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BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1978

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An important monograph on organobismuth compounds appeared in late 1977 [1]. This volume covers the literature as abstracted by *Chemical Abstracts* through May of 1976. There is a Table of Contents in both German and English and a formula index but no author index. The body of the text is in German and covers the synthesis and physical properties of all known organobismuth compounds. In addition to the above monograph, a volume of the familiar Houben-Weyl series on methods of organic synthesis has been published in which the subject matter is devoted to organic compounds of arsenic, antimony, and bismuth [2]. Thirty-six pages (out of a total of 626) are devoted to the synthesis of organobismuth compounds. The text is in German, and there is an author and a comprehensive subject index. Organobismuth compounds have been discussed in the article on bismuth compounds in the recent revision of the *Kirk-Othmer Encyclopedia of Chemical Technology* [3]. Compounds in which organobismuth compounds are coordinated to transition elements were discussed in a recent book [4] by McAuliffe and Levason. These same authors [5] have also published a review article on the coordination chemistry of organostibines. The synthesis of some organobismuth compounds and their use as ligands to transition elements were also discussed in this review. A comparison of organic phosphines, arsines, stibines, and bismuthines in this review was of considerable value. A few organobismuth compounds were mentioned in a review article on organoarsenic, -antimony and -bismuth compounds described in the chemical literature during the year 1976 [6]. This review, however, was not published until 1978. The chemistry of bismin (bismabenzene) has been discussed in a review article on Group V heterobenzenes [7]. One organobismuth heterocyclic compound was mentioned in a review article on six-membered heterocycles containing phosphorus, arsenic, antimony, or bismuth [8].

Bismuth; Annual Survey covering the year 1977 see J. Organometal. Chem., Vol. 163 (1978) p. 141-150.

Wieber and Baudis [9] have noted that the only known compound of the type R_2BiOR' was Et_2BiOEt. They have now prepared four compounds Ph_2BiOR, where R = Me, Et, $CHMe_2$, or Ph, by the reaction:

$$Ph_2BiBr + NaOR \rightarrow Ph_2BiOR + NaBr$$

The compounds were obtained as fine crystals, sensitive to atmospheric moisture and irritating to mucous membranes. Both PMR data and molecular weights from mass spectral data were reported. The compounds reacted with thiols to yield compounds of the type Ph_2BiSR, where R was $CHMe_2$, CMe_3, C_6H_{11} (cyclohexyl), or C_6H_4Me-*p*. Another compound prepared was $Ph_2BiS(CH_2)_5SBiPh_2$. The thio compounds were easily prepared from Ph_2BiOEt which was not isolated:

$$Ph_2BiBr + NaOEt \rightarrow Ph_2BiOEt + NaBr$$

$$Ph_2BiOEt + RSH \rightarrow Ph_2BiSR + EtOH$$

The compounds were characterized by elemental analyses, PMR, and molecular weights (from mass spectral data).

In a second paper from Wieber's laboratory [10] the preparation of the compounds $MeBi(OR)_2$, where R = Me, Et, or $CHMe_2$, was described. The compounds were obtained by means of the following reaction:

$$MeBiBr_2 + 2NaOR \rightarrow MeBi(OR)_2 + 2\,NaBr$$

The solvent for the reaction in each case was the corresponding alcohol, ROH. The compound $MeBi(OEt)_2$ was obtained in crystalline form by recrystallization from ethanol at low temperatures, but the other two compounds could not be crystallized and were obtained as powders by evaporation of the solvent. All three compounds decomposed without melting when heated. Their slight solubility in organic solvents other than alcohols prevented the determination of their molecular weights by cryoscopic methods. It was suggested that the compounds were polymeric in nature. They were, however, sufficiently soluble in $CDCl_3$ to allow determination of their PMR spectra.

The alkoxy compounds reacted with thiols as follows:

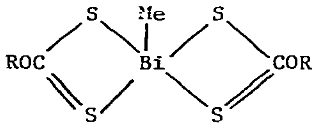
$$MeBi(OR)_2 + 2HSR' \rightarrow MeBi(SR')_2 + 2ROH$$

(where R' = $CHMe_2$, CMe_3, C_6H_{11}, or *o*-C_6H_4Me)

It was not necessary to isolate the alkoxy compound but simply to react $MeBiBr_2$ with an alkoxide (NaOMe) in alcohol and, after removal of the sodium bromide, to add a solution of the mercaptan. The thio compounds $MeBi(SR)_2$ were soluble in organic solvents, could be readily crystallized, and on the basis of mass spectral data were monomeric. The alkoxides $MeBi(OR)_2$ reacted with freshly distilled CS_2 to give xanthates according to the equation:

$$MeBi(OR)_2 + 2CS_2 \rightarrow MeBi(SC(S)OR)_2$$

The PMR spectra of the methyl protons attached to bismuth in the xanthates appeared at lower field (approximately 0.5 ppm) than with the methyl signal of compounds of the type $MeBi(SR)_2$. This result was attributed to a five-coordinate bismuth structure:



Mass spectral data on the mercaptides $MeBi(SR)_2$ gave the molecular ion for the monomeric form, but the molecular ion for the xanthates could not be obtained. The authors were unable to obtain useable mass spectral data for the alkoxy compounds $MeBi(OR)_2$.

A number of interesting compounds containing the Bi–Ge bond have been reported by Bochkarev and coworkers [11]. This paper is a continuation of previous studies from this laboratory on compounds of the type $[(C_6F_5)_3M]_nM'$, where M was Si, Ge, or Sn and M' was either a transition or a main-group element.

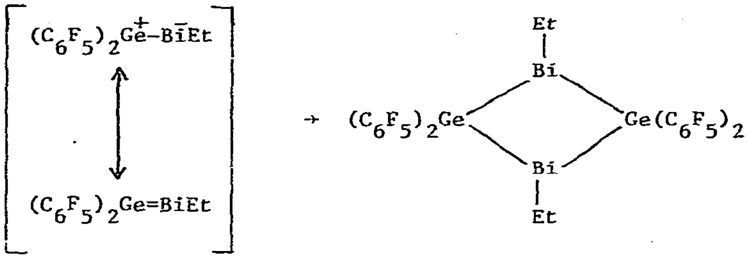
At 90–100°C tris(pentafluorophenyl)germane reacted with triethylbismuthine as follows:

$$(C_6F_5)_3GeH + Et_3Bi \rightarrow [(C_6F_5)_3Ge]BiEt_2 + EtH$$

The reaction was carried out in the absence of a solvent. The same reaction at 170°C gave $[(C_6F_5)_3Ge]_2BiEt$. The authors were unable to replace the third ethyl group and obtained only metallic Bi at higher temperatures. All attempts to obtain $[(C_6F_5)_3Ge]_3Bi$ by an exchange reaction between $(Et_3Ge)_3Bi$ and $(C_6F_5)_3GeBr$ were unsuccessful. Again metallic bismuth was obtained as one of the reaction products. The tin compound $(C_6F_5)_3SnH$ also reacted with Et_3Bi under milder conditions than the corresponding Ge compound, but the product was unstable and could not be isolated in pure form.

The reaction of $(C_6F_5)_2GeH_2$ and Et_3Bi was more complicated. On slow heating in the temperature range 60-105°C, only one ethyl group was evolved as ethane, but two ethyl groups were cleaved at higher temperatures. Rapid heating at 60–105°C, however, resulted in a violent reaction in which two moles of ethane were evolved. The product obtained in both cases was a dimer with the formula $[(C_6F_5)_2GeBiEt]_2$. This was a bright orange crystalline compound after recrystallization from benzene. In addition to the crystalline compound an undistillable liquid, believed to be a polymer of $[(C_6F_5)_2GeBiEt]_2$, was obtained. The material obtained by the loss of one mole of ethane could not be purified and characterized, but the presence of the compound $(C_6F_5)_2Ge(H)BiEt_2$ was suggested by the IR spectrum of the reaction mixture. The following reaction scheme was suggested to account for the results:

$$(C_6F_5)_2GeH_2 + Et_3Bi \rightarrow [(C_6F_5)_2Ge(H)BiEt_2] \longrightarrow$$



The stability of the new compounds was in the order:

$$[(C_6F_5)_2GeBiEt]_2 > [(C_6F_5)_3Ge]_2BiEt > (C_6F_5)_3GeBiEt_2$$

In all three compounds the Bi-Ge bond was cleaved by Br_2 and by HCl, but the stability of the dimeric compound $[(C_6F_5)_2GeBiEt]_2$ to HCl cleavage was surprising in that the cleavage reaction required three days to go to completion at room temperature. The presence of the C_6F_5 group in the two compounds $(C_6F_5)_3GeBiEt_2$ and $[(C_6F_5)_3Ge]_2BiEt$ does not increase the stability of the Ge-Bi bond as indicated by a comparison with the corresponding phenyl compounds.

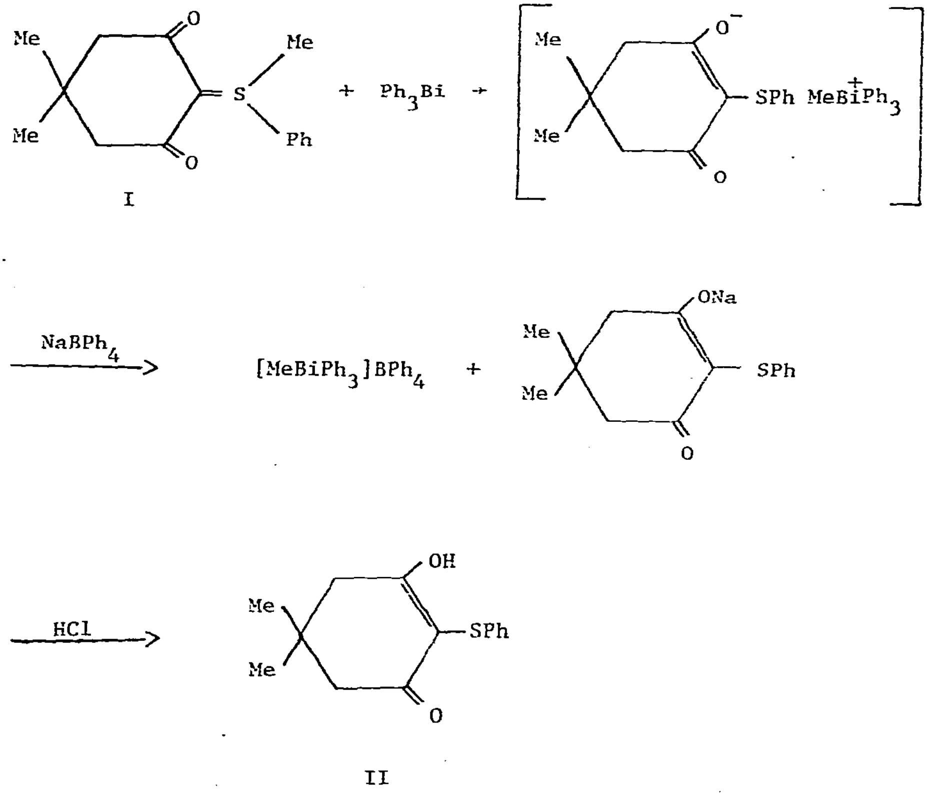
It was the expectation of the authors that compounds containing the Ge-Bi bond would display high reactivity in transmetallation reactions. However, $(C_6F_5)_3GeBiEt_2$ did not react with metallic Hg when the reaction was carried out at 20°C for six days. Under the same reaction conditions $[(C_6F_5)_3Ge]_2BiEt$ reacted as follows:

$$3[(C_6F_5)_3Ge]_2BiEt + 3Hg \rightarrow 3[(C_6F_5)_3Ge]_2Hg + 2Bi + BiEt_3$$

In an investigation devoted to the preparation of mixed triaryl compounds of the type Ar_3EXY, where E was As, Sb, or Bi, Bhattacharya and Singh [12] attempted to prepare $Ph_3Bi(CN)I$ by the reaction between Ph_3Bi and ICN. Instead they isolated Ph_2BiCN and PhI.

In a paper largely devoted to the fluorination of tertiary arsines and stibines, Ruppert and Bastian [13] have reported that Ph_3Bi can be readily fluorinated to Ph_3BiF_2 by a stream of fluorine diluted with argon. The Ph_3Bi was dissolved in $CFCl_3$, and the reaction was carried out at room temperature. Both ^{19}F and ^{13}C NMR were reported for the Ph_3BiF_2. The yield in the reaction was 78%.

Having previously demonstrated that trivalent phosphorus and arsenic compounds will dealkylate carbonyl-stabilized sulfonium ylids, Arbuzov and coworkers [14] have studied the reaction between Ph_3Sb or Ph_3Bi and the sulfur ylid I in the presence of $NaBPh_4$ at 200°C. The authors were unable to isolate either the stibonium or bismuthonium tetraphenylborates. However, they were able to isolate the cleavage product II of these salts which was taken as evidence that the reaction had proceeded in the following manner:



The 2-phenylthiodimedone II was found not to depress the melting point of an authentic sample.

The effect of the Group V triphenyl compounds Ph_3E, where E = P, As, Sb, or Bi, on poisoning of palladium-on-carbon hydrogenation of isoprene has been studied by Fujii and Bailar [15]. In the absence of a Group V triphenyl compound, isoprene was reduced by Pd-on-carbon to form 2-methyl-1-butene, 3-methyl-1-butene, and 2-methyl-2-butene with very little 2-methylbutane. The rate depended upon the hydrogen pressure but not the isoprene concentration. In the presence of Ph_3E the rate of hydrogenation was independent of the hydrogen pressure but was dependent on the isoprene concentration. As with unpoisoned catalysts, butenes were formed and there was comparatively little 2-methylbutane. However, Ph_3P and Ph_3As were more selective than either Ph_3Sb or Ph_3Bi as judged by the ratios between the various butenes formed. More 2-methylbutane was formed when the catalyst was poisoned with Ph_3Sb or Ph_3Bi. The authors suggested that the nature of the active site on the catalyst varied with the different Group V poisons used.

Razuvaev and coworkers [16] have studied the electronic emission spectra of a number of phenyl derivatives of Group IV (C, Si, Ge, Sn, or Pb) and Group V (N, P, As, Sb, or Bi) at 77 K in order to obtain information on donor-acceptor properties of complexes between oxygen and the organometallic species. The luminescence spectra of the organometallic compounds in *n*-hexane were first obtained at 77 K; the spectrum was then obtained after evacuation at 10^{-4} torr and alternate freezing and unfreezing. There was a marked increase in the intensity of the spectrum during this procedure which was reversed by the addition of oxygen. These results were indicative of the reversible formation of a complex between the organometallic compound and oxygen. The bimolecular quenching was found to obey the Stern-Volmer equation:

$$I_p/I_p^{O_2} = 1 + K_q[O_2]$$

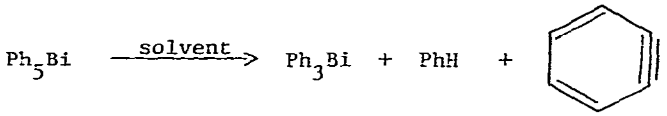
(where K_q was termed the quenching constant)

Values of this constant for the compound Ph_3E, where E = N, P, As, Sb, or Bi, were given and were found to decrease markedly in going from Ph_3N to Ph_3P and then increase slowly between Ph_3P and Ph_3Bi. These results were interpreted in terms of an electron donor-electron acceptor complex, and the variation in K_q was attributed to the amount of d_π-p_π interaction between the phenyl rings and the element E. Thus such interaction was absent where E = N and decreased markedly in the sequence P > As > Sb > Bi.

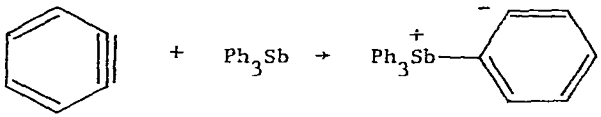
The photoinduced (UV) substitution of CO groups by the ligands ER_3 (where E = As or Sb and R = alkyl, aryl, or ethoxy) and Et_3Bi in the compounds $[Et_4N][V(CO)_6]$ and $[\eta^5\text{-}CpV(CO)_4]$ (Cp = the cyclopentadienyl group) has been studied by Talay and Rehder [17]. With Et_3Bi and $[Et_4N][V(CO)_6]$ the compound $[Et_4N][V(CO)_5BiEt_3]$ was obtained but with $[\eta^5\text{-}CpV(CO)_4]$ two compounds, $[\eta^5\text{-}CpV(CO)_3BiEt_3]$ and *cis*-$[\eta^5\text{-}CpV(CO)_2(BiEt_3)_2]$, were isolated. The IR spectra and ^{51}V NMR spectra of the compounds were given and compared with spectral values of the compounds previously obtained with the corresponding R_3P ligands. From the ^{51}V NMR chemical shift values a sequence of overall increasing ligand strengths in the order $Et_3Bi < R_3As < R_3P < R_3Sb$ was given.

Oxybis(triphenylbismuth) dichloride, $(Ph_3BiCl)_2O$, has been found to be a mild but effective reagent for the oxidation of primary and secondary alcohols to aldehydes and ketones, respectively [18]. The reagent was easily prepared by the hydrolysis of triphenylbismuth dichloride and was readily soluble in dichloromethane, chloroform, or benzene. It was particularly useful for the oxidation of allylic alcohols and was also applicable to the cleavage of 1,2-glycols. The carbonyl compounds formed in these reactions were readily separated from triphenylbismuthine by chromatography on silica gel or by heating the reaction mixture with acetic acid in order to keep the bismuth-containing substances in solution.

The decomposition of pentaphenylbismuth in pyridine, chloroform, or carbon tetrachloride at room temperature has been studied by Razuvaev and coworkers [19]. The decomposition was somewhat more rapid in pyridine solution than in the chlorinated solvents. In every case Ph_3Bi, PhH, and a resinous solid, believed to be formed by the polymerization of benzyne, were obtained:



The formation of benzyne was demonstrated by running the reaction in the presence of furan, *t*-butyl alcohol, or moist pyridine. With THF, the Diels-Alder addition product was isolated, with *t*-BuOH, *t*-BuOPh was obtained, while with moist pyridine the products included phenol and diphenyl ether. When the decomposition of Ph_5Bi was carried out in CCl_4 solution in the presence of Ph_3Sb, an organoantimony product was obtained which was believed to be a dipolar antimony compound (see Antimony section):



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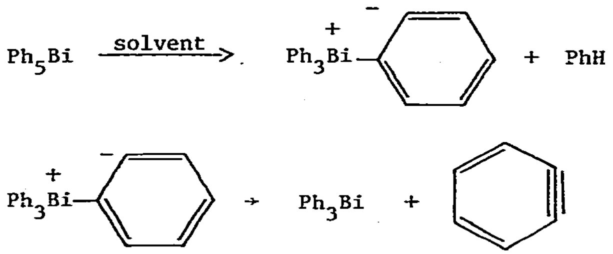
The authors postulated that pentaphenylbismuth decomposed in an organic solvent to give the dipolar bismuth compound which then underwent further decomposition to yield benzyne:



REFERENCES

1 M. Wieber, *Gmelin Handbuch der Anorganischen Chemie*, Bd. 47, *Bismut-Organische Verbindungen*, Springer-Verlag, Berlin, 1977.

2 S. Samaan, *Methoden der organischen Chemie (Houben-Weyl)* Bd. 13, Pt.8: *Metallorganische Verbindungen, As, Sb, Bi*, Georg Thieme Verlag, Stuttgart, 1978, pp. 590-626.

3 G. G. Long, L. D. Freedman, and G. O. Doak, *Kirk-Othmer Encycl. Chem. Technol., 3rd Ed.*, 3 (1978) 921.

4 C. A. McAuliffe and W. Lavason, *Phosphine, Arsine and Stibine Complexes of the Transition Elements*, Elsevier, Amsterdam, 1979. Both *Chem. Abstr.*, 89 (1978) 208395c, and various advertisements for this book indicated that the publication date was 1978.

5 W. Levason and C. A. McAuliffe, *Acc. Chem. Res.*, 11 (1978) 363.

6 J. L. Wardell, *Organomet. Chem.*, 6 (1978) 162.

7 A. J. Ashe, III, *Acc. Chem. Res.*, 11 (1978) 153.

8 R. E. Atkinson in S. Coffey, *ed. Rodd's Chemistry of Carbon Compounds, 2nd ed.*, Vol. *IV*, Pt. G: *Six-membered Heterocyclic Compounds With a Single Hetero-Atom from Group V of the Periodic Table*, Elsevier, Amsterdam, 1978, p. 114.

9 M. Wieber and U. Baudis, *Z. Anorg. Allg. Chem.*, 439 (1978) 134.

10 M. Wieber and U. Baudis, *Z. Anorg. Allg. Chem.*, 439 (1978) 139.

11 M. N. Bochkarev, N. I. Gur'ev, and G. A. Razuvaev, *J. Organomet. Chem.*, 162 (1978) 289.

12 S. N. Bhattacharya and M. Singh, *Indian J. Chem., Sect. A*, 16A (1978) 778.

13 I. Ruppert and V. Bastian, *Angew. Chem., Int. Ed. Engl.*, 17 (1978) 214.

14 B. A. Arbuzov, Yu. V. Belkin, N. A. Polezhaeva, and G. E. Buslaeva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1978) 1643.

15 Y. Fujii and J. C. Bailar, Jr., *J. Catal.*, 52 (1978) 342.

16 G. A. Razuvaev, A. N. Egorochkin, V. A. Kuznetsov, V. N. Glushakova, A. V. Shabanov, Yu. A. Alexandrov, and Yu. Yu. Baryshnikov, *J. Organomet. Chem.*, 148 (1978) 147.

17 R. Talay and D. Rehder, *Chem. Ber.*, 111 (1978) 1978.

18 D. H. R. Barton, J. P. Kitchin, and W. B. Motherwell, *J. Chem. Soc., Chem. Commun.*, (1978) 1099.

19 G. A. Razuvaev, N. A. Osanova, V. V. Sharutin, A. I. Sorokin, and I. E. Okhlopkova, *Dokl. Acad. Nauk SSSR*, 238 (1978) 361.