BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1971

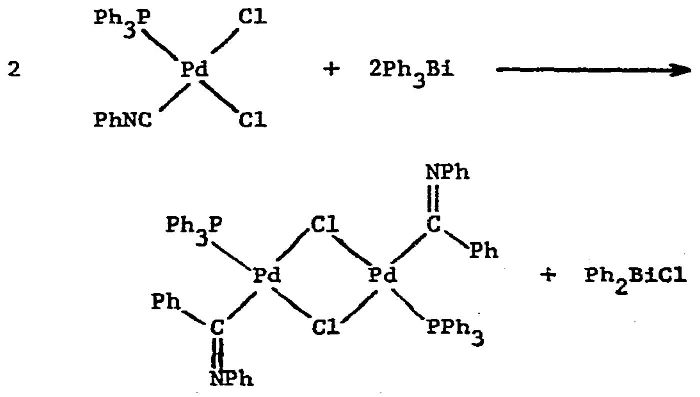
LEON D. FREEDMAN AND G. O. DOAK
Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27607 (U.S.A.)

There have been several recent reviews in which organobismuth compounds were briefly mentioned. Moedritzer [1] has included these substances in a survey of the preparative utility of redistribution reactions of organometallic compounds. Cox and Pilcher [2] in a monograph on the thermochemistry of organic compounds have critically examined the relatively few thermochemical measurements that have been performed on organobismuth compounds. The preparation and properties of substances of the type Ph_2BiM (where M was Li or Na) have been briefly discussed in a review on alkali metal and magnesium derivatives of organic compounds of silicon, germanium, tin, lead, phosphorus, arsenic, antimony, and bismuth [3]. The utilization of trialkylbismuthines for the preparation of compounds containing Bi–Ge bonds has been reviewed in a book on organogermanium chemistry [4]. Organobismuth compounds have also been included in a general survey of sigma-bonded organometallic compounds [5] and in a report on spectroscopic data published in 1970 [6].

Compounds of the type $ArBiX_2$ (where X was Cl, Br, or O_2SPh) have been found to give apparent first order PMR spectra at 60 MHz [7]. For example, the spectrum of phenyldichlorobismuthine in dimethyl sulfoxide exhibited a well-defined doublet at τ 1.00 and two well-defined triplets at τ 2.08 and τ 2.62. The three signals were attributed to the *ortho*, *meta*, and *para* protons, respectively. Solutions in acetonitrile and other donor solvents gave similar spectra, in which the separation between the *meta* and *para* protons was greater than that obtained with benzyl alcohol in the presence of tris(dipivalomethanato)europium, a powerful shift reagent. The PMR spectra of compounds of the type Ar_2BiX, Ar_3Bi, and Ar_3BiX_2 were also investigated; the resolution of the aromatic proton signals was much poorer than that observed with the $ArBiX_2$ compounds.

Müller [8] has obtained azidodimethylbismuthine, Me_2BiN_3, by the interaction of equimolar amounts of trimethylbismuthine and hydrazoic acid in ether. The azide, which precipitated in the form of colorless needles, was insoluble in tetrahydrofuran, ethanol, pyridine, and other common organic solvents. It dissolved with decomposition in inorganic acids, but it was not explosive and only slightly light-sensitive. At about 150° it decomposed and turned gray. The mass spectrum of the azide exhibited a weak molecular ion and relatively strong peaks corresponding to Me_2Bi^+, $MeBi^+$, and Bi^+; no peaks above M + 1 were observed. The IR and Raman spectra of the azide provided additional evidence for the non-ionic, monomeric nature of this compound.

Crociani and co-workers [9] have noted in a preliminary communication that the reaction of a palladium(II) isocyanide complex with triphenylbismuthine (and a variety of phenyl derivatives of other heavy metals) proceeded according to the following equation:



The binuclear palladium compound thus obtained was thoroughly characterized, but no evidence for the formation of the chlorobismuthine was presented.

Deacon and co-workers [10] have described the formation of bismuth-carbon bonds by the thermal elimination of sulfur dioxide from certain arenesulfinatobismuth(III) compounds. For example, when tris(arenesulfinato)bismuthines were heated at 200° for 5 hours, the corresponding triarylbismuthines sublimed from the reaction mixture in 68-85% yield:

$$Bi(O_2SAr)_3 \longrightarrow 3SO_2 + Ar_3Bi$$

(where Ar was Ph or *p*-MeC_6H_4)

Bis(benzenesulfinato)phenylbismuthine and (benzenesulfinato)diphenylbismuthine underwent similar reactions:

$$Ph_{3-n}Bi(O_2SPh)_n \longrightarrow nSO_2 + Ph_3Bi$$

(where n was 1 or 2)

The tris(arenesulfinato)bismuthines could be prepared by two different procedures:

$$Ph_3Bi + 3Hg(O_2SAr)_2 \longrightarrow Bi(O_2SAr)_3 + 3PhHg(O_2SAr)$$

$$Bi(OAc)_3 + 3ArSO_2H \longrightarrow Bi(O_2SAr)_3 + 3HOAc$$

(where Ar was Ph or *p*-Me C_6H_4)

The second reaction tended to give purer products. Bis(benzenesulfinato)phenylbismuthine and (benzenesulfinato)diphenylbismuthine were obtained by the interaction of triphenylbismuthine and benzenesulfinic acid:

$$Ph_3Bi + nPhSO_2H \longrightarrow Ph_{3-n}Bi(O_2SPh)_n + nPhH$$

(where n was 1 or 2)

The IR spectrum of every arenesulfinatobismuth(III) complex exhibited very broad absorption at 970-890 cm^{-1}, which was attributed to $\nu(SO_2)$. It was concluded that *O*-sulfinate coordination was involved and that the complexes probably contained bidentate or bridging bidentate *O*-sulfinate groups.

The *meta* and *para* isomers of tris(chlorophenyl)- and tris(fluorophenyl)bismuthine have been prepared by the interaction of the appropriate arylmagnesium bromide and bismuth trichloride in ether [11]. The PMR spectrum of tris(*p*-fluorophenyl)bismuthine was in agreement with the theoretical spectral pattern expected for an AA'XX' system, and it was possible to calculate all the chemical shifts and coupling constants. The PMR spectrum of the corresponding *p*-chloro isomer consisted of a broad AB type quadruplet; analysis of the spectrum yielded the chemical shifts of the protons *ortho* and *meta* to the bismuth atom and the $^3J(H_o - H_m)$ constant. The PMR spectra of the *meta*-substituted bismuthines were very complex, and only the chemical shift corresponding to the center of the multiplet was obtained. The ^{19}F NMR spectra of the tris(fluorophenyl)bismuthines were also determined, and the chemical shifts and coupling constants were calculated.

Royo and Uson [12] have described the preparation of tris(pentafluorophenyl)bismuthine by means of the Grignard reaction:

$$3C_6F_5MgBr + BiCl_3 \longrightarrow (C_6F_5)_3Bi + 3MgClBr$$

The bismuthine thus obtained was reported to decompose readily in the presence of water to form decafluorobiphenyl and bismuth metal. Bregadze and co-workers [13] have prepared tris(phenylcarboranyl)bismuthine by the interaction of phenylcarboranyllithium and bismuth trichloride. This work has been discussed under Antimony. The reaction of trimethylbismuthine with tetraborane, B_4H_{10}, has been found to give a low yield of 2-methyltetraborane [14].

Davies and Hook [15] have studied the oxidation of trimethyl- and triethylbismuthine with *tert*-butyl hydroperoxide and with oxygen. The interaction of triethylbismuthine and *tert*-butyl hydroperoxide in benzene yielded *tert*-butyl alcohol, ethyl alochol, diethyl ether, and ethyl *tert*-butyl peroxide. Small amounts of alkanes and alkenes derived from the ethyl group were also detected. The oxidation of trimethylbismuthine by *tert*-butyl hydroperoxide yielded an analogous array of volatile products. The authors concluded that the hydrocarbons were formed via ethyl or methyl radicals while the alcohols, ethers, and peroxides were products of a heterolytic process. The autoxidation of the trialkylbismuthines in benzene yielded the corresponding alkyl alcohols, dialkyl ethers, and dialkyl peroxides. Pale yellow nonperoxidic solids separated during the reaction and appeared to be polymeric bismuth oxides containing an average of one (or less than one) alkyl group per metal atom. The effect of inhibitors (such as phenothiazine and galvinoxyl) on the autoxidation of the trialkylbismuthines established unequivocally that these reactions proceeded by a radical chain process. The authors suggested detailed mechanisms for the autoxidations and for the *tert*-butyl peroxide reactions. The reaction of triethylbismuthine with oxygen has also been studied by Winchester [16]. He used cyclohexane as the solvent and found that the major products were ethanol, acetaldehyde, and an insoluble bismuth-containing solid. Minor products included diethyl peroxide, diethyl ether, acetic acid, and probably ethylene. Since the reaction was strongly inhibited by diphenylamine, a radical chain mechanism was proposed. Analysis of the solid formed in the reaction suggested that it was a substance similar to bismuth(III) oxide with some of the oxygen atoms replaced by ethylene or ethylidene groups. The overall reaction scheme was summarized by the following equation:

$$2Et_3Bi + 3O_2 \longrightarrow Bi_2O_{3/2}(C_2H_4)_{3/2} + 3EtOH + 3/2MeCHO$$

Davies and co-workers [17] have included triethylbismuthine in an investigation of the reaction of *tert*-butoxy radicals with a variety of organometallic compounds. In the case of triethylbismuthine, the *tert*-butoxy radicals were generated by the thermal decomposition of di-*tert*-butyl hyponitrite at 80° in *tert*-butylbenzene and underwent an S_H2 reaction with the bismuth compound. The ethyl radicals formed via this reaction were observed by ESR.

The flash photolysis of trimethylbismuthine in argon has been found to produce excited bismuth atoms and a variety of other species [18]. These included Bi_2, Me, and possibly MeBi. In the presence of oxygen or carbon dioxide, the formation of BiO was also observed. The UV absorption spectrum of trimethylbismuthine was reported to exhibit a maximum at 211.5 nm (ε, 1.65×10^4) and shoulders at 222.5 nm (ε, 1.4×10^4) and 260.0 nm (ε, 2.4×10^3).

Marshall and Pollard [19] have included triphenylbismuthine in a study of exchange reactions between metallic mercury and various phenylmetal compounds. The reactions were carried out at 55° by stirring a benzene solution of the organometallic compound with an excess of mercury labelled with the radioactive ^{203}Hg isotope. After 5.0 hours (in the case of triphenylbismuthine), a sample of the supernatant liquid was analyzed for radioactivity. When the initial concentration of triphenylbismuthine was 0.050 M, the following reaction proceeded 20.6% to completion:

$$3Hg + 2Ph_3Bi \longrightarrow 3Ph_2Hg + Bi(amalgam)$$

The relatively large amount of exchange was attributed in part to the "planar structure" of triphenylbismuthine. It is now known, however, that in the solid state there is a pyramidal configuration about the bismuth atom [20].

Several papers published in 1971 have added to our meager knowledge of quaternary bismuthonium salts and of the donor properties of tertiary bismuthines. In attempts to prepare triphenylbismuth diperchlorate and bis(tetrafluoroborate) by the interaction in acetone of triphenylbismuth dichloride and silver perchlorate or tetrafluoroborate, Goel and Prasad [21] obtained derivatives of the acetonyltriphenylbismuthonium cation:

$$Ph_3BiCl_2 + 2AgX + Me_2CO \longrightarrow [Ph_3BiCH_2COMe]X + 2AgCl + HX$$

(where X was ClO_4 or BF_4)

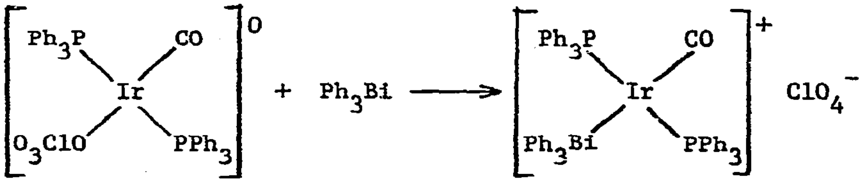
Both compounds were white crystalline solids and were soluble in polar organic solvents and very slightly soluble in benzene. Their PMR spectra exhibited a phenyl multiplet (δ 7.60) and two singlets; one occurred at δ 5.50 for the perchlorate and at δ 5.33 for the tetrafluoroborate, and the other occurred at δ 2.37. The 5.50 or 5.33 peak was assigned to the methylene protons, and the 2.37 peak to the methyl protons. The IR spectra of the bismuthonium salts were also consistent with the proposed structures. The equivalent conductances in acetonitrile showed that the compounds behaved as 1:1 electrolytes in this solvent. Goel and Prasad were unsuccessful in an attempt to prepare acetonyltriphenylbismuthonium nitrate by the reaction between triphenylbismuth dichloride and silver nitrate in acetone; they obtained instead a quantitative yield of triphenylbismuth dinitrate. They also failed to prepare a bismuthonium salt by the direct quaternization of triphenylbismuthine with chloroacetone. In contrast to this result, Schipper and Buck [22] observed the formation of a bismuthonium compound by the interaction of a solution of the 7-norbornadienyl cation and triphenylbismuthine. The required cation was generated by treatment of 7-norbornadienyl chloride in liquid sulfur dioxide with silver tetrafluoroborate at −70°. The reaction of the resulting 7-norbornadienyl cation with triphenylbismuthine (and a number of other nucleophiles) was followed by PMR. This work has been discussed in more detail under Arsenic.

The treatment of tetraphenylbismuthonium tetrafluoroborate with alcoholic sodium hydroxide has been found to give an 82% yield of triphenylbismuthine [23]. The reaction was complete in a few minutes at room temperature. In aqueous sodium hydroxide the decomposition was slow; after a month about 60% of the starting material could be recovered. The bismuthonium compound used in this study was prepared by the interaction of pentaphenylbismuth and hydrogen tetrafluoroborate.

White and Farona [24] have described the synthesis and properties of a 1:1 adduct of triphenylbismuthine and bis(dithioacetylacetonato)-cobalt(II). Analogous complexes of triphenylphosphine, -arsine, and -stibine were also prepared. The adducts were obtained by allowing equimolar amounts of bis(dithioacetylacetonato)cobalt(II) and the ligand to react in benzene for 72 hours at room temperature. The four products were dark red (nearly black) solids and were soluble in a wide range of organic solvents. They were thermally stable and showed no melting or decomposition at 300°. Their optical spectra and magnetic moments indicated that they were five-coordinate, low-spin complexes with square-pyramidal structures.

Complexes containing Bi-Cr, Bi-Mo, and Bi-W bonds have also been reported [25]. They were prepared by the ultraviolet irradiation of benzene solutions of triphenylbismuthine and hexacarbonylchromium, -molybdenum, or -tungsten. The resulting complexes, which were air-stable, crystalline solids, were of the type $Ph_3BiM(CO)_5$. Their stabilities decreased in the order Mo < Cr < W. All three triphenylbismuthine complexes were much less stable than those of triphenylphosphine, -arsine, or -stibine. The mass spectrum of each bismuth complex showed a peak at m/e corresponding to the $Ph_3BiM(CO)_5^+$ parent ion. Other major peaks in the spectrum corresponded to ions resulting from the stepwise loss of carbon monoxide from the parent ion and to the $M(CO)_6^+$ ion, which probably arose from the thermal decomposition of the complexes in the mass spectrometer.

Vaska and Peone [26] have reported the replacement of a coördinated perchlorato ligand in an iridium complex by triphenylbismuthine:



Similar replacements were achieved with triphenylstibine, triphenylarsine, and a number of phosphines and amines. The CO frequencies of the complexes obtained in this manner indicated that the "total electronegativity" of the Group V ligands decreased in the order: $Ph_3N > Ph_3P > Ph_3As > Ph_3Sb > Ph_3Bi$.

Goel and Prasad [27] have prepared and characterized triphenylbismuth carbonate, oxalate, sulfate, selenate, and chromate. The solid state IR spectra of these compounds in the 4000-200 cm^{-1} region indicated that they possessed polymeric structures involving five-coordinate bismuth and bridging anionic ligands. Further evidence for the nonionic nature of these compounds was the low electrical conductivity of the selenate and the chromate in formamide. No suitable solvent could be found for determining the conductivities of the other compounds.

Ferguson, Goel, and co-workers [28] have investigated the IR spectra of oxybis(triphenylbismuth) diperchlorate, $(Ph_3BiClO_4)_2O$, and a dihydrate of this substance. They have also used X-ray diffraction to determine the crystal and molecular structure of the anhydrous material. Although the dihydrate appeared to contain perchlorate ions, the anhydrous oxide was clearly a non-ionic derivative of five-coordinate bismuth. The X-ray analysis showed that the Bi–O–Bi angle was 142.4° and that the two halves of the molecule possessed slightly distorted trigonal-bipyramidal configurations with the bridging oxygen at one apex and a perchlorate oxygen at the other. Similar results were obtained with oxybis(triphenylantimony) diazide. This work has been discussed under Antimony.

REFERENCES

1 K. Moedritzer, in E. I. Becker and M. Tsutsui, eds., *Organometallic Reactions*, Vol. 2, Wiley-Interscience, New York, 1971, pp. 24, 32, 61, 78, 79.

2 J. D. Cox and G. Pilcher, *Thermochemistry of Organic and Organometallic Compounds*, Academic Press, London, 1970, pp. 486–487.

3 D. D. Davis and C. E. Gray, *Organometal. Chem. Rev., Sect. A*, 6 (1970) 283.

4 M. Lesbre, P. Mazerolles, and J. Satgé, *The Organic Compounds of Germanium*, Wiley-Interscience, New York, 1971, pp. 278, 671, 672.

5 W. T. Reichle, in M. Tsutsui, ed., *Characterization of Organometallic Compounds*, Part II, Wiley-Interscience, New York, 1971, pp. 798–807.

6 N. N. Greenwood, ed., *Spectroscopic Properties of Inorganic and Organometallic Compounds*, Vol. 4, The Chemical Society, London, 1971, pp. 197–198, 304.

7 B. C. Smith and C. B. Waller, *J. Organometal. Chem.*, 32 (1971) C11.

8 J. Müller, *Z. Anorg. Allg. Chem.*, 381 (1971) 103.

9 B. Crociani, M. Nicolini, and T. Boschi, *J. Organometal. Chem.*, 33 (1971) C81.

10 G. B. Deacon, G. D. Fallon, and P. W. Felder, *J. Organometal. Chem.*, 26 (1971) C10.

11 R. F. de Ketelaere, F. T. Delbeke, and G. P. van der Kelen, *J. Organometal. Chem.*, 30 (1971) 365.

12 P. Royo and R. Uson, *Rev. Acad. Cienc. Exactas, Fis.-Quim. Natur. Zaragoza*, 24 (1969) 119; *Chem. Abstr.*, 75 (1971) 76963k.

13 V. I. Bregadze, D. N. Sadzhaya, and O. Yu. Okhlobystin, *Soobshch. Akad. Nauk Gruz. SSR*, 63 (1971) 77; *Chem. Abstr.*, 75 (1971) 98644j.

14 F. M. Miller and D. M. Ritter, *Inorg. Chem.*, 9 (1970) 1284.

15 A. G. Davies and S. C. W. Hook, *J. Chem. Soc., C*, (1971) 1660.

16 R. V. Winchester, *Can. J. Chem.*, 49 (1971) 1747.

17 A. G. Davies, D. Griller, and B. P. Roberts, *J. Chem. Soc., B*, (1971) 1823.

18 J. Connor, P. J. Young, and O. P. Strausz, *J. Amer. Chem. Soc.*, 93 (1971) 822.

19 R. A. G. Marshall and D. R. Pollard, *J. Organometal. Chem.*, 27 (1971) 149.

20 D. M. Hawley and G. Ferguson, *J. Chem. Soc., A*, (1968) 2059.

21 R. G. Goel and H. S. Prasad, *J. Chem. Soc., A*, (1971) 562.

22 P. Schipper and H. M. Buck, *Phosphorus*, 1 (1971) 93.

23 O. A. Ptitsyna, M. E. Gurskii, T. D. Maiorova, and O. A. Reutov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1971) 2618; *Chem. Abstr.*, 76 (1972) 113321t.

24 J. F. White and M. F. Farona, *Inorg. Chem.*, 10 (1971) 1080.

25 R. A. Brown and G. R. Dobson, *J. Inorg. Nucl. Chem.*, 33 (1971) 892.

26 L. Vaska and J. Peone, Jr., *Suom. Kemistilehti, B*, 44 (1971) 317.

27 R. G. Goel and H. S. Prasad, *Can. J. Chem.*, 49 (1971) 2529.

28 G. Ferguson, R. G. Goel, F. C. March, D. R. Ridley, and H. S. Prasad, *J. Chem. Soc., D*, (1971) 1547.