

BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1975

G. O. DOAK AND LEON D. FREEDMAN

*Department of Chemistry, North Carolina State University,
Raleigh, North Carolina 27607 (U.S.A.)*

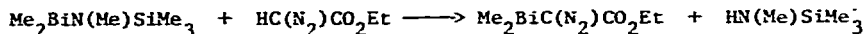
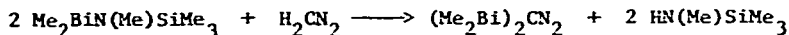
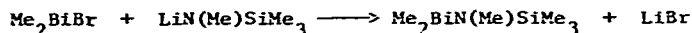
In 1975 no books or critical review articles concerned only with organobismuth compounds have been published but organobismuth compounds are mentioned in a number of more general review articles. Thus such compounds are mentioned briefly in a monograph on arsenic, antimony, and bismuth compounds [1]. 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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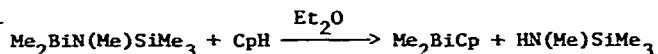
are discussed in greater detail in the Antimony section. The bismuth compounds prepared and characterized were $\text{Ph}_2\text{BiSC}_6\text{H}_4\text{F}$ and $\text{Ph}_2\text{BiSC}_6\text{H}_4\text{F}$.

In a paper devoted to the preparation of diazoalkane derivatives of As, Sb, and Bi, the bismuth compounds $\text{Me}_2\text{BiN}(\text{Me})\text{SiMe}_3$, $(\text{Me}_2\text{Bi})_2\text{CN}_2$, and $\text{Me}_2\text{BiC}(\text{N}_2)\text{CO}_2\text{Et}$, were prepared [13]. The synthesis involved the following reactions:



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:



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 $(\text{Me}_3\text{C})_3\text{BiM}(\text{CO})_5$ where M = Cr, Mo, or W. The reaction of Et_3Bi with Et_3SnH gave the interesting product $(\text{Me}_3\text{Sn})_3\text{Bi}$. This also formed coordination compounds $(\text{Me}_3\text{Sn})_3\text{BiM}(\text{CO})_5$, where again M = Cr, Mo, and W. The known compound $(\text{Me}_3\text{Ge})_3\text{Bi}$ was also found to form similar complexes $(\text{Me}_3\text{Ge})_3\text{BiM}(\text{CO})_5$. In addition to Cr, Mo, and W, the two nickel compounds $(\text{Me}_3\text{Ge})_3\text{BiNi}(\text{CO})_3$ and $(\text{Me}_3\text{C})_3\text{BiNi}(\text{CO})_3$ were prepared. IR, Raman, and PMR

data were given for the various compounds prepared.

The interesting quadridentate ligand, tris(*o*-dimethylarsinophenyl)bismuthine ($o\text{-Me}_2\text{AsC}_6\text{H}_4$)₃Bi, has been synthesized by Levason, McAuliffe and Murray [16]. The complexes [NiLX]BPh₄ were formed with this new ligand and nickel halides. The complex was assigned square-pyramidal geometry. Nickel perchlorate formed the dimer [Ni₂L₃](ClO₄)₄, with square pyramidal geometry and a bridging bismuth atom.

In a study of the behavior of the compounds Ph₃M (M = P, As, Sb, and Bi) in chlorosulfuric acid, it was found that Ph₃Bi did not dissolve appreciably in this solvent and there was essentially no change in conductance of the chlorosulfuric acid on the addition of Ph₃Bi [17].

In a paper devoted largely to the ¹⁹F NMR spectra of fluorine-substituted triarylphosphines of the type R_{3-n}R'_nP (n = 0, 1, 2, R = *p*-FC₆H₄, *m*-FC₆H₄ and R' = Ph) and the oxides, sulfides, and selenides derived from these phosphines, a comparison is made between certain parameters derived from the ¹⁹F chemical shifts and these same parameters derived from values obtained from corresponding As, Sb, and Bi compounds [18]. For example σI (σI = $\frac{\delta m - 0.6}{710}$) and σ_R^o (σ_R^o = $\frac{\delta p - \delta m}{29.5}$) values for -P(*p*-FC₆H₄)₂ compounds were compared with these values for -As(*p*-C₆H₄F)₂, -Sb(*p*-C₆H₄F)₂, and -Bi(*p*-C₆H₄F)₂ compounds, but no definite conclusions were drawn from these comparisons.

Although it was originally believed that Ph₃Bi 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 Ph₃Bi in several different solvents and invariably found a dipole moment close to zero. But both (*p*-MeC₆H₄)₃Bi and (*p*-BrC₆H₄)₃Bi had appreciable dipole moments (0.62 D and 2.52 D, respectively). The authors attribute the zero dipole moment of Ph₃Bi 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 $\text{M} = \text{N}, \text{P}, \text{As}, \text{Sb}, \text{and Bi}$. 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 $(\text{Mes})_3\text{Z}$, (where $\text{Mes} = \text{mesityl}$ and $\text{Z} = \text{B}, \text{CH}, \text{N}, \text{etc.}$), 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 $(\text{Mes})_3\text{N}$, $(\text{Mes})_3\text{SnH}$ and $(\text{Mes})_3\text{Bi}$ 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 $\text{Ph}_3\text{Bi}(\text{O}_2\text{CPh})_2$ 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; $\text{Ph}_3\text{Bi}(\text{O}_2\text{CPh})_2$, 32.9, 6.4, 2.0 and 3.7. In addition the chemical shifts of $\text{Ph}_3\text{Bi}(\text{O}_2\text{CEt})_2$ were listed.

Ouchi and coworkers [23] have found that thio acids would react with pentavalent antimony and bismuth compounds without reduction to form compounds of the type $\text{R}_3\text{Sb}(\text{S}_2\text{CR}')_2$ and $\text{R}_3\text{Bi}(\text{S}_2\text{CR}')_2$. 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 $\text{Ph}_3\text{Sb}(\text{O}_2\text{CCH}_2\text{OPh})_2$ and $\text{Ph}_3\text{Bi}(\text{O}_2\text{CCH}_2\text{OPh})_2$. The results in this and the preceding paper have been described in greater detail in the Antimony section.

REFERENCES

- 1 J. D. Smith, *The Chemistry of Arsenic, Antimony, and Bismuth*, Pergamon, Elmsford, N. Y., 1975; *Chem. Abstr.*, 83 (1975) 70887g.

- 2 J. L. Wardell, *Organometal. Chem.*, 3 (1975) 162.
- 3 A. Morris and B. D. Sowerby, *Inorg. Chem. Main-Group Elem.*, 2 (1974) 430; *Chem. Abstr.*, 83 (1975) 157033z.
- 4 J. Y. Corey, in F. G. A. Stone and R. West, eds., *Advances in Organometallic Chemistry*, Vol. 13, Academic Press, New York, N. Y., 1975 pp. 139-271.
- 5 R. J. Cross, *MTP Int. Rev. Sci., Inorg. Chem., Ser. Two*, 5 (1974) 147.
- 6 A. Haas, *Gmelin Handbuch der Anorganischen Chemie, Ergänzungswerk, Band 24: Perfluorhalogenorgano-Verbindungen der Hauptgruppenelemente, Teil 3: Verbindungen von Phosphor, Arsen, Antimon, und Wismut*, Springer-Verlag, Berlin, 1975, pp. 226-232.
- 7 P. Jutzi, *Angew. Chem., Int. Ed. Engl.*, 14 (1975) 232.
- 8 M. B. Hursthouse, *Mol. Struct. Diffr. Methods*, 2 (1974) 459.
- 9 J. H. Carpenter, *Spectrosc. Prop. Inorg. Organometal. Compounds*, 8 (1975) 178.
- 10 O. A. Reutov and K. P. Butin, *J. Organometal. Chem.*, 99 (1975) 171.
- 11 A. N. Nesmeyanov, D. N. Kravtsov, B. A. Kvasov, S. I. Pombrik, and E. I. Fedin, *J. Organometal. Chem.*, 47 (1973) 367.
- 12 D. N. Kravtsov, B. A. Kvasov, S. I. Pombrik, and E. I. Fedin, *J. Organometal. Chem.*, 86 (1975) 383.
- 13 P. Krommes and J. Lorberth, *J. Organometal. Chem.*, 93 (1975) 339.
- 14 P. Krommes and J. Lorberth, *J. Organometal. Chem.*, 88 (1975) 329.
- 15 H. Schumann and H. J. Breunig, *J. Organometal. Chem.*, 87 (1975) 83.
- 16 W. Levason, C. A. McAuliffe, and S. G. Murray, *J. Chem. Soc., Chem. Comm.*, (1975) 164.
- 17 R. C. Paul, D. S. Dhillon, and J. K. Puri, *Indian J. Chem.*, 13 (1975) 1058.
- 18 R. F. De Ketelaere and G. P. Van der Kelen, *J. Mol. Struct.*, 27 (1975) 33.

- 19 I. P. Romm, V. I. Lodochnikova, O. P. Syutkina, E. N. Gur'yanova, and E. M. Panov, *Zh. Strukt. Khim.*, 16 (1975) 498.
- 20 R. H. Lema and J. C. Scaiano, *Tetrahedron Lett.*, (1975) 4361.
- 21 M. R. Kates, J. D. Andose, P. Finocchiaro, D. Gust, and K. Mislow, *J. Amer. Chem. Soc.*, 97 (1975) 1772.
- 22 A. Ouchi, T. Uehiro, and Y. Yoshino, *J. Inorg. Nucl. Chem.*, 37 (1975) 2347.
- 23 A. Ouchi, H. Honda, and S. Kitazima, *J. Inorg. Nucl. Chem.*, 37 (1975) 2559.