BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1979 *

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Except for the Annual Survey covering the year 1978, there were no review articles published in 1979 that were devoted only to organobismuth compounds. However, both organic antimony and bismuth compounds were discussed in considerable detail in Volume III of *Comprehensive Organic Chemistry*, a new six volume work on organic chemistry [1]. In a review on recent compounds of Group V by Sowerby [2], both organic and inorganic compounds were mentioned. A critical review of organic compounds of arsenic, antimony, and bismuth was published in 1978 [3].

In a continuing study of organobismuth compounds, Goel and Prasad [4] have prepared a series of diphenylbismuth halides and diphenylbismuth pseudohalides and have reported their IR and Raman spectra. The compounds prepared were Ph_2BiX, where X = Cl, Br, CN, SCN, SeCN, or N_3. The selenocyanate was unstable and decomposed on standing at room temperature, but the remaining compounds were stable. Their high melting points and low solubilities in both polar and non-polar organic solvents suggested that these compounds were associated in the solid state. Molecular weight determinations in acetone, however, indicated that all the compounds were monomolecular in this solvent. The compounds were also non-electrolytes in acetone solution. The IR and Raman spectra of diphenylbismuth cyanide were in accord with organotin and organolead compounds which are known to be polymeric in the solid state with bridging CN groups. Similar results were found for diphenylbismuth azide.

Raman and IR (to 200 cm^{-1}) spectra were reported and assignments of bands below 400 cm^{-1} were made. The Bi-Ph stretching frequencies in all of the compounds were similar to the Bi-Ph stretching frequencies

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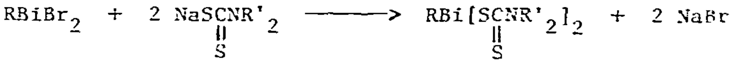
* Bismuth, Annual Survey covering the year 1978 see J. Organometal. Chem., 180 (1979) p. 143 - 151.

in Ph_3Bi and Ph_3BiX_2. The spectra of these compounds in solution were in accord with the presence of monomeric species, but there was a marked difference between the solution spectra and the solid state spectra, again suggesting association in the solid state.

Allman, Goel, and Prasad [5] have reported on compounds of bismuth in which the bismuth atom is either anionic or cationic. The two compounds $[Et_4N][Ph_2BiCl_2]$ and $[Et_4N][Ph_2BiBr_2]$ were prepared from Ph_2BiCl or Ph_2BiBr by the addition of Et_4NCl or Et_4NBr, respectively. From $[Et_4N][Ph_2BiCl_2]$, the three compounds $[Et_4N][Ph_2Bi(CN)_2]$, $[Et_4N][Ph_2Bi(SCN)_2]$, and $[Et_4N][Ph_2Bi(N_3)_2]$ were obtained. The reaction involved metathasis with NaCN, NaSCN, and NaN_3, respectively. The interesting compound $[Ph_2Bi(OAsPh_3)_2]ClO_4$ was obtained by the reaction between a solution of Ph_2BiClO_4 and two equivalents of Ph_3AsO. The Ph_2BiClO_4 was obtained in solution from Ph_2BiCl.and silver perchlorate and subsequent removal of the precipitated silver chloride by filtration. Conductometric studies demonstrated that all of the compounds were 1:1 electrolytes in acetone solution. Vibrational spectra, both IR and Raman, were carried out in the solid state and in solution. The Bi-O, Bi-X, and Bi-Ph stretching frequencies were assigned. It was suggested that in all of these compounds the bismuth atom was a distorted tetrahedron with C_{2v} skeletal symmetry.

Wieber and Basel [6] have reported on a series of compounds of the type $RBi[SC(S)NR'_2]_2$, where R was methyl or phenyl and R' was methyl or ethyl. The compounds in which R was Me or Ph and NR'_2 was a piperidinyl group were also prepared. The synthesis involved the reaction of the dibromobismuthine with the sodium salt of the dithiocarbamate:



$$RBiBr_2 + 2\ Na\underset{\overset{\|}{S}}{SC}NR'_2 \longrightarrow RBi[\underset{\overset{\|}{S}}{SC}NR'_2]_2 + 2\ NaBr$$

The new compounds were quite stable and possessed sharp melting points. The PMR spectra of the compounds were reported.

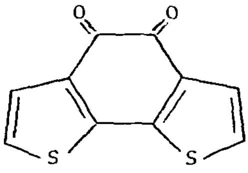
The crystal structure of methylbismuth bis(diethyldithiocarbamate) $MeBi[SC(S)NEt_2]_2$ has been reported by Burschka and Wieber [7]. The compound was monomeric in benzene solution but in the crystalline state was a dimer with Bi-S bridges. Each bismuth atom was a slightly distorted pentagonal pyramid. The free electron pair on each bismuth atom was presumably opposite the apical carbon atom of the methyl group.

In an attempt to prepare the compounds $(C_6Cl_5)_3E$, where E = As, Sb, or Bi, three molecular equivalents of C_6Cl_5Li were allowed to react with $AsCl_3$, $SbCl_3$, or $BiCl_3$, respectively [8]. With $SbCl_3$ and $BiCl_3$, the desired $(C_6Cl_5)_3Sb$ and $(C_6Cl_5)_3Bi$ were obtained, but with $AsCl_3$, only $(C_6Cl_5)_2AsCl$ could be isolated regardless of the amount of C_6Cl_5Li used in the reaction. In contrast to $(C_6Cl_5)_3Sb$, which was oxidized by Cl_2 or Br_2 to the corresponding $(C_6Cl_5)_3SbCl_2$ and $(C_6Cl_5)_3SbBr_2$, the C-Bi bond in $(C_6Cl_5)_3Bi$ was cleaved by Cl_2 or Br_2 to give unidentified decomposition products. All of the compounds were stable in the air and were non-electrolyts in nitromethane solution.

Juhlke and coworkers [9] have described an interesting new method of preparing metal alkyls by cocondensing a metal vapor and an alkyl radical on a cold finger at -196°C. The alkyl radicals were generated in a radio frequency glow discharge apparatus which was described. The radicals generated were $CH_3\cdot$, $CF_3\cdot$ and $SiF_3\cdot$, obtained from C_2H_6, C_2F_6, and Si_2F_6, respectively. The bismuth compounds prepared were $(CF_3)_3Bi$ and Me_3Bi in 31% and 13% yields, respectively.

In a patent devoted to the preparation of organometallic compounds by the uncatalysed addition of metallic hydrides to olefins, the preparation of organobismuth compounds was mentioned [10].

Several organometallic free radicals containing Sb(III) and Bi(III) have been prepared by the high-temperature reactions of SbF_3, $SbCl_3$, or Ph_3Bi with phenanthraquinone or with the dione I [11]. The reactions were carried out by heating the antimony or bismuth compound in diglyme solution with the dione in the cavity of an ESR spectrometer. In every case the dominant feature of the ESR spectrum was hyperfine coupling to the metal nucleus. In the spectra of the bismuth-containing species, the hyperfine decet showed a pronounced variation in line width which was attributed to nuclear quadrupole relaxation. The ESR spectral results were assigned to the radicals II and III:



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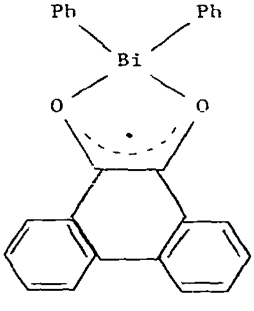
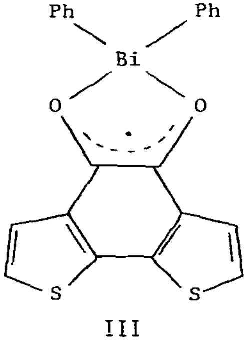


II



III

In a paper largely devoted to the preparation of bismuth trialkanoates $Bi(O_2CR)_3$, it was reported that Ph_3Bi underwent reaction with $ClCH_2CO_2H$ to yield $Bi(O_2CCH_2Cl)_3$ in 90% yield [12]. This same compound was also prepared from bismuth oxide Bi_2O_3 and $ClCH_2CO_2H$. Bismuth oxide was also used in the preparation of other alkanoates $Bi(O_2CR)_3$ (where R = H, Me, Me_2CHCH_2, or *n*-C_5H_{11}). An attempt was then made to convert the bismuth trialkanoates to a triarylbismuthine by reaction with either a tetraarylstannane or a dialkyldiarylstannane. This type of reaction had been successfully used with alkanoates of mercury, thallium, or lead. The reaction was not successful, however, with the bismuth trialkanoates. On the other hand, it was found that bismuth tribromide could be arylated to phenylbismuth dibromide by heating with tetraphenylstannane or with diethyldiphenylstannane:

$$2BiBr_3 + Et_2Ph_2Sn \longrightarrow 2PhBiBr_2 + Et_2SnBr_2$$

In the above reaction, the yield of phenylbismuth dibromide was 94%.

Unlike triphenylarsine and triphenylstibine, which have been found to react with tetramethyl-1,2-dioxetane to give 2,2-dihydro-4,4,5,5-tetramethyl-2,2,2-triphenyl-1,3,2-dioxarsolane and -stibolane, respectively, the interaction of triphenylbismuthine and the same dioxetane slowly yielded two moles of acetone [13].

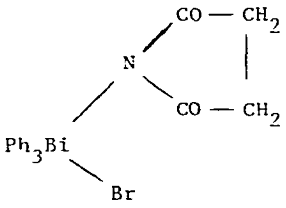
The degree to which ns_σ and nd_π orbitals of the Group V elements, P, As, Sb, and Bi, contribute to the ground state in compounds where the Group V element is a ligand to a transition element has been the subject of considerable controversy. Carty and coworkers [14] have now reported on X-ray crystallographic studies of compounds of the type $[Cr(CO)_5(EPh_3)]$ (where E is As, Sb, or Bi) and have compared bond angles and bond distances in these compounds with those of the previously reported phosphorus compound $[Cr(CO)_5(PPh_3)]$. There was a marked decrease in the C-E-C average bond angle in going from phosphorus to bismuth and a parallel increase in the Cr-E-C angle. The authors concluded that the Bi-Cr bond had greater *s*-character than the P-Cr or As-Cr bond. The authors also concluded that the Cr-CO bond distances (*trans* to E) suggested an increase in structural *trans*-influence down the series $PPh_3 < AsPh_3 < SbPh_3 \sim BiPh_3$.

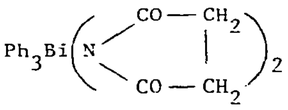
In a paper devoted to the crystal structure of tri-*p*-tolylstibine [15], a comparison was made of the covalent radii of heteroatoms in triphenyl derivatives of Group V compounds including triphenylbismuthine. The change in the valence angle C-E-C in going from phosphorus to bismuth and the change in the long wavelength band in the UV spectra were also mentioned.

The mean bond dissociation energy <D>(E-R), where R is Me, Et, or Ph and E is a Group V element (N, P, As, Sb, or Bi), is quite erratic in going from nitrogen to bismuth. In contrast, the tetra-substituted Group IV elements give a smooth decline in descending the periodic table. Steele [16] believes that the older work on standard enthalpies of formation of group V compounds, obtained by static bomb calorimetry, is in error, and he has set out to redetermine these thermodynamic quantitites. The present paper deals with the energy of combustion of triphenylbismuthine in a previously described rotating bomb calorimeter. Values for the standard molar energy of combustion (ΔE_c^o), standard molar enthaply of combustion (ΔH_c^o), and the standard molar enthalpy of formation (ΔH_f^o) were given. The mean gas-phase bond dissociation energy <D>(Ph-Bi) was calculated to be 193.9 ± 10.8 kJ mol^{-1}. A plot of bond dissocation energies for the triphenyl compounds Ph_3N to Ph_3Bi showed a smooth linear decrease as one descends the periodic table except for the value of <D>(Ph-Sb) which the author believes is in error due to the presence of various oxides of antimony in the combustion products when the combustion is carried out in a static bomb.

The hydrogen bond strengths of a series of alcohols have been studied by gas chromatography over squalene containing Group V compounds, Ph_3E, where E was P, As, Sb, or Bi [17]. The hydrogen bond strengths decreased in the order P>As>Sb>Bi. This order was supported by NMR data for complexes of Ph_3E with 2,6-$(Me_3C)_2C_6H_3OH$. The results were interpreted in terms of p_π conjugation in the Ph_3E compounds.

The following new bismuth compounds have been reported by Dahlmann and Winsel [18]:





The first was formed from triphenylbismuthine and N-bromosuccinimide, the second from triphenylbismuth dibromide and silver succinimide. Both PMR and IR (carbonyl stretching frequencies) data were reported. The paper is discussed in considerable detail in the Antimony section.

Barton and coworkers [19] have recently shown that μ-oxo-bis(chlorotriphenylbismuth) is a very effective reagent for the oxidation of the hydroxy group, especially in allylic and benzylic alcohols. The work has now been extended to other Bi(V) organic compounds [20]. By allowing two triaryl compounds Ar_3BiCl_2 and Ar'_3BiCl_2 to compete in the oxidation of a limited amount of allylic alcohol, it was demonstrated that the rate of oxidation increased in the order (p-$MeC_6H_5)_3BiCl_2$ < Ph_3BiCl_2 < (p-$ClC_6H_5)_3BiCl_2$, in a ratio of approximately 1:1.5:6. They also studied the effect of the leaving group X in compounds Ph_3BiX_2, where X was Cl, Br, or NO_3. However, under the standard reactions conditions used, namely in the presence of carbonate or bicarbonate ion, no difference was found with Cl, Br, or NO_3. When pyridine or collidine was used as the base, no oxidation of the alcohol occurred. From these results, the authors concluded that Ph_3BiCO_3 was the active oxidizing agent. Accordingly, Ph_3BiCO_3 was prepared and proved to be an efficient oxidizing agent, not only for allylic alcohols, but for 1,2-diols, hydrazones, and mercaptans. For example, geraniol was oxidized to geranial in 95% yield at room temperature. The reagent was remarkably selective. Thus cholest-4-en-3β-ol (1 equivalent) was oxidized to cholest-4-en-3-one in the presence of one equivalent of thiophenol, without oxidation of the thiol. In addition to Ph_3BiCO_3, the authors found that esters such as $Ph_3Bi(OAc)_2$, $Ph_3Bi(OCOPh)_2$, and $Ph_3Bi(OCOCF_3)_2$, in the presence of strong base such as tetramethylguanidine, were also effective oxidizing agents.

REFERENCES

1 R. C. Poller in D. N. Jones, ed., *Comprehensive Organic Chemistry*, Vol. 3, Pergamon, Oxford, 1979, pp. 1111-1125.

2 D. B. Sowerby, *Coord. Chem. Rev.*, 30 (1979) 234.

3 F. Bickelhaupt and H. Vermeer, *Method. Chim.*, 7 (Part B) (1978) 549.

4 R. G. Goel and H. S. Prasad, *Spectrochim. Acta, Part A*, 35A (1979) 339.

5 T. Allman, R. G. Goel, and H. S. Prasad, *J. Organomet. Chem.*, 166 (1979) 365.

6 M. Wieber and A. Basel, *Z. Anorg. Allg. Chem.*, 448 (1979) 89.

7 C. Burschka and M. Wieber, *Z. Naturforsch. B: Anorg. Chem., Org. Chem.*, 34B (1979) 1037.

8 A. Otero and P. Royo, *J. Organomet. Chem.*, 171 (1979) 333.

9 T. J. Juhlke, R. W. Braun, T. R. Bierschenk, and R. J. Lagow, *J. Amer. Chem. Soc.*, 101 (1979) 3229.

10 A. Ross (M and T Chemicals Inc.) Can. Pat. 1,057,296; *Chem. Abstr.*, 91 (1979) 140999m.

11 A. Alberti and A. Hudson, *J. Organomet. Chem.*, 182 (1979) C49.

12 N. I. Anishchenko, E. M. Panov, O. P. Syutkina, and K. A. Kocheshkov, *Zh. Obshch. Khim* 49 (1979) 1185.

13 A. L. Baumstark, M. E. Landis, and P. J. Brooks, *J. Org. Chem.*, 44 (1979) 4251.

14 A. J. Carty, N. J. Taylor, A. W. Coleman, and M. F. Lappert, *J. Chem. Soc., Chem. Commun.*, (1979) 639.

15 A. N. Sobolev, I. P. Romm, V. K. Belsky, and E. N. Guryanova, *J. Organomet. Chem.*, 179 (1979) 153.

16 W. V. Steele, *J. Chem. Thermodyn.*, 11 (1979) 187.

17 V. K. Pogorelyi, V. I. Bogillo, G. V. Filonenko, and A. E. Lutskii, *Teor. Eksp. Khim.*, 15 (1979) 175; *Chem. Abstr.*, 91 (1979) 38700v.

18 J. Dahlmann and K. Winsel, *J. Prakt Chem.*, 321 (1979) 370.

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

20 D. H. R. Barton, D. J. Lester, W. B. Motherwell, and M. T. B. Papoula, *J. Chem. Soc., Chem. Commun.*, (1979) 705.