BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1988

G.O. DOAK AND LEON D. FREEDMAN

Department of Chemistry, North Carolina State University, Raleigh, North Carolina 27695-8204 (U.S.A.)

Although no books or reviews dealing exclusively with organobismuth compounds, other than our Annual Survey, were published in 1988, a review on newer methods of arylation [1] was devoted in large part to the use of organobismuth compounds for this purpose. Wardell [2] has reviewed the literature on organoarsenic, -antimony, and -bismuth compounds described in 1986. The chemistry of both inorganic and organic bismuth compounds (particularly their use as ligands to transition elements) described in 1985 has been reviewed [3]. The preparation of two organobismuth compounds has been described in volume 4 of *Organometallic Syntheses* [4,5]. A few organobismuth compounds were mentioned in the *Annual Reports on the Progress of Chemistry* [6].

Three organobismuth(III) compounds, $MeBi(SMe)_2$, $MeBi(SC_6H_4NH_2\text{-}4)_2$, and $MeBi(SC_6H_4NH_2{}^+Me\text{-}4)_2\ 2I^-$, have been tested for antitumor activity [7]. The assay for activity employed the Ehrlich ascites tumor in the peritoneal cavity of mice. All three compounds were 100% effective in doses ranging from 2.5 to 160 mg/kg. Because of its lower toxicity the anilinium compound $MeBi(SC_6H_4NH_2{}^+Me\text{-}4)_2\ 2I^-$ possessed the most favorable therapeutic index. In doses between 60-80 mg/kg this compound effected 100% cure of the tumor with no deaths due to toxicity of the compound.

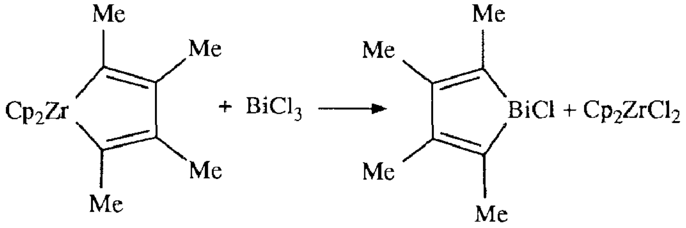
Bis[(2,6-dichlorophenyl)thio]methylbismuthine was prepared by means of the following reaction [8]:

$$MeBiBr_2 + 2\ 2,6\text{-}Cl_2C_6H_3SLi \xrightarrow[THF]{PhH} MeBi(SC_6H_3Cl_2\text{-}2,6)_2 + 2LiBr$$

The $2,6\text{-}Cl_2C_6H_3SLi$ was prepared from $2,6\text{-}Cl_2C_6H_3SH$ and BuLi, and the reaction was carried out in an argon atmosphere. The product, mp 202°C, was characterized by IR, PMR, and mass spectrometry and by elemental analysis. The biological activity of the compound was tested against bacteria (*B. subtilis* and *E. coli*), yeasts (*C. tropicalis*), and molds (*P. camembertii*). Against bacteria it was considerably more active than $PhBi(SC_6H_4Cl\text{-}4)_2$.

Fagan and Nugent [9] have found that easily prepared zirconium heterocyclic compounds could be used for the preparation of a variety of heterocyclic compounds of the main group elements. Thus, 1-chloro-2,3,4,5-tetramethylbismole was readily prepared according to the following equation:

Previous review see J. Organomet. Chem., 360(1989)297-317.



(where Cp was cyclopentadienyl)

Treatment of the chloro compound with phenyllithium gave 1-phenylbismole. The zirconium compound was prepared by reduction of Cp_2ZrCl_2 with either magnesium or butyllithium in the presence of 2-butyne.

Huber and coworkers have investigated the crystal structure of two organobismuth carboxylates by means of X-ray diffraction. The first paper [10] described the crystal and molecular structure of diphenylbismuth *N*-benzoylglycinate, $Ph_2BiO_2CCH_2NHCOPh$. The compound was prepared from Ph_2BiOEt and *N*-benzoylglycine in ether solution, and recrystallized from methanol. The bismuth atom was found to be in the center of a heavily distorted ψ-trigonal bipyramid. Two phenyl groups and a stereochemically active inert pair occupied equatorial positions. The apical positions were occupied by one oxygen(O) of the carboxyl group and one oxygen (O′) from the carboxyl group of a neighboring atom. The O-Bi-O′ angle was 160.63°. The compound thus existed as a one-dimensional polymer. The structure was similar to that previously found for bismuth(III) formate. The Bi-O′ distance was smaller than the sum of the Van der Waals radii but longer than the Bi-O distance. There is a similar weak interaction between the Bi atom and the oxygen of a carboxylate group of a third molecule, so that these interactions formally extended the coordination of the bismuth to seven.

In the second paper [11] the crystal and molecular structure of bis[2-furoato(1^-)]-triphenylbismuth was described. The compound was prepared from triphenylbismuth carbonate and 2-furancarboxylic acid, and the product was recrystallized from ethanol. The polyhedron around each Bi atom was that of a distorted pentagonal pyramid, with four carboxylate oxygens and one phenyl group in equatorial positions, and two phenyl groups in apical positions. The C-Bi-C angle of the apical phenyl groups was 148.23°. From the Bi-O distances between the Bi and the carboxylate oxygens, it was concluded that the carboxylate ligand possessed considerable ionic character.

Calderazzo and coworkers [12] have reported a greatly improved method for the preparation of tetraphenyldibismuthine and have studied a number of reactions of this compound. The new preparation of the dibismuthine involved the reduction of Ph_2BiI with bis(cyclopentadienyl)cobalt(II):

$$2Ph_2BiI + 2CoCp_2 \xrightarrow{THF} Ph_4Bi_2 + 2CoCp_2I$$

(where Cp was cyclopentadienyl)

The above reaction was carried out at room temperature. The insoluble $CoCp_2I$ was removed by filtration, and the dibismuthine was obtained from the filtrate in 80% yield. If Ph_2BiCl was used, no straightforward reaction was obtained. However, when the reduction of Ph_2BiCl was carried out in the presence of NaI, Ph_4Bi_2 was obtained in 54% yield. Tetraphenyldibismuthine reacted with diphenyldichalcogenides to form compounds of the type Ph_2BiEPh (where E was S, Se, or Te). The resulting colored compounds were characterized by elemental analyses, IR, ^{13}C NMR, and, for the tellurium compound only, mass spectrometry. In addition, an X-ray diffraction study of $Ph_2BiSePh$ was carried out. The geometry of the Bi atom was pyramidal. The angles around the Bi atom were significantly less than the tetrahedral value, indicating considerable *s* character for the lone pair on the bismuth atom.

The tellurium compound $Ph_2BiTePh$ reacted with diazomethane with insertion into the BiTe bond:

$$Ph_2BiTePh + CH_2N_2 \longrightarrow Ph_2BiCH_2TePh + N_2$$

The product was obtained as an oil, but PMR and mass spectral results (including the molecular ion, 0.5%) were in agreement with the proposed formula. There was also PMR evidence for a similar insertion reaction for diazomethane and $Ph_2BiSePh$, but no insertion was found when Ph_2BiSPh was used. Another insertion reaction involved Ph_4Bi_2 and elemental selenium:

$$Ph_2BiBiPh_2 + Se \xrightarrow{MePh} Ph_2BiSeBiPh_2$$

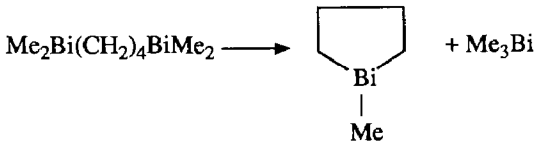
The product was characterized by elemental analyses and IR spectroscopy.

Alkali dialkylbismuthides are known to react with 1,2-dihaloethanes with the formation of ethylene and tetralkyldibismuthines:

$$2R_2BiM + XCH_2CH_2X \longrightarrow R_2BiBiR_2 + CH_2{=}CH_2 + 2MX$$

(where R was an alkyl group, M was an alkali metal, and X was a halogen)

Wieber and Rudolph [13] have now investigated the reaction of sodium dimethylbismuthide with α, ω-dibromoalkanes $Br(CH_2)_nBr$, where $n = 3,4,5$. Only in the case where $n = 5$ was the pure product $Me_2Bi(CH_2)_5BiMe_2$ obtained. Where $n = 3$, a non-separable mixture of the desired product together with 10-30% of tetramethyldibismuthine resulted. The composition of this mixture was determined both from its PMR spectrum and elemental analysis. The product mixture decomposed in a few minutes at room temperature and in a few weeks at -78°C. When $n = 4$, a mixture of the desired product, $Me_2Bi(CH_2)_4BiMe_2$, and a bismuth-containing heterocycle, 1-methylbismolane, was obtained. The dibismuthine was unstable and dismutated to the bismolane when allowed to stand at room temperature (in the dark under argon) for six days:



The same dismutation occurred after 2-3 h at 70-90°C under vacuum, or after standing for several weeks at -78°C. The latter result allowed the cyclic compound to be obtained in a pure form. The dibismuthine $Me_2Bi(CH_2)_5BiMe_2$ also gave a cyclic compound 1-methylbismane under similar reaction conditions. Finally, both heterocyclic compounds were prepared from dimethylbromobismuthine and the Grignard reagents $BrMg(CH_2)_nMgBr$, where $n = 4$ or 5. The two cyclic compounds were remarkably stable. They could be distilled *in vacuo* without decomposition. They were characterized by PMR and mass spectrometry, as well as by elemental analyses.

In addition to the above reaction, the authors employed sodium dimethylbismuthide for the preparation of unsymmetrical bismuth-silicon, -germanium, and -tin compounds:

$$Me_2BiNa + XCH_2EMe_3 \longrightarrow Me_2BiCH_2EMe_3 + NaX$$

(Where E was Si or Ge, X was Cl; and where E was Sn, X was Br)

All three compounds were obtained as colored fluids, characterized by PMR spectra, elemental analyses, and, in the case of the silicon compound, mass spectrometry. All three compounds were thermolabile. The Si and Ge compounds decomposed at room temperature in the dark after several hours. The Sn compound decomposed after several minutes, and all three compounds decomposed slowly at -78°C.

When Ph_2BiI was treated with samarium, europium, or ytterbium in THF, Ph_3Bi, $(PhBi)_x$, and biphenyl were formed [14].

Benson and coworkers [15] have found a linear or near-linear correlation between the average differences in the gas phase heats of formation on homologous substitution (Me for H, Et for Me) and the Pauling electronegativity of the main group elements. For alkyl substitutions, Pr for Et and higher, no such correlation was found. This result suggested that an atom's influence extended only up to its next-nearest neighbors. Several trialkylbismuthines were included in the study.

Yablokov and coworkers [16] have investigated the kinetics of the thermal decomposition of Et_3As, Et_3Sb, and Et_3Bi in the gas phase under comparable conditions. The principal products of the reaction were ethane and butane, with smaller amounts of ethylene and butylenes. The decomposition followed a first order reaction rate up to a conversion of 60-70% completion. These results were consistent with a free radical mechanism for the decomposition. The activation energies for the three compounds were 50.4, 45.3, and 26.5 kcal/mol, respectively.

In a U.S. patent on the disposal of solid propellants without atmospheric pollution or destruction of the outer casing, one of the ingredients in the propellant tested was triphenylbismuthine (0.03%) [17].

A Japanese patent described the preparation of electrostatographic toners with improved triboelectric properties by incorporating triarylbismuth compounds, such as triphenylbismuthine, into the toner [18].

Chemical vapor deposition of diamond-like carbon films was achieved by directing a supply of energy to an organometallic compound, the amount of energy corresponding to the dissociation energy of the C-metal bond [19]. Thus, triphenylstibine or -bismuthine in a reaction chamber treated with a 5300Å YAG laser beam gave a film with a Vickers hardness of 8000.

Japanese patents [20,21] have been issued for the preparation of electrically conducting films formed from trialkylbismuthines such as Me_3Bi. Thus, the organobismuth compound was deposited on the substrate and heated to < 300°C. In a paper from a Japanese laboratory [22], a method for the formation of epitaxial films using the metallorganic chemical vapor deposition technique and employing Me_3Bi and $(MeO)_4Si$ or $(EtO)_4Si$ as metal sources and oxygen or N_2O as oxidizing agents.

A combustion tube method for the simultaneous determination of carbon, hydrogen, and bismuth in organobismuth compounds has been reported by Hassan and coworkers [23]. After combustion the bismuth was determined by the weight of Bi_2O_3. Triphenylbismuthine was the only compound containing a C-Bi bond among the various compounds, all of which gave satisfactory analytical results.

An oxygen flask method for the combustion of organobismuth compounds followed by the micro or submicro spectrophotometric determination of bismuth as the orange-yellow iodide complex ion, BiI_4^-, at 465 nm has also been described [24]. Analysis of twelve compounds including triphenylbismuthine gave satisfactory results with a standard deviation of 0.4%.

In continuation of previous work on the polymerization of substituted alkynes by WCl_6 or $MoCl_5$ with various organometallic compounds, including triarylbismuthines, as cocatalysts, Masuda and coworkers have published seeral further papers on this subject. In one paper [25] the polymerization of silylacetylenes of the type $HC{\equiv}CSiMe_2R$, where R was an alkyl or aryl group, was described. Another paper [26] dealt with the polymerization of $2\text{-}CF_3C_6H_4C{\equiv}CH$. Yet another paper [27] dealt with the copolymerization of $Me_3SiC{\equiv}CCH_3$ with $MeC{\equiv}CPh$, $BuC{\equiv}CPh$, 2-octyne, or 4-octyne. In this last paper the catalysts were $TaCl_5$ or $NbCl_5$, and the cocatalyst was Ph_3Bi.

Acidic additives such as 3,5-dinitrosalicylic acid have been found to activate triphenylbismuthine as a catalyst for the reaction of diols with isocyanates [28].

In a paper largely devoted to organoantimony compounds, Rüther and coworkers [29] have described the preparation and properties of six organobismuth compounds of the type $(Ph_3BiO_3SR)_2O$, where R was CF_3, $2,4\text{-}(O_2N)_2C_6H_3$, $4\text{-}MeC_6H_4$, Ph, Me, and CH_2CH_2OH. These compounds were obtained by means of the following reaction:

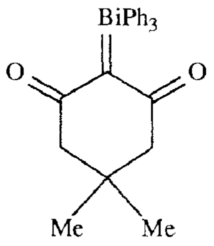
$$(Ph_3BiCl)_2O + 2RSO_3H + Ag_2O \longrightarrow (Ph_3BiO_3SR)_2O + 2AgCl + H_2O$$

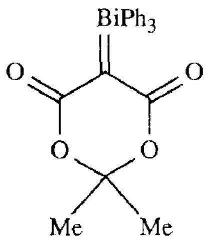
The compounds were characterized by elemental analyses and IR spectroscopy. Molecular weight determinations in methanol solution gave values which were from one-third to one-quarter of those calculated for the monomers. It was also found that $(Ph_3BiO_3SPh)_2O$ was a 1:2 electrolyte in methanol solution. The molecular weight results accordingly were assigned to the following solvolysis reaction:

$$(Ph_3BiO_3SR)_2O + 2MeOH \rightleftarrows 2[Ph_3BiBiOMe]^+ + 2RSO_3^- + H_2O$$

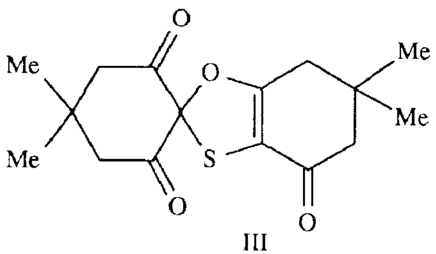
On the basis of the IR spectra, the compounds were believed to contain a pentacoordinate Bi atom containing μ-oxygen and SO_3-oxygen atoms in apical positions.

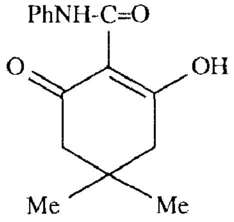
Although two bismuthonium ylides had been reported in the chemical literature, they were not obtained in pure crystalline form. Suzuki and coworkers [30] have now reported the preparation of two stable bismuthonium ylides I and II:


I


II

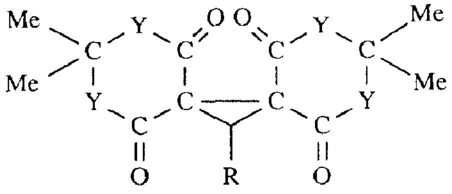
Compound I was obtained as pale yellow crystals, mp 72-75°C, by the reaction between Ph_3BiCO_3 and 5,5-dimethylcyclohexane-1,3-dione. Compound II was similarly prepared from Ph_3BiCO_3 and 2,2-dimethyl-1,3-dioxane-4,6-dione. Both compounds were characterized by elemental analyses and by IR, UV, ^1H and ^{13}C NMR spectroscopy. Compound I reacted with phenylisothiocyanate in benzene solution at 80°C in the presence of catalytic amounts of $Cu(acac)_2$ in a nitrogen atmosphere to yield the spiran III and the amide IV.

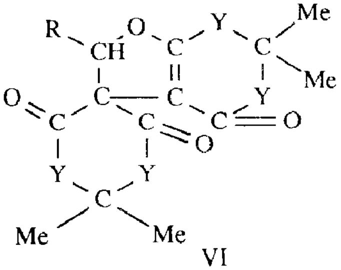

III

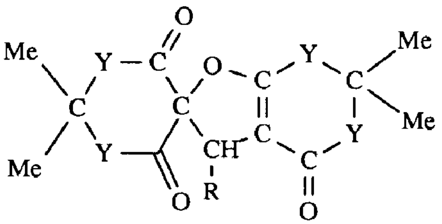

IV

The same product III was obtained from methylisothiocyanate together with the *N*-methyl amide corresponding to IV. There was no reaction between acetophenone or 4-phenyl-3-penten-2-one and either of the ylides I or II.

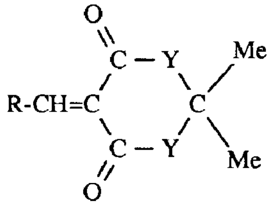
In addition to the reactions of the two stable bismuthonium ylides with isothiocyanates, described in the preceding report, the reaction of these ylides with a number of aldehydes, both aromatic (ArCHO, where Ar was 4-$MeOC_6H_4$, 4-MeC_6H_4, Ph, 4-ClC_6H_4, 4-NCC_6H_4, and 4-$O_2NC_6H_4$) and aliphatic ($PhCH_2CH_2CHO$ and PhCH=CHCHO), was investigated [31]. From these reactions four different types of products were obtained, V, VI, VII and/or VIII.


V


VI



VII



VIII

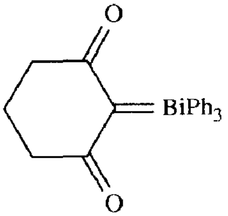
(where Y was CH_2 or O and R was an aryl or alkyl group corresponding to the aldehyde used in the reaction)

The product obtained depended not only on the ylide used, but also on the aldehyde and on the reaction conditions employed. Thus, with ylide I and $4\text{-}MeOC_6H_4CHO$ at 70°C, the only product obtained was the dihydrofuran VI ($R = MeOC_6H_4$, $Y = CH_2$). However, with the same ylide and the aldehydes $4\text{-}MeC_6H_4CHO$, $4\text{-}ClC_6H_4CHO$, or PhCHO, again at 70°C, mixtures of the two dihydrofurans, VI and VII ($Y = CH_2$) in a ratio of 2:1, respectively, were formed. When the reaction of the same ylide and $4\text{-}ClC_6H_4CHO$ was carried out at room temperature, the cyclopropane derivative V (43%, $Y = CH_2$) and the dihydrofurans VI and VII (7%) were isolated. With aldehydes containing negative groups on the benzene ring ($4\text{-}NCC_6H_4CHO$ and $4\text{-}O_2NC_6H_4CHO$), the only products obtained were those corresponding to V. A product of type V was also the sole material obtained from the aldehyde $PhCH_2CH_2CHO$, while PhCH=CHCHO gave only the dihydrofurans of types VI and VII. In all of these reactions with ylide I, benzene was the solvent. With ylide II the reactions were carried out in CH_2Cl_2 at 45°C and the same aldehydes were used. The results, however, were quite different. With the aldehydes $4\text{-}MeOC_6H_4CHO$ and PhCH=CHCHO, the olefins corresponding to product VIII (Y = O), the normal Wittig-reaction products, were obtained. With all of the other aldehydes only the cyclopropanes corresponding to product V (Y = O) were found. The authors suggested that in all cases the aldehydes first reacted with the ylides by a Wittig reaction to form olefins of type VIII. Except in two cases, this olefin then reacted with a second mol of ylide to form the cyclopropane derivative of type V. Reaction pathways involving opening of the cyclopropane ring followed by rearrangements, were suggested to account for the formation of the two dihydrofurans of types VI and VII. The products were characterized by IR and PMR spectroscopy and, in some cases, by elemental analyses. Representative spectra and analytical data on some of the compounds were reported in the present communciation.

An excellent general method for the preparation of ylides from diazo compounds has been devised by Glidewell and coworkers [32]. The method employed bis(hexafluoroacetylacetonato)copper(II) as the catalyst. It was believed that the thermal decomposition of the diazo compound produced a carbene which was then trapped by an appropriate reagent (*e.g.* Ph_3Bi) to form the ylide. It was suggested that the catalyst acted to bring the reactants in close proximity by their coordination at *cis*-sites at the copper in a six-coordinate intermediate. Use of the catalyst allowed the reaction to take place at much lower temperatures and was thus of particular value for the preparation of thermally unstable ylides. Two unstable bismuthonium ylides, IX and X, were prepared by the above method.

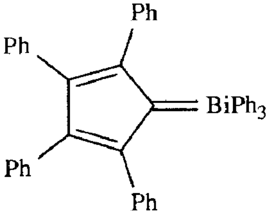
$(PhSO_2)_2C{=}BiPh_3$

IX



X

The chemistry of the two bismuthonium ylides, whose synthesis was described in the previous paper, has now been reported in a paper largely devoted to the chemistry of stibonium ylides [33]. Ylide IX decomposed slowly in the solid state, whereas X appeared to be more stable. Both compounds were khaki colored. Thus, they differed considerably from the previously known bismuthonium ylide XI which was deep blue and was also solvatochromic.



XI

It was suggested that in IX and X there was considerable intramolecular interaction between the bismuth atom and an oxygen atom of the sulfonyl or carbonyl group. In the IR spectrum of X the carbonyl group gave a broad peak centered at 1440 cm^{-1}, a much lower wavenumber than that found for the stibonium analog. This result suggested a very polarized carbonyl group. There was no reaction between ylide X and 2,4-dinitrobenzaldehyde.

A method for the preparation of triphenylbismuth dicarboxylates based on the oxidation of triphenylbismuthine in the presence of an acid anhydride has been reported by Dodonov and coworkers [34]:

$$Ph_3Bi + Me_3COOH + (RCO)_2O \longrightarrow Ph_3Bi(O_2CR)_2 + Me_3COH$$

(where R was Me, Pr, or Ph)

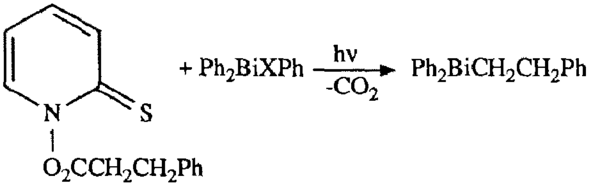
The most effective solvent for the reaction was ether. In this solvent the yields were 50-65%. Other organic solvents were much less effective.

In contrast to the antimony compound, $Ph_3Sb(OOCMe_3)_2$, the corresponding bismuth diperoxide has been found to be unstable; it decomposed homolytically to yield phenyl- and oxygen-centered radicals. Dodonov and coworkers [35] have now found that the bismuth compound oxidized primary and secondary alcohols to the corresponding aldehydes and ketones, respectively. With BuOH, Me_2CHCH_2OH, and $PhCH_2OH$, up to two molar equivalents of aldehyde were formed per mole of peroxide used. The yields of ketones from secondary alcohols were slightly less. The bismuth peroxide was also found to oxidize toluene and ethylbenzene to benzaldehyde and acetophenone, respectively.

Barton and coworkers have previously reported the arylation of amines (*N*-arylation), phenols and enols (*O*-arylation) by arylbismuth compounds of the types Ar_3BiY_2 and Ar_4BiY (where Y was a negative group such as 0.5 CO_3, O_2CMe, O_2CCF_3, etc.) in the presence of a copper catalyst. It was later found that triphenylbismuthine, in the presence of $Cu(OAc)_2$ or $Cu(O_2CCF_3)_2$, was an effective agent for the *N*-phenylation of amines [36]. There was evidence, however, that the active phenylating agent was a Bi(V) compound. Barton and coworkers [37] have now investigated the alkylation of amines using Bi(III) compounds of the type Ph_2BiR and R_3Bi (where R was Me or CH_2CH_2Ph). The authors noted that, unlike arylbismuth(III) compounds, alkylbismuth(III) compounds cannot be oxidized to stable alkylbismuth(V) compounds. Nevertheless, they were successful in *N*-alkylating amines using alkylbismuth(III) compounds in the presence of $Cu(OAc)_2$. In addition to the known compounds, Me_3Bi and Ph_2BiMe, two new alkylbismuth compounds, $Ph_2BiCH_2CH_2Ph$ and $Bi(CH_2CH_2Ph)_3$, were synthesized for use in this study. These were prepared from Ph_2BiCl or $BiCl_3$ and 2-phenylethylmagnesium bromide in 76 and 50% yields, respectively. A second synthesis of $Ph_2BiCH_2CH_2Ph$ involved a free radical substitution reaction:

$$Ph_3Bi + CF_3CO_2H \longrightarrow Ph_2BiO_2CCF_3$$

$$Ph_2BiO_2CCF_3 + PhXH \longrightarrow Ph_2BiXPh$$

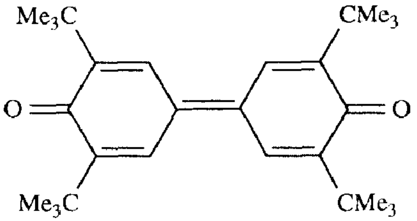


(where X was S or Se)

The compound $Bi(CH_2CH_2Ph)_3$, when refluxed in toluene for 2 h, gave a quantitative yield of styrene. By contrast, $Ph_2BiCH_2CH_2Ph$ was stable, even when heated neat at 160°C.

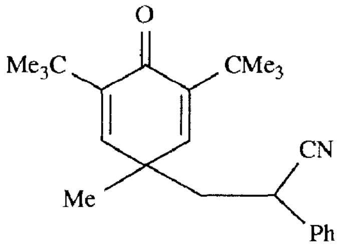
The amines used in the alkylation experiments were aniline, 4-anisidine, butylamine, piperidine, pyrrolidine, and morpholine. The reactions involved stirring 1 mmol of the amine, 1.2 mmol of the bismuth reagent, and 1 mmol of $Cu(OAc)_2$ at room temperature under argon for 24 h. The results showed that *N*-alkylation, *N*-arylation, or both could occur, depending on the amine used. Thus, with aniline and $Ph_2BiCH_2CH_2Ph$ both $PhNHCH_2CH_2Ph$ (11%) and $Ph_2NCH_2CH_2Ph$ (18%) were obtained. Similarly, butylamine gave $BuNHCH_2CH_2Ph$ (8%) and $BuN(Ph)CH_2CH_2Ph$ (28%). With the same bismuth reagent, piperidine gave only the *N*-alkylated amine (51%), whereas morpholine gave only the *N*-arylated amine (50%). This rather surprising result was also observed with Ph_2BiMe; piperidine gave only the alkyl and morpholine gave only the aryl product. All six amines were treated with $Bi(CH_2CH_2Ph)_3$; only the monoalkyl products were obtained. With trimethylbismuthine, however, aniline or 4-anisidine gave principally the dialkylated product (tertiary amine). Piperidine, pyrrolidine, and morpholine were alkylated in yields of 49, 47, and 52%, respectively, by the same regent.

Barton and coworkers have written extensively on the *O*- and *C*-phenylation of phenols by organobismuth(V) reagents. With unhindered phenols under neutral conditions, *O*-phenylation generally predominated, whereas under basic conditions *C*-phenylation generally occurred. Quite different results were obtained with highly hindered phenols. Thus, 2,6-di-*tert*-butylphenol and triphenylbismuth carbonate, in the presence of BTMG (*N*-*tert*-butyl-*N*′,*N*′,*N*″,*N*″-tetramethylguanidine), gave the following diphenoquinone:

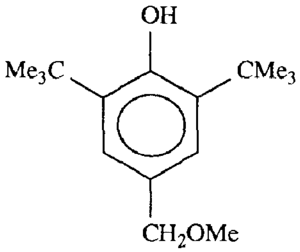


XII

2,6-Di-*tert*-butyl-4-methylphenol, triphenylbismuth dichloride, and BTMG in acrylonitrile gave the following product:



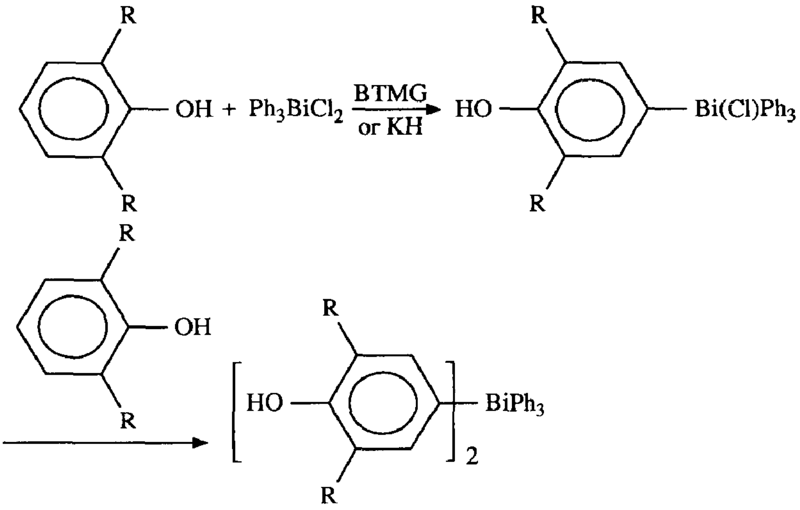
If the solvent used was benzene-methanol rather acrylonitrile, the following product was obtained:



Other hindered phenols giving somewhat similar results were 2,4,6-trimethylphenol and 2,6-dimethyl-4-methoxyphenol. In an effort to explain these results several mechanistic pathways had been previously considered [38]. In one such pathway formation of an aryloxy radical with subsequent dimerization was postulated. Another pathway considered the formation of an aryloxybismuth intermediate as the first step of the reaction:

$$\mathrm{ArOH} + \mathrm{Ph_3BiX_2} \longrightarrow \mathrm{ArOBi(X)Ph_3}$$

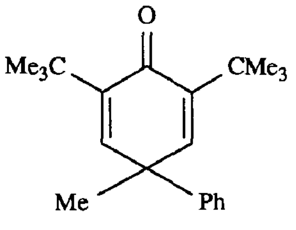
A third mechanism, and the one favored by Barton and coworkers, involved attack of the bismuth reagent at the 4-position of the phenol as the first step of the reaction:



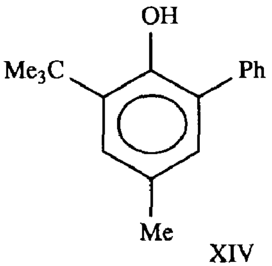
(where R was *tert*-Bu)

Barton and coworkers [39] have now reported further studies in an effort to distinguish between the three proposed mechanisms. One such study involved the effect of radical scavengers on the course of the reactions. For example, the effect of two radical scavengers (2,2,6,6-tetramethyl-1-piperidinyloxy and 1,1-diphenylethylene) on the reaction of 2,6-di-*tert*-butylphenol with triphenylbismuth dichloride in the presence of BTMG was studied. While the results did not rule out a radical mechanism, they were considered to be best explained by the third proposed mechanism, *i.e.* attack of the bismuth reagent at the 4-position of the phenol. Further evidence for this mechanism was suggested by the observation that 2,6-di-*tert*-butylphenol, and tetraphenylbismuth 4-toluenesulfonate in the presence of BTMG gave 2,6-di-*tert*-butyl-4-phenylphenol (33%) (together with traces of XII). The authors noted that this was the first example of the 4-phenylation of a phenol by an organobismuth reagent. This same product, however, in 37% yield, together with 3,3′,5,5′-tetra-*tert*-butyl-4,4′-biphenol (15%) was obtained when 2,6-di-*tert*-butylphenol was treated first with potassium hydride and then with triphenylbismuth dichloride.

Although most of the experiments reported in this paper gave results that were best explained by the mechanism involving attachment of the bismuth reagent at the 4-position of the phenol, several experiments were not compatible with this mechanism. Thus, when 2,6-di-*tert*-butyl-4-methylphenol was treated with tetraphenylbismuth 4-toluenesulfonate and BTMG, both 2,6-di-*tert*-butyl-4-methyl-4-phenylcyclohexa-2,5-dien-1-one(XIII) and 2-*tert*-butyl-4-methyl-6-phenylphenol (XIV) were obtained.



XIII



XIV

In a similar manner the reaction of triphenylbismuth dichloride and 2,4,6-tri-*tert*-butylphenol in the presence of KH gave 2,4-di-*tert*-butyl-6-phenyl- and 2,6-di-*tert*-butyl-4-phenylphenols. The products in which phenylation occurred in the 2-positions suggested the involvement of an O-Bi type intermediate (mechanism 2).

In addition to the above (and many other) synthesis experiments, the authors investigated ESR spectra of the various reactions studied in the present work. Thus, the aryloxyl radical was detected in a solution of 2,6-di-*tert*-butyl-4-methylphenol. The intensity of the signal was increased by the addition of BTMG, but no significant modification occurred after the addition of triphenylbismuth dichloride. A stable, colored radical was found in a solution of 2,4,6-tri-*tert*-butylphenol, BTMG, and triphenylbismuth dichloride. An equimolar solution of the three components, when measured by UV-visible spectroscopy, showed that the radical was present in a 1.8% concentration. It was pointed out that observation of small concentrations of aryloxy radicals did not necessarily mean that they played a part in the reactions leading to the isolated products.

The authors concluded that the abnormal 2- and 4-phenylation reactions found in the present study could be accommodated by mechanisms involving Bi-O or Bi-C intermediates, respectively. Nevertheless, they "considered the hypothesis that extreme steric hindrance has finally produced a new mechanism in which electron transfer between BTMG (or other base) and a Bi(V) reagent leads to fragmenting to aryl radicals".

Since the copper-catalyzed arylation of amines, phenols, and enols by organobismuth reagents almost certainly involved an arylcopper intermediate, Barton and coworkers [40] reasoned that if a metal such as palladium or nickel, rather than copper, was used, coupling to form biaryls might occur as the principal reaction. This indeed proved to be the case with palladium (but not with nickel). When triphenylbismuthine was allowed to react with an equimolar amount of $Pd(OAc)_2$ and triethylamine (2 molar equivalents) in THF solution, a 97% yield of biphenyl was produced, based on the reaction:

$$2Ph_3Bi \xrightarrow[Et_3N]{Pd(OAc)_2} 3Ph_2 + 2Bi$$

A 100% yield of the same product was obtained in hexamethylphosphoramide, $(Me_2N)_3PO$, after heating for 10 minutes at 65°C. In addition to triphenylbismuthine, tri-4-tolylbismuthine and tris(4-methoxyphenyl)bismuthine gave the corresponding biaryls in essentially quantitative yields. Nor was the reaction confined only to organobismuth compounds. Thus, triphenylstibine, hexaphenyldilead, and tetraphenyllead all gave good yields of biphenyl when treated with $Pd(OAc)_2$ and triethylamine. In all of the above reactions equimolar quantities of $Pd(OAc)_2$ and arylmetal compounds were used. The authors found, however, that, with a few exceptions, almost quantitative yields of biaryls could be obtained with only 0.05 molar equivalent of $Pd(OAc)_2$ when any of the following arylbismuth compounds were used to produce biaryls: Ph_2BiX (X = Cl, OAc, O_2CCF_3), Ph_3BiX_2 (X = Cl, OAc, O_2CCF_3), and Ar_3BiCl_2 (Ar = 4-$MeOC_6H_4$, 4-MeC_6H_4). In the case of Ph_3BiCO_3, however, the yield of biphenyl was only 52%. In addition to palladium, the authors used bis(1,5-cyclooctadiene)nickel and triphenylbismuthine in a 1:1 molar ratio. After stirring at room temperature for 52 h in THF solution, the yield of biphenyl was only 4%. In addition, it was found that tris(2-phenylethyl)bismuthine and $Pd(OAc)_2$ gave a 74% yield of 1,4-diphenylbutane.

In addition to the use of organobismuth compounds and palladium to form biaryls, the authors investigated the reaction of these reagents with acyl chlorides (as well as with benzoyl chloride) to form phenyl ketones:

$$Ph_3Bi + 3RCOCl \xrightarrow[Et_3N]{Pd(OAc)_2} 3RCOPh + BiCl_3$$

(where R was Ph, $PhCH_2$, Me, Et, $Me(CH_2)_{14}$, Me_3C, or 1-adamantyl)

The reactions were carried out at 65°C for 5 h with HMPA as the solvent. The yields of ketones varied from 89-96%.

In another paper from Barton's laboratory [41], the copper-catalyzed reactions of organobismuth(V) reagents with indole and derivatives of indole were investigated. The most effective catalysts were copper metal and $Cu(O_2CCF_3)_2$; $Cu(OAc)_2$ was less effective. Indole, $Ph_3Bi(O_2CCF_3)_2$ and Cu(0.01 molar equivalent) gave a 50% yield of 3-phenylindole. In the absence of any added catalyst a 41% yield of the same product was obtained. This result was attributed to traces of copper in the solvent (CH_2Cl_2) used. Larger amounts of catalyst (0.1 molar equivalent of Cu or $Cu(O_2CCF_3)_2$) gave complex mixtures from which no pure compounds could be obtained. With indoles where the 3-position was blocked, *N*-phenylation occurred. Thus, 3-methylindole, $Ph_3Bi(O_2CCF_3)_2$ and $Cu(O_2CCF_3)_2$ gave a 21% yield of 1-phenylindole. No phenylation occurred with $Cu(OAc)_2$ as the catalyst. 1,2,3,4-Tetrahydrocarbazole gave a 15% yield of the *N*-phenyl derivative. Carbazole gave a maximum yield of 84% of the *N*-phenyl derivative. Neither carbazole nor the 1,2,3,4-tetrahydro derivative reacted when $Cu(OAc)_2$ was the catalyst. As might be predicted, no phenylation occurred when 1,3-dimethylindole was the substrate; 1,2-dimethylindole gave a 94% yield of the 3-phenyl derivative. An exception to the *C*-phenylation of indoles unsubstituted in the 3-position was found with ethyl 2-indolylacetate. This compound gave the *N*-phenyl derivative in 30 and 31% yield; the catalysts were $Cu(OAc)_2$ and Cu, respectively. Two reaction pathways involving a phenyl copper intermediate and leading to either *C*- or *N*-phenylation were suggested.

The oxidation of olefins to ketones by molecular oxygen in anhydrous ethanol solution was catalyzed by complexes containing palladium chlorides, lithium chloride, and a bismuth chloride [42]. Although bismuth trichloride was generally used as the bismuth compound, one effective catalyst was Li_2PdCl_4-Ph_3BiCl_2-LiCl. This catalyst produced the highest yield of octanones when 1-octene was the olefin. The principal product was 2-octanone, but both 3- and 4-octanones as well as acetaldehyde and its diethyl acetal were also formed.

In addition to the wide variety of organic compounds phenylated by other organobismuth(V) reagents, Sharutin and Ermoshkin [43] have reported that pentaphenylbismuth reacted with liquid SO_2 to form benzene, diphenylsulfone, and an unidentified bismuth compound which analyzed for the empirical formula $C_{12}H_9BiO_4S_2$.

REFERENCES

1 R.A. Abramovitch, D.H.R. Barton, and J.-P. Finet, *Tetrahedron*, **44** (1988) 3039.

2 J.L. Wardell, *Organomet. Chem.*, **16** (1987) 142.

3 M.F.A. Dove and D.B. Sowerby, *Coord. Chem. Rev.*, **85** (1988) 289.

4 H.J. Breunig, D. Müller, W.W. Du Mont, and T. Severengiz, *Organomet. Synth.*, **4** (1988) 596.

5 D. Hellwinkel, *Organomet. Synth.*, **4** (1988) 599.

6 P.G. Harrison, *Annu. Rep. Prog. Chem., Sect. A: Inorg. Chem.*, **84** (1988) 85.

7 P. Köpf-Maier and T. Klapötke, *Inorg. Chim. Acta*, **152** (1988) 49.

8 T. Klapötke and P. Gowik, *Z. Naturforsch., B: Chem. Sci.*, **42B** (1987) 940.

9 P.J. Fagan and W.A. Nugent, *J. Am. Chem. Soc.*, **110** (1988) 2310.

10 F. Huber, M. Domagala, and H. Preut, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, **C44** (1988) 828.

11 M. Domagala, H. Preut, and F. Huber, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, **C44** (1988) 830.

12 F. Calderazzo, A. Morvillo, G. Pelizzi, R. Poli, and F. Ungari, *Inorg. Chem.*, **27** (1988) 3730.

13 M. Wieber and K. Rudolph, *Z. Naturforsch., B: Chem. Sci.*, **43B** (1988) 739.

14 E.A. Fedorova, O.A. Trokhaeva, G.S. Kalinina, M.N. Bochkarev, and G.A. Razuvaev, *Metalloorg. Khim.*, **1** (1988) 397; *Chem. Abstr.*, **110** (1989) 192964b.

15 S.W. Benson, J.T. Francis, and T.T. Tsotsis, *J. Phys. Chem.*, **92** (1988) 4515.

16 V.A. Yablokov, I.A. Zelyaev, E.I. Makarov, and N.S. Lokhov, *Zh. Obshch. Khim.*, **57** (1987) 2034.

17 D.C. Sayles, U.S. Pat. US 4,758,387; *Chem. Abstr.*, **109** (1988) 173018j.

18 K. Tanaka, Jpn. Kokai Tokkyo Koho JP 63 15,260 [88 15,260]; *Chem. Abstr.*, **109** (1988) 101793k.

19 N. Kurihara, M. Sugata, H. Sugata, T. Den, and K. Ando, Jpn. Kokai Tokkyo Koho JP 63 89,665 [88 89,665]; *Chem. Abstr.*, **109** (1988) 181119h.

20 M. Okada and K. Tomita, Jpn. Kokai Tokkyo Koho JP 62 67, 175 [87 67,175]; *Chem. Abstr.*, **108** (1988) 122969s.

21 M. Futaki, Jpn. Kokai Tokkyo Koho JP 62 182, 279 [87 182,279]; *Chem. Abstr.*, **108** (1988) 30363m.

22 Y. Nagao and Y. Mimura, *IEEE J. Quantum Electron.*, **QE-23** (1987) 2152.

23 H.N.A. Hassan, M.E.M. Hassouna, and Y.A. Gawargious, *Microchem. J.*, **37** (1988) 51.

24 H.N.A. Hassan, M.E.M. Hassouna, and Y.A. Gawargious, *Talanta*, **35** (1988) 311.

25 H. Tajima, T. Masuda, and T. Higashimura, *J. Polym. Sci., Part A: Polym. Chem.*, **25** (1987) 2033.

26 T. Masuda, T. Hamano, T. Higashimura, T. Ueda, and H. Muramatsu, *Macromolecules*, **21** (1988) 281.

27 T. Hamano, T. Masuda, and T. Higashimura, *J. Polym. Sci., Part A: Polym. Chem.*, **26** (1988) 2603.

28 B.D. Nahlovsky and G.A. Zimmerman, *Int. Jahrestag.-Fraunhofer-Inst. Treib-Explosivst.*, **39** (1987) 12; *Chem. Abstr.*, **108** (1988) 56652e.

29 R. Rüther, F. Huber, and H. Preut, *J. Organomet. Chem.*, **342** (1988) 185.

30 H. Suzuki, T. Murafuji, and T. Ogawa, *Chem. Lett.*, (1988) 847.

31 T. Ogawa, T. Murafuji, and H. Suzuki, *Chem. Lett.*, (1988) 849.

32 C. Glidewell, D. Lloyd and S. Metcalfe, *Synthesis*, (1988) 319.

33 G. Ferguson, C. Glidewell, I. Gosney, D. Lloyd, S. Metcalfe, and H. Lumbroso, *J. Chem. Soc., Perkin Trans. 2*, (1988) 1829.

34 V.A. Dodonov, A.V. Gushchin, and M.B. Ezhova, *Zh. Obshch. Khim.*, **58** (1988) 2170.

35 V.A. Dodonov, T.I. Zinov'eva, and N.N. Osadchaya, *Zh. Obshch. Khim.*, **58** (1988) 712.

36 D.H.R. Barton, J.-P. Finet, and J. Khamsi, *Tetrahedron Lett.*, **28** (1987) 887.

37 D.H.R. Barton, N. Ozbalik, and M. Ramesh, *Tetrahedron Lett.*, **29** (1988) 857.

38 D.H.R. Barton, N. Yadav-Bhatnagar, J.-P. Finet, J. Khamsi, W.B. Motherwell, and S.P. Stanforth, *Tetrahedron*, **43** (1987) 323.

39 D.H.R. Barton, J.-P. Finet, C. Giannotti, and F. Halley, *Tetrahedron*, **44** (1988) 4483.

40 D.H.R. Barton, N. Ozbalik, and M. Ramesh, *Tetrahedron*, **44** (1988) 5661.

41 D.H.R. Barton, J.-P. Finet, and J. Khamsi, *Tetrahedron Lett.*, **29** (1988) 1115.

42 J.-M. Brégeault, M. Faraj, J. Martin, and C. Martin, *New J. Chem.*, **11** (1987) 337.

43 V.V. Sharutin and A.E. Ermoshkin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1987) 2598.