BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1985

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In addition to our Annual Survey covering the year 1983, several review articles dealing with organobismuth compounds have appeared in 1985. The annual survey of organometallic compounds [1] and the *Annual Reports on the Progress of Chemistry* [2], both published by the Royal Society of Chemistry, included short sections on organobismuth compounds. Organic compounds containing Bi-Si bonds were described in an annual survey of the "silicon group" [3]. The use of organic compounds of Bi(V) for the oxidation of alcohols has been reviewed by Barton and coworkers [4]. Much of the pioneer work on the use of organic Bi(V) compounds in organic synthesis originated with this research group. The structures, dipole moments, and electronic spectra of compounds of the type Ar_3E, where E was N, P, As, Sb, and Bi, have been reviewed in the Russian chemical literature [5]. In a review article on metal-ligand bond energies in organometallic compounds [6], bond dissociation energies of the Bi-H, Bi-Me, Bi-Et and Bi-Ph bonds were given, and these values were then plotted against the energy of atomization values for E-H, E-Me, E-Et, and E-Ph compounds, where E was P, As, Sb, and Bi. In general, bond energies increased as the energy of atomization increased, not only for the main group elements but also for the transition group elements.

Organobismuth compounds were briefly discussed in a review article on organometallic compounds of the main group elements, published in *Coordination Chemistry Reviews* [7]. This article covered only papers published in 1983. Scherer [8] has reviewed multiply-bonded compounds of the Group V elements, P, As, Sb, and Bi, with coordination numbers of 1, 2, or 3. The author points out that many of these types of compounds (Group V compounds with multiple bonds) were long thought to be incapable of being prepared, and he predicts that more such compounds will be discovered.

Ashe and coworkers have previously reported that 2,2',5,5'-dimethylbistibole (I) was markedly thermochromic, whereas the corresponding arsenic compound was not. Ashe and Drone [9] have now reported the

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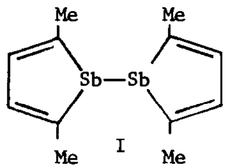
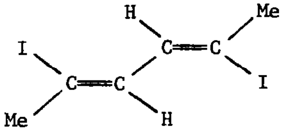
*Previous survey see J.Organomet.Chem., 298(1986)67-73.


I

synthesis of the bismuth analog of I. The method used for preparing the stibole could not be used for the preparation of the bismuth compound because of the failure of diiodo(phenyl)bismuthine to undergo exchange with 1,1-dibutyl-2,5-dimethylstannole to yield 1-phenyl-2,5-dimethylbismole. A similar reaction with diiodo(phenyl)stibine was a key step in the preparation of the bistibole. It was found, however, that 1,1-dibutyl-2,5-dimethylstannole, when treated with iodine, gave


II

2(Z),5(Z)-diiodohexa-2,4-diene (II). When II was treated with butyllithium, a 1,4-dilithiobutadiene was obtained. This latter compound proved to be an effective reagent for preparing five-membered ring heterocycles. With diiodo(phenyl)bismuthine it gave the desired 1-phenyl-2,5-dimethylbismole. This new bismole was characterized by PMR and mass spectromety. When treated with sodium in liquid ammonia the phenyl group was cleaved to yield the 1-sodio derivative which gave the desired 2,2',5,5'-tetramethylbibismole on treatment with 1,2-dichloroethane. The bibismole was characterized by NMR (^1H and ^{13}C) and mass spectrometry, and by elemental analysis. It was an air-sensitive solid which could be stored in the solid state at room temperature. It was, like the corresponding bistibole, thermochromic. Crystals of the bibismole were black with a greenish luster but a solution in cyclohexane was red. The reflectance spectrum showed a broad absorption maximum centered at 690 nm. In cyclohexane solution λ_{max} = 230 nm (ε 14600) with a shoulder at 320 nm and a low intensity tail out to 700 nm.

Since both dibismuthines, R_2BiBiR_2, and ditellurides show thermochromic effects and give different colors in solution than in the solid state, du Mont and Severengiz [10] decided to investigate a compound containing a Bi-Te bond. The compound prepared was $Pr_2BiTeC_6H_4Me$-*p*. It was prepared in an argon atmosphere as follows:

$$Pr_2BiBiPr_2 + (p\text{-}MeC_6H_4)_2Te \xrightarrow{Ar} 2\ Pr_2BiTeC_6H_4\text{-}p$$

The PMR spectrum of the new compound was consistent with the above structure. The ^{125}Te NMR signal was shifted 385 ppm to higher field than in the ditelluride. The compound was also characterized by its mass spectrum and by elemental analysis. At room temperature the new compound was a red-brown liquid; solutions in benzene, toluene, or pentane were orange. On cooling the compound the thermochromic effect was as small as that previously observed for the corresponding Sb-Te compound. The compound was stable when kept in an inert atmosphere, but in solution decomposition occurred at 25°C. In the light, the compound decomposed rapidly with formation of the ditelluride.

Cowley and coworkers [11] have previously reported the preparation of compounds containing P=P, P=As, and As=As bonds, but attempts to prepare compounds with Sb=Sb and Bi=Bi bonds were not successful. The authors have now attempted to obtain compounds with Bi=Bi bonds by the attachment of transition-metal fragments to the bismuth atoms [12]. They first prepared the compound $(Me_3Si)_2CHBiCl_2$ by the reaction between $(Me_3Si)_2CHMgCl$ and $BiCl_3$. The product was a yellow oil, bp 108-110°C/10^{-4} torr. It was not further characterized. The dichlorobismuthine was treated with $Na_2[W(CO)_5]$ in THF solution to yield two compounds, $[\{W(CO)_5\}_3(\mu_3-\eta^2-Bi_2)]$ and $[W_2(CO)_8(\mu_2-\eta^2-Bi)(\mu-Bi)MeW(CO)_5]$. The compounds were separated by column chromatography and recrystallized from organic solvents. The first of these compounds had been previously prepared by Huttner and coworkers [13] from $BiCl_3$ and $[W(CO)_5]^{2-}$, and was known to contain a Bi-Bi bond. The structure of the second compound was determined by X-ray diffraction and was also shown to possess a Bi-Bi bond. The authors speculated that the methyl group was obtained by successive Cl^- attacks at a $(Me_3Si)_2C(H)Bi$ moiety. The presence of the Me-Bi group was confirmed by IR spectroscopy.

In continuation of their research on organobismuthdithiocarbamates and -xanthates, Wieber and coworkers [14] have investigated the reactions of the metal carbonyl compound $[Cp(CO)_2Fe]_2$ (where Cp = the cyclopentadienyl group) with compounds of the type $RBiY_2$, where R = Me or Ph and Y = $SC(S)NEt_2$ or $SC(S)OMe$. The reactions took an unexpected course with cleavage of the Bi-C bond, rather than substitution of a carbonyl group:

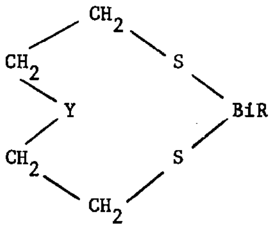
$$[Cp(CO)_2Fe]_2 \ + \ 2\ RBiY_2 \longrightarrow 2\ Cp(CO)_2FeBiY_2 \ + \ R_2$$

The authors then found that even simple bismuth compounds such as $MeBiBr_2$ reacted in a similar manner:

$$[Cp(CO)_2Fe]_2 \ + \ 2\ MeBiBr_2 \longrightarrow 2\ Cp(CO)_2FeBiBr_2 \ + \ MeMe$$

The IR and NMR spectra of the new bismuth compounds (which do not contain a Bi-C bond) were reported, and the structure of one compound, $Cp(CO)_2FeBi[SC(S)NEt_2]_2$, was determined by X-ray diffraction.

In continuation of previous work on 8-membered heterocyclic rings containing such elements as Ge, Sn, Pb, As, or Sb, Dräger and Schmidt [15] have now prepared four new 8-membered heterocyclic ring compounds in which Bi was the metal. These compounds were of the type:



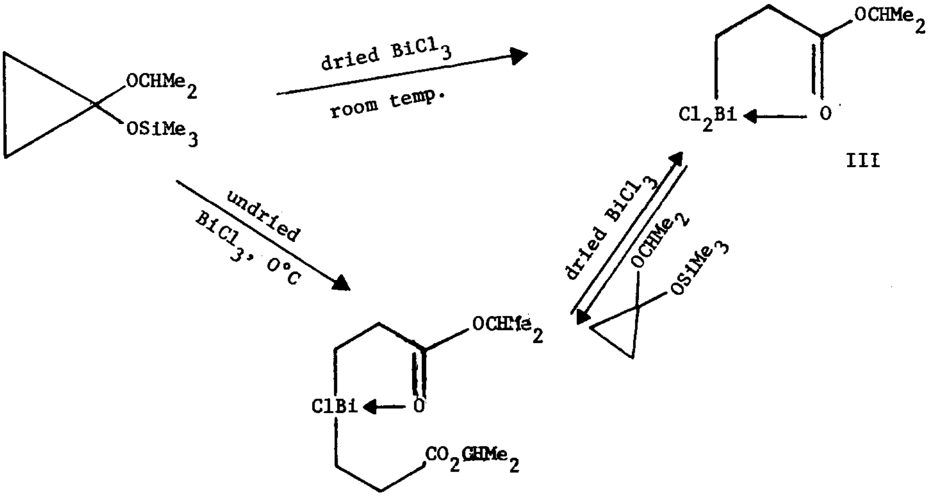
(where Y was O or S, and R was Me or Ph).

They were prepared by the condensation of the appropriate diethoxybismuthine $RBi(OEt)_2$ with the appropriate dithiol. The phenyl compounds were prepared at -40°C and the methyl compounds at room temperature. The diethoxybismuthines were not isolated but prepared and used *in situ*. The new bismocanes were yellow, crystalline, light-sensitive compounds. Their decomposition temperatures were determined thermogravimetrically. All of the compounds melted with decomposition at temperatures ranging from 125-150°C. They were characterized by mass spectrometry, IR and Raman spectroscopy, and ^{13}C NMR spectrometry. In the mass spectra all of the compounds gave molecular ions; the percentages of molecular ions were considerably larger for the two compounds where Y was oxygen (18 and 22%) than where Y was sulfur (2 and 4%).

The crystal structure of one compound (Y = O, R = Ph) was determined by X-ray diffraction. The 8-membered ring possessed the chair-chair configuration. Besides the three covalent bonds (two Bi-S and one Bi-C) there was a transannular Bi-O bond and two intermolecular Bi-S contacts. This resulted in the Bi atom attaining a ψ-monocapped octahedral coordination sphere. These polyhedra were connected by sharing two different edges, and the crystal structure exhibited double chains of molecules.

The reaction of 1-isopropoxy-1-trimethylsiloxycyclopropane with $SbCl_5$ to form a chelate-ring compound containing an Sb-C bond has been described in the Antimony section. The authors, Nakamura and coworkers

[16], also described the formation of two compounds, both of which contained Bi-C bonds. These were made from the same cyclopropane compound by reaction with $BiCl_3$. One compound, similar to the Sb compound, was obtained when $BiCl_3$, previously heated at 300°C *in vacuo*, was treated, at -60°C in $CDCl_3$ solution, with 1-isopropoxy-1-trimethylsiloxycyclopropane. The reaction mixture was stirred at room temperature for 1.5 hours under untrasonic irradiation, and the crystalline product III was recrystallized from benzene. It was characterized by IR spectroscopy, ^1H and ^{13}C NMR spectrometry, and by elemental analysis. The mp of III was 144-145°C. If the same reaction was carried out with $BiCl_3$ which had not been previously heated *in vacuo*, an oily dialkyl bismuth compound IV was first formed. The oily product decomposed on heating and could not be purified by distillation *in vacuo*. If the reaction of the siloxycyclopropane compound with $BiCl_3$ (not previously heated *in vacuo*) was allowed to continue for 8 hours, only the crystalline product III was obtained. Both reactions were reversible; *i.e.* III could be converted into IV by treating it with 1-isopropoxy-1-trimethylsiloxycyclopropane at room temperature, and IV could be converted into III by treatment with dried $BiCl_3$. The formation of III and IV are summarized in the following equations:



III

IV

The IR spectrum of the oily product IV showed two carbonyl stretching bands of equal intensity at 1660 and 1708 cm^{-1}. These data confirmed the monochelated structure assigned to IV.

A number of organometallic azides of the type R_2EN_3 (R=Me, E=Sb or Bi; R = Et, E=Sb) and Re_3EN_3 (R=Me, E=Pb) have been prepared and their PMR, IR and Raman spectra reported [17]. The crystal structures of several of these compounds were determined by X-ray diffraction. The bismuth compound was prepared by means of the following reaction:

$$Me_2BiN(SiMe_3)_2 + HN_3 \xrightarrow[0°C]{Et_2O} Me_2BiN_3 + HN(SiMe_3)_2$$

The crystal structure of the compounds showed that the metal atoms were linked *via* the α-N atoms of the azido groups to form endless zig-zag chains. In the Bi compound the Bi-N distances were equal, in contrast to Me_2SbN_3 where the Sb-N distances alternated with two different lengths.

Wieber and coworkers [18] have prepared a series of antimony and bismuth compounds of the type $RE(SR')_2$, where R was Me or Ph, R' was a heterocyclic nitrogen group, and E was Sb or Bi. The bismuth compounds were obtained by means of the following reaction:

$$RBiBr_2 + 2\ NaSR' \longrightarrow RBi(SR')_2 + 2\ NaBr$$

(where R was Me or Ph, NaSR' was either sodium pyrimidine-2-thiolate or sodium 1-methylimidazole-2-thiolate; and where R was Ph and NaSR' was sodium 1-phenyl-1,2,3,4-tetrazole-2-thiolate)

The products were recrystallized from ethanol and were characterized by PMR spectroscopy, differential thermal analysis, and elemental analysis.

Trialkylbismuthines containing two different alkyl groups are relatively few in number. Similarly, mixed alkyl-arylbismuthines are but little known. In 1985, however, two different research groups have reported the preparation of a number of compounds of these two types. Wieber and Sauer [19] have prepared trialkyl compounds of the type Me_2BiR, where R was Et, Pr, Bu, allyl, or isopropyl. They were obtained from Me_2BiNa and the appropriate alkyl bromide in liquid ammonia solution:

$$Me_2BiNa + RBr \longrightarrow Me_2BiR + NaBr$$

The yields varied from 70-90%. The new bismuthines were obtained as liquids which were spontaneously inflammable in air. They could be distilled at low temperatures *in vacuo*. The compound $Me_2CHBiMe_2$ was stable when heated to 100°C for 3-4 hours, but the other compounds started to decompose when heated to 50-60°C. In solution at room temperature some disproportionation occurred after 1-2 days and was 60-80% complete after 14 days:

$$2\ Me_2BiBr \rightleftharpoons MeBiBr_2 + Me_3Bi$$

The Me_2BiNa was prepared from Me_2BiBr and sodium in liquid ammonia solution. The resulting dark-red solution faded on standing, and from the solution Me_4Bi_2 could be obtained in about 60% yield.

From methylene chloride and Me_2BiNa the compound $(Me_2Bi)_2CH_2$ was obtained as an orange-red liquid which could be distilled *in vacuo*. Above 100°C, or after 3-4 weeks at -30°C, or after 3-4 days in CH_2Cl_2 solution, the $(Me_2Bi)_2CH_2$ began to decompose into a dark-colored polymer. It reacted with RLi (R = Bu or Ph) with cleavage of the Bi-C bond:

$$(Me_2Bi)_2CH_2 + RLi \longrightarrow Me_2BiR + Me_2BiCH_2Li$$

The reaction of Me_2BiNa with aryl bromides to yield mixed alkyl-aryl bismuthines proceeded only to about 3-5%. The principal product of the reaction was Me_4Bi_2:

$$Me_2BiNa + ArBr \xrightarrow{NH_3} Me_2BiBr + ArNa$$

$$Me_2BiBr + ArNa + Me_2BiNa + NH_3 \longrightarrow Me_4Bi_2 + ArH + NaBr + NaNH_2$$

(where Ar was p-MeC_6H_4, p-$MeOC_6H_4$, or 2,4,6-$Me_3C_6H_2$)

The desired bismuthines, however, were readily prepared from Me_2BiBr, lithium metal, and excess aryl bromide:

$$Me_2BiBr + 2\ Li + ArBr \longrightarrow Me_2BiAr + 2\ LiBr$$

The bismuthines could be distilled *in vacuo*, but even at room temperature some disproportionation occurred after standing for one day:

$$2\ Me_2BiAr \rightleftharpoons MeBiAr_2 + Me_3Bi$$

The diaryl compounds formed in the above reaction could be obtained in a pure state. The Me_2BiAr compounds were allowed to stand for 3-4 weeks at room temperature, then warmed to 90°C in a stream of nitrogen, and finally cooled to room temperature. The resulting $MeBiAr_2$ compounds were obtained as solids in quantitative yields. All of the new compounds were characterized by PMR and mass spectra and by elemental analysis.

In addition to the above paper describing the preparation of aryldimethylbismuthines, Kauffmann and Steinseifer [20] have described the preparation of a series of new alkyldiarylbismuthines. The only previous attempt to prepare compounds of this type had resulted in disproportionation:

$$Ph_2BiBr \xrightarrow{EtMgBr} Ph_3Bi + Et_3Bi$$

In the present paper chlorodiphenylbismuthine and an alkyllithium compound were allowed to react at low temperatures:

$$Ph_2BiCl + RLi \xrightarrow[-70°C]{Et_2O} Ph_2BiR + LiCl$$

(R = Me, Et, Bu, n-C_5H_{11}, n-C_6H_{13}, or cyclopentyl)

The yields varied between 61 and 92%. The compounds were purified by vacuum distillation. In every case a forerun was obtained which appeared to be a mixture of the dialkylphenyl- and alkyldiphenylbismuthines, as judged by the PMR spectrum of the forerun. The authors believed that the dialkylphenyl compounds were produced in the following manner:

$$Ph_2BiR + RLi \rightleftharpoons [Ph_2BiR_2]Li \rightleftharpoons PhBiR_2 + PhLi$$

They suggested that the previous failure to obtain alkyldiphenylbismuthines was due to a similar type of reaction rather than to disproportionation:

$$Ph_2BiEt + PhMgBr \rightleftharpoons [Ph_3BiEt]MgBr \rightleftharpoons Ph_3Bi + Et_3Bi$$

The alkyldiphenylbismuthines obtained in the present study were unpleasant smelling liquids, which were characterized by NMR (^{13}C and ^1H) and IR spectra, as well as by mass spectra and elemental analysis. Although the compounds were air-sensitive, they were surprisingly stable to heat, decomposing only when heated to ∿170°C. In the PMR spectra of these compounds the chemical shifts of the β-protons of the alkyl groups were at lower fields than expected. Thus, in the spectrum of Ph_2BiBu, the δ values for the α,β,γ and δ protons were (in ppm referred to TMS) 2.29, 2.10, 1.42 and 0.95, respectively. This effect was not found for the corresponding As or Sb compounds. However, the chemical shifts of the α and β protons in $(CH_3CH_2)_4Pb$ were approximately equal. The authors attributed these results to the inductive effect of the bismuth (or lead) atom. A similar result was noted for the β- and γ-carbon atoms in the ^{13}C NMR spectra. The alkyl groups in the alkyldiphenylbismuthines were readily cleaved by halogens. Thus, the addition of one equivalent of bromine to one equivalent of Ph_2BiR in dichloromethane at -70°C gave the corresponding bromoalkane and bromodiphenylbismuthine. Small amounts of bromobenzene were also formed. When the same experiments were carried out with sulfuryl chloride, the chloroalkane and chlorodiphenylbismuthine were obtained. The use of sulfuryl chloride resulted in less cleavage of the phenyl-bismuth bond, whereas the use of chlorine (in ether solution) gave considerably more cleavage of the phenyl-bismuth bond.

The compound $(Ph_2Bi)_2CH_2$ has been synthesized by Kauffmann and coworkers [21] from bromo- or iododiphenylbismuthine:

$$Ph_2BiX + 2\ Na \xrightarrow[NH_3]{liquid} Ph_2BiNa + NaX$$

$$2\ Ph_2BiNa + CH_2Cl_2 \longrightarrow (Ph_2Bi)_2CH_2 + 2\ NaCl$$

(where X = Br or I)

The compound was obtained in 53% yield after recrystallization from petroleum ether. It was characterized by NMR (^1H and ^{13}C) and IR spectroscopy, mass spectroscopy, and elemental analysis. It was sensitive to oxygen. When treated with one molar equivalent of phenyllithium in THF it was converted to the methyllithium derivative:

$$(Ph_2Bi)_2CH_2 + PhLi \longrightarrow Ph_2BiCH_2Li + Ph_3Bi$$

The lithium compound was not isolated but was converted to the methyldiphenylbismuthine by water or methanol. The yield of the latter bismuthine was 70-72%. The compound Ph_2BiCH_2Li was considerably less stable than the corresponding As or Sb compound. The half-life was estimated to be 34 min. in THF solution at 25°C. The lithium compound reacted with aldehydes or ketones as follows:

$$Ph_2BiCH_2Li + R^1R^2CO \longrightarrow Ph_2BiCH_2C(OLi)R^1R^2$$

(where $R^1 = H$, $R^2 = Ph$ or C_6H_{13}; $R^1 = R^2 = Ph$)

The adducts were treated with $HClO_4$ to yield the corresponding alkenes:

$$Ph_2BiCH_2C(OLi)R^1R^2 \xrightarrow{HClO_4} Ph_2BiOH + H_2C{=}CR^1R^2$$

Hydrolysis of the benzophenone adduct gave the interesting bismuth compound $Ph_2BiCH_2C(OH)Ph_2$. This compound was characterized, after recrystallization from petroleum ether, by PMR and mass spectroscopy and by elemental analysis. It reacted with $HClO_4$ to yield $Ph_2C{=}CH_2$ in 61% yield, and with SiO_2 suspended in $CHCl_3$ (at room temperature for 24 hours) to yield the same product in 16% yield.

Al-Jabar and Massey [22] have prepared a number of perfluoro-1,6-disubstituted triptycenes which contained P, As, Sb, or Bi in the 1,6-positions. They were all obtained from 1,2-dibromobenzene which was converted to 1-bromo-2-lithiobenzene by treatment with BuLi at -78°C. Subsequent treatment with the appropriate halide ($BiCl_3$ in the case of the bismuth compound) gave the 1,6-disubstituted triptycene. The structure of the bismuth compound was confirmed by elemental analysis, ^{13}C NMR and IR spectra, and by accurate mass spectrum measurements. Thus, for the Bi compound the calculated molecular ion value was 861.942 and the observed value was 861.9425. Chemical shifts for the C(1), C(2), and C(3) atoms were 157.2, 150.8, and 140.2 ppm, respectively, relative to TMS. The mp of the bismuth compound was 314°C without decomposition but with partial sublimation. All of the triptycene compounds retained solvent of crystallization tenaciously. This was particularly true of the bismuth compound. Thus, when recrystallized from Et_2O and dried in the oven for 2 hours, it still retained 0.5 mole of Et_2O.

The formation of $(2\text{-}ClC_6H_4)_3Sb$ from $2\text{-}ClC_6H_4Li$ and $SbCl_3$ in the presence of $Me_2N(CH_2)_2NMe_2$ has been described in the Antimony section. None of the desired stibine was formed in the absence of $Me_2N(CH_2)_2NMe_2$. With success in preparing $(2\text{-}ClC_6H_4)_3Sb$, the authors [23] extended the reaction to the preparation of other $(2\text{-}ClC_6H_4)_3E$ compounds, where E was P, As, or Bi. Thus, $(2\text{-}ClC_6H_4)_3Bi$ was obtained in 63% yield, mp 140-141°C. The compound was characterized by IR spectroscopy and elemental analysis.

The reaction between tributylbismuthine and either CCl_4 or $CHCl_3$ has been investigated by Dodonov and coworkers [24]. The reactions were carried out in sealed ampoules in an argon atmosphere at 80°C for 60 hours and the products were identified by gas chromatography. With some exceptions, the products of the reactions with CCl_4 and $CHCl_3$ were the same and the yields were similar. The principal products were 1-chloro-1-pentene and butyldichloribismuthine, with trace amounts of 4-nonene. However, the reaction with CCl_4 gave 0.82 molar equivalents of 1-chloro-1-butene, whereas only 0.18 molar equivalents of this compound were obtained from $CHCl_3$. Trace amounts of 1-butene were found with CCl_4 only, whereas $CHCl_3$ gave trace amounts of 1-pentene. With $CHCl_3$, 0.86 molar equivalent of butane was obtained, but CCl_4 gave only 0.01 molar equivalent of this hydrocarbon. Finally, traces of $CHCl_3$ were found when CCl_4 was used as the reactant. The butyldichlorobismuthine was obtained as an unstable yellow crystalline compound, characterized by elemental analysis.

The authors suggested a number of reaction sequences to account for the various products obtained. With CCl_4 the suggested first step was the following:

$$Bu_3Bi + CCl_4 \longrightarrow [Bu_3BiCCl_3]Cl \longrightarrow BuCl + Bu_2BiCCl_3$$

To account for the large amount of butane formed when $CHCl_3$ was used, the following reaction was suggested:

$$\mathrm{Bu_3Bi + CHCl_3 \longrightarrow BuH + Bu_2BiCCl_3}$$

In accordance with the known decomposition of other organometallic compounds containing the metal-$\mathrm{CCl_3}$ grouping, it might be expected that $\mathrm{Bu_2BiCCl_3}$ would decompose as follows:

$$\mathrm{Bu_2BiCCl_3 \longrightarrow Bu_2BiCl + :CCl_2}$$

However, when the reactions were carried out in the presence of cyclohexene, the yield of dichloronorcarane was only 0.02 molar equivalent. This result indicated that the dichlorocarbene was only formed in very small amounts. Accordingly, the authors suggested that $\mathrm{Bu_2BiCCl_3}$ rearranged and then decomposed as follows:

$$\mathrm{Bu_2BiCCl_3 \longrightarrow BuBi(Cl)C(Bu)Cl_2 \longrightarrow BuBiCl_2 + Bu\underset{\cdot\cdot}{C}Cl}$$

$$\mathrm{MeCH_2CH_2CH_2\underset{\cdot\cdot}{C}Cl \longrightarrow MeCH_2CH_2CH{=}CHCl}$$

This reaction scheme accounted for the large amount of 1-chloro-1-pentene formed with both $\mathrm{CCl_4}$ and $\mathrm{CHCl_3}$. The small amount of 4-nonene formed was accounted for by the reaction between $\mathrm{Bu_3Bi}$ and the chlorocarbene $\mathrm{Bu\underset{\cdot\cdot}{C}Cl}$.

In a series of previously published papers, Nikitas and coworkers have reported on the adsorption of $\mathrm{Ph_3P}$, $\mathrm{Ph_3As}$, and $\mathrm{Ph_3Sb}$ on the mercury electrode in both aqueous and methanol solution. The present paper [25] extends the study to $\mathrm{Ph_3Bi}$.

The adsorption of $\mathrm{Ph_3Bi}$ on the polarized mercury electrode was first studied in a 0.1 M LiCl-methanol solution by means of electrocapillary measurements using a nonsiliconized capillary and varying the $\mathrm{Ph_3Bi}$ concentration from 0.2 - 10 mmol/$\mathrm{dm^{-3}}$. From the resulting curves it was determined that $\mathrm{Ph_3Bi}$ was strongly adsorbed on the mercury electrode in the region of the electrocapillary maximum. Thus $\mathrm{Ph_3Bi}$ was similar to $\mathrm{Ph_3P}$, $\mathrm{Ph_3As}$, and $\mathrm{Ph_3Sb}$.

The effect of the four triphenyl compounds on the evolution of hydrogen at the mercury electrode in methanolic HCl (1.0×10^{-3} M HCl) was then determined. In each case the polarographic hydrogen wave was shifted towards less negative potentials. It was found that $\mathrm{Ph_3Bi}$ had the strongest catalytic effect on hydrogen evolution. The effect of $\mathrm{Ph_3P}$ was similar, but not as strong as with $\mathrm{Ph_3Bi}$, while $\mathrm{Ph_3As}$ and $\mathrm{Ph_3Sb}$ showed a weaker catalytic effect.

The effect of the four triphenyl compounds on the polarographic reduction of *o*-dinitrobenzene, and the reduction of oxygen and of the cations Cd^{2+} and Zn^{2+} at the mercury electrode was also investigated. With *o*-dinitrobenzene the reductions were carried out in both neutral and acidic methanol solutions of 0.1 M LiCl. In neutral solution Ph_3Bi was found to have the strongest inhibitory activity of the four substances under investigation. The effect of the Ph_3Bi on the reduction of *o*-dinitrobenzene in acid solution was complicated. The inhibitory action of these substances on the reductions studied were interpreted as due to a reduction of the interfacial concentration of H^+ in the case of *o*-dinitrobenzene or to the blocking of the electrode surface in the case of the reduction of oxygen, Cd^{2+}, and Zn^{2+}.

Spin trapping, column chromatography, and ESR spectroscopy have been used to study the reactive intermediates formed in the photolysis of the compounds Ph_3E, where E was N, P, As, Sb, or Bi [26]. The free radical Ph• was detected in the P, As, Sb, and Bi compounds. It was concluded that the initial step in the photolysis was homolysis of the Ph_3E compounds.

Although $TaCl_5$ was an effective agent for the polymerization of 1-phenyl-1-propyne, the polymer underwent degradation after all the monomer had been consumed. Masuda and coworkers [27] have now found that when several organometallic compounds were used as cocatalysts, polymerization was effected without degradation of the polymer. Although Ph_3P and Ph_3As were ineffective, Ph_3Sb and Ph_3Bi (as well as Bu_4Sn, Me_4Sn and Ph_4Sn) were excellent cocatalysts with $TaCl_5$. The yield of polymer having molecular weights of 1.6×10^6 to 1.8×10^6 was 80-90%.

The low temperature polymerization of methyl methacrylate was effected by the use of two types of catalysts, namely, trialkylbismuthines (Bu_3Bi or $(Me_2CH)_3Bi$) and silicon or germanium compounds of the type $(Me_3COO)_xER_{4-x}$, where E was Si or Ge, R was Me, Et, or Ph, and x was 1 or 2 [28]. The reaction involved the formation of a pentacoordinate Bi compound which gave free alkyl radicals by homolytic decomposition. The radicals promoted the polymerization. The conversion of the monomer to polymer was 94-96%.

The rate of acrylonitrile photopolymerization in the presence of a number of compounds of the type Ph_3E, where E was N, P, As, Sb, Bi, has been studied [29]. Ph_3Bi was the least effective of the compounds investigated.

In continuation of previous work on compounds of the type $Ph_3Bi(O_2CR)_2$, Dodonov and coworkers [30] have prepared several such compounds from triphenylbismuthine, *tert*-butylhydroperoxide, and a carboxylic acid:

$$Ph_3Bi + \textit{tert}\text{-BuOOH} + 2\ RCO_2H \longrightarrow Ph_3Bi(O_2CR)_2 + \textit{tert}\text{-BuOH} + H_2O$$

(where R = Me, Ph, Bu, or $CH{=}CH_2$)

The reactants were used in the molar ratio 1:1:2. When oxalic acid was used (molar ratio 1:1:1), the product obtained was $Ph_3Bi(-OC(O)C(O)O-)$. The compounds obtained from valeric and acrylic acids have not been previously described. All of the products were crystalline solids, soluble in some organic solvents, and they gave sharp mp's. The authors were unable to isolate a crystalline product when capric acid was used in the above reaction. However, the crude reaction mixture was converted into $Ph_3Bi(O_2CMe)_2$ or Ph_3BiCl_2 when treated with acetic or hydrochloric acid, respectively. The authors concluded, therefore, that compounds of the type $Ph_3Bi(O_2CR)_2$, where R was a long hydrocarbon chain, were unstable. As further proof of this conclusion they were unable to isolate the compound $Ph_3Bi(O_2CC_{11}H_{23})_2$ from Ph_3Bi and dilauroyl peroxide, although the crude reaction product was converted to $Ph_3Bi(O_2CMe)_2$ with acetic acid. Furthermore, the crude reaction products, in both of the above reactions, were readily hydrolyzed in contrast to the finding that the compounds $Ph_3Bi(O_2CR)_2$, where R is a short chain hydrocarbon, were stable to hydrolysis.

The compound $Ph_3Bi(O_2CMe)_2$ was found to decompose when heated at 155°C for 3 hours to yield Ph_3Bi, $MeCO_2Ph$, and C_6H_6. The compounds $Ph_3Bi(O_2CR)_2$ (where R = Me, Ph, or $C_{11}H_{23}$) also decomposed when heated in organic solvents (toluene, cyclohexene, or ether). In each case the phenyl esters RCO_2Ph were obtained in approximately quantitative yields; Ph_3Bi was also formed. The authors proposed the following scheme for the decomposition:

$$Ph_3Bi(O_2CR)_2 \xrightarrow[\text{solvent}]{\Delta} PhOC(O)R + Ph_2BiO_2CR$$

$$2\ Ph_2BiO_2CR \longrightarrow Ph_3Bi + PhBi(O_2CR)_2$$

The decomposition of these compounds was markedly accelerated by the addition of copper salts. Thus, one mole of $Ph_3Bi(O_2CMe)_2$ and CuCl (0.5 mole) in toluene at room temperature gave 0.65 mole of $MeCO_2Ph$ in 24 hours.

In addition to the reaction of Ph_3Bi with the above peroxides, the authors attempted two other reactions, namely, the reaction between Ph_3Bi and dicyclohexyl peroxydicarbonate and between Ph_3BiCl_2 and $C_6H_{11}OLi$ (where C_6H_{11} = cyclohexyl). The products from both reactions were similar and included cyclohexanone, cyclohexanol, Ph_3Bi, C_6H_6, and (after hydrolysis) $Bi(OH)_3$. Carbon dioxide was also obtained in the reaction between Ph_3Bi and dicyclohexyl peroxy dicarbonate. The authors have proposed a complicated reaction sequence to explain the products of these two reactions:

$$\mathrm{Ph_3Bi} + \underset{\mathrm{V}}{\mathrm{C_6H_{11}OC(O)OOC(O)OC_6H_{11}}} \longrightarrow [\mathrm{Ph_3Bi(O_2COC_6H_{11})_2}]$$

$$\mathrm{V} \longrightarrow 2\ \mathrm{CO_2} + [\mathrm{Ph_3Bi(OC_6H_{11})_2}]$$

$$[\mathrm{Ph_3Bi(OC_6H_{11})_2}] \longrightarrow \mathrm{PhH} + \text{Cyclohexanone} + \mathrm{Ph_2BiOC_6H_{11}}$$

$$3\ \mathrm{Ph_2BiOC_6H_{11}} \longrightarrow 2\ \mathrm{Ph_3Bi} + \mathrm{Bi(OC_6H_{11})_3}$$

Finally, the authors reinvestigated the oxidation of alcohols with diacetoxytriphenylbismuth. In a previous short communication [31] they had reported that this bismuth(V) compound readily oxidized primary and secondary alcohols to aldehydes or ketones, respectively, and that tertiary alcohols were unaffected. The following equation was proposed for the oxidation of 1-butanol:

$$\mathrm{BuOH} + \mathrm{Ph_3Bi(O_2CMe)_2} \longrightarrow \mathrm{PrCHO} + \mathrm{BuO_2CMe} + \mathrm{PhH} + \mathrm{Ph_xBi(O_2CMe)_y}$$

(where $x = 0$, 1 or 2, and $y = 3-x$)

In addition to 1-butanol, ethyl, benzyl, *sec*-butyl, and isobutyl alcohols were similarly oxidized. In each case, the yields of benzene were in excess of 2 molar equivalents. Thus, from 1-butanol, 2.2 and from *sec*-butyl alcohol, 2.8 molar equivalents of benzene were obtained, respectively. The yield of ester, however, was usually about 1 molar equivalent. In addition, small amounts of the ether ROPh were sometimes found. The formation of ester cannot be explained by a simple redox reaction:

$$\mathrm{Ph_3Bi(OAc)_2} + \mathrm{Me_2CHOH} \longrightarrow 2\ \mathrm{PhH} + \mathrm{Me_2CO} + \mathrm{PhBi(OAc)_2}$$

Accordingly, the authors proposed the following reactions to account for the products:

$$\mathrm{PhBi(O_2CMe)_2} + \mathrm{AcOH} \longrightarrow \mathrm{Bi(O_2CMe)_3} + \mathrm{PhH}$$

$$\mathrm{ROH} + \mathrm{MeCO_2H} \rightleftharpoons \mathrm{RO_2CMe} + \mathrm{H_2O}$$

In order to test this proposal the oxidations were carried out in various solvents in the presence of a base ($\mathrm{Et_3N}$, NaOH, or $\mathrm{K_2CO_3}$), to react with the acetic acid. Under these reaction conditions the yields of reaction products changed considerably. The amounts of benzene and ester were markedly reduced, but the yield of aldehyde or ketone was not affected. In addition, in the presence of a base, Ph_3Bi was found in substantial amounts. Again, traces of an ether ROPh were found in some reactions. The authors then proposed the following reaction sequence to explain the results (with Me_2CHOH as the example):

$$Me_2CHOH + Ph_3Bi(O_2CMe)_2 \rightleftharpoons MeCO_2H + Ph_3Bi(O_2CMe)OCHMe_2$$

$$Ph_3Bi(O_2CMe)OCHMe_2 \longrightarrow PhH + Me_2CO + Ph_2BiO_2CMe$$

$$2\ Ph_2BiO_2CMe \longrightarrow Ph_3Bi + PhBi(O_2CMe)_2$$

$$Ph_3Bi(O_2CMe)OCHMe_2 \longrightarrow Me_2CHOPh + Ph_2BiO_2CMe$$

In addition to primary and secondary alcohols the reaction of $Ph_3Bi(O_2CMe)_2$ with two tertiary alcohols, pinacol and *tert*-butyl alcohol, was investigated, both in the presence and in the absence of base. Without base *tert*-butyl alcohol gave traces of benzene but no other product, while pinacol gave 0.64 and 2.06 molar equivalents of acetone and benzene, respectively. In the presence of K_2CO_3, *tert*-BuOH gave 0.34 and 0.66 molar equivalents of *tert*-BuOPh and Ph_3Bi, respectively, but no benzene or carbonyl compound. Pinacol, in the presence of K_2CO_3, gave 1.65, 0.15, and 0.88 molar equivalents of Me_2CO, PhH, and Ph_3Bi, respectively.

In continuation of previous studies on the phenylation of organic substrates with diacetoxytriphenylbismuth, Dodonov and coworkers [32] have reported the phenylation of primary and secondary amines with the bismuth compound in the presence of trace amounts of copper(II) acetate:

$$Ph_3Bi(OAc)_2 + 2\ RNH_2 \xrightarrow{Cu(OAc)_2} PhNHR + Ph_2BiOAc + RNH_2\cdot HOAc$$

The amine was used in a five fold molar excess to neutralize the acetic acid formed in the reaction. The yields of secondary or tertiary amines formed were satisfactory (generally 69-82%). However, phenylation of Ph_2NH occurred only to 3%. Primary amines phenylated by this procedure included isopropylamine, isobutylamine, *tert*-butylamine and aniline; secondary amines included diethyl- and dibutylamine. Neither urea nor acetamide was phenylated under these reaction conditions.

The preparation of dinaphthyltriphenylbismuth was described in the Russian chemical literature in a journal unavilable to the authors [33].

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