PdCl_4]Na_2$ and the bismuthine in 1-butanol solution and in the presence of $NaBPh_4$ gave $[Pd(PhAsMe_2)_3Cl]BPh_4$ and metallic bismuth. In a similar manner tris(3-dimethylarsinopropyl)bismuthine and $PdCl_4^{2-}$ gave $[Pd(Me_2AsCH_2CH_2CH_3)_3Cl]^+$ compounds.

Cullen and Wu [13] have reported on the reaction between 1,2-dilithiotetrafluorobenzene and trihalides of the Group V elements As, Sb, or Bi to form triptycene-like compounds (see Antimony section). With the bismuth compound only the yield, m.p., ^{19}F NMR spectrum, and carbon analyses were reported. It was stated, however, that all of the compounds were stable.

The reaction of pentacarbonyl(ylid)metal complexes of the type $(CO)_5CrC(R')(R'')$ with tertiary arsines, stibines, and bismuthines has been reported by Fischer and Richter [14]. The bismuthines reacted in a different manner than the arsines and stibines to give pentacarbonyl trialkylbismuthine complexes. Thus from Me_3Bi, Et_3Bi, and $(C_6H_{11})_3Bi$ the compounds $(CO)_5Cr(BiR_3)$ were obtained (where C_6H_{11} = cyclohexyl).

In an interesting paper Levason, McAuliffe, and Sedgwick [15] have reported the synthesis of several new organobismuth compounds of potential importance as ligands in coordination chemistry. Thus *o*-$C_6H_4(PPh_2)BiPh_2$ and *o*-$C_6H_4(AsPh_2)BiPh_2$ were obtained from *o*-bromodiphenylphosphine and *o*-bromodiphenylarsine. These were converted to the lithium compounds that were then treated with chlorodiphenylbismuthine. The compound $Ph_2Bi(CH_2)_3BiPh_2$ however, could not be prepared. The mass spectra of the new compounds were reported.

In a paper devoted to oxidative-addition reactions of triphenyl derivatives of Group V, the reactions of Ph_3Bi with such compounds as S_2Cl_2, SCl_2, and $Pb(OAc)_4$ have been described [16]. From S_2Cl_2 and SCl_2, Ph_3BiCl_2 was obtained. The hydrolysis of $Ph_3Bi(OAc)_2$, obtained from Ph_3Bi and $Pb(OAc)_4$, gave a precipitate of metallic Bi. A mass spectrometric examination of the organic residue suggested the presence of Ph_2BiOAc, PhOAc, PhCl, and biphenyl. The mass spectra of Ph_3Bi and $Ph_3Bi(OAc)_2$ were reported.

The crystal structure of μ-oxobis(perchloratotriphenylbismuth) has been reported by March and Ferguson [17]. The molecule was a distorted trigonal bipyramid. However, the Bi-O bond distance was extremely long for a covalently bonded perchlorato group, and the authors suggested that the bonds were intermediate in character between covalent and ionic bonds.

The IR and Raman spectra of a series of bismuth(V) compounds of the type Ph_3BiX_2, where X = F, Cl, Br, NCO, ONO_2, and O_2CCH_3, have been reported by Goel and Prasad [18]. The IR studies were carried out in the region below 700 cm^{-1}, and Bi-X and Bi-Ph stretching frequencies have been assigned. In addition to the above compounds IR and Raman spectra of the compounds Ph_3BiO, $(Ph_3BiCl)_2O$ and $(Ph_3BiBr)_2O$ were determined, and assignments of the various bands were made. It was concluded that Ph_3BiO possessed a five-coordinate polymeric structure which involved bent Bi-O-Bi bonds.

It has been reported by Razuvaev and coworkers [19] that pentaphenylbismuth, in contrast to the pentaphenyl compounds of phosphorus, arsenic, and antimony, was cleaved by such reagents as isopropyl alcohol, phenol, dry pyridine, and water, with the formation of triphenylbismuthine. The reaction with isopropyl alcohol proceeded as follows:

$$Ph_5Bi + Me_2CHOH \longrightarrow Ph_3Bi + Me_2CO + 2C_6H_6$$

The reaction with phenol was more complicated and in addition to triphenylbismuthine, diphenyl ether, phenol, and unidentified tarry products were obtained. The reaction with triphenylsilanol proceeded as follows:

$$Ph_5Bi + Ph_3SiOH \longrightarrow Ph_4BiOSiPh_3 + C_6H_6$$

The silanol derivative may then be cleaved by HCl:

$$Ph_4BiOSiPh_3 + 2HCl \longrightarrow Ph_3BiCl_2 + Ph_3SiOH + C_6H_6$$

In a paper devoted to complexes of the type R_3ML_2 (where R was an alkyl or aryl group, M was antimony or bismuth, and HL was a phenol or carboxylic acid), Ouchi and coworkers [20] have discussed the IR and NMR spectra of the complexes. The paper has been described in some detail in the Antimony section.

The photodissociation of phenyl derivatives Ph_3M, where M = N, P, As, Sb, and Bi, has been studied by Smirnov and coworkers [21]. This paper has been discussed in considerable detail in the Antimony section. It was noted that under the reaction conditions studied no radicals were detected from Ph_3N and the concentration of radicals was too low to measure with Ph_3P, whereas the quantum yield of radicals was the highest with Ph_3Bi.

In a second paper from the same laboratory as the preceding paper, Rogozhin and coworkers [22] have discussed the increase in the energy of the lowest singlet and triplet excited levels of aromatic compounds of Group IV (C, Si, Ge, and Sn) and Group V(N, P, As, Sb, and Bi) elements. This paper is also discussed in considerable detail in the Antimony section. The bismuth compounds studied were Ph_3Bi, $(2,4,6\text{-}Me_3C_6H_2)_3Bi$, and $(1\text{-}C_{10}H_7)_3Bi$.

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