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BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1989

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Several review articles on the use of organobismuth compounds in organic synthesis have appeared in 1989 [1-3]. The first of these covered both organoantimony and organobismuth compounds. The second article dealt only with organobismuth compounds in arylation reactions. The third article (which was in Japanese and was unavailable to the present authors) dealt with both organobismuth compounds and metallic bismuth in organic synthesis. A few organobismuth compounds were mentioned in both the organic [4] and the inorganic [5] sections of *Annual Reports on the Progress of Chemistry.* Wardell, in *Organometallic Chemistry*, has summarized the organobismuth compounds described in the chemical literature appearing in 1987 [6]. In the same volume of *Organometallic Chemistry* several organobismuth compounds, whose structures have been determined by diffraction methods, were listed [7]. In a review article on the preparation of organometallic compounds by direct synthesis from the metal, the preparation of organobismuth compounds was mentioned [8]. Klapötke [9] has written a comprehensive review on the biological activity of organobismuth compounds. A great many of the compounds discussed were synthesized in his laboratory. Organic compounds of metals (including bismuth) that have an uncommon valence were mentioned in a review written in Japanese [10]. In a long review article on the mechanisms of reactions of organometallic compounds [11], organobismuth compounds were briefly described. A great deal of the work on organometallic compounds exhibiting thermochromism has originated in Breunig's laboratory. Organobismuth compounds were mentioned in a symposium article by Breunig on thermochromism [12]. Organobismuth compounds containing a Bi-Si bond were reviewed in a book on organic silicon compounds [13].

Jutzi and Schwartzen [14] have found that 5-bromopentamethyl-1,3-cyclopentadiene reacted with such metals as antimony, bismuth, tin, or magnesium to form organometallic compounds. Thus, powdered bismuth reacted with the cyclopentadiene as follows:

$$4Me_5C_5Br + 2Bi \longrightarrow 2Me_5C_5BiBr_2 + (Me_5C_5)_2$$

The two reactants were stirred together in hexane-diethyl ether for 3 days at 20°C to yield a red-brown solid. This was washed with hexane-diethyl ether, dried, and then dissolved in THF to separate the product from excess bismuth. After removal of the solvent, the product could no longer be completely dissolved. From this result the authors concluded that the product was

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Previous review see J. Organomet. Chem., 380 (1990) 35–49 polymeric. It melted at 230°C with decomposition, and was characterized by elemental analyses, ^{1}H and ^{13}C NMR, and mass spectroscopy.

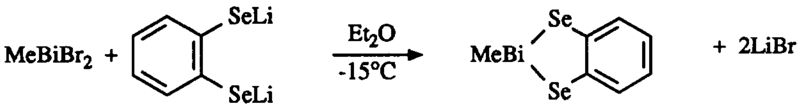
The use of a domestic microwave oven to increase the rate of reactions has been described [15]. Thus, the reaction time for the following reaction was decreased from 2-3 h to 6 minutes when carried out in the oven:

$$Ph_3Bi + 2BiCl_3 \xrightarrow{Me_2CHOH} 3PhBiCl_2$$

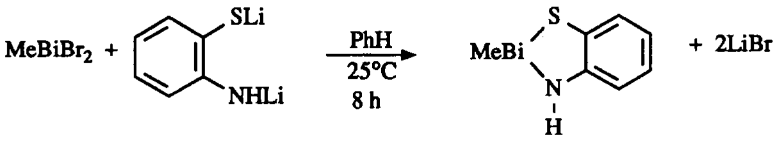
The yield, however, was essentially the same as that obtained by conventional reaction methods. Although the interaction of tetraphenyltin and bismuth trichloride was also very rapid in the microwave oven, it was found difficult to separate the products of the reaction:

$$3Ph_4Sn + 2BiCl_3 \longrightarrow 3Ph_2SnCl_2 + 2Ph_3Bi$$

Klapötke has described the preparation of several organobismuth(III) compounds containing Bi-Se and Bi-S bonds [16]. The reaction of dibromomethylbismuthine with the dilithium compound derived from 1,2-benzenediselenol gave a heterocyclic bismuth compound:



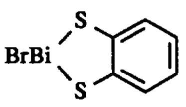
Dibromomethylbismuthine reacted with the dilithium compound derived from 2-aminothiophenol in a similar manner:

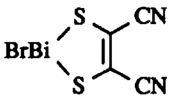


Triphenylbismuthine was found to react with 2-aminothiophenol with loss of one phenyl group:

$$Ph_3Bi + 2\text{-}H_2NC_6H_4SH \xrightarrow[\text{reflux}]{PhH} 2\text{-}H_2NC_6H_4SBiPh_2 + PhH$$

In addition to the above organobismuth compounds, the following two inorganic heterocyclic bismuth compounds were prepared from bismuth tribromide:





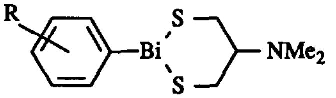
All of the compounds were characterized by elemental analyses, IR, and mass spectroscopy and, where applicable, PMR spectroscopy.

In continuation of previous work on the microbiological activity of organobismuth compounds, Klapötke [17] has prepared the compound $MeBi(SMe)_2$ by means of the following reaction:

$$MeBiBr_2 + 2MeSLi \longrightarrow MeBi(SMe)_2 + 2LiBr$$

The resulting compound was characterized by elemental analyses, mass spectra, and PMR. The labelled compound $^{13}CH_3Bi(SMe)_2$ was also prepared as an aid to interpreting the mass spectrum of the compound. The new compound was tested against *B. subtilis, E. coli, Candida tropicalis* and *Penicillium camembertii* and shown to be quite active against these organisms *in vitro.*

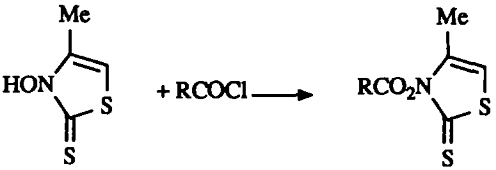
A Japanese patent described the preparation of monoarylbismuth compounds of the following type for use as anticoccidial and insecticidal agents [18]:



(where R was H, halogen, or a lower alkyl group)

The compounds were obtained by reaction of the appropriate dibromoarylbismuthine with 2-(*N,N*-dimethylamino)-1,3-propanedithiol in the presence of a base. The compound where R = H was effective against several microorganisms.

Barton and coworkers have previously described, in a number of papers, reactions involving the formation of radicals produced by the decomposition of thiohydroxamate esters of carboxylic acids. A paper from Barton's laboratory has now described attempts to prepare organoarsenic, -antimony, and -bismuth compounds of the type $RE(SPh)_2$ (where R was an alkyl or alicyclic group such as pentadecyl, 2,2-diphenylethyl, cyclohexyl, or adamantyl and E was As, Sb, or Bi) by means of the above mentioned radical reaction [19]. The thiohydroxamate esters were prepared from 3-hydroxy-4-methylthiazole-2(3*H*)-thione and various acid chlorides:



I

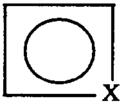
It was hoped that a radical reaction of compounds of type I with arsenic, antimony, or bismuth compounds of type $E(SPh)_3$ would yield the desired organometallic compounds $RE(SPh)_2$. Although there was evidence that the desired compounds $RE(SPh)_2$ (where E was Sb) were formed, the organic product produced after the reaction mixture was worked up was the *nor*-alcohol ROH. The only antimony-containing product isolated was Sb_2O_3. The authors then used this reaction for the preparation of a number of alcohols in almost quantitative yield.

Similar reaction products were produced, although in somewhat lower yields, when the arsenic compound $(PhS)_3As$ was employed.

When the bismuth compound $(PhS)_3Bi$ was heated at 100°C with compound I (R = Ph_2CHCH_2) in chlorobenzene for 2 h under anaerobic conditions and the yellow reaction mixture exposed to the air for several hours, the alcohol Ph_2CHCH_2OH was produced. However, if the yellow reaction mixture was subjected to flash chromatography under nitrogen, the desired intermediate $Ph_2CHCH_2Bi(SPh)_2$ was isolated. This product was characterized by PMR and mass spectroscopy and by elemental analyses, which approached the theoretical values. An attempt was then made to prepare nitropentadecane from I (R = $CH_3(CH_2)_{13}CH_2$) and $(PhS)_3Bi$ by treating the reaction mixture with N_2O_4. The yields of nitropentadecane, however, were small (5-35%), and the principal product was palmitic acid. Attempts to prepare compounds of the type $(PhS)_2BiR$, where R was derived from a secondary or tertiary carboxylic acid (*e.g.* dibenzylacetic acid), were unsuccessful.

In a paper devoted largely to inorganic compounds containing Bi-Fe and Sb-Fe bonds, Whitmire and coworkers [20] have described the reaction of $BiCl_3$ and $SbCl_3$ with $[Et_4N]_2[Fe_2(CO)_8]$. The product from $BiCl_3$ tended to be an oil in most solvents. IR data were obtained with a solution of the compound in methylene dichloride. It was believed to possess the structure $[Et_4N][BiClFe_3(CO)_{12}]$. The analogous antimony compound was obtained in crystalline form and was characterized by elemental analyses and IR spectral results, but structure determination by X-ray diffraction was unsuccessful. When the bismuth compound was treated with methyl iodide in acetone solution, a solid crystalline compound $Bi_2Fe_2(CO)_8Me_2$ was obtained. The compound was characterized by elemental analyses, PMR, IR, and mass spectrometry and by an X-ray diffraction study. The structure contained an Fe_2Bi_2 parallelogram with each Bi atom possessing a methyl group. The methyl groups were oriented *trans* to each other with respect to the Bi_2Fe_2 ring. The bismuth atoms were pyramidal with one coordination site occupied by an electron lone pair. The PMR spectrum of a freshly prepared solution of the compound in CD_2Cl_2 gave a singlet at 2.53 ppm, but on warming a second signal at 2.75 ppm grew very slowly. On further standing in solution the compound was slowly converted into $Bi_2Fe_3(CO)_9$.

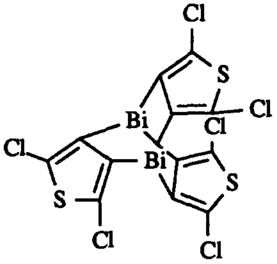
A critical assessment of closed- and open-shell heterocyclobutadienes of the following type has been made [21]:



(where X was N, P, As, Sb, or Bi)

The definition of topological resonance energy (TRE) was modified and new TRE values for both closed- and open-shell configurations were calculated. A non-uniform charge distribution was obtained for the closed-shell configuration, whereas an apparently smoothed-out charged distribution was observed for the open-shell configurations. The mobile bond orders for the heterocyclobutadienes suggested a symmetrical four-membered ring with strongly distorted diagonal distances for all the molecules.

Al-Soudani and Massey [22] have synthesized 2,5-dichloro-3,4-dilithiothiophene by the reaction of butyllithium with either 3,4-diiodo- or 3,4-dibromo-2,5-dichlorothiophene. Reaction of the dilithio compound with elemental halides then led to the formation of heterocyclic compounds. Thus, the reaction of 2,5-dichloro-3,4-dilithiothiophene with bismuth trichloride gave the following product:



It melted at 322-323°C with decomposition and was characterized by elemental analyses. The molecular ion could not be detected in the mass spectrum of the bismuth compound. Other heterocycles, using halides of elements such as sulfur, selenium, tellurium, phosphorus, arsenic, tin, and mercury, were also prepared.

Tyrra and Naumann [23] have studied the reactions of two perfluoroorganobismuth compounds, $(CF_3)_3Bi$ and $(C_6F_5)_3Bi$, with halogens, interhalogens (ICl and IF_5), and two xenon compounds, XeF_2 and $[XeF][TaF_6]$. Only in the reaction of $(C_6F_5)_3Bi$ with XeF_2 or $[XeF][TaF_6]$ was an organobismuth(V) compound, *viz.* $(C_6F_5)_3BiF_2$, formed. The reaction was carried out by adding XeF_2 to $(C_6F_5)_3Bi$ in MeCN at -196°C. The reaction mixture was then warmed to -30°C and stirred at this temperature until $(C_6F_5)_3Bi$ could no longer be detected spectroscopically. After removing the solvents, the product, $(C_6F_5)_3BiF_2$, was characterized by ^{19}F and ^{13}C NMR and mass spectroscopy. The reactions of $(CF_3)_3Bi$ with Cl_2, Br_2, or I_2 gave $BiCl_3$, $BiBr_3$, or BiI_3, respectively, and the corresponding trifluoromethyl halides. The intermediate compounds, $(CF_3)_2BiX$ and CF_3BiX_2 (where X was Cl, Br, or I), could be detected by ^{19}F NMR spectroscopy, and the peaks in the spectra assigned to each compound. The reactions of $(C_6F_5)_3Bi$ with Cl_2, Br_2, or I_2 similarly gave $BiCl_3$, $BiBr_3$, or BiI_3, respectively, but the intermediates could not be clearly distinguished by ^{19}F NMR spectroscopy. The reactions of $(CF_3)_3Bi$ or $(C_6F_5)_3Bi$ with the interhalogen ICl gave $BiCl_3$ in both cases. The intermediates $(CF_3)_2BiCl$ and CF_3BiCl_2 (as well as CF_3I) were identified by ^{19}F NMR spectroscopy. With $(C_6F_5)_3Bi$ only C_6F_5I was identified. Similar results were obtained with IF_5 and the two bismuthines. Thus, $(CF_3)_3Bi$ gave BiF_3, $(CF_3)_2BiF$, and CF_3IF_4; $(C_6F_5)_3Bi$ gave BiF_3 and $C_6F_5IF_4$. These results with interhalogens were taken as evidence that the reactions of $(CF_3)_3Bi$ and $(C_6F_5)_3Bi$ with the halogens Cl_2, Br_2, and I_2 probably occurred by a polar mechanism (rather than by formation of an intermediate organobismuth(V) compound). Thus, if intermediates such as $(CF_3)_3Bi(I)Cl$ or $(C_6F_5)_3Bi(I)Cl$ were formed, perfluoroorgano chlorine compounds would have been expected as reaction products. Although $(C_6F_5)_3Bi$ was oxidized by XeF_2 to $(C_6F_5)_3BiF_2$, $(CF_3)_3Bi$ was cleaved by this reagent to give BiF_3, CF_4, and Xe. Similar results were obtained with $[XeF][TaF_6]$.

Attempts to form acyl Sb(V) and Bi(V) compounds of the type $Ar_3Sb(COR)Cl$ and $Ar_3Bi(COR)Cl$ have been reported by Asthana and Srivastava [24]. When triphenylbismuthine was heated with MeCOCl or PhCOCl in refluxing carbon tetrachloride, or with $ClCH_2COCl$ or 1-chloropyridine in refluxing dichloromethane, the reactants were recovered unchanged. However, under the same reaction conditions triphenylbismuthine and 3,5-dinitrobenzoyl chloride reacted with cleavage of one Ph-Bi bond:

$$Ph_3Bi + 3{,}5\text{-}(O_2N)_2C_6H_3COCl \xrightarrow{CH_2Cl_2} Ph_2BiCl + 3{,}5\text{-}(O_2N)_2C_6H_3COPh$$

Triphenyl derivatives of the Group V elements, P, As, Sb, and Bi, form dihalogenides which, on the basis of their ionic character, can be considered as onium salts, $[Ph_3EX]X$. The bismuth compound $[Ph_3BiI]I$ was stable only in solution at -70°C and decomposed into diphenyliodobismuthine and iodobenzene at higher temperatures. Tornieporth-Oetting and Klapötke [25] have now converted all of the iodo compounds $[Ph_3EI]I$ into the corresponding hexafluoroarsenates by the following metathetical reaction:

$$[Ph_3EI]I + AgAsF_6 \longrightarrow [Ph_3EI][AsF_6] + AgI$$

(where E was P, As, Sb, or Bi)

The bismuth compound was a bright yellow solid, mp 47°C. It was characterized by PMR, IR, and Raman spectra. The antibacterial properties of the bismuth compound were tested against *E. coli*. Although possessing some activity it was less active than the compound $[MeBi(SC_6H_4NH_2Me\text{-}4)_2][I]_2$, previously studied by one of the authors (Klapötke).

Ogawa and coworkers [26] have described the preparation of esters of diarylbismuthinic acids, $Ar_2Bi(O)OR$. These were obtained by heating triarylbismuthines with sodium *N*-chloro-4-toluenesulfonamide (chloramine-T hydrate) in a mixture of benzene and methanol:

$$Ar_3Bi + 4\text{-}MeC_6H_4SO_2NClNa \xrightarrow[MeOH]{PhH} Ar_2Bi(O)OMe + ArH + 4\text{-}MeC_6H_4SO_2NH_2$$

The reaction was successful when Ar was Ph, $4\text{-}MeC_6H_4$, $3{,}4\text{-}Me_2C_6H_3$, 1-naphthyl, or 4-Me-1-naphthyl. The yields varied from 10% ($4\text{-}MeC_6H_4$) to 80% (1-naphthyl and 4-Me-1-naphthyl). When Ar was $2\text{-}MeC_6H_4$, di-2-tolylbismuthinic acid was obtained (rather than the ester). When Ar was 3-trifluoromethylphenyl or 4-chlorophenyl, the corresponding esters were not obtained and the triarylbismuthines were recovered in about 60% yields. There was evidence, however, that the reaction proceeded to give the esters, which then underwent a disproportionation reaction during work-up to yield the triarylbismuthines. The other product (or products) of this disproportionation was stated to be a colorless solid of unknown structure. When Ar was 2-thienyl, the only reaction product was a colorless solid, again of unknown structure. The authors suggested the following reaction series to explain their results:

$$Ar_3Bi + 4\text{-}MeC_6H_4SO_2NClNa \longrightarrow Ar_3Bi{=}NSO_2C_6H_4Me\text{-}4 + NaCl$$

$$Ar_3Bi{=}NSO_2C_6H_4Me\text{-}4 + MeOH + H_2O \longrightarrow Ar_3Bi(OH)OMe + 4\text{-}MeC_6H_4SO_2NH_2$$

$$Ar_3Bi(OH)OMe \longrightarrow Ar_2Bi(O)OMe + ArH$$

After recrystallization from benzene-methanol, the esters were obtained as crystalline solids which melted with decomposition in the range 90-150°C. They were characterized by elemental analysis, PMR, and IR spectroscopy. The methyl signal of the methoxy group was a broad singlet occurring in the range $\delta = 3.5\text{-}3.6$. The esters underwent ester exchange reactions when recrystallized from alcohols. Thus, the methyl ester gave the ethyl and isopropyl esters of diphenylbismuthinic acid in 60 and 52% yields, respectively. Methyl diphenylbismuthinate was hydrolysed in water to give diphenylbismuthinic acid in 90% yield.

Since organobismuth(V) compounds are known to be excellent oxidizing agents, methyl di-1-naphthylbismuthinate was examined for its oxidizing ability. When heated with benzoin in benzene for 2 h, benzil was obtained. The other products of the reaction, in addition to unchanged benzoin, were naphthalene and metallic bismuth. 1,1,2,2-Tetraphenylethanediol gave benzophenone; hydrazobenzene gave azobenzene. Both were obtained in quantitative yields. In a surprising result, 1,2-diphenyl-1,2-ethanedione dihydrazone reacted to give diphenylacetylene in 50% yield. Cyclohexane-1,2-diol and 1-phenylethane-1,2-diol were unaffected when heated with methyl di-1-naphthylbismuthinate.

The results reported in the above paper are somewhat surprising. Although organobismuth(V) compounds containing three, four, or five organic groups attached to bismuth are all well known, all previous attempts to prepare organobismuth(V) compounds containing two organic groups attached to bismuth have been unsuccessful. The authors suggested that reactions involving highly reactive bismuthonium imines may lead to the preparation of a variety of pentavalent organobismuth compounds.

A paper reviewed in the Antimony section has described the tributylstibine-promoted reaction between electron-deficient olefins and compounds such as diethyl dibromomalonate to form 1,1,2-trisubstituted cyclopropanes. The above type of reaction has also been studied with tributylbismuthine, but the bismuthine was less effective than the stibine [27].

The rate of exchange of phenyl radicals between triphenylbismuthine and phenyllithium (and between triphenylstibine and phenyllithium) in the binary solvent system, pentane-diethyl ether, was studied in the temperature range 248-307 K [28]. The reaction rate was determined by the use of ^{14}C labelled triphenylbismuthine:

$$(^{14}C_6H_5)_3Bi + 3C_6H_5Li \rightleftarrows (C_6H_5)_3Bi + 3\,^{14}C_6H_5Li$$

Samples were withdrawn at intervals and the phenyllithium converted to benzoic acid with carbon dioxide. The amount of $^{14}C_6H_5Li$ was thus proportional to the radioactivity of the benzoic acid. No exchange occurred in pentane alone, and the exchange rate increased as the mole fraction of ether increased in the binary solvent mixture. The exchange rate constant for the antimony system was 2 orders of magnitude greater than for the bismuth system. The enthalpy and entropy of activation decreased with increasing dielectric constant values of the solvent system. The exchange rate was found to obey second order kinetics, first order with respect to each reactant.

The temperature dependence of the specific heat of triethylbismuthine has been studied in an adiabatic vacuum calorimeter between 12 and 329 K [29]. Rapid cooling of the liquid bismuthine from room temperature to 78 K produced a glass transition. A number of thermodynamic functions were calculated for the crystalline, the liquid, and the glass state, and also for the supercooled liquid state. The standard entropy and the Gibbs free energy of formation at 298.15 K were also calculated.

Shima and coworkers [30] have reported a new type of laser-induced decomposition of organometallic compounds with the production of fine metal particles. A single laser pulse was used to produce the ignition of a thermal chain reaction. Trimethylbismuthine was one of the compounds used in this investigation. The purity of this compound was stated to be 99.9999%, based on metal analysis, and it was further purified by five freeze-pump-thaw cycles, followed by trap-to-trap distillation *in vacuo* before being transferred to the reaction cell.

Two papers have described the use of triphenylbismuthine as a source of bismuth in the preparation of thin films of superconducting bismuth strontium calcium copper oxide [31, 32]. The thin films were prepared by metalorganic chemical vapor deposition.

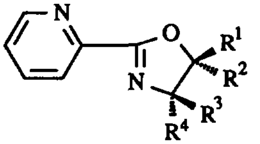
Triphenylbismuthine has found potential medical use as a radiopacifying agent for polymers which were used as radiopaque resins [33]. A copolymer of methyl methacrylate and styryldiphenylbismuthine was used to prevent leaching of the radiopacifying agent into nonaqueous media.

The preparation of bidentate ligands containing trivalent phosphorus, arsenic, antimony, or bismuth which were useful catalysts for such organic reactions as low-pressure formylations has been described in a European patent application [34].

A Japanese patent [35] described a number of organobismuth(III) and organobismuth(V) compounds containing 1-3 phenyl or substituted phenyl groups which were useful as anticoccidial drugs. The preparation of tris(3-trifluoromethylphenyl)bismuthine was described. This compound gave complete control of *Eimeria tenella* in chickens. Another Japanese patent described the use of triphenylbismuthine, as well as other triphenyl Group V compounds, as catalysts for the disproportionation of halosilanes [36].

The reaction of triphenylbismuth diacetate with glycols results in the phenylation of one hydroxy group to produce hydroxy ethers. If the glycol is a *meso* compound the product is a mixture of two enantiomeric pairs. In a previous paper Brunner and coworkers [37] have reported on the phenylation of *cis*-cyclohexane-1,2-diol and *meso*-butane-2,3-diol by triphenylbismuth diacetate, catalyzed by copper(II) acetate, in the presence of a number of chiral 2-pyridyl oxazolines. Although the overall yield of the ether was greatly reduced, the presence of the oxazoline resulted in an optical induction which varied from 13 to 30.2% , depending on the particular oxazoline used. The reaction has now been extended to the monophenylation of 11 *meso*-diols, and to racemic *trans*-cyclohexane-1,2-diol [38]. Nine of the *meso* diols were vicinal diols, the other two diols were *meso*-pentane-2,4-diol and *cis*-1,2-bis(hydroxymethyl)-

cyclohexane. Several of these diols were commercial products; the synthetic methods used to prepare the other compounds were given. The monophenylation of all of these glycols was carried out, both in presence of, and in the absence of, a chiral agent. Catalytic amounts of copper(II) acetate were also employed. A total of 14 chiral 2-pyridyl oxazolines (II) of the following type were the principal chiral agents used in this study:



II

(where R^1, R^2, R^3, and R^4 were hydrogen, and groups such as alkyl, aryl, SCHMeEt, CH_2CH_2SMe, or CH_2OMe, such that one or both carbon atoms bearing R groups were chiral)

The synthesis of these chiral compounds is to be described in a forthcoming paper. The monophenylation of the glycols in the absence of a chiral agent was carried out in methylene dichloride with equal amounts of the diol and triphenylbismuth diacetate and 0.03 molar equivalent of copper(II) acetate. The resulting hydroxy ethers were purified first by column chromatography and then by high vacuum distillation. They were all obtained as colorless liquids and were characterized by elemental analysis, PMR, and mass spectrometry. Only one of the twelve diols, 2,2,5,5-tetramethyl-3,4-hexanediol, could not be phenylated by the above procedure (presumable due to steric hindrance). In the presence of a chiral agent, the reactions were carried out with degassed methylene dichloride in the absence of air. In order to determine the enantiomeric excess, the hydroxy ethers were converted to urethanes, usually by treatment with isopropyl isocyanate. With 1-hydroxy-2-phenoxycyclohexane, the urethanes obtained from methyl, ethyl, or phenyl isocyanate gave better results. The enantiomeric excess induced by the chiral agent was then determined on the urethanes by gas chromatography. On the chirasil-L-val column used, the (*S*)-alcohols were known to have longer retention times than those of (*R*)-alcohols, and the configurations of seven of the phenoxy alcohols were assigned tentatively on this basis. It was not possible to obtain base-line separation of four of the enantiomers with the chirasil-L-val column. However, with the uracil of 2-phenoxy-1,2-diphenylethanol, base-line separation of the enantiomers was achieved by HPLC on a hypersil-Pirkle-*T* column. With the diol *exo*-*cis*-bicyclo[2.2.1]heptane-2,3-diol, the racemic mixture of hydroxy ethers could be obtained in the absence of a chiral agent, but the reaction in the presence of a chiral agent resulted in cleavage of the central C-C bond, and the product was *cis*-cyclopentane-1,3-dicarbaldehyde. Apparently, separation of the enantiomeric pairs was not effected with three of the hydroxy ethers, namely those obtained from *cis*-cyclooctane-1,2-diol, *meso*-diethyl tartrate, and *cis*-1,2-bis(hydroxymethyl)cyclohexane. In addition to the chiral agents of the 2-pyridyl oxazoline type, the phenylation of two of the diols was carried out in the presence of a number of other chiral agents. None of these agents gave the enantioselective monophenylation achieved with the 2-pyridyl oxazolines.

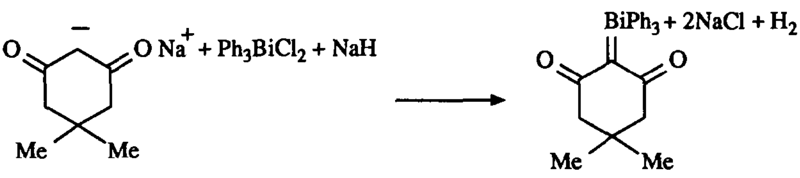
With the isopropyl urethane of 1-hydroxy-2-phenoxycyclopentane, the phenylation reaction was carried out in the presence of all fourteen 2-pyridyl oxazolines. The largest enantiomeric excess (50.4 and 49.6% 1*R*, 2*S*, from two runs) was obtained with oxazoline II, where R^1, R^2, and R^3 were hydrogens, and R^4 was $CHMe_2$. With the urethanes from 1-hydroxy-2-phenoxycyclohexane, twelve of the 2-pyridyl oxazolines were used. The best enantiomeric excess (31.9 and 29.0% 1*R*, 2 *S*, from 2 runs) was with oxazoline II, where R^1, R^2, and R^3 were hydrogen and R^4 was SCHMeEt. (In the above configurations the carbon atom bearing the OPh group was defined as C1.) With five other urethanes of hydroxy ethers, the phenylation reaction was carried out in the presence of three 2-pyridyl oxazolines, and the enantiomeric excess of each reaction determined. No clear relationship between the nature of the substituents and the substitution pattern of the oxazoline ring, on the one hand, and the enantiomeric excess of the product, on the other hand, was found.

The chemical yield of hydroxy ether was always considerably lower in the presence of a 2-pyridyl oxazoline. This was not due to a side reaction, since unreacted diol could be recovered in essentially quantitative yield (after subtracting the amount of ether formed). If the $Ph_3Bi(OAc)_2$, the 2-pyridyl oxazoline, and copper(II) acetate were stirred for 1 h before adding the diol, no phenylation of the diol occurred. However, if the diol, oxazoline, and copper(II) acetate were stirred for 1 h, and the $Ph_3Bi(OAc)_2$ then added, the reaction proceeded as usual.

In addition to the *meso*-diols discussed above, the phenylation of racemic *trans*-cyclohexane-1,2-diol in the presence of the oxazoline II (where R^1, R^2, and R^3 were hydrogen and R^4 was SCHMeEt) and varying amounts of $Ph_3Bi(OAc)_2$ (from 0.1 to 0.9 molar equivalent) was carried out. The phenyl ether and excess diol were then separated by column chromatography. The enantiomeric excess of each compound was determined by conversion to the urethane and diurethane, respectively, followed by gas chromatographic separation on a chirasil-L-val column. The enantiomeric excess of the 1*R*, 2*R* enantiomer of the phenyl ether was found to decrease as the ratio of $Ph_3Bi(OAc)_2$: diol increased, whereas the enantiomeric excess of the diol increased. The best enantioselectivity obtained for the 1*S*, 2*S* enantiomer of the diol was 65.5% excess with a chemical yield of 26%. For the phenyl ether the best enantiomeric excess was 50.9% for the 1 *R*, 2*R* enantiomer with a chemical yield of 8% (based on the amount of diol used). The enantiomeric yields of both ether and diol increased as the temperature was lowered, and most of the experiments were carried out at 0°C. No such temperature effect was noted in the phenylation of the *meso*-diols.

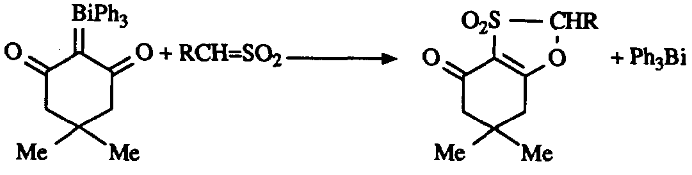
In a paper largely devoted to organoantimony(V) compounds of the type $R_3Sb(O_2CR')_2$, where R was an alkyl or aryl group and R′ was a 5-membered heterocyclic ring, Domagala and coworkers [39] have included 10 similar organobismuth(V) compounds, $R_3Bi(O_2CR')_2$ and $R_3Bi(O_2CCH_2R')_2$, where R was Ph or $4\text{-}MeC_6H_4$ and R′ was 2-furyl, 2-thienyl, 2-pyrryl or 2-*N*-methylpyrryl. The compounds were prepared from triarylbismuth carbonate and 2 equivalents of the carboxylic acid in chloroform solution. They were characterized by elemental analyses and IR spectra. As with the organoantimony compounds (described in the Organoantimony Section in this journal), the υ(C=)O-Bi and υ(C-)O-Bi absorption bands in the IR spectra, both in the solid state and in solution, as well as the differences υ[C=)O-Bi] - [υ(C-)O-Bi], both in the solid state ($\Delta\upsilon_F$) and in solution ($\Delta\upsilon_L$), were listed. Finally, the magnitude of the difference, $\Delta\upsilon_L-\Delta\upsilon_F$, was taken as a measure of the amount of interaction between the carbonyl oxygens and the bismuth atom. In the case of the ten organobismuth(V) compounds studied, all of these values for $\Delta\upsilon_L-\Delta\upsilon_F$ were positive, but considerably smaller than those for the corresponding antimony compounds. It would appear, accordingly, that the interaction between the carbonyl oxygen atoms and the bismuth atom was considerably less than was the case with the antimony atoms. The authors attributed this result to the greater mass of the bismuth atom.

Only a few bismuthonium ylides have been prepared, and the methods used for the preparation were not general reactions but were limited to the preparation of only a few types of ylides. Ogawa and coworkers [40] have now developed a more general method for preparing bismuthonium ylides. This involved the reaction of the sodium salts of 1,3-dicarbonyl compounds with either dichlorotriphenylbismuth or triphenylbismuthine oxide. Thus, the sodium salt of dimedone (5,5-dimethylcyclohexane-1,3-dione), generated from the dione and sodium hydride in THF, was treated with dichlorotriphenylbismuth under nitrogen at -20°C:



III

The resulting ylide III was purified by chromatography on a silica-gel column with $MeOH-CH_2Cl_2$ as the eluent. The stable ylide, mp 75°C, was obtained in 52% yield. If triphenylbismuthine oxide, rather than the dichloride, was used, the yield was 84%. Stable crystalline ylides were also obtained from cyclohexane-1,3-dione and cyclopentane-1,3-dione. Dichlorotriphenylbismuth was used for the preparation of these two compounds. It was found that these ylides reacted with sulfenes, generated from sulfonyl chlorides and triethylamine, to form 1,3-oxathiole-3,3-dioxides:

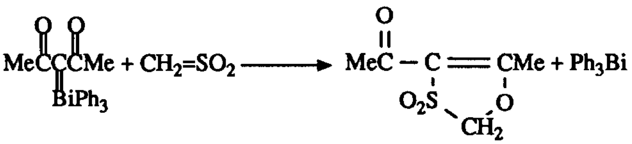


III

(where R was H, Ph, Pr, or Hep)

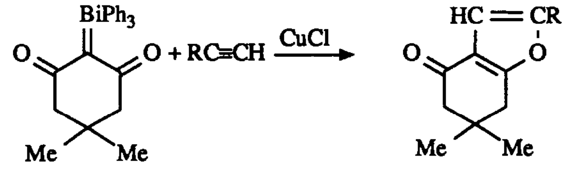
Similar compounds were prepared from the bismuthonium ylides obtained from cyclohexane-1,3-dione or cyclopentane-1,3-dione and $CH_2=SO_2$.

When the sodium salt of acetylacetone was treated with dichlorotriphenylbismuth, the ylide was generated as demonstrated by TLC and ^{13}C NMR studies of the crude reaction product. Attempts to isolate the ylide, however, were unsuccessful. The only products were 3-phenylpentane-2,4-dione and triphenylbismuthine. But when the crude reaction mixture was treated with methanesulfonyl chloride and triethylamine, the 1,3-oxathiole-3,3-dioxide was obtained in 65% yield:



Similar oxathioles were obtained when 1-phenylbutane-1,3-dione or 1-methoxybutane-1,3-dione was used as the substrate. When any of these three open chain diones was treated with dichlorotriphenylbismuth and the mixtures allowed to stand, the 3-phenyl-2,4-diones were isolated from the reaction mixtures. This finding strongly suggested that the *C*-arylation of 1,3-dicarbonyl compounds with organobismuth(V) compounds proceeded through the intermediate formation of a bismuthonium ylide, rather than by any of the different mechanistic pathways suggested by Barton and coworkers [41].

Ogawa and coworkers have previously reported on the reactions of the stable crystalline ylide III with aromatic and aliphatic aldehydes. In a paper from the same laboratory, the reaction of III with a number of alkynes was reported [42]:

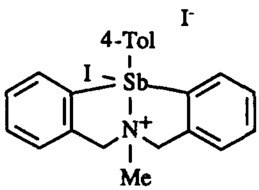


III IV

(where R was Ph, 4-MeC$_6$H$_4$, 4-ClC$_6$H$_4$, Hex, or PhCOCH$_2$)

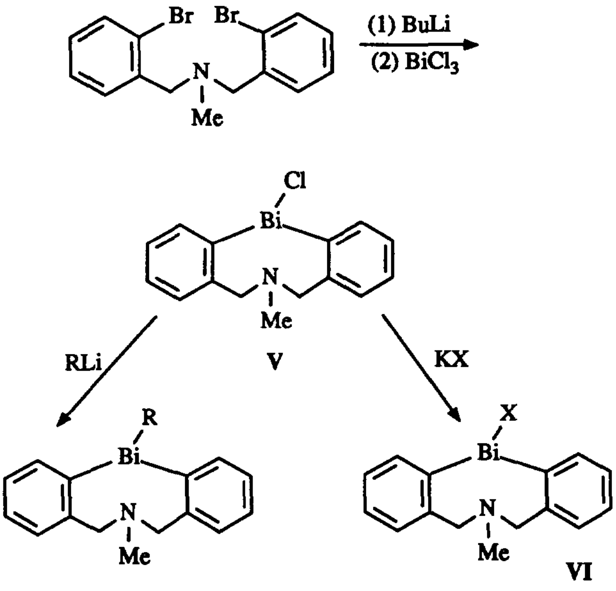
The reactions were carried out by heating the reactants in benzene in the presence of catalytic amounts of copper(I) chloride for 1 h. In addition to the furan product IV, dimedone, triphenylbismuthine, and an unidentified organic solid containing copper were obtained. Two of the products (R = Hex or PhCO$_2$CH$_2$) were obtained only as oils; the other three products were crystalline solids. Complex mixtures were obtained with the alkyne RC≡CH, where R was MeO$_2$C, and with 4-octyne and 1,2-diphenylethyne. No reaction occurred in the absence of the copper salt. The authors proposed a mechanism involving reaction of copper(I) chloride with the ylide to form a carbene by loss of triphenylbismuthine. The reaction products were characterized by ^{1}H and ^{13}C NMR and IR spectroscopy.

Several previously published papers from Akiba's laboratory in Japan have described the preparation and properties of derivatives of bicylic systems exhibiting transannular interactions. Thus, one such compound described in a recent publication [43] was the following:



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

This compound was described as a 10-Sb-5 compound, where 10 was the number of electrons and 5 the number of ligands surrounding the antimony atom. Another paper from Akiba's laboratory has now described the preparation and properties of 10-Sb-4 and 10-Bi-4 transannular compounds [44]. Five 12-substituted dibenz[*c*, *f*][1,5]azabismocine compounds were prepared by means of the following series of reactions:



V

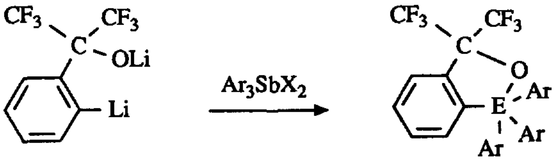
VI

(where R was Me or Ph)

(where X was F or I)

The chloro compound V failed to react with methyl iodide to give methylated derivatives, but rather gave the iodo derivative VI (X = I). The authors suggested that V underwent oxidative addition to the bismuth atom followed by loss of methyl chloride. ^{1}H and ^{13}C NMR data on all of the new bismocine compounds were given. It was noted that there was a linear relationship between the *N*-methyl proton NMR signals and the Hammett σ_m constants for the various substituents on the bismuth atom. A similar linear relationship existed for the ^{13}C *N*-methyl NMR signals and the Hammett σ_m constants. These results suggested that a transannular bond existed between the nitrogen and bismuth atoms, *i.e.*, the bismuth possessed a 10-Bi-4 configuration.

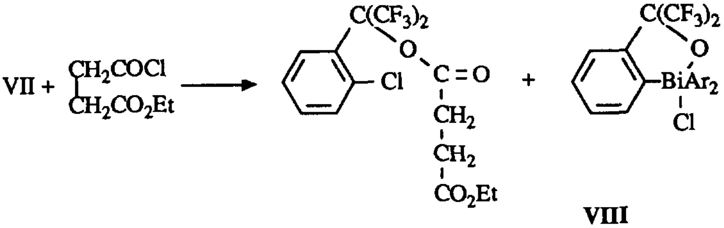
Akiba and coworkers have previously described in considerable detail the preparation of the benzoxastibole compound VII:



(where E was Sb)

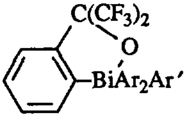
VII

In a new paper from Akiba's laboratory, the preparation of two bismuth compounds VII (E = Bi, Ar = 4-tolyl or 4-$CF_3C_6H_4$) has been described [45]. The compounds were stable to atmospheric *moisture and melted at 207-209 and 199-201°C, respectively, without* decomposition. Compound VII (Ar = 4-tolyl) reacted with ethyl succinyl chloride as follows:



VIII

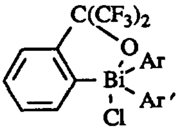
By contrast, *reaction of VII (Ar = 4-tolyl) with sulfuryl chloride gave VIII and ArCl.* Compound VIII reacted with 4-$CF_3C_6H_4Li$ to give compound IX:



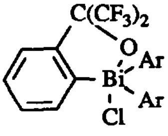
IX

(where Ar was 4-tolyl and Ar′ was 4-$CF_3C_6H_4$)

Compound IX was then allowed to react with sulfuryl chloride to give two products Xa and Xb in a ratio of *>10:1.*



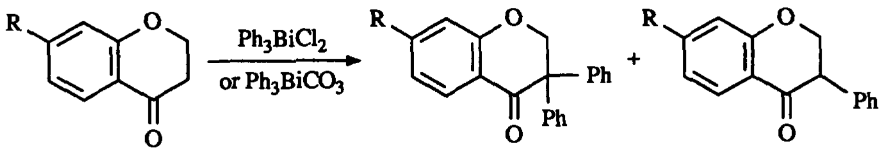
Xa



Xb

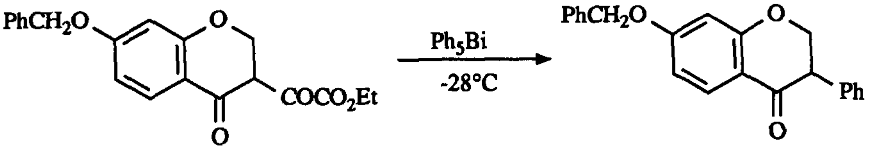
(where Ar was 4-tolyl and Ar′ was 4-$CF_3C_6H_4$)

Barton and coworkers have published extensively on the use of organobismuth(V) compounds in organic synthesis, particularly on their use as oxidizing or arylating agents. Because of the mild conditions employed, these compounds were of particular value with sensitive natural products. The present paper deals with the use of tri-, tetra, or pentaarylbismuth(V) compounds for the arylation of chroman-4-one or 4-hydroxycoumarin derivatives [46]. For this purpose a variety of organobismuth(V) compounds were used, *e.g.* Ph_3BiX_2 (where X was Cl, OAc, $O_3SC_6H_4Me$-4, NO_3), $Ph_4BiO_3SC_6H_4Me$-4, or Ph_5Bi. Phenylation of the potassium enolate of chroman-4-one (XI, R = H) with either Ph_3BiCl_2 or Ph_3BiCO_3 gave modest yields of the 3,3-diphenyl compound with only small amounts of the monophenyl compound:



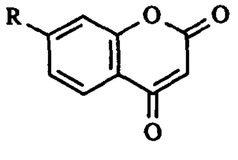
XI

Further studies were carried out with two substituted chroman-4-ones, (XI, R = OCH_2Ph or OMe). The best yield of a monophenyl compound (88%) was obtained with Ph_5Bi and the 3-oxalyl derivative of XI (R = OCH_2Ph):



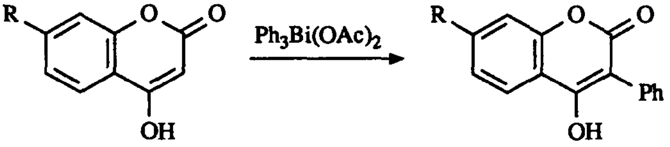
Under the reaction conditions used, the protecting oxalyl group was lost. Only 3% of the diphenyl derivative was obtained.

In addition to the phenylation of chroman-4-ones to give isoflavanones, the phenylation of 4-hydroxycoumarins XII (R = H or OMe) was studied.



XII

The best results with XII (R = H) were obtained (92%) when the substrate was heated in refluxing CH_2Cl_2 with $Ph_3Bi(OAc)_2$ in the dark for 16 h. Under similar conditions XII (R = OMe) gave an 85% yield of the monophenyl compound:

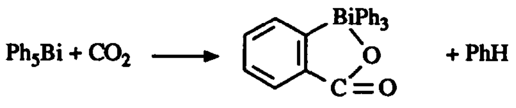


(where R was H or OMe)

In addition to the 3-phenyl derivatives, both substrates (R = H and R = OMe) gave the 3-(4′-tolyl) derivatives in 85 and 80% yields, respectively, when $(4\text{-MeC}_6H_4)_3Bi(OAc)_2$ was used as the arylating agent. In yet another reaction, XII (R = H) was arylated with tris(3-nitrophenyl)bismuth diacetate to yield the 3-(3′-nitrophenyl) derivative. After acetylation of the hydroxy group, the nitro group was reduced with $SnCl_2$ in HCl solution, the resulting amine, without isolation, was diazotized, and then treated with acetic anhydride-pyridine. Two products were obtained, 4-acetoxy-3-(3′-chlorophenyl)coumarin and 4-acetoxy-3-(3′-acetoxyphenyl)coumarin, in 35 and 61% yields, respectively.

A paper by Knop and coworkers [47] was devoted to a comparison of the molecular structures of compounds of the type R_4EX, where R was an alkyl or aryl group, E was P, As, Sb, or Bi, and X was a relatively small negative group. The authors noted that compounds of this type, whose crystal structures were known and where E was P or As, were all ionic. By contrast, most compounds of this type where E was Sb or Bi were trigonal-bipyramidal. Tetraphenylbismuthonium perchlorate, however, was ionic. The authors apparently had not seen a paper published in 1988 [48] where the crystal structures of Ph_4SbClO_4, as well as of Ph_4SbBr, were reported. Thus, the determination, reported in this paper [47], of the crystal structure of the latter compound duplicated work previously published. When the bond lengths and bond angles of all R_4SbX and R_4BiX compounds, whose molecular structures were known, were tabulated and compared, it was apparent that the Sb-C_{axial} and Bi-C_{axial} distances decreased with increasing Sb-X and Bi-X distances. With antimony this fact could be quantified as Sb-C_{axial} is proportional to 2.4 $(\text{Sb-X})^{1/9}$. This, and other geometric relationships, showed that there was a limiting E-X bond length (about 3.3 Å for Sb and 3.5 Å for Bi) at which the trigonal bipyramid became unstable and changed to a tetrahedral R_4E form. This was accompanied by a rearrangement to an ionic $R_4E^+X^-$ species, with E-X distances no shorter than about 4 Å (for E-Sb or Bi and X = O). The Sb-Br bond length in Ph_4SbBr, 2.990 Å, was the longest known for any Sb(V)-Br compound. This length and the long Sb-Cl bond length in Ph_4SbCl (2.740 Å) suggested that these species were well en route from molecular to ionic compounds.

In an article devoted to steric factors associated with the thermal decomposition of pentaphenyl derivatives of phosphorus, arsenic, antimony, and bismuth, Sharutin [49] has noted that the thermal stability of triphenyl compounds was in the order P>As>Sb>Bi, whereas in the pentaphenyl series the order was Sb>As>P>Bi. The relative instability of the phosphorus compound was attributed to steric hindrance; the instability of the pentaphenylbismuth was attributed to "low coordination saturation of the bismuth atom". Thus, addition of a sixth ligand to pentaphenylbismuth should result in a more stable compound. The formation of the more stable lithium hexaphenylbismuthate from phenyllithium and pentaphenylbismuth was cited as an example of this effect. The author then gave a number of reactions of pentaphenylbismuth which probably occurred through addition of a sixth ligand to the bismuth atom. Some of these reactions were not described in the experimental part. The reaction of pentaphenylbismuth with carbon dioxide at -10°C (described in a previous paper) was considered in some detail:



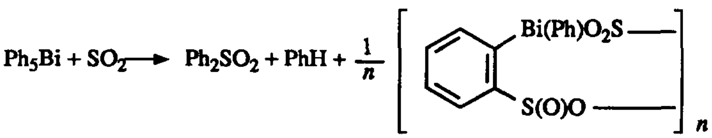
The author suggested that the first step in this reaction was the addition of CO_2 to the bismuth as a sixth ligand. (A similar reaction occurred with pentaphenylphosphorus at 80-110°C but did not occur with pentaphenylantimony.) Another reaction considered was that involving pentaphenylbismuth and triphenylstibine (also reported in a previous paper [50] in which a mechanism involving the formation of benzyne was suggested to explain the results). In the present paper it was reported that when the reaction was carried out in toluene, the product was pentaphenylantimony. The author suggested that this reaction involved formation of a 6-covalent bismuth atom followed by transfer of two phenyl groups to the antimony atom:

$$Ph_5Bi + Ph_3Sb \rightarrow Ph_5Bi\text{----}SbPh_3 \rightarrow Ph_3Bi + Ph_5Sb$$

If a tritolystibine was used in the above reaction, the yield of arylated product was lower, and with such bulky stibines as tricymanthrenyl- or trinaphthylstibine, no reaction occurred. Two other reactions which may have involved a similar arylation mechanism were the following:

$$Ph_5Bi + Cp_2WH_2 \rightarrow Cp_2W(H)Ph + Ph_3Bi + PhH$$

(where Cp was cyclopentadienyl)



Finally, the author speculated that the many reactions of organobismuth(V) compounds with alcohols, enols, phenols, and other organic substrates, involving oxidation, arylation, or both involved the addition of a sixth ligand to a "recess" in the surroundings of the bismuth atom. "The dimensions and configuration of the "recess", the distribution of electron density at its edges, and the peculiar features of the electron structure of the incoming ligand determine the structure of the final reaction product."

Pentaphenylbismuth is an unstable violet-colored solid which exhibits dichroism. These properties are in sharp contrast to the corresponding phosphorus, arsenic, and antimony pentaphenyl compounds which are stable colorless or pale yellow (Ph_5Sb) solids. Schmuck and coworkers previously determined the crystal structure of Ph_5Bi and showed it to be square pyramidal with four long Bi-C bonds. These authors suggested that the differing properties (dichroism and color) could be attributed to a charge transfer complex, $Ph_5Bi \rightarrow Ph_4Bi^-Ph^+$. Schmuck and Seppelt [51] have now prepared several new pentaarylbismuth compounds and determined their crystal structures. An attempt to obtain penta-4-tolylbismuth was unsuccessful. The reaction between dichloro-tri-4-tolylbismuth and 4-tolylithium gave a violet-colored solution which decomposed with loss of color above -20°C. Tris(pentafluorophenyl)difluorobismuth was prepared by the fluorination of tris(pentafluorophenyl)bismuthine with xenon difluoride. However, reaction of this bismuth(V) compound with excess pentafluorophenyllithium in ether solution gave a yellow uncrystallizable oil, from which not all the ether could be removed. An attempt to prepare pentakis(4-fluorophenyl)bismuth was also unsuccessful. Bis(4-fluorophenyl)triphenylbismuth was obtained as an orange-colored crystalline solid; its crystal structure could not be determined because of crystal twinning. Bis(4-fluorophenyl)tri-4-tolylbismuth was obtained as violet-colored crystals, which like Ph_5Bi exhibited dichroism. These crystals were also twinned, preventing determination of the crystal structure. Three new stable crystalline compounds were prepared and their crystal structures determined by X-ray diffraction. Bis(pentafluorophenyl)tri-4-tolylbismuth was obtained as a yellow crystalline compound, stable at room temperature. Like pentaphenylbismuth it was a slightly distorted tetragonal pyramid. The largest angle (162.6°) was between the two pentafluorophenyl groups. Bis(pentafluorophenyl)tris(4-fluorophenyl)bismuth, a yellow crystalline solid, was an almost perfect quadratic pyramid. The third compound, triphenylbis(2,6-difluorophenyl)bismuth, an orange-red crystalline solid, contained two different molecules in the unit cell; both of these possessed square pyramidal geometry. Since none of these new compounds exhibited the deep violet color or the dichroism of pentaphenylbismuth, the results reported in the present paper do not add information as to the reason for these properties of the pentaphenyl compound.

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