

BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1974

LEON D. FREEDMAN AND G. O. DOAK

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

There have been several reviews in which organobismuth compounds were briefly mentioned. Thus, these substances were included in two short surveys of organoarsenic, -antimony, and -bismuth chemistry [1,2], a comprehensive summary of the synthesis and preparative uses of organoarsenides, -stibides, and -bismuthides [3], and review articles on the vibrational spectra of organic derivatives of phosphorus, arsenic, antimony, and bismuth [4,5], biological effects of organometallic compounds [6], NMR spectroscopy of inorganic and organometallic compounds [7,8], X-ray structures of Group V compounds [9], and bond strengths in organic compounds of non-transition elements [10]. In addition, organobismuth compounds have been incidentally mentioned in books on organometallic reaction mechanisms [11] and stereochemistry in inorganic chemistry [12].

A study has been made of the effect of electrolyte composition on the formation of organobismuth compounds at a bismuth cathode [13]. The compounds prepared included the tertiary bismuthine $(\text{NCCH}_2\text{CH}_2)_3\text{Bi}$ and the halo-bismuthines $(\text{NCCH}_2\text{CH}_2)_2\text{BiI}$ and Me_2BiBr . The electrochemical synthesis of organobismuth compounds at a tungsten cathode has been described in a Russian patent [14].

Rossi and Bunnett [15] have included triphenylbismuthine in a study of the cleavage of substituted benzenes by potassium metal in liquid ammonia containing the acetone enolate ion. They isolated 2.7 moles of benzene per mole of bismuth compound. This observation contrasted sharply with the

Bismuth, Annual Survey covering the year 1973 see *J. Organometal. Chem.*, 89 (1975) 183-192.

References p. 257

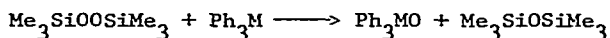
results obtained with triphenylphosphine, -arsine, and -stibine, which were cleaved to diphenylphosphide, -arsenide, and -stibide anions, respectively:



(where M was P, As, or Sb and e^- was a solvated electron)

In these cases, less than one mole of benzene per mole of substrate was formed. Good yields of diphenylphosphinic, diphenylarsinic, and diphenylstibinic acids were obtained from these reaction mixtures.

Brandes and Blaschette [16] have found that bis(trimethylsilyl) peroxide readily oxidized triphenylphosphine, -arsine, and -stibine to the corresponding oxides in high yields:



(where M was P, As, or Sb)

In contrast, triphenylbismuthine was unaffected by refluxing with the peroxide in petroleum ether (bp 110-130°) for 4 hours.

The molecular structure of trimethylbismuthine in the gas phase has been determined by electron diffraction [17]. The only surprising feature of the structure was that the Bi-C distance (2.267 Å) was significantly longer than the Pb-C distance (2.238 Å) previously reported in a gas-phase electron diffraction study of tetramethyllead. The position of bismuth to the right of lead in the periodic table would lead one to expect the Bi-C bond to be slightly shorter than the Pb-C bond. The C-Bi-C and Bi-C-H intervalency angles were found to be $96.7 \pm 1.0^\circ$ and $107.6 \pm 1.0^\circ$, respectively, and the C-H bond length was 1.101 Å.

Evidence for the gas-phase formation of Ph_3BiTl^+ has been obtained by inserting an intimate mixture of triphenylbismuthine and (hexafluoroacetylacetonato)thallium(I) into a mass spectrometer [18]. Analogous results were

obtained when mixtures of the latter compound with triphenylphosphine or triphenylarsine were used.

The transmission of electronic effects through the bismuth-aryl bond has been investigated by ^{19}F NMR spectroscopy [19]. The compounds studied were tertiary bismuthines of the type $4\text{-FC}_6\text{H}_4\text{Bi}(\text{C}_6\text{H}_4\text{Y})_2$, where Y was H, 4-F, 4-Cl, 4-Me, 4-MeO, or 4-Me₂N. A linear correlation was found between the chemical shift values and the σ° constants of the substituents Y:

$$\delta_{\text{F}} = -2.53 \sigma^\circ + 0.08$$

It was concluded that the electronic effects of the substituents were transmitted mainly by an inductive mechanism, since the correlation of chemical shifts with σ_{p} constants was relatively poor.

Several papers in which organobismuth compounds were mentioned have been reviewed under Antimony. Described in these publications were the preparation and ^{19}F NMR spectrum of diphenyl(*p*-fluorophenylthio)bismuthine [20], the reaction of triphenylbismuthine with chloramine-T [21,22], the IR and Raman spectra of the *meta* and *para* isomers of tris(chlorophenyl)- and tris(fluorophenyl)bismuthine [23], the NQR spectra of triphenyl-, tris(*m*-chlorophenyl)-, tris(*m*-fluorophenyl)-, and tris(*p*-fluorophenyl)bismuthine [24], the mass spectrum of triphenylbismuthine [25], and the use of triphenylbismuth dihalides as analytical reagents [26].

REFERENCES

- 1 D. Millington, *Annu. Rep. Prog. Chem., Sect. A*, 70 (1974) 315.
- 2 L. C. Duncan, *Annu. Rep. Inorg. Gen. Syn.*, 1 (1973) 225.
- 3 G. O. Doak and L. D. Freedman, *Synthesis*, (1974) 328.
- 4 E. Maslowsky, Jr., *J. Organometal. Chem.*, 70 (1974) 153.
- 5 S. R. Stobart, *Spectrosc. Prop. Inorg. Organometal. Compounds*, 7 (1974) 255.
- 6 J. S. Thayer, *J. Organometal. Chem.*, 76 (1974) 265.

- 7 B. E. Mann, *Spectrosc. Prop. Inorg. Organometal. Compounds*, 7 (1974) 1.
- 8 L. J. Todd and J. R. Wilkinson, *J. Organometal. Chem.*, 77 (1974) 1.
- 9 M. B. Hursthouse, *Mol. Struct. Diffraction Methods*, 1 (1973) 756.
- 10 V. I. Tel'noi, *Tr. Khim. Khim. Tekhnol.*, (1974) 28.
- 11 D. S. Matteson, *Organometallic Reaction Mechanisms of the Nontransition Elements*, Academic Press, New York, N. Y., 1974, pp. 267, 285.
- 12 J. E. Fergusson, *Stereochemistry and Bonding in Inorganic Chemistry*, Prentice-Hall, Englewood Cliffs, N. J., 1974, pp. 167, 185.
- 13 I. N. Chernykh and A. P. Tomilov, *Elektrokhimiya*, 10 (1974) 1424; *Chem. Abstr.*, 82 (1975) 91701 m.
- 14 A. P. Tomilov and I. N. Chernykh, U.S.S.R. Pat. 415, 271; *Chem. Abstr.*, 80 (1974) 133627 h.
- 15 R. A. Rossi and J. F. Bunnett, *J. Amer. Chem. Soc.*, 96 (1974) 112.
- 16 D. Brandes and A. Blaschette, *J. Organometal. Chem.*, 73 (1974) 217.
- 17 B. Beagley and K. T. McAloon, *J. Mol. Struct.*, 17 (1973) 429.
- 18 H. Nakayama, C. Nishijima, and S. Tachiyashiki, *Chem. Lett.*, (1974) 733
- 19 D. N. Kravtsov, B. A. Kvasov, S. I. Pombrik, and É. I. Fedin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1974) 234.
- 20 D. N. Kravtsov, B. A. Kvasov, S. I. Pombrik, and É. I. Fedin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1974) 927.
- 21 D. K. Padma, R. A. Shaw, A. R. V. Murthy, and M. Woods, *Phosphorus*, 4 (1974) 25.
- 22 S. S. Pahil and K. D. Sharma, *Fresenius' Z. Anal. Chem.*, 270 (1974) 127; *Chem. Abstr.* 81 (1974) 114248 q.
- 23 R. F. De Ketelaere and G. P. Van der Kelen, *J. Organometal. Chem.*, 73 (1974) 251.
- 24 G. P. Van der Kelen and R. F. De Ketelaere, *J. Mol. Struct.*, 23 (1974)
- 25 V. K. Potapov, A. N. Rodionov, T. I. Evlasheva, and K. L. Rogozhin, *Khim. Vys. Energ.*, 8 (1974) 559; *Chem. Abstr.*, 82 (1975) 57009 g.
- 26 M. Benmalek, H. Chermette, C. Martelet, D. Sandino, and J. Tousset, *J. Inorg. Nucl. Chem.*, 36 (1974) 1359.