BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1975

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In 1975 no books or critical review articles concerned only with organobismuth compounds have been published but organobismuth compounds are mentioned in a number of more general review articles. Thus such compounds are mentioned briefly in a monograph on arsenic, antimony, and bismuth compounds [1]. In survey articles devoted in whole or in part to organoarsenic, -antimony, and -bismuth compounds, some mention of bismuth compounds were made [2,3]. In addition, some information on organobismuth compounds has been given in review articles on the following subjects: unsaturated organometallic heterocyclic compounds [4], transition metal complexes of Group VA donor ligands [5], organo perfluoro compounds of phosphorus, arsenic, antimony, and bismuth [6], novel (p-p)π bonds between carbon and elements of Group IIIA, IVA, or VA [7], X-ray diffraction studies of the molecular structures of a number of nitrogen, phosphorus, arsenic, antimony, and bismuth compounds [8], NQR spectroscopy [9] and "organo calomels" and other organobimetallic compounds as intermediates in transmetallation reactions of organometallic compounds with mercury metal [10].

The ground-state electronic effect of Ar_2Sb- and Ar_2Bi- as substituents directly bonded to the aromatic ring has previously been shown to be mainly inductive in nature [11]. This work has now been extended to Sb and Bi compounds containing O and S linkages to the Sb and Bi [12]. The results

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[*] Bismuth, Annual Survey covering the year 1974, see J. Organometal. Chem., 106 (1976) 255-258.

are discussed in greater detail in the Antimony section. The bismuth compounds prepared and characterized were $Ph_2BiSC_6H_4F$-*m* and $Ph_2BiSC_6H_4F$-*p*.

In a paper devoted to the preparation of diazoalkane derivatives of As, Sb, and Bi, the bismuth compounds $Me_2BiN(Me)SiMe_3$, $(Me_2Bi)_2CN_2$, and $Me_2BiC(N_2)CO_2Et$, were prepared [13]. The synthesis involved the following reactions:

$$Me_2BiBr + LiN(Me)SiMe_3 \longrightarrow Me_2BiN(Me)SiMe_3 + LiBr$$

$$2\ Me_2BiN(Me)SiMe_3 + H_2CN_2 \longrightarrow (Me_2Bi)_2CN_2 + 2\ HN(Me)SiMe_3$$

$$Me_2BiN(Me)SiMe_3 + HC(N_2)CO_2Et \longrightarrow Me_2BiC(N_2)CO_2Et + HN(Me)SiMe_3$$

NMR and IR spectroscopic data as well as other physical properties for all of the compounds prepared were listed.

In a paper devoted to cyclopentadienyl compounds of In, Sb, and Bi, Krommes and Lorberth [14] have described the preparation of the thermally labile bismuth compound Me_2BiCp (where Cp = cyclopentadienyl). The compound was prepared by the following synthesis:

$$Me_2BiN(Me)SiMe_3 + CpH \xrightarrow{Et_2O} Me_2BiCp + HN(Me)SiMe_3$$

Mass spectral and IR data were given for all of the compounds prepared.

The Grignard reaction employing bismuth trichloride and *tert*-butylmagnesium chloride gave tri-*tert*-butylbismuthine [15]. The bismuthine was obtained as a yellow liquid, bp 43-52°/0.2 torr. It formed coordination compounds of the type $(Me_3C)_3BiM(CO)_5$ where M = Cr, Mo, or W. The reaction of Et_3Bi with Et_3SnH gave the interesting product $(Me_3Sn)_3Bi$. This also formed coordination compounds $(Me_3Sn)_3BiM(CO)_5$, where again M = Cr, Mo, and W. The known compound $(Me_3Ge)_3Bi$ was also found to form similar complexes $(Me_3Ge)_3BiM(CO)_5$. In addition to Cr, Mo, and W, the two nickel compounds $(Me_3Ge)_3BiNi(CO)_3$ and $(Me_3C)_3BiNi(CO)_3$ were prepared. IR, Raman, and PMR data were given for the various compounds prepared.

The interesting quadridentate ligand, tris(*o*-dimethylarsinophenyl)bismuthine $(o\text{-}Me_2AsC_6H_4)_3Bi$, has been synthesized by Levason, McAuliffe and Murray [16]. The complexes $[NiLX]BPh_4$ were formed with this new ligand and nickel halides. The complex was assigned square-pyramidal geometry. Nickel perchlorate formed the dimer $[Ni_2L_3](ClO_4)_4$, with square pyramidal geometry and a bridging bismuth atom.

In a study of the behavior of the compounds Ph_3M(M = P, As, Sb, and Bi) in chlorosulfuric acid, it was found that Ph_3Bi did not dissolve appreciably in this solvent and there was essentially no change in conductance of the chlorosulfuric acid on the addition of Ph_3Bi [17].

In a paper devoted largely to the ^{19}F NMR spectra of fluorine-substituted triarylphosphines of the type $R_{3-n}R'_nP$ (n = 0, 1, 2, R = $p\text{-}FC_6H_4$, $m\text{-}FC_6H_4$ and R' = Ph) and the oxides, sulfides, and selenides derived from these phosphines, a comparison is made between certain parameters derived from the ^{19}F chemical shifts and these same parameters derived from values obtained from corresponding As, Sb, and Bi compounds [18]. For example σI ($\sigma I = \frac{\delta m - 0.6}{710}$) and σ°_R ($\sigma^{\circ}_R = \frac{\delta p - \delta m}{29.5}$) values for $-P(p\text{-}FC_6H_4)_2$ compounds were compared with these values for $-As(p\text{-}C_6H_4F)_2$, $-Sb(p\text{-}C_6H_4F)_2$, and $-Bi(p\text{-}C_6H_4F)_2$ compounds, but no definite conclusions were drawn from these comparisons.

Although it was originally believed that Ph_3Bi was planar, based on a dipole moment of zero, later X-ray diffraction studies demonstrated that the molecule was pyramidal. Romm and coworkers [19] have measured the dipole moment of Ph_3Bi in several different solvents and invariably found a dipole moment close to zero. But both $(p\text{-}MeC_6H_4)_3Bi$ and $(p\text{-}BrC_6H_4)_3Bi$ had appreciable dipole moments (0.62 D and 2.52 D, respectively). The authors attribute the zero dipole moment of Ph_3Bi to mutual compensation of the phenyl-bismuth dipoles and the dipole of the lone pair of electrons which possesses approximately 20% p-character.

Lema and Scaiano [20] have studied the quenching of fluorenone fluorescence in benzene and in DMF by the trivalent Group V compounds Ph_3M, where M = N, P, As, Sb, and Bi. Although the rate of quenching for Ph_3Sb was higher than for Ph_3As, the value for Ph_3Sb and Ph_3Bi were almost identical. The authors suggest that the lack of rate increase for Ph_3Bi should be attributed to the lack of p-character of the lone pair of electrons on bismuth.

By means of an empirical force-field calculation for the activation energies of stereoisomerization of mesityl compounds of the type $(Mes)_3Z$, (where Mes = mesityl and Z = B, CH, N, etc.), Mislow and coworkers [21] have concluded that a two-ring flip mechanism of isomerization is the pathway of lowest energy (compared with a one-ring or three-ring flip mechanism). Predicted activation energies for $(Mes)_3N$, $(Mes)_3SnH$ and $(Mes)_3Bi$ were 25-27, 5-7 and 3-5 kcal/mole, respectively.

In a paper devoted largely to the ^{13}C NMR spectroscopy of organoantimony compounds, the NMR spectra of the two organobismuth compounds Ph_3BiBr_2 and $Ph_3Bi(O_2CPh)_2$ were studied [22]. The chemical shifts of the C_1, *ortho*, *meta* and *para* carbons referred to C_6H_6 as 0 (downward: + from benzene as 0) were as follows: Ph_3BiBr_2, 28.6, 7.1, 4.3 and 4.3; $Ph_3Bi(O_2CPh)_2$, 32.9, 6.4, 2.0 and 3.7. In addition the chemical shifts of $Ph_3Bi(O_2CEt)_2$ were listed.

Ouchi and coworkers [23] have found that thio acids would react with pentacovalent antimony and bismuth compounds without reduction to form compounds of the type $R_3Sb(S_2CR')_2$ and $R_3Bi(S_2CR')_2$. A number of thio acids were used. Phenoxyacetic acid also reacted with Ph_3SbCl_2 and Ph_3BiCl_2 to form compounds of the type $Ph_3Sb(O_2CCH_2OPh)_2$ and $Ph_3Bi(O_2CCH_2OPh)_2$. The results in this and the proceeding paper have been described in greater detail in the Antimony section.

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