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BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1990

G.O. DOAK AND LEON D. FREEDMAN

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

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In addition to our Annual Survey covering the year 1989, only one review dealing exclusively with organobismuth compounds was published in 1990 [1]. This was a discussion of the relationship between color and C-Bi bonding in pentaarylbismuth compounds and was published in the proceedings of the Second International Conference on Heteroatom Chemistry. A second paper presented at the same conference reviewed ligand coupling in organobismuth and organolead compounds [2]. Wardell, in *Organometallic Chemistry*, has reviewed organobismuth compounds described in the chemical literature in 1989 [3]. Sowerby, in a paper reviewing the organic compounds of the Group V elements, has described organobismuth compounds prepared in 1986-1987 [4]. In a Japanese journal not available to the present authors, a review of hypervalent and hypercoordinate compounds used in organic synthesis included Ph-Bi(V) compounds [5]. The properties of thermochromic distibines and dibismuthines have been reviewed by Ashe [6]. A great deal of the work described in this review originated in Ashe's laboratory.

In a review paper, presented at the Fifth International Symposium on Organometallic Chemistry Directed Toward Organic Synthesis, Brunner [7] has discussed enantioselective catalysts developed in his laboratory. Among the various reactions outlined was the monophenylation of *meso*-cyclopentane-1,2-diol by triphenylbismuth diacetate and copper(II) diacetate to give a racemic mixture of the phenoxycyclopentanol. When the reaction was carried out in the presence of an enantiomeric pyridineoxazoline, a 50% enantiomeric excess could be obtained. References were cited to the scope of the reaction in the monophenylation of a number of *meso*-diols.

Organobismuth compounds containing both Bi-C and Bi-M bonds, where M was Mo or Co, have been prepared by Clegg and coworkers [8]. The reaction between $BiCl[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$ and $K[BHEt_3]$ in THF at -78°C gave the crystalline complex $Bi[Mo(CO)_3(\eta\text{-}C_5H_5)]_3$ and a small amount of $Mo_2(CO)_6(\eta\text{-}C_5H_5)_2$. The IR spectrum

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*Bismuth, Annual Survey covering the year 1989, see J. Organomet. Chem., 404 (1991) 87. Reprints for this Survey are not available.

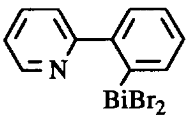
of the mother liquors, after removal of the above two compounds, showed the presence of $K[Mo(CO)_3(\eta\text{-}C_5H_5)]$ and a fourth complex. From these mother liquors, after removal of more of the solvent and cooling to -30°C, dark red crystals of the compound $EtBi[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$ were obtained. This material was characterized by IR and ^1H NMR spectroscopy, by elemental analyses, and by a determination of the crystal structure by X-ray diffraction. It was shown that the reaction to give the ethyl compound resulted from direct reaction of $K[BHEt_3]$ with $BiCl[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$ and not from BEt_3 formed by oxidation of $K[BHEt_3]$, since the molybdenum complex was completely unreactive to BEt_3. An attempt to prepare the complex $PhBi[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$ from the chloro compound and PhLi gave principally $Bi[Mo(CO)_3(\eta\text{-}C_5H_5)]_3$, together with unidentified products. The desired phenyl compound was prepared in 80% yield from $PhBiBr_2$ and two equivalents of $Na[Mo(CO)_3(\eta\text{-}C_5H_5)]$ in THF at 0°C. It was characterized by IR, ^1H, and ^{13}C NMR spectroscopy and by elemental analyses. The cobalt complex $PhBi[Co(CO)_3PPh_3]_2$ was similarly prepared from $PhBiBr_2$ and $K[Co(CO)_3PPh_3]$. It was characterized by IR, ^1H, ^{13}C, and ^{31}P NMR spectroscopy and by elementary analyses.

Although the cyclopentadienylbismuth compounds Cp_3Bi and Cp_2BiCl (Cp = cyclopentadienyl) are known, a monocyclopentadienyl compound has hitherto not been prepared. Frank [9] has now obtained $CpBiCl_2$ as a thermolabile, light-sensitive compound by means of the following reaction:

$$CpNa + BiCl_3 \xrightarrow[-70°C]{Et_2O} CpBiCl_2 + NaCl$$

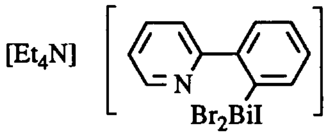
The desired product was separated from sodium chloride by extraction with Et_2O-THF (9:1) and recrystallization at low temperature. It was obtained as red crystals, which changed slowly at room temperature, more rapidly at higher temperatures and especially when exposed to X-rays, into a black amorphous form, insoluble in organic solvents. The red crystalline form was characterized by PMR and by elemental analyses. It was monomolecular in benzene. This substance was subjected to X-ray diffraction at -130°C. The structure was built up of distorted $TcCl_4$-type polymeric chains with Cp rings π-bonded to bismuth. Pseudorotational disorder, which was attributed to packing requirements, resulted in both η^2- and η^3-bonded states in a 1:1 ratio along the chains. The bond order of the Cp-Bi bond was calculated to be ~ 1.5. Bond distances and bond angles were listed. The PMR spectrum (in solution) suggested that there was a fast rotation of the cyclopentadienyl ring even at -70°C.

Ali and coworkers [10] have prepared dibromo-2-(2′-pyridyl)phenylbismuthine (I) by the reaction between 2-(2′-pyridyl)phenylmercury chloride and bismuth tribromide in dioxane. The new compound was characterized by IR and ^{13}C NMR spectroscopy, and by elemental analyses.

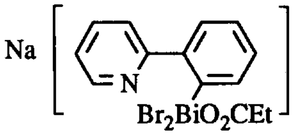


I

The IR data suggested two different environments for the 2-pyridylphenyl group, one weakly coordinated to the nitrogen, the other uncoordinated. The Lewis acidity of the compound was investigated by studying its reaction with tetraethylammonium iodide, with sodium propionate, and with sodium diethyldithiocarbamate. With the first two compounds, salts II and III were formed, respectively.

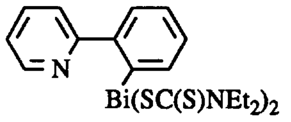


II



III

^{14}N NMR in DMSO solution was used to confirm the presence of the cation of compound II. The authors were unable to determine the structure of this compound by X-ray diffraction. In compound III the IR data suggested that the carboxylato group was symmetrically bidentate. In both compounds II and III, the nitrogen of the pyridyl group appeared to be less coordinated than in compound I (as judged by the IR data). The reaction of compound I with sodium diethyldithiocarbamate in acetonitrile led to the formation of compound IV.



IV

This compound was characterized by IR and ^{13}C NMR spectroscopy, and by elemental analyses. The IR data suggested that the pyridyl nitrogen coordinated to the bismuth atom to a greater extent than in the other 2-pyridylphenyl compounds reported in this paper. The molecular structure of the compound was determined by X-ray diffraction. The coordination around the bismuth atom was pseudopentagonal-bipyramidal with four sulfur atoms and the pyridyl nitrogen atom forming the equatorial plane. The phenyl group and the bismuth lone pair were located axially to the equatorial plane. Each thiocarbamato group was linked to the bismuth by one long and one short Bi-S bond. The Bi-N distance was considerably longer than the sum of the covalent radii, but was well within the van der Waals distance.

Triphenylbismuthine (5.7 mmol) and maleic acid (11.5 mmol) were refluxed in ether solution in a dinitrogen atmosphere to yield the dimaleate PhBi-$(O_2CCH{=}CHCO_2H)_2$ and a second uncharacterized product. The dimaleate was characterized by ^{13}C NMR and IR spectroscopy, and by elemental analyses. When this compound was refluxed with sodium diethyldithiocarbamate in DMSO-$MeNO_2$-H_2O solution, bis(diethyldithiocarbamato)phenylbismuthine was obtained (together with some triphenylbismuthine). The molecular structure of this compound was also determined by X-ray diffraction. It was dimeric with a similar structure to bis(diethyldithiocarbamato)-2-(2′-pyridyl)phenylbismuthine (IV). The coordination around the bismuth atom was pseudopentagonal-pyramidal, with four sulfur atoms, together with a fifth sulfur atom from a centrosymmetrically related molecule of the dimer, forming the equatorial plane. The phenyl group and the bismuth lone pair, located axially, completed the pentagonal bipyramid.

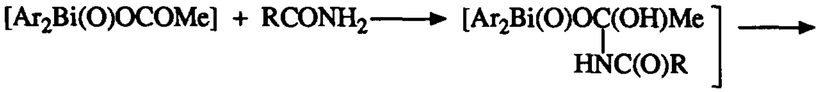
Ogawa and coworkers have recently described compounds of the type $Ar_2Bi(O)OMe$ and outlined several reactions where they served as oxidizing agents in organic syntheses. A new paper [11] described the use of these organobismuth(V) reagents for the acylation of amides and thioamides:

$$RC(Y)NH_2 + MeCO_2H \xrightarrow{Ar_2Bi(O)OMe} RC(Y)NHCOMe$$

(where R was phenyl and Y was O or S; or where R was methyl and Y was O; and where Ar was 1-naphthyl)

The yields varied from 76% ($PhCSNH_2$) to 89% ($PhCONH_2$). In addition to these amides, 2-piperidone was acylated to *N*-acetyl-2-piperidone in 84% yield. Other than these simple amides, two substituted ureas and two substituted thioureas, $CO(NHR)_2$ and $CS(NHR)_2$, where R was cyclohexyl or phenyl, were acylated by the use of the bismuth reagent. The yields for the two ureas were 76 and 84%, respectively, and for the two thioureas, 68 and 48%, respectively. The authors suggested the following mechanism for the acylation:

$$\mathrm{Ar_2Bi(O)OMe + MeCO_2H \longrightarrow [Ar_2Bi(O)OCOMe] + MeOH}$$



$$\mathrm{[Ar_2Bi(O)OCOMe] + RCONH_2 \longrightarrow \left[\begin{array}{r}\mathrm{Ar_2Bi(O)OC(OH)Me}\\ |\quad\;\;\\ \mathrm{HNC(O)R}\end{array}\right] \longrightarrow}$$

$$\mathrm{Ar_2Bi(O)OH + RC(O)NHCOMe}$$

The acetylated amides were identified by PMR spectroscopy and by comparison of their mps or bps with literature values.

Massey and coworkers have previously described the preparation of dodecafluorotriptycenes containing P, As, Sb, or Bi atoms in the 1,6-positions. Triptycenes containing two different Group V elements, P/Sb or As/Sb in the 1,6-positions, were also prepared. The present paper from the same laboratory described, in more detail, the mass spectra and ^{19}F NMR spectra of the compounds [12]. A comparison of the mass spectra obtained under both electron impact (EI) and fast atom bombardment (FAB) conditions was made. In the case of the bismuth compound $Bi_2(C_6F_4)_3$, the peak for the molecular ion under EI conditions was considerably greater (relative intensity 18.4) as compared with that obtained under FAB conditions (relative intensity 3.5). This result was not the case with some other Group V triptycenes. The ^{19}F NMR spectrum, both observed and calculated for $Sb_2(C_6F_4)_3$, but not for the corresponding Bi compound, was illustrated.

Previous attempts to prepare $Bi_2(C_6F_4)_3$, from granular bismuth metal and 1,2-diiodotetrafluorobenzene were unsuccessful. The authors have now succeeded in obtaining the triptycene by heating finely powdered bismuth with 1,2-diiodotetrafluorobenzene in a sealed tube. The yield was almost 20%. The crude product was extracted with hexane, boiled with charcoal, and the solvent removed until crystallization occurred. The desired material, mp 318°C, was purified by sublimation and any solvent removed by heating in an oven at 90°C for 12 h. Treatment of the triptycene with chlorine, followed by the addition of water, gave BiOCl. However, boiling the compound with water after moistening with ethanol, or refluxing it with iodine in carbon tetrachloride, gave no reaction.

In a paper largely devoted to the reaction of phenyldichlorostibine and diphenylchlorostibine with the $[Ni_6(CO)_{12}]^{2-}$ dianion, Dahl and coworkers [13] reported that 4-tolyldibromobismuthine gave no isolatable carbonyl-containing products when allowed to react with $[NMe_3Ph]_2$ $[Ni_6(CO)_{12}]$. The preparation of tri-4-tolylbismuthine from 4-tolyllithium and bismuth tribromide and its conversion to 4-tolyldibromobismuthine were described in detail. PMR data were given for tri-4-tolylbismuthine.

In recent years the use of triarylbismuth(V) and triarylbismuth(III) compounds as arylating agents for compounds containing an active hydrogen atom (alcohols, phenols, water, glycols, enols, and amines) in the presence of copper salts has been the subject of a number of investigations. Many of the reports on this subject have come from the laboratory of V.A. Dodonov in Russia. When triphenylbismuthine was used, a twofold excess of copper(II) acetate was necessary, and only one phenyl group participated in the phenylation reaction while two phenyl groups were converted to benzene. Dodonov and coworkers [14] have now studied the reaction of triphenylbismuthine (or triphenylstibine) with acetic acid in the presence of copper salts with 2-propanol as the solvent:

$$Ph_3Bi + 3\,MeCO_2H \xrightarrow[\substack{Me_2CHOH \\ 50°C,\ 6\ h}]{Cu(O_2CMe)_2} Bi(O_2CMe)_3 + 3\,PhH$$

A quantitative yield of $Bi(O_2CMe)_3$ was obtained, and the yield of PhH was 2.95 mol per mol of Ph_3Bi. The ratio of Ph_3Bi:$MeCO_2H$:$Cu(O_2CMe)_2$ was 1:3.3:0.02. Similar results were obtained when 1-butanol was used as the solvent. However, when the solvent was methylene dichloride or toluene, the yield of benzene was reduced to 1.10 and 1.00 mol, respectively. Copper compounds other than $Cu(O_2CMe)_2$ were less active. Thus, the yields of benzene with copper(II) chloride, stearate, nitrate, or copper metal were 2.78, 2.35, 2.89, and 0.46 mol per mol of Ph_3Bi used. All of the above results were obtained when the reactions were carried out in the absence of oxygen. In the presence of oxygen, the yields of benzene were greatly reduced. Thus, the yield in 2-propanol or 1-butanol was reduced from 2.95 mol to 0.74-0.72 mol. In addition, phenylation of the alcohol to the corresponding phenyl ethers was observed. When pyridine was added to the reaction mixture, the yields of benzene were increased, both in the presence and absence of oxygen. However, addition of 2,2′-dipyridyl prevented the formation of benzene almost completely. These results suggested to the authors that Cu(I) was the active catalyst in all of the reactions.

The *d* core level photoionization and subsequent fragmentation process have been studied for the compounds $GaMe_3$, $GeMe_4$, $SnMe_4$, $PbMe_4$, and $BiMe_3$ by using the threshold photoelectron-photoion coincidence (TPEPICO) technique [15]. Threshold electron spectra (TES) for trimethylbismuthine gave four sharp bands which were assigned to photoionization from the Bi *5d* core orbitals. Photoionization curves were given for Me_3Bi^+, Me_2Bi^+, $MeBi^+$, and Bi^+. The fragmentation mechanism for Me_3Bi was statistical in all probabilities and differed from the specific fragmentation mechanism found for the four other compounds studied in the present paper. Since the Me_3Bi^+ ion in the *d* core ionized state belongs to the same point group (C_{3v}) as trimethylbismuthine in the ground state, upon excitation the angles remained essentially unchanged, in contrast to the cases of the other molecules studied. This explained the different fragmentation pattern for Me_3Bi.

A large number of papers have been published by Masuda and coworkers on the polymerization of substituted acetylenes by such transition metal catalysts as WCl_6 or $MoCl_5$, usually in the presence of a cocatalyst such as Et_3SiH or Ph_3Bi. The present paper [16] described the preparation and properties of poly[trimethylsilylphenyl-acetylene] by WCl_6. Triphenylbismuthine was one of the effective cocatalysts used. In another paper [17] from Masuda's laboratory, the polymerization of a number of 1-alkyl-1-propynes with $MoCl_5$ as the catalyst and the addition of various cocatalysts. Triphenylbismuthine was one of the cocatalysts used, but the yield was somewhat smaller than that obtained with Ph_3SiH or Ph_3Sb as the cocatalysts.

Anastopoulos and Moumtzis [18] have studied the reduction of Cd^{2+} ions in the presence of the inhibitors Ph_3As, Ph_3Sb, or Ph_3Bi in methanol by means of *dc*-polarography. The cadmium compound used was $Cd(O_2CMe)_2$. The inhibition efficiency was in the order $Ph_3Bi > Ph_3Sb > Ph_3As$. The dependence of the logarithms of the apparent rate constant $\ln k_{app.}$ was linearly dependent on the concentration of the inhibitors.

In a paper devoted to the ruthenium-catalysed hydrogenation of alkynes, such catalysts as $[RuH(COD)(Me_2PPh)_3]PF_6$ (where COD was 1,5-cyclooctadiene) were investigated [19]. The effect of adding Group 5 ligands Ph_3E, where E was P, As, Sb, or Bi, on the rate of hydrogenation was investigated. The most effective catalyst was Ph_3P.

Triphenylbismuthine in a stream of air has been used for preparing bismuth oxide films on glass heated on a block to 950°F [20].

A triphenylbismuthine-maleic anhydride catalyst was one ingredient in burn-inhibiting coatings for rocket motors [21].

In a paper devoted to the volatility of compounds useful for the preparation of superconducting thin films, the latent heat of evaporation of triphenylbismuthine was found to be 32.5 kcal/mol [22].

Fine metal particles have been deposited on a surface by the explosive decomposition of organometallic compounds with single pulse laser irradiation [23]. Trimethylbismuthine was one of the organometallic compounds used for this purpose.

A U.S. patent covering the use of polyesters or polyisocyanates in rocket engines claimed triphenylbismuthine as a curing agent [24].

Two papers describing the use of trimethylbismuthine for producing bismuth monofluoride lasers have been published [25,26].

Triphenylbismuthine has been incorporated into polymers of methyl methacrylate to produce radioopaque materials useful as medical and dental resins for fabricating radiation-shielding devices [27].

Both trialkylbismuthines [28] and triarylbismuthines [29-35] have found extensive use as raw materials in the preparation of superconductors of the type Bi, Ca, Cu, Sr, O. Several patents have been issued on this use of organobismuth compounds.

Delaviz and coworkers [36] have found that triphenylbismuthine and other organobismuth compounds were effective as radiopacifying additives for polymeric materials. Triphenylbismuthine gave homogeneous mixtures with such polymers as polystyrene, PVC, polyacrylates, and polyethylenes. The radiopacifities of the mixtures were proportional to the molar content of the Ph_3Bi. Leaching by organic solvents could be prevented by covalently binding the bismuth to the polymer by the use of styryldiphenylbismuthine.

In continuation of their studies on the stability of heterocyclobutadienes, Mishra and coworkers [37] have generated polynomials of a series of heterocyclobutadienes and analyzed their graph spectra. The cyclobutadienes contained either one or two heteroatoms and were of the following type:

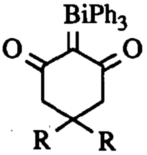
or

The bismuth compounds listed were those where M^1 was Bi, or where M^1 was Bi and M^2 was N, P, As, Sb, or Bi. The reactivity and stability of the system were given by the ΔE value, where $\Delta E = E_{LUMO} - E_{HOMO}$. In the monosubstituted cyclobutadienes, the stability was in the decreasing order N > P > Sb > Bi > As. The unsubstituted cyclobutadiene was the least stable and most reactive in the series.

Tri-, tetra-, and pentaethylbismuth compounds have been patented as non-toxic antiknock agents for gasoline [38].

In a paper largely devoted to the preparation of bridged metal cluster compounds obtained by the reactions of the anion $[HOs_3(CO)_{11}]^-$ with antimony halides, the preparation of three complexes obtained by the reaction of the same anion with the bismuth halides, $BiCl_3$, $BiBr_3$, or $[C_6H_6BiCl_2]$ $[AlCl_4]$, was described [39]. Thus, when a solution of $[N(PPh_3)_2]$ $[HOs_3(CO)_{11}]$ in THF was added to a THF solution of $[C_6H_6BiCl_2]$ $[AlCl_4]$ there was an immediate color change from red to bright yellow. The IR spectrum of the resulting solution indicated that the complex $HOs_3(CO)_{11}BiCl_2$ was present. The complex was not isolated and decomposed completely on standing overnight.

Suzuki and coworkers [40,41] previously described the preparation of the pure crystalline bismuthonium ylides V and VI.



V, R = H
VI, R = Me

The crystal structure of VI has now been determined by X-ray diffraction [42]. The dioxocyclohexane ring was almost planar, and the Bi atom was in this plane with a deviation of only 0.036 Å. The Bi atom possessed a distorted tetragonal configuration with (phenyl)C-Bi-C(phenyl) angles of 101.6 - 103.1°; the (cyclohexane)C-Bi-C-(phenyl) angles were 111.8 - 119.6°. The Bi-C(cyclohexane) bond distance (2.16 Å) was only slightly shorter than the Bi-C(phenyl) bond distances (2.21 - 2.22 Å), suggesting that the former linkage had a large degree of ionic character. Ferguson and coworkers [43] had previously shown by X-ray diffraction studies that in arsonium and stibonium ylides containing suitable placed carbonyl or sulfonyl groups, there was considerable overlap of a carbonyl or sulfonyl oxygen atom with the arsenic or antimony atom. They also suggested, without proof, a similar O-Bi overlap for the compound V. Indeed, the present investigation showed that one O-Bi distance (3.019 Å) was considerable shorter than the other (3.352 Å). However, the C-O distance (1.261 Å) involving the oxygen with the longer O-Bi distance, was also longer than the other C-O distance (1.236 Å). This result was in marked contrast to the corresponding arsonium and stibonium ylides, where the C-O bond distance for the O atom with the longer O-As or O-Sb bond distance was considerably shorter than the other C-O bond distance. Suzaki and coworkers suggested that the unsymmetrical structures of these ylides were the consequence of both electrostatic and steric factors, and thus do not reflect electron density distributions directly. Ferguson and coworkers, who originally prepared compound V, described it as a kahki-colored solid, insoluble in common organic solvents and non-reactive with 2,4-dinitrobenzaldehyde. The pure crystalline ylides V and VI, described in the present paper, were soluble in most organic solvents and reacted smoothly with a variety of organic compounds including the less reactive 4-methoxybenzaldehyde.

Suzuki and Murafuji [44] have prepared four new bismuthonium ylides $Ph_3Bi{=}CR^1R^2$ (where $R^1 = R^2 = MeCO$; $R^1 = MeCO$, $R^2 = PhCO$; $R^1 = MeCO$, $R^2 = MeOCO$; and $R^1 = R^2 = PhSO_2$). The ylides were prepared from the corresponding methylene compounds by converting the latter to their sodium salts which were subsequently treated with triphenylbismuth dichloride (or triphenylbismuthine oxide) in THF solution:

$$R^1R^2CH_2 + 2\,NaH \xrightarrow[N_2]{O°C} R^1R^2CNa_2 + 2\,H_2$$

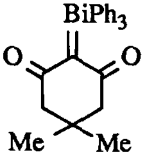
$$R^1R^2CNa_2 + Ph_3BiCl_2 \longrightarrow R^1R^2C{=}BiPh_3 + 2\,NaCl$$

Attempts to isolate the ylides from solution were unsuccessful. The major decomposition products were triphenylbismuthine and the *C*-phenylated 1,3-dicarbonyl compounds. However, the ylides were moderately stable in benzene solution, prepared by removing the THF under reduced pressure and dissolving the oily product in dry benzene. The four ylides in solution reacted with dimethyl sulfide with exchange of the ylide function:

$$R^1R^2C{=}BiPh_3 + Me_2S \xrightarrow[PhH,\ RT]{CuCl} R^1R^2C{=}SMe_2 + Ph_3Bi$$

The yields in this reaction were largest when the ylide where $R^1 = R^2 = MeCO$ was used (81%) and were quite small (20-32%) with the other three ylides. No ylide exchange occurred in the absence of CuCl. The reaction also failed when diphenyl sulfide was used. In addition to dimethyl sulfide, the reaction of one ylide ($R^1 = R^2 = MeCO$) with triphenylarsine, triphenylphosphine, and triphenylstibine was investigated. With triphenylarsine a 52% yield of the arsonium ylide $Ph_3As{=}C(OCMe)_2$ was obtained. Triphenylphosphine, however, gave only an 18% yield of $Ph_3P{=}C(OCMe)_2$.

The main product of this latter reaction was 3-phenyl-2,4-pentanedione (63%). No ylide exchange occurred when $(MeCO)_2C{=}BiPh_3$ was treated with triphenylstibine. *C*-phenylated active methylene compounds and bismuth-containing polymeric substances were formed. In all of these exchange reactions, CuCl was used as the catalyst. Finally, the ylide $(MeCO)_2C{=}BiPh_3$ was treated with dimedone in the presence of an equal amount of triethylamine. The known, stable ylide VI was obtained in 69% yields.



VI

Ylide VI was found to be considerably less active in ylide exchange reactions than $(MeCO)_2C{=}BiPh_3$. It reacted sluggishly with dimethyl sulfide to give the sulfur ylide in 35% yield, and with triphenylarsine to give the arsonium ylide in 25% yield. With triphenylphosphine and triphenylstibine no ylide exchange occurred. Dimedone was the principal product obtained in each case.

In a paper devoted to a comparison of the nitration of the Group V compounds Ph_3E (where E was N,P, As, Sb, or Bi) in 96% sulfuric acid or in acetic anhydride, triphenylbismuth diacetate was the sole product obtained by nitrating triphenylbismuthine in acetic anhydride at 0°C [45]. The diacetate was also prepared from triphenylbismuthine oxide and acetic anhydride. The diacetate was converted to the oxide by heating *in vacuo*. Because of extensive decomposition in sulfuric acid, nitration in this solvent was not investigated.

The phenylation of alcohols ROH to the corresponding phenyl ethers ROPh has been readily achieved by the use of $Ph_3Bi(O_2CMe)_2$ and catalytic copper salts [46]. The activity of the alcohols increased in the following order $Me_3C < Me_2CH <$ cyclohexyl < Bu < Me. Alcohols were also converted to phenyl ethers by Ph_3Bi and $Cu(O_2CMe)_2$. A similar order of activity of alkyl groups was also observed. Primary and secondary amines were also phenylated by $Ph_3Bi(O_2CMe)_2$ and copper salts. The amines were more active than the alcohols. Phenyl radicals were found to be involved by the use of spin trapping methods.

The phenylation of isatin and a large number of isatin derivatives by $Ph_3Bi(O_2CMe)_2$ and copper powder has been the subject of a European patent application [47]. The $Ph_3Bi(O_2CMe)_2$ was prepared from Ph_3BiCl_2 and AgO_2CMe.

In a paper described in greater detail in the Antimony section, the preparation of two new bismuth(V) compounds, $Ph_3Bi(O_2CR)_2$ and $(4\text{-}MeC_6H_4)_3Bi(O_2CR)_2$, where R was 2-pyridyl, was given [48]. The two compounds were characterized by elemental analyses, Raman, and IR spectroscopy. They were prepared by the condensation of triphenylbismuth carbonate or tri-4-tolylbismuth carbonate with 2-pyridinecarboxylic acid. The two bismuth compounds were unstable and decomposed in daylight with development of a brown color. On the basis of the IR spectra, it was concluded that there was coordination between the bismuth atoms and the carbonyl oxygen of one pyridine carboxylate group, and coordination between the bismuth atoms and the pyridine nitrogen of the other pyridine carboxyate group. This structure was also suggested by the X-ray diffraction study of one of the antimony compounds, $Ph_3Sb(O_2CR)_2$, where R was 2-pyridyl.

In a paper devoted to the preparation of tritium-labelled onium cations of Group V (P, As, Sb, or Bi), Group VI (O, S, Se, or Te), and Group VII (F, Cl, Br, or I) elements from tritium-labelled phenyl cations, $[C_6{}^3H_5]^+$, the preparation of the bismuthonium compound $[C_6{}^3H_5Ph_3Bi]ClO_4$ was described [49]. Some of this compound underwent decomposition to yield tritium-labelled triphenylbismuthine:

$$[C_6{}^3H_5Ph_3Bi]^+ \rightarrow [C_6{}^3H_5]^+ + Ph^+ + C_6{}^3H_5Ph_2Bi + Ph_3Bi$$

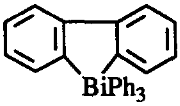
The yield of $[C_6{}^3H_5Ph_3Bi]ClO_4$ isolated was 10.7%, and the yield of $C_6{}^3H_5Ph_2Bi$ was 22.2%. In a second paper on the same subject, the yield data were used to compare the relative donor capacity of the compounds Ph_3E and the relative stabilities of the cations $[C_6{}^3H_5Ph_3E]^+$, where E was P, As, Sb, or Bi [50]. The stabilities were in the order $P > Sb > As > Bi$.

Schmuck, Seppelt, and coworkers have previously published several papers on the preparation and structure of pentaarylbismuth compounds. All such compounds were colored and, with those whose crystal structures could be determined, possessed square-pyramidal geometry. A new paper from this group described the preparation of two new compounds bis(2-fluorophenyl)triphenylbismuth and bis(2-fluorophenyl)tri-4-tolylbismuth [51]. The first compound was violet and dichroic in the solid state, but was reddish colored in solution. The second compound formed orange crystals but was also reddish in solution. Since both compounds were the same color in solution, it was argued that the energy barrier for Berry pseudorotation must be quite small. ^{19}F NMR on both compounds at the lowest achievable temperature gave only a single peak, in further confirmation of a low energy barrier for pseudorotation. X-ray diffraction studies of the two compounds revealed that the triphenyl compound possessed square-pyramidal geometry around the Bi atom, whereas the tritolyl compound possessed trigonal bipyramidal geometry. Since the energy barrier for pseudorotation was small, these differences in geometry must have been determined by lattice forces. IR and UV-visible spectra of both compounds were reported. The UV-visible spectra of both compounds in THF at -40°C were almost identical, but the absorption of the tritolyl compound was considerably weaker. The λ_{max} values were 487 nm (triphenyl compound) and 475 nm (tritolyl compound).

In addition to the experimental work, extended Hückel MO calculations with relativistic corrections were carried out for the hypothetical molecule BiH_5 (assuming ideal D_{3h} or C_{4v} symmetry) and for BiH_6^- (O_h symmetry). Extended Hückel calculations were also carried out for BiH_5 without relativistic corrections. Those without relativistic corrections gave qualitatively similar diagrams but with smaller HOMO-LUMO splitting for the C_{4v} model. However, the HOMO-LUMO splitting changed by about 27% on applying the relativistic correction for the C_{4v} model but only 14% for the D_{3h} model. The authors suggested that nonrelativistic pentaphenylbismuth might not be violet colored. They also pointed out that since the color of the pentaarylbismuth compounds correlated with weakness and ease of excitement of the basal Bi-C bonds, compounds with weaker Bi-C bonds, which would be expected to be even more deeply colored, might no longer be stable at room temperature.

In another paper by Schmuck and coworkers [52], the preparation and molecular structures of several additional Ar_5Bi compounds have been reported. Because Ph_5Sb possesses a different geometry (square-pyramidal) than penta-4-tolylantimony (trigonal-bipyramidal), an attempt was made to prepare penta-4-tolylbismuth. However, this compound could only be obtained as a crystalline adduct $(4\text{-}MeC_6H_4)_5Bi{\bullet}LiCl{\bullet}2$ THF. The compound was violet-colored and dichroic. The UV spectrum of the compound gave a λ_{max} of 521 nm compared to a value of 532 nm for Ph_5Bi. The compound, like pentaphenylbismuth, is thermally unstable, both in solution and in the solid state. The crystal structure of the compound was determined by X-ray diffraction. The geometry around the Bi atom was intermediate between square-pyramidal and trigonal-bipyramidal.

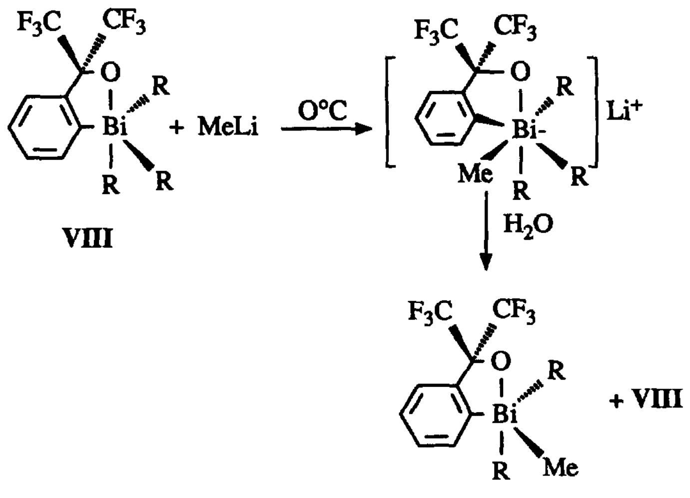
A second compound prepared was bis(2,6-difluorophenyl)tri-4-tolylbismuth. It was an orange-red crystalline solid. The molecular structure of the compound was that of a quadratic pyramid. Both in structure and in color, this compound was almost identical to the previously reported bis(2,6-difluorophenyl)triphenylbismuth. It thus differs from the previously reported pair, bis(2-fluorophenyl)tri-4-tolylbismuth and bis(2-fluorophenyl)triphenylbismuth, which have different colors, violet and orange, respectively, as well as different structures (quadratic-pyramidal and trigonal-bipyramidal, respectively). The authors also prepared the known compound, 5,5-dihydro-5,5,5-triphenyl-5-*H*-dibenzobismole (VII), and determined its crystal structure.



VII

The compound was orange-red and dichroic. Structurally, the compound was a distorted quadratic pyramid with the biphenyl group occupying two basal positions. All attempts to prepare $(C_6F_5)_5Bi$ have so far been unsuccessful. The preparation of $(C_6F_5)_3BiF_2$ from $(C_6F_5)_3Bi$ and XeF_2 has been previously described. When this compound was crystallized from CH_2Cl_2 at -10°C, some of the compound decomposed to give a yellowish precipitate which no longer dissolved when the solvent was warmed. In one case, after standing for 2 days, colorless crystals, mp 159°C, were obtained. In contrast to $(C_6F_5)_3BiF_2$ these crystals were no longer moisture sensitive. The ^{19}F NMR spectrum of the material gave signals for $(C_6F_5)_3BiF_2$ and $(C_6F_5)_3Bi$ in a ratio of 1:2. The structure of this material was also determined by X-ray diffraction. The geometry of the Bi atom in $(C_6F_5)_3BiF_2$ was an almost perfect trigonal bipyramid. The F-Bi-F angle was 180°. The $(C_6F_5)_3Bi$ structures were pyramidal with C-Bi-C angles which varied from 93 - 98°.

In continuation of previously reported work on hypervalent organobismuth compounds, Akiba and coworkers [53] have described their investigations on the preparation and spectral properties of several 12-Bi-6 compounds. They first attempted the preparation of an ate complex by means of the following reaction:

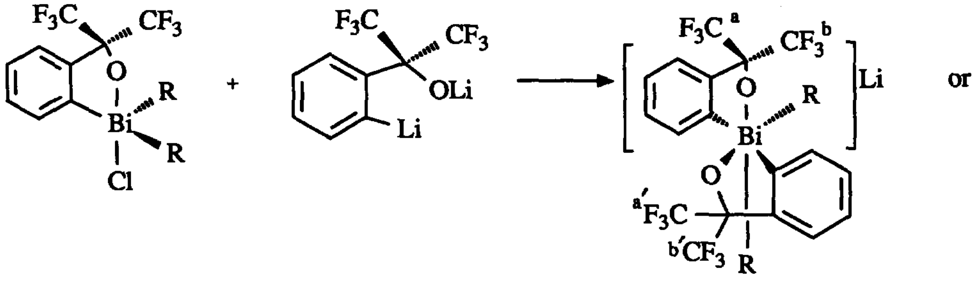


VIII

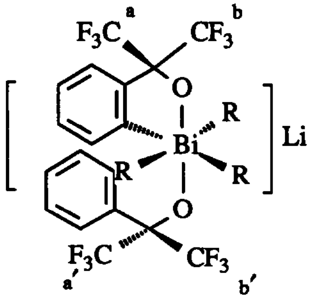
IX

(where R was 4-MeC$_6$H$_4$)

After stirring a mixture of the two reactants for 1.5 h, then quenching the solution with water, compounds VIII and IX were recovered in 10 and 70% yields, respectively. However, if the mixture was stirred for 1 day and then quenched with water, a 20% yield of VIII was the sole material isolated. This result in was in contrast to a similar reaction, in which the heteroatom was Sb rather than Bi, which, after stirring for 1 day, yielded two products, corresponding to VIII and IX in 97% total yield. Apparently, the 12-Bi-6 ate complex was formed but decomposed slowly. Accordingly, the authors attempted to obtain a stable ate complex by using two bidentate ligands to form a spiran-type complex such as X or XI:

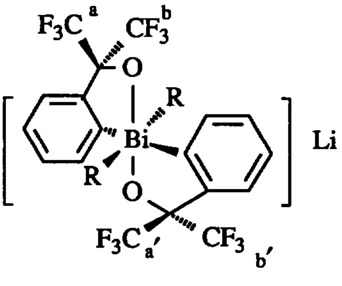


X

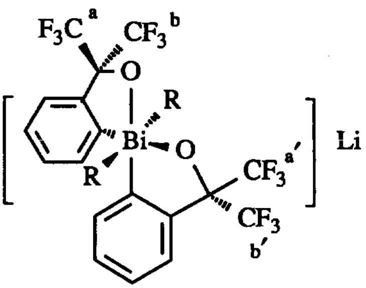


XI (where R was 4-MeC_6H_4)

The two reactants were stirred together in THF solution at -78°C for 10 minutes. A small sample was then withdrawn for ^{19}F NMR spectrum determination and the remaining mixture stirred at room temperature for 24 h. A ^{19}F NMR spectrum taken at this time was identical to that taken at 10 minutes indicating that the product was stable at room temperature. The ^{19}F NMR spectrum gave a pair of quartets indicating two pairs of CF_3 groups, with each pair (a = a′, b = b′) being magnetically equivalent. The hexacoordinate ate compounds X and XI both fulfilled these requirements. In order to distinguish between X and XI the preparative reaction was repeated in the presence of 12-crown-4 in order to deprive the ate complex of the lithium ion. The ^{19}F spectrum of the resulting solution gave a sharp singlet. This result suggested that the complex prepared without the 12-crown-4 contained the lithium ion complexed to two *cis* oxygen atoms, a result which excluded XI as the structure. Two possible structures were suggested for the isomer obtained when 12-crown-4 was used in the synthesis, namely XII or XIII (a = a′ = b = b′).

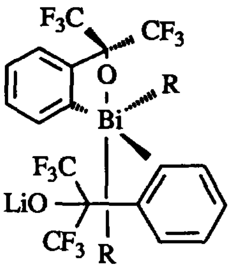


XII



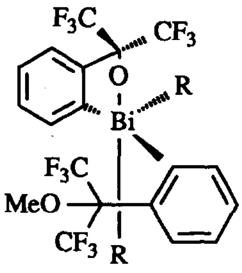
XIII

In both complexes all four CF_3 groups would be magnetically equivalent. The authors were unable to distinguish between structures XII and XIII. Finally, the authors considered the pentacoordinate Bi structure XIV for the compound that had been obtained in the absence of 12-crown-4.



XIV

Accordingly, they synthesized the pentacoordinate Bi compound XV.

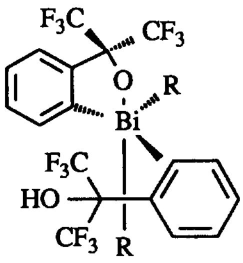


XV

Compound XV was characterized by elemental analyses and ^{19}F NMR. The ^{19}F NMR spectrum at room temperature gave two singlets at δ = -66.6 (6F), and δ = -73.4 (6F). Each signal was split into a pair of quartets at -67 and -40°C, respectively. This result suggested weak coordination between oxygen and bismuth. The above results indicated that structure XIV was not the correct structure for the reaction product.

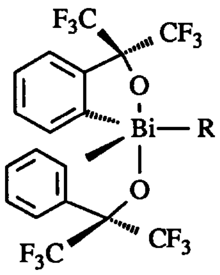
The ate complex X was remarkably stable to 150°C. At 70°C the pair of quartets coalesced to a singlet but reverted to the pair of quartets when the solution was cooled to 0°C. The activation energy of the equilibrium was calculated to be 18 kcal/mol at 70°C. A mechanism for the isomerization was suggested, namely X $\rightleftarrows$ XIV, followed by Berry pseudorotation of the pentacoordinate Bi compound XIV. The ate complex X did not react with most electrophilic reagents such as 4-$CF_3C_6H_4COCl$ in refluxing THF. Nor did it react with 4-ClC_6H_4COCl in the presence of 12-crown-4.

It did react with water to give the alcohol XVI.



XVI

The ^{19}F NMR spectrum of XVI gave a singlet at 0°C, suggesting rapid intramolecular prototropy between the two oxygen atoms. Compound XVI was unstable and lost toluene to give XVII.



XVII

Compound XVII reacted with 4-MeC_6H_4Li to yield X.

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