BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1987

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A paper published in 1987 reviewed the researches of Barton and coworkers [1] on the use of organobismuth(V) compounds as reagents in organic synthesis. These dealt principally with the oxidation of primary and secondary alcohols to aldehydes and ketones, and the *O*-, *C*-, *N*-, and *S*-arylation of a wide variety of organic compounds. A closely related publication [2], a chapter in a book dealing with oxidations of organic compounds by metal compounds, described the use of both inorganic and organic bismuth compounds as oxidizing agents for organic compounds. In a newly published series of books devoted to coordination chemistry, the use of bismuth compounds, both inorganic and organic, has been dealt with in two separate volumes. In volume 2 of the series the bonding of bismuth to the main group elements of Groups IV-VII was described in considerable detail [3]. In volume 3, the use of bismuth compounds as ligands to transition elements was briefly considered [4]. Wardell has reviewed the literature on organoarsenic, -antimony, and -bismuth compounds published in 1985 [5]. In two other reviews in the same volume bismuth compounds were briefly mentioned. One of these deals with organic compounds containing metal-metal bonds [6]; the other deals with ligand substitution reactions of metal or organometal compounds with Groups V and VI donor ligands [7]. Organobismuth compounds were also mentioned in a review of the structure of organometallic compounds by diffraction methods [8]. In the *Annual Reports on the Progress of Chemistry*, both in the organic [9] and inorganic [10] sections, organobismuth compounds have been mentioned. In a review devoted principally to arsonium ylides, the few known bismuth ylides were discussed [11].

Tetrapropyldibismuthine has been found to react with chalcogens with cleavage of the Bi-Bi bond and insertion of the chalcogen [12]:

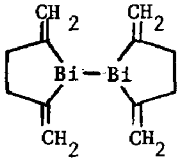
$$\mathrm{Pr_2Bi{-}BiPr_2 + Y \longrightarrow Pr_2BiYBiPr_2}$$
$$\text{(where Y = O, S, Se, and Te)}$$

The formation of the oxide was carried out in petroleum ether at -30°C and the product was characterized by elemental analysis, PMR, Raman, and mass spectrometry. The reactions of S were also carried out in petroleum ether at -30°C, as well as at room temperature without solvent in the dark. The reactions with Se and with Te were carried out only at room temperature in the dark. The sulfide, selenide, and telluride were unstable at room temperature. They decomposed to give Pr_3Bi and unidentified products. It was also found that $(Pr_2Bi)_2$ reacted with $(Me_2Sb)_2$ in benzene solution according to the equation:

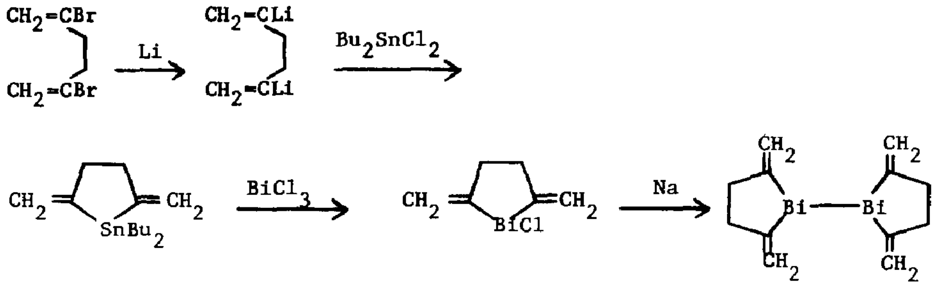
$$(Pr_2Bi)_2 + (Me_2Sb)_2 \rightleftharpoons 2\ Pr_2BiSbMe_2$$

The product could not be isolated but was identified in the mixture by means of the PMR spectrum. It was found that the Me signal of the $(Me_2Sb)_2$ moiety differed from the Me signals for the same methyl groups in the compound $Pr_2BiSbMe_2$. From these data the equilibrium constant for the reversible equation was calculated and found to be 0.7. In addition to PMR data the mass spectrum of the reaction mixture gave the molecular ion of the $Pr_2BiSbMe_2$ species as well as several fragments containing an Sb–Bi bond.

In a paper largely devoted to the thermochromic effect in distibines, Ashe and coworkers [13] have described the preparation of the following bibismolane:



The synthesis was carried out in the following manner:



The chlorobismuthine was obtained as yellow crystals that could be stored at 0°C but decomposed at 25°C. It was characterized by PMR and mass spectrometry. The bibismolane was obtained by treating the chlorobismuthine with sodium in liquid ammonia and recrystallizing the product from pentane at -78°C. It decomposed on warming to 0°C and was characterized by PMR and mass spectrometry. Suitable crystals for X-ray diffraction studies could not be obtained. In contrast to the corresponding bistibolane (described in the Antimony section) Hückel calculations were carried out on the bibismolane.

In continuation of previous work on the reactions of dibismuthines, Wieber and Sauer [14] have prepared $[(4\text{-MeC}_6H_4)_2Bi]_2$ and studied its reactions with the chalcogens S and Se and with disulfides, diselenides, and ditellurides. Bromodi-4-tolylbismuthine was prepared in 94% yield from $(4\text{-MeC}_6H_4)_3Bi$ and $BiBr_3$:

$$2\ (4\text{-MeC}_6H_4)_3Bi + BiBr_3 \longrightarrow 3\ (4\text{-MeC}_6H_4)_2BiBr$$

When treated with sodium in liquid ammonia, tetra-4-tolydibismuthine was produced:

$$2\ (4\text{-MeC}_6H_4)_2BiBr + 2\ Na \longrightarrow [(4\text{-MeC}_6H_4)_2Bi]_2 + 2\ NaBr$$

Tri-4-tolylbismuthine was a byproduct of this reaction. The dibismuthine was unstable and decomposed to $(4\text{-MeC}_6H_4)_3Bi$ and a dark polymeric material. At 0°C, the decomposition occurred in about 30 minutes. It was more stable in solution; the half-life in CH_2Cl_2 was about 2 days or 5-6 days in PhH. It reacted with sulfur in CH_2Cl_2 solution at -10°C to yield $[(4\text{-MeC}_6H_4)_2Bi]_2S$ and with selenium at 0°C to give $[(4\text{-MeC}_6H_4)_2Bi]_2Se$. No similar product was obtained with tellurium; only the decomposition products of the dibismuthine were observed. The sulfur and selenium insertion products slowly decomposed in the following manner:

$$3\ [(4\text{-MeC}_6H_4)_2Bi]_2S \longrightarrow Bi_2S_3 + 4\ (4\text{-MeC}_6H_4)_3Bi$$

The dibismuthine reacted with disulfides, diselinides, and ditellurides as follows:

$$[(4\text{-MeC}_6H_4)_2Bi]_2 + PhEEPh \longrightarrow 2\ (4\text{-MeC}_6H_4)_2BiEPh$$

(where E was S, Se, or Te)

These compounds were also unstable and disproportionated as follows:

$$2\ (4\text{-MeC}_6H_4)_2BiEPh \longrightarrow (4\text{-MeC}_6H_4)_3Bi + 4\text{-MeC}_6H_4Bi(EPh)_2$$

The sulfur compound was the most stable (2-3 days), while the tellurium compound was visually decomposed in about 40 minutes. The decomposition of all three compounds occurred much more rapidly in solution. Thus, the sulfur compound was 40% decomposed in CH_2Cl_2 solution after 10 h. Another compound prepared from the dibismuthine was $1,4\text{-C}_6H_4[OBi(C_6H_4Me\text{-}4)_2]_2$. It was obtained as a yellow powder by the interaction of the dibismuthine and 1,4-benzoquinone in CH_2Cl_2 at -20°C. All of the compounds were characterized by elemental analyses, PMR, and mass spectrometry.

Two new thiophenolato compounds of Bi(III) have been reported by Klapotke [15]. They were prepared according to the following equations:

$$PhBiBr_2 + 2\ 4\text{-}ClC_6H_4SLi \longrightarrow PhBi(SC_6H_4Cl\text{-}4)_2 + 2\ LiBr$$

$$MeBiBr_2 + 2\ 4\text{-}H_2NC_6H_4SLi \longrightarrow MeBi(SC_6H_4NH_2\text{-}4)_2 + 2\ LiBr$$

The compounds were characterized by elemental analyses, PMR, and IR spectrometry and by their mass spectra. They were obtained as yellow $PhBi(SC_6H_4Cl)_2$ or orange $MeBi(SC_6H_4NH_2)_2$ crystalline solids which melted with decomposition at 165 and 220°C, respectively. When treated with MeI, the NH_2 group of the methyl compound was methylated to yield the compound $[MeBi(SC_6H_4NH_2Me\text{-}4)_2]I_2$. The compounds were tested against several bacteria and found to be effective, particularly the two methyl compounds $MeBi(SC_6H_4NH_2\text{-}4)_2$ and $[MeBi(SC_6H_4NH_2Me\text{-}4)_2]I_2$.

Organocadmium compounds of the type $Cd(R_f)_2$, where R_f was a perfluoroalkyl group such as CF_3, C_2F_5, $n\text{-}C_3F_7$, have recently been used with considerable success for the preparation of perfluoroalkyl derivatives of a number of elements. Naumann and Tyrra [16] have now reported on the preparation, spectra, and chemical properties of a number of compounds of the type $Bi(R_f)_3$ (where R_f was CF_3, C_2F_5, $n\text{-}C_3F_7$, $n\text{-}C_4F_9$, $n\text{-}C_6F_{13}$, $n\text{-}C_8F_{17}$, and C_6F_5), prepared from the corresponding Cd compounds. The progress of the reaction was followed for $Cd(CF_3)_2 + BiBr_3$ by means of ^{19}F NMR spectral studies. All of the intermediates in the reaction were identified in the NMR spectrum. The reaction proceeded in a stepwise manner, as shown by signals of CF_3BiBr_2, $(CF_3)_2BiBr$, and $(CF_3)_3Bi$ in the ^{14}F spectrum at various stages of the reaction. The solvent used was MeCN. The two compounds $(CF_3)_3Bi$ and $(C_2F_5)_3Bi$ were colorless liquids, the other compounds were white to pale yellow solids. They were rapidly decomposed in air, but the compounds $Bi(C_nF_{2n+1})_3$, where n was 1, 2, or 3, could be stored for several days in MeCN or EtCN solution, and the other compounds, when pure, were stable for several weeks. The ^{19}F and ^{13}C NMR, IR, Raman, and mass spectra for $(CF_3)_3Bi$ were reported, and the ^{19}F NMR and mass spectra (Bi containing fragments only) for the other compounds were also reported. All of the $(R_f)_3Bi$ compounds reacted with water or alcohols to form compounds of the type R_fH. The reactions of $(CF_3)_3Bi$ with PhI, $AgNO_3$, and ICl were also studied. No reaction occurred with PhI, but the C-Sb bond was cleaved to yield $Ag[Ag(CF_3)_4]$, $[Ag(CF_3)_2]^-$, and CF_3NO with $AgNO_3$, and CF_3I with ICl. These results suggested that $(CF_3)_3Bi$ underwent polar rather than radical-type reactions.

The reaction of ketene and diphenylketene with several amino, alkoxy, and alkylthio arsines and stibines as well as with two tris(dialkylamino)-bismuthines has been described by Ando and coworkers [17]. Thus, $Bi(NR_2)_3$, R = Me and Et, reacts with ketene at -50°C in the following manner:

$$Bi(NR_2)_3 + 3\ CH_2{=}C{=}O \longrightarrow Bi(CH_2CONR_2)_3$$

The methyl compound was a red solid and the ethyl compound was a red oil. Neither compound could be purified by vacuum distillation. At 250°C they decomposed into dialkylacetamides and black metal-containing residues. The ^1H and ^{13}C NMR spectra of both compounds were reported. The IR carbonyl frequency of both compounds occurred at 1640 cm^{-1}.

Organic mercury compounds have been used for many years for the preparation of organometallic compounds by means of metal-exchange reactions. This procedure has been employed for the preparation of heterocyclic compounds by the reaction between *o*-phenylenemercurials and Group V and VI main group elements [18]. Thus, P, As, Sb, and Bi react with $(o\text{-}C_6H_4Hg)_3$ to yield the Group V triptycenes:

$$(o\text{-}C_6H_4Hg)_3 + 2\ E \longrightarrow 3\ Hg + E_2(C_6H_4)_3$$

The reactions were carried out in evacuated sealed pyrex tubes which had previously been rigorously dried by baking *in vacuo*. The bismuth compound was prepared from finely powdered Bi and $(o\text{-}C_6H_4Hg)_3$ at 250°C for 2 h. The resulting bismuth triptycene was thermally unstable and longer heating decreased the yield (0% yield after 24 h). The reaction products were extracted with petroleum ether and subjected to preparative TLC. The triptycene $(C_6H_4)_3Bi_2$, triphenylene, and hexaphenylene were obtained and identified by mass spectrometry. Even when the optimum yield was obtained there was too little Bi triptycene for elemental analysis. Much better results were obtained when $(o\text{-}C_6Cl_4Hg)_3$ was used. The bismuth compound was obtained in yields of 60-70% after extraction with DMF or $PhNO_2$. The same triptycene was also obtained by reaction of $1,2\text{-}I_2C_6Cl_4$ with bismuth:

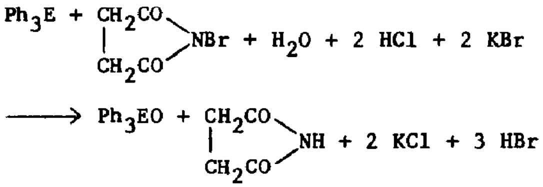
$$3\ 1,2\text{-}I_2C_6Cl_4 + 4\ Bi \longrightarrow (C_6Cl_4)_3Bi_2 + 2\ BiI_3$$

The triptycene held solvents tenaciously. It was purified by crystallization from $PhNO_2$, washing with Me_2CO, and drying at 75°C for 72 h. Elemental analyses and the IR spectrum of this compound were reported.

The reaction between $PhBiCl_2$ and an excess of cymanthrenyllithium led to the formation of dicymanthrenylphenylbismuthine, $PhBi[C_5H_4Mn(CO)_3]_2$ [19]. The compound occurred as yellow crystals, mp 120°C, and was characterized by elemental analysis and IR spectroscopy. When treated with $CuCl_2$, the Bi-C bonds were cleaved to yield chlorocymanthrene (58%), PhCl (21%), dicymanthrenyl (3%) and traces of Ph_2, while the $CuCl_2$ was reduced to CuCl. Since Ph_3Bi and $CuCl_2$ reacted to give Ph_2 and PhCl, the authors suggested the two reactions occurred by the same mechanism.

The reaction of organobismuth(III) compounds with IF_5 has been described in a paper which also included the reaction of IF_5 with organoarsenic and organoantimony compounds [20]. In contrast to the arsenic and antimony compounds, R_3As and R_3Sb, which reacted with IF_5 to give R_3AsF_2 and R_3SbF_2, respectively, the reaction of R_3Bi compounds varied with the nature of the R group. Thus, Ph_3Bi gave Ph_3BiF_2, but $(C_6F_5)_3Bi$ and $(4\text{-}FC_6H_4)_3Bi$ reacted with cleavage of the Bi-C bond to yield $C_6F_5IF_4$ or $4\text{-}FC_6H_4IF_4$ and BiF_3. With $(4\text{-}CF_3C_6H_4)_3Bi$, both oxidation and cleavage reactions occurred to give a mixture of products. At -30°C, Bu_3Bi reacted with IF_5 to give Bu_3BiF_2, identified by the ^{19}F NMR spectrum. This product, however, was unstable even at -30°C and decomposed with the formation of BuF, BiF_3, and other products. The reaction of Ph_2BiCl and IF_5 led to the formation of a mixture of Ph_2BiF, $PhBiF_2$, and BiF_3.

A method for the micro and submicro determination of P, As, Sb, and Bi in the triphenyl derivatives of these elements involved titration of an acidic methanol solution of the compound with *N*-bromosuccinimide in the presence of KBr [21]. Methyl red was used as the indicator. The reaction involved was the following:



$$Ph_3E + \begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix}\!\!>\!NBr + H_2O + 2\ HCl + 2\ KBr \longrightarrow Ph_3EO + \begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix}\!\!>\!NH + 2\ KCl + 3\ HBr$$

Formation of the oxides Ph_3EO was confirmed by extraction and crystallization of the four products individually from benzene. They were identified by mp's and mixed mp's.

A paper by Eng and coworkers [22] was devoted to the relationship between molecular conformation and chromatographic parameters. The total surface area (TSA) in Å^2 for each of five compounds of the type Ph_3E, where E was N, P, As, Sb, or Bi, in three different conformations (flat, propeller, and twisted) was calculated from conventional bond distances, bond angles, and Van der Waals radii. A mixture of all five compounds was separated chromatographically by means of the HLPC-GFAA system with a reversed-phase bonded octadecylsilane column and with methanol-water (70:30) as the mobile phase. The results obtained were then used to calculate the capacity factor (k') for each of the compounds. A plot of log k' vs the TSA for each of the three conformations gave a very poor correlation. However, when log k' was plotted *vs.* the preferred conformation for each of the five triphenyl compounds, an excellent correlation ($r^2 = 0.990$) was obtained. It was concluded that chromatographic retention time was dependent on the conformation of the molecule.

In continuation of previously reported work, Bulgakov and coworkers [23] have measured the kinetic dependence of the intensity of chemiluminescence produced by the O_2 oxidation of a number of organometallic compounds. In each case a maximum of the chemiluminescence occurred during the oxidation. This result confirmed the participation of organometallic peroxides during the oxidation. One of the compounds used in this study was Et_3Bi.

In a theoretical paper from Razuvaev's laboratory, the hyperconjugative effect of organometallic substituents EX_n in compounds of the type $PhEX_n$ or $PhCH_2EX_n$ was investigated [24]. In these compounds E was a Group II-V main group element with a valence of n and X was one of a number of substituents attached to E. A linear relationship between the bond refractivities R_D and the Hammett-Taft constant differences, $\sigma_p^+ - \sigma_p$, was taken as evidence of the hyperconjugative effect. One of the substituents EX_n was $BiPh_2$.

Since the lone pair of electrons in Bi is relatively inert, only a few coordination compounds of trivalent Bi are known. Baker and Fraser [25] have now reported a number of new compounds in which Ph_3Bi acts as a donor ligand to molybdenum or tungsten. Thus, $MoI_2(CO)_3(MeCN)_2$ in CH_2Cl_2 solution, when treated with one molar equivalent of Ph_3Bi, gave $MoI_2(CO)_3(MeCN)(Ph_3Bi)$. The reaction was carried out at room temperature for 25 h, and the brown crystalline product was recrystallized from CH_2Cl_2. When 2 molar equivalents of Ph_3Bi were used $MoI_2(CO)_3(Ph_3Bi)_2$ was obtained. Similar reactions with $WI_2(CO)_3(MeCN)_2$ gave the corresponding two tungsten complexes. When the complex $MoI_2(CO)_3(MeCN)(Ph_3Bi)$ was dissolved in CH_2Cl_2 and stirred for 5 h it dimerized to yield the complex $[Mo(\mu\text{-}I)I(CO)_3(Ph_3Bi)]_2$, but the corresponding tungsten complex failed to dimerize. The ease of dimerization of the complexes $MoI_2(CO)_3(MeCN)(Ph_3E)$, where E was P, As, Sb, or Bi, was in the same order. The Ph_3Bi complex dimerized so readily that the monomer was difficult to obtain in a pure state. Other molybdenum and tungsten complexes reported were the following: $MoI_2(CO)_3[P(OPh)_3](Ph_3Bi)$, $WI_2(CO)_3[P(OPh)_3](Ph_3Bi)$, $MoI_2(CO)_3(Ph_3As)$-(Ph_3Bi), and $[WI_2(CO)_3(Ph_3P)(Ph_3Bi)]MeCN$. The compounds were characterized by elemental analyses (C, H, and N), IR, and for some compounds, PMR spectrometry.

The Mo-Mo bond in the complex $[CpMo(CO)_3]_2$, where Cp was the cyclopentadienyl group, was cleaved by ferricinium fluoroborate in the presence of Group V ligands, Ph_3E (E = P, As, Sb, and Bi) and $Ph_2PCH_2CH_2PPh_2$, under photochemical radiation to produce mononuclear cationic complexes of the type $[CpMo(CO)_2(Ph_3E)_2]BF_4$ and $[CpMo(CO)_2(Ph_2PCH_2CH_2PPh_2)]BF_4$ [26]. The bismuth compound was obtained as a yellow-brown solid, characterized by elemental analyses, IR, and ^1H and ^{13}C NMR spectrometry. The reactions were carried out in CH_2Cl_2 in an argon atmosphere at room temperature. The yield of the bismuth compound was 86%.

Ahrland and Hultén [27] have pointed out that the stability of complexes formed between donor ligands and acceptor metals depends, not only on the affinity between the reacting species, but also on the solvation of each in the reaction solvent. In order to study the effect of solvation on complex formation with compounds of the type Ph_3E, where E = N, P, As, Sb, or Bi, the authors determined the enthalpies of solvation of these ligands in five polar solvents (MeOH, Me_2SO, MeCN, pyridine, and tetrahydrothiophene) and in two nonpolar solvents (PhH and CCl_4). It was found that, with two minor exceptions, the enthalpies of solvation increased monotonally from Ph_3N to Ph_3Bi in all solvents. All values were small, however, and were all of the same magnitude in both the polar and nonpolar solvents. It was concluded that the solvation was due essentially to London forces. The two minor exceptions were the values for Ph_3Bi in PhH and CCl_4, where the enthalpies of solvation were slightly smaller than those for Ph_3Sb. The authors suggested that for Ph_3Bi the donor properties of the solvent might be of some importance. They concluded, however, that for these ligands, with a certain acceptor, no change in stability sequence would be expected between various solvents.

In a paper devoted principally to equilibrium and enthalpy measurements on complexes formed between Ag+ and phosphorus or antimony donor ligands (tri- and dialkylphosphines and tributylstibine), the complex formed between $AgClO_4$ and Ph_3Bi was mentioned [28].

In a paper largely devoted to bismuth as a bridging ligand to organoiron complexes, one organobismuth complex, $[CpFe(CO)_2]_2BiEt$ (Cp = cyclopentadienyl), was described [29]. The compound was prepared by the reaction of $[CpFe(CO)_2]_2BiBr$ with one equivalent of Et_3Al. It was obtained as dark red, metallic crystals. It was characterized by elemental analyses, PMR and IR spectrometry.

In a paper largely devoted to the IR and Raman spectra of 2-phenyl-1,3,6-trithia-2-stibocane and 5-phenyl-1-oxa-4,6-dithia-5-stibocane, the vibrational spectra of the two corresponding bismocanes were described [30].

The polymerization of acetylenic compounds by compounds of transistion metals, particularly compounds of Nb, Ta, Mo, and W, was usually greatly enhanced by the use of an organometallic compound as a cocatalyst. One of the best of these cocatalysts was Ph_3Bi. Several papers on this subject have appeared in 1987 [31-34].

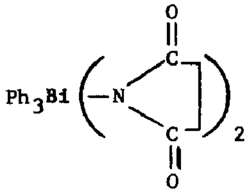
A recent paper from Schmidbaur's laboratory has described the preparation and crystal structures of two stable arene-$BiCl_3$ complexes where the arenes were hexamethylbenzene and mesitylene [35]. This work has now been considerably expanded by including complexes of the same two arenes with $BiBr_3$, $SbCl_3$, and $SbBr_3$. In the first of two papers [36], the four hexamethylbenzene compounds were desribed. These are of the type $C_6Me_6(EX_3)_2$ (E = Bi or Sb, X = Cl or Br). The complex $C_6Me_6(BiBr_3)_2$ was a yellow crystalline solid, mp 162°C, characterized by elemental analysis. Because of intense x-ray absorption, determination of its crystal structure was not attempted. The crystal structure of the $C_6Me_6(BiCl_3)_2$ complex was described in the earlier paper[35], but considerably more crystal structure data were included in the present paper. The structure consisted of cyclic $(BiCl_3)_4$ units containing four equivalent Bi atoms with bridging Cl atoms, all combined to form a flat square. Each Bi atom coordinated by η^6-bonding a C_6Me_6 ring. The center of each C_6Me_6 ring formed a crystallographic inversion center, so that a $BiCl_3$ unit was found on the other side of each ring. Each $(BiCl_3)_4$ unit was thus cross-linked by double-sided C_6Me_6 coordination at each Bi atom with four other $(BiCl_3)_4$ units to give a three-dimensional organometallic polymer.

The second paper from Schmidbaur's laboratory described the preparation of the four mesitylene compounds $C_6H_3Me_3\cdot EX_3$, where E = Sb or Bi and X = Cl or Br [37]. The compound $C_6H_3Me_3\cdot BiBr_3$, not previously described, consisted of yellow crystals, mp 118°C, characterized by elemental analysis. Its crystal structure was not determined. The crystal structure of the compound $C_6H_3Me_3\cdot BiCl_3$ was determined by x-ray diffraction and the data in the present paper were essentially the same as that given in the earlier paper [35]. The crystal structure consisted of two crystallographically independent sheets of $BiCl_3$ networks with many bridging Cl atoms forming two-dimensional polymers. Each sheet contained two non-equivalent types of Bi atoms. These Bi atoms had three strongly bonded Cl atoms and either two or three loosely bonded Cl atoms, so that a Bi atom was essentially either 5 or 6 coordinate. In addition, each Bi atom had an η^6- bonded $C_6H_3Me_3$ ring. These rings were alternately above or below the $BiCl_3$ sheets.

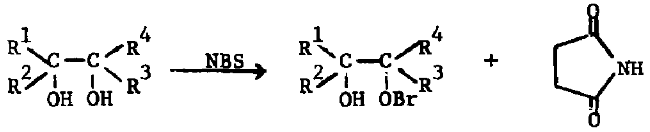
In addition to the two η^6-arene-bismuth halide compounds described by Schmidbaur and coworkers, two new η^6-arene-$BiCl_2^+$ complexes have been prepared by Frank and coworkers [38]. The arenes were toluene and C_6Me_6 and both compounds contained $AlCl_4$ anions. The toluene complex was a yellow crystalline compound, mp 83°C; the C_6Me_6 complex was orange, mp 180°C. Both complexes occurred as twin crystals, but only the C_6Me_6 crystals could be split in order to prepare samples for crystal analysis. An x-ray diffraction study of this compound showed that it occurred as a dimer $\{[C_6Me_6BiCl_2][AlCl_4]\}_2$. Each Bi atom had 2 strongly bonded Cl atoms and 3 weakly bonded Cl atoms, two of which were attached to one $AlCl_4^-$ and the other Cl to the second $AlCl_4^-$. In addition, each Bi atom was attached to the arene by η^6-bonding. The Bi-arene center distance was considerably shorter than in the two complexes 1,3,5-$Me_3C_6H_3BiCl_3$ and $C_6Me_6(BiCl_3)_2$ described by Schmidbaur and coworkers [36,37]. Each Bi atom in this complex possessed essentially strongly distorted octahedral geometry.

Singhal and coworkers have described organobismuth(V) dioximates of the type $Ph_3Bi(ON{=}CRR')_2$ where R,R' = Me,Me; Me,Ph; Me,Et; Me,Pr; Ph,Ph; and $(CH_2)_5$ [39]. They were prepared from Ph_3BiCl_2 and the oxime in the presence of Et_3N or from Ph_3BiCl_2 and the sodium salt of the oxime. Both types of reactions were carried out in benzene under anhydrous conditions. The resulting compounds were hygroscopic, crystalline solids. They were monomolecular in benzene and were non-electrolytes in nitrobenzene. They were characterized by elemental analyses, IR, and PMR spectrometry. A band at 445-460 cm^{-1} was assigned to νBi-C and a band at 1570-1610 cm^{-1} to the C=N stretching mode. In the PMR spectrum of $Ph_3Bi(ON{=}CMe_2)_2$ the methyl signals occurred as a doublet due to the non-equivalence of the methyl groups.

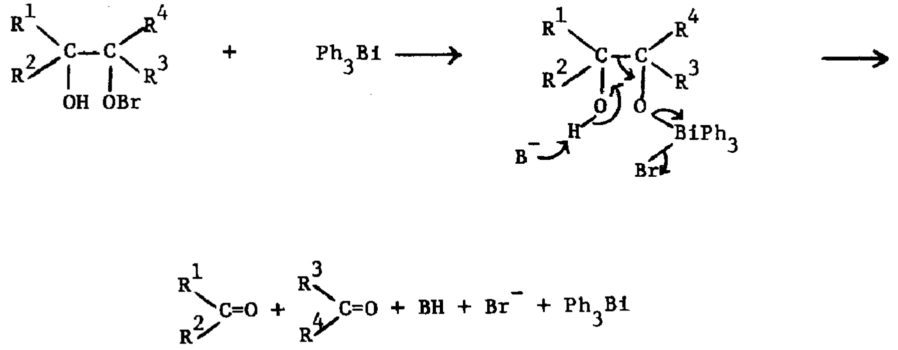
Barton and coworkers have written extensively on the use of organobismuth(V) reagents in organic synthesis. Among the successful reactions previously reported was the cleavage of vicinal glycols to yield aldehydes and/or ketones. It was also found that Ph_3Bi and an oxidizing agent (*N*-bromosuccinimide or *N*-bromoacetamide) in the presence of K_2CO_3 could be used in place of an organobismuth(V) compound [40]. Although, in general, the results obtained with most glycols were the same with either method, the cleavage of *trans*-decalin-1,2-diol (but not the corresponding *cis* isomer) proved to be quite different. Thus, the *cis*-isomer was readily cleaved by Ph_3BiCO_3, whereas the *trans* isomer was unaffected by this reagent. By contrast, both isomers were cleaved at essentially the same rate by Ph_3Bi and NBS. Barton and coworkers [41] have now reported further studies on the cleavage of vicinal glycols by the two methods. They first confirmed that glycols such as *meso*-hydrobenzoin, *cis*-decalin-1,2-diol, and benzopinacol were readily cleaved by organobismuth(V) reagents such as Ph_3BiCO_3 and Ph_3BiCl_2 in the presence of BTMG (2-*tert*-butyl-1,1,3,3-tetramethylguanidine) and also by Ph_3Bi and NBS in the presence of K_2CO_3, with approximately the same yields. *trans*-Decalin-1,2-diol, however, was unaffected by Ph_3BiCO_3 and was scarcely cleaved by Ph_3BiCl_2 and BTMG (6% after 3 h), but was readily cleaved by Ph_3Bi and NBS in the presence of K_2CO_3. Two other organobismuth(V) reagents which failed to cleave the *trans* compound were Ph_3BiO and the following succinimide compound:



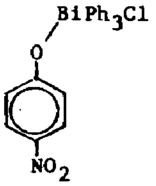
The authors believed these results excluded the formation of an organobismuth(V) intermediate (formed from Ph_3Bi and NBS) which then reacted with the glycol. They suggested rather that NBS first reacted with the glycol to form a hypobromite and succinimide:



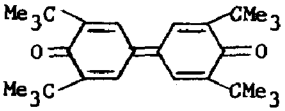
In confirmation of this suggestion, succinimide was recovered in 90 and 80% yields, respectively, when NBS and K_2CO_3 were added to *meso*-hydrobenzoin or *trans*-decalin-1,2-diol. Furthermore, one of the two hydroxyl hydrogen signals in the PMR spectrum of *meso*-hydrobenzoin was shifted downfield (4.7 to 5.9 ppm) on the addition of NBS. It was suggested that the hypobromite then reacted with Ph_3Bi in the following manner:



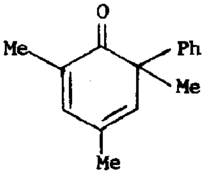
Another paper from Barton's laboratory described the *O*-phenylation and *C*-phenylation of a variety of phenols by treatment with organobismuth(V) reagents [42]. 4-Nitrophenol and Ph_3BiCl_2 in the presence of BTMG gave the following stable aryloxybismuth derivative:



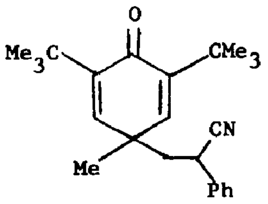
Thermal decomposition of this adduct in refluxing PhH gave biphenyl (26%) and 4-nitrophenyl phenyl ether (2%). A similar aryloxybismuth derivative from $Ph_3Bi(O_2CCF_3)_2$ gave, on thermal degradation in PhH, 69% biphenyl and no phenyl ether. By contrast, three other phenols, 4-RC_6H_4OH (R = CO_2Me, CN, and CF_3) gave the corresponding phenyl ethers in 88, 91, and 70% yields, respectively, when refluxed in solution with Ph_3BiCl_2 and BTMG. With 3-nitrophenol, under the same conditions, a mixture of 3-nitrophenyl phenyl ether (54%), 2-phenyl-5-nitrophenol (13%), and 2,6-diphenyl-3-nitrophenyl-phenol (9%) was formed. 3,5-Dichlorophenol gave 60% of the corresponding phenyl ether with small amounts of 2-phenyl- and 2,6-diphenyl-3,5-dichlorophenols. It would thus appear that phenols, substituted with electron-attracting groups in *m*- or *p*-position, give exclusively or predominantly the corresponding phenyl ethers, with only minor amounts of *C*-phenylated phenols, when treated with organobismuth(V) reagents under basic conditions. By contrast, the reaction of phenols substituted with electron-repelling groups usually gave *C*-phenylated compounds as the principal reaction products. Thus, 3,5-dimethoxyphenol gave 2-phenyl- (45%) and 2,6-diphenyl-3,5-dimethoxyphenol (30%), but only 10% 3,5-dimethoxyphenyl phenyl ether, when treated with Ph_3BiCl_2 under basic conditions (BTMG). 2,4-Di-*tert*-butylphenol give the 6-phenyl derivative in 81% yield, with only 3% of the corresponding phenyl ether, when treated with $Ph_3Bi(O_2CCF_3)_2$ and BTMG. The reactions of phenols substituted in the 2,6-positions were more complicated. Thus, 2,6-di-*tert*-butylphenol and Ph_3BiCO_3 gave the following diphenoquinone:



2,4,6-Trimethylphenol and Ph_3BiCl_2 in THF under basic conditions (BTMG) gave only a poor yield (15%) of the following cyclohexadienone:



A much larger yield (88%) of the same product was obtained when Ph_5Bi in PhH was used as the phenylating agent. If, instead of THF, MeOH was used as the solvent in the reaction of 2,4,6-trimethylphenol with Ph_3BiCl_2, 2,6-dimethyl-4-methoxymethylphenol was obtained in 82% yield. In a similar manner, 2,6-di-*tert*-butyl-4-methylphenol, Ph_3BiCl_2, and BTMG in MeOH-PhH solution gave 2,6-di-*tert*-butyl-4-methoxymethylphenol. If acrylonitrile, rather than MeOH, was used in this last reaction, the following product was obtained:



Finally, the phenylation of phenol itself was investigated. With Ph_3BiCl_2 and BTMG, 2-phenylphenol (30%), 2,6-diphenylphenol (7%), and diphenyl ether (8%) were obtained (after work-up with HCl). If, instead of Ph_3BiCl_2, $Ph_4BiO_2CCF_3$ or $Ph_4BiOSO_2C_6H_4Me$-4 was used as the phenylating agent, diphenyl ether was the principal product (35–42%), with smaller amounts of 2-phenylphenol (29%) and 2,6-diphenylphenol (3%). The authors proposed several different reaction mechanisms to account for the results obtained.

In a number of research papers from Barton's laboratory dealing with the *O*-phenylation and *C*-phenylation of various substrates, several different pathways for these reactions have been suggested. In the case of phenols, two mechanisms were preferred by Barton and coworkers depending on whether the reaction occurred under basic conditions (usually leading to the *C*-phenylation of phenols) or under neutral (or acid) conditions (usually leading to the *O*-phenylation of phenols). Neither of these two reaction pathways involved free radicals and, although not entirely ruled out, Barton's group has always believed that radicals were not involved in these reactions. Considerable evidence against a free radical mechanism has now been presented in a lengthy paper from Barton's laboratory [43].

In preliminary experiments the ESR spectra of the reactions involving the phenylation of 1,1,3,3-tetraphenylacetone by $Ph_4BiOSO_2C_6H_4Me$-4, both in the presence of, and in the absence of the radical-trapping agent phenyl-*tert*-butylnitrone, were obtained. In both cases the spectra consisted of a triplet of doublets, evidence for the formation of radicals. The same spectrum was also observed in the absence of $Ph_2CHCOCHPh_2$, but not in the absence of $Ph_4BiOSO_2C_6H_4Me$-4. It was then decided to follow the reaction quantitatively by substituting nitrosobenzene (as a trapping agent) for the phenyl-*tert*-butylnitrone. The total reaction mixture was then reduced with iron-acetic acid-acetic anhydride. In this manner any unchanged PhNO would yield PhNHAc, while any phenylated PhNO would yield Ph_2NAc. From the ratio of the two products the amount of phenyl radicals could be determined. It was found that $Ph_2CHCOCHPh_2$ in THF at room temperature, when treated with $Ph_4BiOSO_2C_6H_4Me$-4 and BTMG, gave an 88% yield of $Ph_2CHCOCPh_3$ in the absence of PhNO and a 90% yield, in the presence of 2 equivalents of PhNO. In the latter case 83% PhNHAc and 3% Ph_2NAc were obtained. In the absence of $Ph_2CHCOCHPh_2$ 87% PhNHAc and 3% Ph_2NAc were obtained. From these experiments it was concluded that, although $Ph_4BiOSO_2C_6H_4Me$-4 does yield some phenyl radicals when stirred with BTMG in THF solution, the amount of radical formation is small and radicals are not involved in the phenylation of $Ph_2CHCOCHPh_2$.

The authors then extended the radical-trapping technique to a number of the *C*-, *O*- , and *N*-phenylation reactions (involving organobismuth(V) reagents) reported during the last ten years from Barton's laboratory. The radical-trapping agents PhNO and $Ph_2C{=}CH_2$ were employed. With the latter agent the amount of $Ph_2C{=}CHPh$ formed was indicative of the amount of phenyl radicals produced. A number of organobismuth(V) reagents of the types Ph_3BiX_2, Ph_4BiX, and Ph_5Bi were used and most of the reactions were carried out in the presence of BTMG. In no case was the amount of *C*-, *O*-, or *N*-phenylated product appreciably affected by the presence of the radical-trapping reagent. It was concluded, therefore, that none of these reactions proceeded by mechanisms involving phenyl radicals. The authors also extended the radical-trapping technique to phenylation reactions involving such reagents as Ph_2ICl, Ph_2IOAc, $PhPb(OAc)_3$, and Ph_3SBr. The results were similar to those found for organobismuth(V) reagents and again it was concluded that phenyl radicals were not involved. Finally, two reactions known to occur by mechanisms involving free radicals were investigated. The decomposition of *N*-nitrosoacetanilide, which occurs by two competing routes (ionic and radical), gave 2% $Ph_2C{=}CHPh$ when carried out in the presence of $Ph_2C{=}CH_2$, while 40% Ph_2NAc was obtained when the same reaction was run in the presence of PhNO. In another example PhN_2BF_4 was decomposed by copper in DMF solution in the presence of $Ph_2C{=}CH_2$ to yield 43% $Ph_2C{=}CHPh$. The authors suggested that many reactions for which free radical mechanisms have been suggested actually occur by other mechanisms.

The oxidation of alcohols by organobismuth(V) reagents has been reported by Barton and coworkers in several preliminary papers. This reaction, as well as the *O*-phenylation of alcohols to produce phenyl ethers by organobismuth compounds of the type Ph_4BiX, has now been reported in considerable detail by Barton and coworkers [44]. Thus, $Ph_4BiO_2CCF_3$, when refluxed in benzene or toluene with a number of primary alcohols, gave satisfactory yields of ethers (65-75%). Allylic alcohols and diols gave smaller yields (45-60%), while secondary alcohols gave poor yields (15-30%). Tertiary alcohols gave only intractable mixtures. With two diols, *cis*-cyclohexane-1,2-diol and 2,2-dimethylpropane-1,3-diol, small amounts (13%) of the diphenylated ethers were also produced. The phenylation reaction was always accompanied by a competing reaction, the trifluoroacetylation of the alcohol:

$$Ph_4BiO_2CCF_3 \xrightarrow{\Delta} Ph_3Bi + CF_3CO_2Ph$$
$$CF_3CO_2Ph + ROH \longrightarrow CF_3CO_2R + PhOH$$

With primary alcohols ether formation was the principal reaction, but with secondary alcohols trifluoroacetylation predominated. Another by-product of the reaction was diphenyl ether which was believed to be produced in the following manner:

$$Ph_4BiO_2CCF_3 + H_2O \longrightarrow Ph_4BiOH + CF_3CO_2H$$
$$Ph_4BiOH \xrightarrow{\Delta} Ph_3Bi + PhOH$$
$$PhOH + Ph_4BiO_2CCF_3 \longrightarrow Ph_2O + Ph_3Bi + CF_3CO_2H$$

Thorough drying of the $Ph_4BiO_2CCF_3$ essentially eliminated this side reaction. The rate of the reaction between $Ph_4BiO_2CCF_3$ and alcohols to produce ethers was accelerated by the addition of Cl_3CCO_2H, but the yields were not affected. In the above experiments a number of simple alcohols (MeOH, Me_3CCH_2OH, $Me(CH_2)_{16}CH_2OH$, $PhCH_2CH_2OH$, $PhCH_2OH$, cyclohexanol, 2,2-dimethylpropane-1,3-diol, *cis*-cyclohexane-1,2-diol, and 1-methyl-*trans* cyclohexane-1,2-diol) as well as more complex natural products (geraniol, 3β-cholestanol, 3α-cholestanol, and 1,2:5,6-diisopropylidene-D-glucofuranose) were used. Because of the rather poor yields of ethers from secondary alcohols and $Ph_4BiO_2CCF_3$, a number of other reagents of the type Ph_4BiX (X = $OSO_2C_6H_4Me$-4, OAc, OSO_2CF_3, 2,4,6-$(NO_2)_3C_6H_2O$, O_2CCCl_3, O_2CCH_2Cl, and O_2CCHPh_2) were tried as phenylating agents, using 3 β-cholestanol as the substrate. In no case was the yield of the phenyl ether as good as that obtained with $Ph_4BiO_2CCF_3$ (26%). Neither Ph_4BiOAc nor $Ph_4OSO_2CF_3$ yielded any ether; $Ph_4BiO_2CCCl_3$ gave 3β-cholestanyl trichloroacetate (4%) and cholestanone (30%), but none of the phenyl ether. In all of these reactions considerable amounts of unreacted 3β-cholestanol were recovered.

Barton and coworkers had previously shown that Ph_5Bi and Ph_3BiCO_3 were excellent reagents for the oxidation of primary and secondary alcohols to aldehydes and ketones. Compounds of the type Ph_3BiX_2 (where X is an electronegative group) were also used to oxidize alcohols under basic conditions. In the present paper $Ph_4BiO_2CCF_3$ was used to oxidize 3β-cholestanol under basic conditions (BTMG). Cholestanone was obtained in 92% yield, slightly better than the yield obtained with Ph_3BiCl_2 (88%) or $Ph_3Bi(O_2CCF_3)_2$ (80%), while Ph_3BiCO_3 and Ph_5Bi gave yields of 75 and 70%, respectively. The tosyl compound $Ph_3Bi(OSO_2C_6H_4Me\text{-}4)_2$ gave the ketone in only 43% yield.

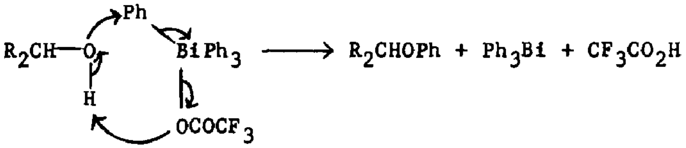
In addition to alcohols, the use of $Ph_4BiO_2CCF_3$ and $Ph_4BiOSO_2C_6H_4Me$-4 for the phenylation of several nitrogen compounds was investigated. No identifiable phenylated products were obtained from cholestanone oxime when it was treated with $Ph_4BiO_2CCF_3$ under neutral or basic conditions. Succinimide and phthalimide gave the corresponding *N*-phenyl derivatives in 34 and 57% yields, respectively, when refluxed with $Ph_4BiO_2CCF_3$ for several days.

N-Phenylacetamide gave *N,N*-diphenylacetamide in 21% yield under similar reaction conditions. *N*-Methylbenzamide gave only traces of *N*-methyl-*N*-phenylbenzamide when refluxed with $Ph_4BiO_2CCF_3$ for 4 days in PhH solution under basic conditions (LiH).

Two different mechanisms have been proposed for the reaction of Ph_4BiX compounds with alcohols, depending on whether the reaction occurred under basic or neutral (or acid) conditions. Under basic conditions it was suggested that a Bi-O bond was formed which subsequently broke to form the carbonyl compound, PhH, and Ph_3Bi:

$$R_2CHOH + Ph_4BiX + B^- \longrightarrow R_2CHOBiPh_4 + BH + X^-$$
$$R_2CHOBiPh_4 \longrightarrow R_2CO + [Ph_4BiH] \longrightarrow Ph_3Bi + PhH$$

In the reaction under neutral or acid conditions, a direct aromatic S_N2 displacement was suggested:



Barton and coworkers [45] had previously reported the *N*-phenylation of primary and secondary amines by organobismuth(V) reagents in the presence of Cu or Cu compounds. They have now reported [46] that the yields in this reaction sometimes exceeded 100% based on the following equation:

$$RNH_2 + Ph_3Bi(O_2CR')_2 \longrightarrow RNHPh + Ph_2BiO_2CR' + R'CO_2H$$

This observation suggested that an organobismuth(III) compound could act as a phenylating agent, and they further suggested that this phenylating agent might be Ph_3Bi formed by the dismutation of Ph_2BiO_2CR':

$$3\ Ph_2BiO_2CR' \longrightarrow 2\ Ph_3Bi + Bi(O_2CR')_3$$

Accordingly, the authors investigated the phenylation of amines by Ph_3Bi in the presence of 0.5 equivalent of $Cu(OAc)_2$. The reactions were carried out in CH_2Cl_2 at room temperature under argon with 1.2 equivalents of Ph_3Bi. The reaction times varied from 18-24 h. In general the yields of secondary amines from both aromatic and aliphatic primary amines were excellent (48-90%). Butylamine gave a 60% yield of *N*-butylaniline and a 13% yield of *N,N*-dibutylaniline, but no other tertiary amines as reaction products were reported. Amines which gave poor yields of secondary amines were 2,4,6-trimethylaniline (25%), and 4-nitroaniline (6%). Two secondary amines, tetrahydroisoquinoline and piperidine, gave satisfactory yields of the corresponding tertiary amines (90% and 56%, respectively). *N,N*-Diphenylhydrazine gave a 60% yield of the triphenyl compound, but benzophenone hydrazone gave only a 16% yield of the *N*-phenylated derivative. In all of the above reactions $Cu(OAc)_2$ or $Cu(O_2CCF_3)_2$ was an effective catalyst; Cu, or Cu oxides, chlorides, or triflates (OSO_2CF_3) gave no phenylation. Although these reactions were carried out in an argon atmosphere, an oxygen atmosphere scarcely affected the yields. By contrast, if oxygen was rigorously excluded, the yield of phenylated amine was dependent on the amount of $Cu(OAc)_2$ present. Thus, under these conditions, the yields of *N*-phenyl-*p*-anisidine (from *p*-anisidine) was 25, 42, and 60% in the presence of 0.5, 1, and 1.5 equivalents of $Cu(OAc)_2$, respectively. A possible mechanism for the *N*-phenylation reaction by Ph_3Bi in the presence of $Cu(OAc)_2$ was suggested.

In addition to the work of Barton and coworkers on the phenylation of alcohols to form alkyl phenyl ethers, Dodonov and coworkers have contributed extensively to this subject. In a recent preliminary communication [47] they reported that Ph_3Bi, in the presence of two molar equivalents of $Cu(OAc)_2$, phenylated primary alcohols to ethers and that the yields were increased when the reactions were carried out in the air rather than in a sealed ampoule. These authors have now reported on this reaction in much greater detail [48]. It was first shown that both primary alcohols (MeOH, EtOH, BuOH and $Me_2CHCH_2CH_2OH$) and secondary alcohols (Me_2CHOH and cyclohexanol) gave satisfactory yields (43-91%) of ethers when heated at 50°C for 2-6 h in sealed ampoules in the presence of 2 molar equivalents of $Cu(OAc)_2$ according to the equation:

$$Ph_3Bi + 2\ Cu(OAc)_2 + ROH \longrightarrow PhOR + PhH + PhBi(OAc)_2 + 2\ CuOAc$$

In addition to PhOR and PhH, considerable amounts of AcOH were usually produced in the reaction. Experiments were also carried out (both in the presence and absence of air and at several different temperatures) with equimolar amounts of two different alcohols. In this manner the reactivity of different alcohols was shown to be as follows: *tert*-BuOH << Me_2CHOH = cyclohexanol < BuOH < MeOH. It was also found that water was considerably more reactive (to give phenol) than the alcohols. The following mechanism involving a phenyl radical was suggested for the reaction:

$$\begin{gathered}
Ph_3Bi + Cu(OAc)_2 \longrightarrow [PhCuOAc] + Ph_2BiOAc \\
PhCuOAc \longrightarrow Ph^{\bullet} + CuOAc \\
Ph^{\bullet} + Cu(OAc)_2 + ROH \longrightarrow PhOR + CuOAc + AcOH
\end{gathered}$$

The formation of radicals in these reactions was proved by obtaining the ESR spectrum in the presence of the spin trapping agents Me_3CNO and $PhCH{=}N(O)CMe_3$.

Further experiments were then carried out to determine the effect of changing the concentration of $Cu(OAc)_2$ on the yields of ethers. The alcohols used were MeOH and EtOH and the amount of $Cu(OAc)_2$ was varied from 0.1 to 4 equivalents per mole of Ph_3Bi. The yields of PhOMe and PhOEt were found to increase markedly with increased concentrations of $Cu(OAc)_2$, reaching 1.59 equivalents for PhOMe and 1.33 equivalents for PhOEt. The yields of PhH and AcOH also increased with increasing copper concentration. All of these reactions were carried out in the absence of air. If the reactants were heated in the air at 50°C for 3-6 h, the yields of ethers were found to increase markedly. Thus, 1.78 molar equivalents of MeOPh were obtained under these conditions with 2 molar equivalents of $Cu(OAc)_2$ compared with 0.50 molar equivalent of MeOPh when the reaction was run in the absence of air at 50°C for 2 h. The largest yield (2.36 molar equivalents of PrOPh) was obtained with PrOH and $Cu(OAc)_2$ (2 molar equivalents) heated at 100°C for 1.5 h. Even reactions employing small amounts of $Cu(OAc)_2$ gave significant amounts of ethers when heated in the air. Thus, MeOH, $Cu(OAc)_2$ (0.1 molar equivalent), and 1 molar equivalent of Ph_3Bi gave 0.31 molar equivalent of MeOPh under these reaction conditions compared with 0.05 molar equivalent in the absence of air. In all of these reactions significant amounts of PhH were nearly always found. The formation of benzene was believed to occur by the dephenylation of Ph_3Bi:

$$Ph_3Bi + AcOH \longrightarrow Ph_2BiOAc + PhH$$

This reaction scarcely occurred in the absence of copper compounds, but on the addition of CuCl, CuBr, or $Cu(OAc)_2$ it occurred at room temperature, and at 50°C Ph_3Bi was completely dephenylated. A number of other experiments were reported in this paper including the effect of moisture on the phenylation reaction, the effect of other copper comounds, as well as the effect of salts of other transition metals.

The violet color of Ph_5Bi, as compared with the colorless compounds Ph_5P, Ph_5As, and Ph_5Sb, has long been the subject of speculation. Schmuck and coworkers [49] have now prepared crystals of Ph_5Bi suitable for X-ray diffraction study. They were obtained as large rhombic crystals from concentrated THF solution. Since the color was the same in the dissolved state as in the solid state, the color could not be ascribed to paramagnetism or impurities. X-ray diffraction studies revealed that the geometry about the Bi atom was that of a square pyramid, similar to Ph_5Sb. The angles between opposite equatorial groups were 163.5° and 150.3° and the equatorial bonds were considerably longer (232 pm) than the axial bond (221 pm). Since Ph_5Sb is colorless, the crystal structure of Ph_5Bi does not offer a solution to the violet color of this compound.

However, a violet/colorless dichroism was observed with well-formed crystals. Maximum absorption was found in the direction parallel to the axial Bi-C bond and maximum transmission in the plane perpendicular thereto. Light was transmitted through the crystal unhindered in this plane, but was strongly polarized. When the electric vector vibrated parallel to this plane the crystal appeared violet, when perpendicular the crystal appeared colorless. The authors suggested that the nature of the chromophore could be ascribed to a charge transfer transition by excitation of the 4 long equatorial bonds:

$$(C_6H_5)_4Bi{-}C_6H_5 \longrightarrow (C_6H_5)_4Bi^- \; C_6H_5^+$$

These bonds were much more strongly polarized in Ph_5Bi than in Ph_5Sb because of the poorer shielding of the Bi nucleus by the filled $4f$ shell. If the suggestion of the authors is correct, strong electron-withdrawing groups on the aryl groups should make the charge-transfer transition more difficult. Accordingly, the authors prepared $Ph_3Bi(C_6F_5)_2$ from Ph_3BiCl_2 and C_6F_5Li. It was obtained as orange crystals, mp 104°C.

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