BISMUTH

ANNUAL SURVEY COVERING THE YEAR 1986

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Except for our Annual Survey covering the year 1984, no review articles dealing solely with organobismuth compounds have appeared in 1986. Several review articles, however, have included material on such compounds. Thus, the annual survey of organometallic compounds [1] and the *Annual Reports on the Progress of Chemistry*, both organic [2] and inorganic [3], have all briefly mentioned organobismuth compounds. An excellent review of inorganic and organometallic bismuth compounds covering research published in 1984 has appeared in *Coordination Chemistry Reviews* [4]. Organobismuth compounds have been treated in considerable detail in a recently published text on organometallic chemistry [5], a revision of a text originally published in the Romanian language. The chemical properties of a number of recently prepared organobismuth compounds have been given in the second supplement to the *Dictionary of Organometallic Compounds* [6]. The Raman and infrared stretching frequencies of Bi-C bonds in a number of organobismuth compounds have been tabulated in a new edition of a well-known monograph devoted to vibrational spectra of inorganic and coordination compounds [7]. The crystal structures of a number of organobismuth compounds have been given in a report devoted to the structures of compounds determined by diffraction methods [8]. In a review article on the fluxionality of η^1 - cyclopentadienyl compounds of the main group elements, the fluxionality of organobismuth compounds such as $C_5H_5BiMe_2$ has been discussed [9]. The displacement of carbonyl groups attached to transition metals by tertiary bismuthines was mentioned in a review on ligand displacement reactions of metal carbonyls by Group V and VI donor ligands [10]. A review article on distibines, dibismuthines, and related compounds has been written by Ashe [11] ; most of the work reviewed in this report originated in his laboratory. In a review article devoted to multiple bonding between main group elements, Cowley has mentioned unsuccessful attempts to prepare compounds with Bi-Bi multiple bonds [12]. These attempts involved efforts to stabilize such bonds by coordination with transition elements such as tungsten. Two other review papers by Huttner have also summarized recent work on multiple bonding between Group V elements including bismuth [13, 14].

The reactions of triphenylbismuthine with either sulfur trioxide [15] or sulfur dioxide [16] have been formulated as addition compounds, $Ph_3Bi{\cdot}SO_3$ or $Ph_3Bi{\cdot}2SO_2$, respectively. It was later demonstrated, however, that the product from sulfur dioxide was actually $PhBi(O_2SPh)_2$ [17]. Deacon and coworkers [18] have now reinvestigated the reaction of triphenylbismuthine (and also tri-*p*-tolylbismuthine) with sulfur trioxide. It was first shown that both triarylbismuthines reacted with benzenesulfonic or *p*-toluenesulfonic acids to give the diarylbismuth sulfonates:

$$Ar_3Bi + Ar'SO_3H \longrightarrow Ar_2Bi(O_3SAr') + ArH$$

Under more vigorous reaction conditions tri-*p*-tolylbismuthine reacted with benzenesulfonic acid to give an impure product which contained both *p*-$MeC_6H_4Bi(O_3SPh)_2$ and (presumably) $BiO(O_3SPh)$. The proposed compositions were based on the PMR spectra of the products since resonances of the different aryl groups could be distinguished owing to the downfield shifts of *ortho*-protons of arylbismuth(III) compounds, and to further downfield shifts of arylbismuth resonances as aryl groups were replaced by anionic ligands. Thus, although *p*-$MeC_6H_4Bi(O_3SPh)_2$ was not obtained in a pure state, it was clearly identified as a reaction product by comparison of the *ortho*-protons with the *ortho*-protons of (*p*-$MeC_6H_4)_2BiO_3SPh$. In those compounds where Ar and Ar' differed, the presence of both groups was established by IR spectroscopy.

The compounds Ph_2BiO_3SAr' were unstable, losing phenyl groups attached to the bismuth atom on storage. This was believed to be due to hydrolysis:

$$Ph_2BiO_3SAr' + H_2O \longrightarrow 2\ PhH + BiO(O_3SAr')$$

In addition to hydrolytic products, small amounts of Ph_3Bi were detected in the products obtained on storage. Having characterized the diarylbismuth sulfonates (by PMR, IR, and elemental analyses) the authors then showed that the reaction between Ph_3Bi [or (*p*-$MeC_6H_4)_3Bi$] and SO_3 gave the corresponding diarylbismuth sulfonates as the principal products of the reaction. It was also shown that the formation of Ph_3Bi, previously reported as formed from $Ph_3Bi{\cdot}SO_3$ and boiling water [15], was actually due to a rearrangement:

$$2\ Ph_2BiO_3SPh \longrightarrow Ph_3Bi + PhBi(O_3SPh)_2$$

In continuation of earlier work on the use of organometallic compounds such as Ph_3Bi as cocatalysts for the polymerization of alkynes, Masuda and coworkers [19] have reported on the polymerization of 1-trimethylsilyl-1-

propyne with 1:1 $TaCl_5$-Ph_3Bi or 1:1 $NbCl_5$-Ph_3Bi. Other cocatalysts used were Ph_3Sb, Ph_4Sn, Bu_4Sn, Ph_3SiH, and Et_3SiH. The combination $TaCl_5$-Ph_3Bi produced a polymer with the highest molecular weight ($M_w \leq 4 \times 10^6$) of any of the catalyst-cocatalyst combinations used. The effect of temperature and solvents on the polymerization of $CH_3C \equiv CSiMe_3$ with $TaCl_5$-Ph_3Bi was also reported.

The use of Ph_3Bi as a cocatalyst with $TaCl_5$ for the polymerization of $MeC \equiv CSiMe_2CH_2CH_2SiMe_3$ was included in an article on the polymerization of Si-containing acetylenes [20]. Triphenylbismuthine was less effective as a cocatalyst than Ph_4Sn.

Two organobismuth(III) compounds, Ph_3Bi and $(p\text{-}MeC_6H_4)_3Bi$, and two inorganic bismuth compounds, bismuth chlorosulfide and tris(8-quinolinolato)bismuth, have been tested as fungicides against two diseases of the coffee tree, *viz.* coffee berry disease and coffee leaf rust [21]. Only tris(8-quinolinolato)bismuth showed any marked effectiveness against these two diseases. This compound gave 96% inhibition at the 1% formulation.

Bulgakov and coworkers [22] have described the chemiluminescence produced in the reaction of a number of organometallic compounds when they were oxidized with XeF_2 or O_2. The chemiluminescence was measured quantitatively by means of a photoelectronic multiplier. Among the organometallic compounds used in this study was Et_3Bi.

A number of tertiary bismuthines (triaryl, trialkyl, or alkylaryl) have been included in a paper devoted to the cone angle of 610 ligands of Group IV and Group V elements [23]. The cone angle is defined as the steric characteristic expressing the degree of filling out by the ligand of the coordination sphere. The ligands all had the formulas AX_3 or $A(OX)_3$ and possessd tetrahedral geometry with respect to A in that fragment of the complex M-AX_3, where M was the coordinating metal. It was found that as the atomic number of A increased, the cone angle decreased.

Electrostatographic developers which give high resolution and gradation images without fog and which have excellent durability have been described in a Japanese patent [24]. A triarylbismuthine was one of the principal ingredients.

Triarylbismuthines have also been used as toners for electrostatographic developers which showed improved performance over controls containing ingrosine dyes without the organobismuth compound [25].

A number of hybrid organometallic compounds of the type $MR_xR'_y$, where M was any one of a number of metals including Bi, R and R' were H, alkyl, phenyl, substituted phenyl, or cyclopentadienyl, and x and y were 1 or 2, have been found useful in vapor deposition processes for optoelectronic materials [26].

Trimethylbismuthine was one of a number of organometallic compounds mentioned in a Japanese patent describing materials for forming patterned deposits on a suitable substrate [27].

Bismuth(III) chloride has been shown to form crystalline arene complexes with mesitylene or with hexamethylbenzene [28]:

$$BiCl_3 + 1,3,5\text{-}Me_3C_6H_3 \longrightarrow [1,3,5\text{-}Me_3C_6H_3][BiCl_3]$$

$$2\ BiCl_3 + Me_6C_6 \xrightarrow{\text{toluene}} [Me_6C_6][BiCl_3]_2$$

The mesitylene complex crystallized in colorless platelets, m.p. 157° C (decomp.); the hexamethylbenzene complex consisted of bright yellow crystals, m.p. 212-215° C (decomp.). They were characterized by elemental analyses. Their IR and PMR spectra were similar to the spectra of the components. Their crystal structures were determined by x-ray diffraction. The mesitylene complex consisted of alternating, crystallographically-independent sheets of $BiCl_3$ networks, which, in turn, each contained two non-equivalent Bi atoms. Each Bi atom was pseudo octahedral with three strongly bound chlorine atoms, two more loosely bound (bridging) chlorine atoms, and a η^6-bound mesitylene molecule. The mesitylene rings were alternately above and below the $BiCl_3$ sheets. The hexamethylbenzene structure contained tetrameric $(BiCl_3)_4$ units, and each of the four crystallographically equivalent Bi atoms coordinated a hexamethylbenzene ligand. The centers of the arene molecules formed crystallographically inversion centers, so that an equivalent bismuth halide unit was found on the other side of the ring. By virtue of η^6- bonding, the structure differed from tha analogous Mentshutkin complexes.

It is well known that a variety of distibines and dibismuthines show thermochromic effects, whereas diarsines and diphosphines do not. Ashe and Ludwig [29] have now prepared (as mixtures) compounds of the type $Me_2EE'Me_2$, where E and E' were Group V elements, P, As, Sb, or Bi. They were obtained by the following exchange reaction:

$$Me_4E_2 + Me_4E'_2 \rightleftharpoons 2\ Me_2EE'Me_2$$

The bismuth compounds prepared were $Me_2BiSbMe_2$ and $Me_2BiAsMe_2$. Because of the lability of the equilibrium, the mixed compounds could not be prepared in a pure state but only as a mixture of all three components. The equilibrium constant K was calculated using the expression

$$K = \frac{[Me_2EE'Me_2]^2}{[Me_4E_2][Me_4E'_2]}$$

Data for calculating the equilibrium constants were obtained (for the two bismuth components) from the PMR data. The two methyl signals for the mixed compound lay between the signals for the pure Me_4E_2 and $Me_4E'_2$ compounds. Thus, for $Me_2BiSbMe_2$, two signals at $\delta = 1.23$ and 1.17 ppm were found, whereas the signals for Me_4Bi_2 and Me_4Sb_2 were at 1.55 and 0.84 ppm, respectively. The signals for the mixed compound $Me_2BiAsMe_2$ occurred at 1.42 and 1.14 ppm, whereas the signal for Me_4As_2 occured at 0.96 ppm. The equilibrium constants for the two compounds $Me_2BiSbMe_2$ and $Me_2BiAsMe_2$ were found to be 1.2 and 9×10^{-3}. These values were considerably less than the value of 4 expected on simple probability considerations. The authors noted that these findings violated the Pauling postulate that heteronuclear bonding is stronger than homonuclear bonding. They attributed this result to the fact that, since electronegativity values for the Group V elements are so close together, other factors may influence the equilibria. No mixed compounds could be detected when Me_4Bi_2 and Me_4P_2 (or Me_4Sb_2 and Me_4P_2) were mixed, although Me_4P_2 and Me_4As_2 did undergo exchange. The Raman spectra of the mixed compounds (as well as those of Me_4P_2, Me_4As_2 and Me_4Sb_2, but not of Me_4Bi_2) gave two stretching bands which were assigned to E-E or E-E' stretching frequencies. It was suggested that the two frequencies for all of the compounds (other than Me_4Bi_2) were due to *trans* and *gauche* conformations of the compounds.

The authors then extended their exchange reactions to the preparation of compounds of the type Me_2EAMe, where E was again P, As, Sb, or Bi, and A was S, Se, or Te [30]:

$$Me_4E_2 + Me_2A_2 \longrightarrow 2\ Me_2EAMe$$

The use of this exchange reaction to prepare sulfides, selenides, and tellurides had been used previously by other investigators. However, the two bismuth compounds, $Me_2BiSeMe$ and $Me_2BiTeMe$, had not been previously reported:

$$Me_4Bi_2 + Me_2A_2 \longrightarrow 2\ Me_2EAMe$$

(where A was Se or Te)

With the diselenide and ditelluride, the reaction apparently was complete, *i.e.* the equilibrium constant was in excess of 10^3. With Me_2S_2 and Me_4Bi_2, the authors were unable to detect exchange, but they believed the equilibrium was highly favorable. Both ^1H and ^{125}Te NMR data were reported. The ^1H signals for the two bismuth compounds consisted of broad singlets, so broad that the Te-H coupling constants could not be determined. There was a progressive Te shielding in the series Me_2ETeMe, as E varied from P to Bi. Thus the δ value for Me_2PTeMe occurred at 90 ppm and was -277 ppm for $Me_2BiTeMe$. The authors also reported Raman spectra for these compounds. Stretching frequencies for E-A bonds were found to lie between those for E-E bonds and A-A bonds. They were unable to obtain values for Bi-A bonds, however; apparently the deeply colored bismuth compounds were destroyed by the lasar radiation. Nor could the mass spectra of the two bismuth compounds be determined, apparently due to their lability.

In a preliminary paper Arif, Cowley, and coworkers [31] described their unsuccessful attempts to prepare compounds containing Bi=Bi bonds by stabilization through attachment of transition element groups. They did succeed, however, in obtaining two interesting cluster compounds with Bi-Bi bonds. One of these, $[\{W(CO)_5\}_3(\mu_3\text{-}\eta^2\text{-}Bi_2)]$ had been prepared by other workers and its structure had been determined. The crystal structure of the second compound, $[W_2(CO)_8(\mu_2\text{-}\eta^2\text{-}Bi_2)(\mu\text{-}Bi)MeW(CO)_5]$, has now been described in a second paper from Cowley's laboratory [32]. In addition to the two bismuth compounds the preparation, properties, and crystal structure of a stibinidine complex was also described. In neither case were compounds containing Sb=Sb or Bi=Bi compounds obtained.

Cleavage of C-Bi and Ge-Bi bonds by vanadocene Cp_2V (where Cp= cyclopentadienyl) has been reported by Pankratov and coworkers [33]. The authors first demonstrated that vanadocene and triethylbismuthine did not react when heated at 50-60°C for 40-50 hours. However, when $(C_6F_5)_3GeBiEt_2$ and vanadocene were allowed to react in toluene at room remperature, both the C-Bi and Ge-Bi bonds were cleaved with the formation of metallic bismuth in 100% yield. The reaction of $[(C_6F_5)_3Ge]_2BiEt$ with vanadocene was even faster, again with cleavage of the C-Bi and Ge-Bi bonds:

$$[(C_6F_5)_3Ge]_n\ BiEt_{3-n} + 3\ Cp_2V \longrightarrow Bi\ + n\ Cp_2VGe(C_6F_5)_3 + 3\text{-}n\ Cp_2VEt$$

$$(\text{where } n = 1 \text{ or } 2)$$

The reaction of vanadocene with the tricyclic compound $[(C_6F_5)_2Ge]_3Bi_2$ was also investigated and found to yield a complex mixture of compounds containing V-Ge bonds and metallic bismuth. A number of other reactions between vanadocene and germanium compounds were also reported in this paper.

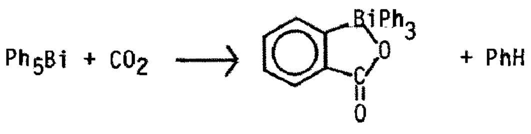
Two interesting organobismuth(V) compounds, $Ph_3Bi(I)N_3$ and $Ph_3Bi(I)NCO$, have been obtained by the reaction between Ph_3Bi and iodine azide (IN_3) or iodine isocyanate (INCO) [34]. The reactions in MeCN or CCl_4 were carried out at -10°C. The resulting bismuth compounds were yellow solids, which were stable at room temperature but decomposed on heating. Some selected IR data on the two compounds were reported, and their molar conductances were also given. The compounds were also characterized by elemental analyses and IR spectra.

A number of triphenylbismuth disulfonates, $Ph_3Bi(O_3SR)_2$, where R was Me,CF_3,CH_2CH_2OH, Ph, 4-MeC_6H_4, or 2,4-$(NO_2)_2C_6H_3$, have been prepared by Rüther and coworkers [35]. All of the compounds were prepared from Ph_3BiCO_3 and the appropriate sulfonic acid. The solvent employed was either acetone or chloroform. The compound $Ph_3Bi(O_3SCH_2CH_2OH)_2$ was isolated only after concentration of the solvent (Me_2CO) to a small volume and the addition of $MeCO_2Et$. All of the compounds were crystalline solids, characterized by elemental analyses, molecular weight determinations, IR, and Raman spectra. On the basis of the vibrational spectral data it was concluded that all of the compounds contained a trigonal bipyramidal Bi atom with unidentate sulfonato groups in axial positions. Molecular weight determinations in $CHCl_3$ were also in agreement with a monomolecular structure. The compound $Ph_3Bi(O_3SPh)_2$ underwent reaction with ethanolic HCl with cleavage of the Bi-O bonds:

$$Ph_3Bi(O_3SPh)_2 + 2\ Cl^- \longrightarrow 2\ Ph_3BiCl_2 + 2\ PhSO_3^-$$

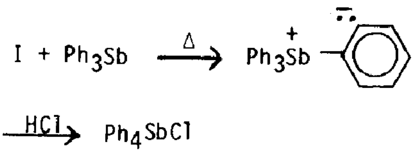
The crystal structure of $Ph_3Bi(O_3SPh)_2$ was determined by X-ray diffraction. The molecular structure was that of a trigonal bipyramid with two axial sulfonato groups and three equatorial phenyl groups. There was, however, some distortion of the equatorial angles, and there was also some shortening of one of the Bi-O contact distances with a non-bonding oxygen atom. These results suggested a weak interaction between the Bi atom and a second oxygen atom.

When pentaphenylbismuth in toluene solution at -20°C was treated with CO_2, the interesting bismole I was formed [36]:



I

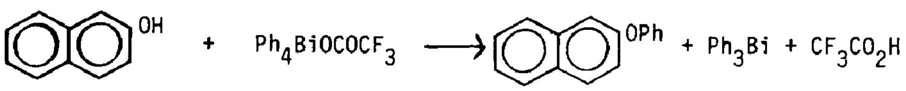
This bismole decomposed on heating in an argon atmosphere to yield triphenylbismuthine, CO_2, and benzyne. The formation of benzyne as a product of the thermolysis was demonstrated by carrying out the decomposition reaction in the presence of *tert*-butyl alcohol; *tert*-butyl phenyl ether was formed. The IR spectrum of I contained a strong, broad band at 1600 cm^{-1}, characteristic of the C=O stretching vibration. It was also found that when I was decomposed in the presence of triphenylstibine, the antimony atom was arylated:



It was also shown that triphenylstibine was similarly arylated when heated in the presence of $2\text{-}C_6H_4(N_2^+)(CO_2^-)$. Thermal decomposition of the latter substance is known to proceed with the formation of benzyne.

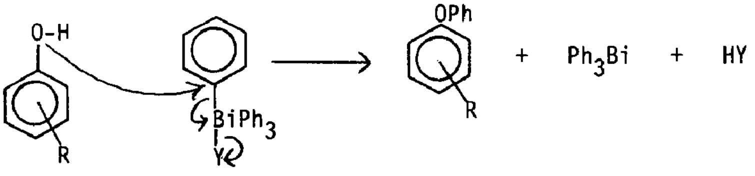
When the thermal decomposition of I in the presence of triphenylstibine was carried out with an excess of I, the known compound 5,5-dihydro-5,5,5-triphenyl-5*H*-dibenzostibole was formed. When this was warmed with dilute hydrochloric acid, 2-biphenylyltriphenylantimony chloride was obtained.

In continuation of earlier work (reported in preliminary communications) on the reactions of organobismuth(V) reagents with phenols, Barton and coworkers [37] have now reported in considerable detail on the reactions of a variety of organobismuth(V) compounds (Ph_3BiY_2, Ph_4BiY, and Ph_5Bi, where Y was an electron-attracting group) with a number of phenols under various reaction conditions. They have found that the products of the reactions varied, not only with the reagents employed, but with the reaction conditions. They have also suggested several reaction mechanisms to explain their results. With phenols, not containing an electron-withdrawing group, the reactions with Ph_4BiY under neutral conditions (boiling benzene) led primarily to the formation of an O-phenylated product, *e.g.* :



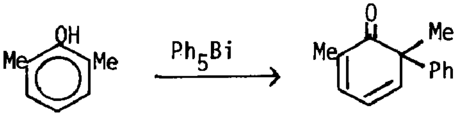
$$Ph_3Bi + CF_3CO_2H \longrightarrow Ph_2BiOCOCF_3 + PhH$$

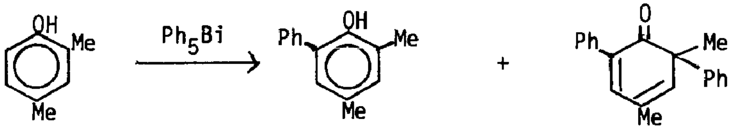
The yield of 2-naphthyl phenyl ether under these conditions was 77% with a 4% yield of 1-phenyl-2-naphthol. Under the same reaction conditions phenol gave 100% yield of diphenyl ether. It was postulated that the reaction involved an S_N2-type displacement reaction:



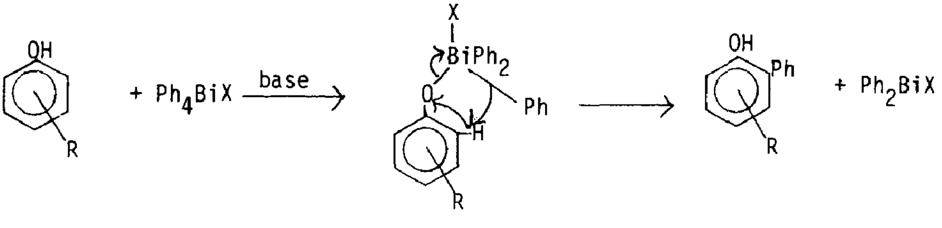
However, the nature of the product and the yields depended to some extent on the Y group. For example, when Y was OCOMe, more 1-phenyl-2-naphthol was obtained (from 2-naphthol) than when Y was $OCOCF_3$. When Y was OSO_2CF_3, no reaction occured.

When Ph_5Bi was used as the organobismuth(V) reagent under neutral conditions (benzene at room temperature), only C-phenylation occured. Thus, 2-naphthol gave a 48% yield of 1-phenyl-2-naphthol. In some cases Ph_5Bi also acted as an oxidizing agent. Thus, the secondary alcohol group of estradiol was oxidized to the corresponding ketone with this reagent. When phenols, in which an *ortho*-position was blocked, were treated with Ph_5Bi, C-phenylation still occured with the formation of a phenylated cyclohexa-2,4-dienone:





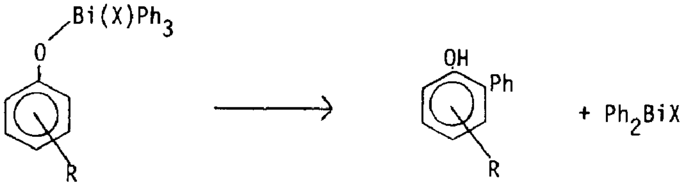
The reactions of organobismuth(V) reagents with phenols under basic conditions resulted in C-phenylation exclusively. The bases used were NaH, 1,1,3,3-tetramethylguanidine, and 1,1,3,3-tetramethyl-2-*tert*-butylguanidine; the solvents used were THF, benzene, and methylene dichloride, and the reactions were carried out at room temperature. In addition to the previously mentioned reagents, Ph_4BiY and Ph_5Bi, compounds of the type Ph_3BiY_2 (where Y was CF_3CO_2, Cl, NO_3, OTs, and 1/2 CO_3) were employed. The yields of C-phenylated products were usually quite large. Thus 2-naphthol and Ph_3BiCl_2 in benzene, with the addition of 1,1,3,3-tetramethyl-2-*tert*-butylguanidine, gave a 90% yield of 1-phenyl-2-naphthol. Even compounds that did not react under neutral or acid conditions underwent reaction under basic conditions. Thus 2-naphthol and $Ph_4BiOSO_2CF_3$ gave an 86% yield of the 2-phenylated product. The authors believed that the reaction proceeded by a different mechanism under basic conditions than under neutral or acid conditions, *i.e.*:



II

The authors also suggested that the C-phenylation that occurred with phenols and Ph_5Bi (without base) proceeded by the same mechanism (*i.e.* X = Ph in the above reaction). Considerable credence for this mechanism was given by the isolation and characterization of the postulated intermediate (II) obtained from 8-hydroxyquinoline and either Ph_3BiCl_2 or $Ph_3Bi(OCOCF_3)_2$. Thermal decomposition of the isolated intermediate II gave the C-phenylated 8-hydroxyquinoline. Finally, the authors found that reaction of an organobismuth(V) reagent with *p*-nitrophenol under basic conditions gave only the O-phenylated product. In this case they were able to isolate the adducts *p*-$O_2NC_6H_4OBi(Y)Ph_3$ (where Y was Cl or CF_3CO_2) and to show that thermal decomposition of these adducts gave only *p*-$O_2NC_6H_4OPh$.

In conclusion, the authors commented briefly on the final step of the C-phenylation reaction, *i.e.* :



They raised the question as to whether this occurred by a radical or a concerted reaction. Because only *ortho* C-phenylation occurred, and also because no trapping of radicals by the solvents (PhH, THF, etc.) occurred, they were inclined to favor the concerted mechanism.

In a second paper from Barton's laboratory on O-phenylation *vs.* C-phenylation, the authors considered principally the reaction between organobismuth(V) reagents and enols or enolate anions [38]. They first noted that triphenylbismuth carbonate under neutral conditions (boiling methylene dichloride) acted both as an oxidizing and a phenylating agent.

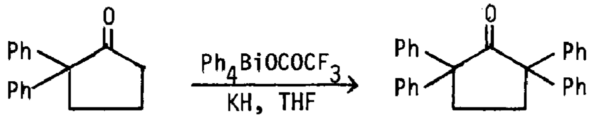
Thus, quinine gave a mixture of diastereomeric phenylated quininones under these conditions, and 1,2-diphenylethanol was similarly oxidized and phenylated:

$$PhCH_2CH(OH)Ph \xrightarrow[CH_2Cl_2]{Ph_3BiCO_3} Ph_2CHCOPh$$

The authors next studied the reaction between Ph_3BiCO_3 and a series of enolate anions formed from ketones and potassium hydride. In each case the substrate was perphenylated, *e.g.*:

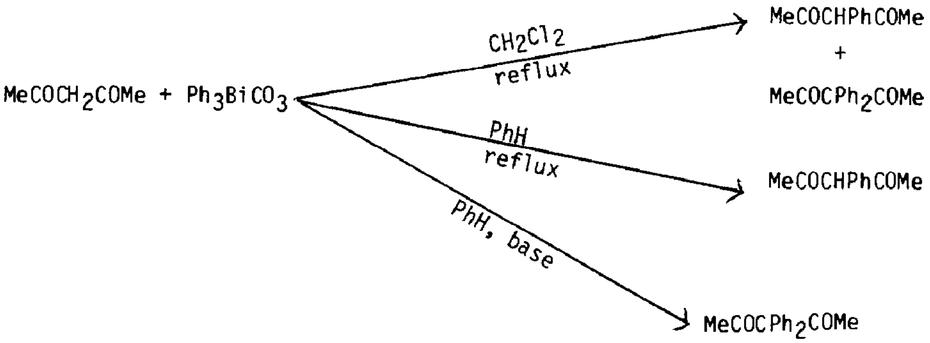
$$PhCH_2COCH_2Ph \xrightarrow[KH,\ THF]{Ph_3BiCO_3} Ph_2CHCOCPh_3$$

Other ketones that underwent perphenylation were acetophenone, cyclohexanone, cholestan-3-one, 4,4-dimethylcholest-5-en-3-one, and 3β-ethoxymethoxyandrost-5-en-17-one. In addition to Ph_3BiCO_3, two tetraphenylbismuth compounds (Ph_4BiY, where Y = *p*-$MeC_6H_4SO_3$ or CF_3CO_2) were used as phenylating agents with similar results:



The authors then studied the reaction between organobismuth(V) reagents and 1,3-dicarbonyl compounds under a variety of reaction conditions. The compounds included acetylacetone, ethyl acetoacetate, ethyl cyclopentanone-2-carboxylate, ethyl cyclohexanone-2-carboxylate, diethyl malonate, and dimedone. Depending both on the organobismuth(V) reagent used and on reaction conditions, mono- and/or diphenylation occurred. Thus, acetylacetone and Ph_3BiCO_3 in refluxing CH_2Cl_2 gave a mixture of 3-phenylpentane-2,4-dione (38%) and 3,3-diphenylpentane-2,4-dione (40%), but only 3-phenylpentane-2,4-dione (34%) was obtained in refluxing benzene, and only

3,3-diphenylpentane-2,4-dione in benzene under basic conditions:

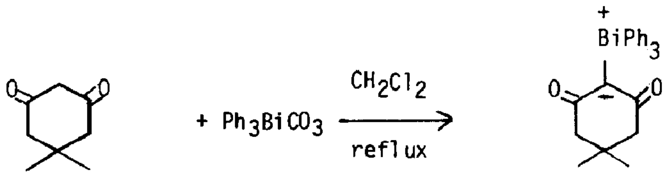


Ethyl acetoacetate, in addition to mono-and diphenylated products, gave a 21% yield of ethyl diphenylacetate when refluxed in CH_2Cl_2 in the presence of Ph_3BiCO_3:

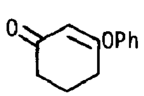
$$MeCOCH_2CO_2Et + Ph_3BiCO_3 \xrightarrow[reflux]{CH_2Cl_2}$$

$$MeCOCHPhCO_2Et + MeCOCPh_2CO_2Et + Ph_2CHCO_2Et$$

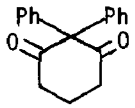
An unexpected product was obtained from dimedone and Ph_3CO_3 in refluxing methylene dichloride;



The product, which was a bismuth ylid, was characterized by its IR, mass, and PMR spectra, and by elemental analysis. With organobismuth(V) reagents other than Ph_3BiCO_3, dimedone gave quite different products. Thus, with $Ph_4BiOCOCF_3$ in benzene alone, or in benzene with the addition of trifluoroacetic acid, the product III was obtained in 56 and 88% yields, respectively, but under basic conditions (1,1,3,3-tetramethyl-2-*tert*-butylguanidine) the diphenylated product IV was obtained.

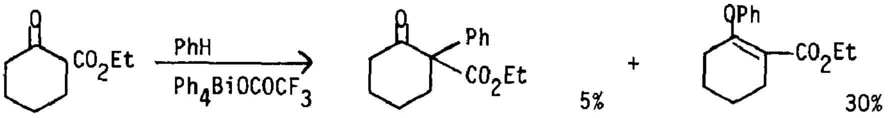


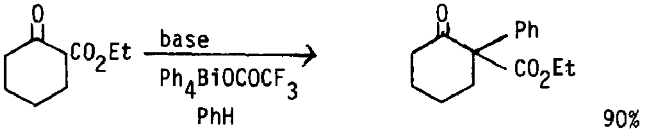
III



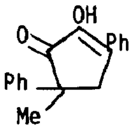
IV

Somewhat similar results were obtained with ethyl cyclohexanone-2-carboxylate, in that C-phenylated, O-phenylated, or both products could be obtained, depending on the reaction conditions (acid, neutral, or basic):

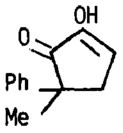




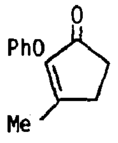
The last enol to be used in these reactions was 2-hydroxy-3-methylcyclopent-2-en-1-one. Under neutral conditions Ph_5Bi or Ph_3BiCO_3 gave 2-hydroxy-5-methyl-3,5-diphenylcyclopent-2-en-1-one (V) in 30 and 25% yields, respectively. The same product in 44% yield was obtained when $Ph_4BiOSO_2C_6H_4Me$-*p* was used as the bismuth(V) reagent under basic conditions. A 10% yield of 2-hydroxy-5-methyl-5-phenylcyclopent-2-en-1-one(VI) was also obtained. Finally, the use of tetraphenylbismuth trifluoroacetate under neutral conditions (refluxing benzene) gave only the O-phenylated product VII in 84% yield.



V



VI



VII

In addition to enolate anions, a number of other anions were phenylated by organobismuth(V) reagents. 2-Nitropropane, potassium hydride, and Ph_3BiCO_3 gave 2-phenyl-2-nitropropane in 80% yield. Potassium triphenylmethanide similarly gave tetraphenylmethane. Methyl octadecanoate, lithium methyldisilazide, and Ph_3BiCO_3 gave the 2-phenyl compound, $Me(CH_2)_{15}CH(Ph)CO_2Me$. *p*-Toluenesulfinic acid and its sodium salt were both phenylated to phenyl *p*-tolyl sulfone by the use of several different organobismuth(V) reagents. The best yield (87%) was obtained from *p*-toluenesulfinic acid and pentaphenylbismuth. Thiophenol and $Ph_4BiOCOCF_3$ gave a 70% yield of Ph_2S with a 15% yield of Ph_2S_2. Similarly, *o*-MeC_6H_4SH gave an 80% yield of *o*-MeC_6H_4SPh. However, PhSNa and Ph_3BiCl_2 gave a nearly quantitative yield of Ph_2S_2.

The last compound considered in this paper was indole (and the indole anion). Indole and $Ph_4BiOCOCF_3$ in refluxing benzene gave 3,*N*-diphenylindole (2%) and 3-phenylindole (43%). Indole and $Ph_4BiOSO_2C_6H_4Me$-*p* gave 3-phenylindole in 36% yield. Under basic condtions (NaH), indole and $Ph_4BiOSO_2C_6H_4Me$-*p* gave 3-phenylindole (5%) and 3,3-diphenyl-3*H*-indole (61%).

Another paper from Barton's laboratory considered (in preliminary form) the O-phenylation of glycols [39]. Although O-phenylation of ordinary alcohols with $Ph_3Bi(OAc)_2$ had previously been shown to be unsatisfactory, David and Thieffry [40] reported in 1983 that glycols [$HO(CH_2)_nOH$, where n = 2-6] underwent mono-O-phenylation with this reagent. Barton and coworkers have now reinvestigated the reactions reported by David and Thieffry. They first demonstrated that groups other than hydroxyl were capable of promoting phenylation. Thus, both 2-phenoxy- and 2-methoxyethanol were readily O-phenylated in high yields. Ethanolamine gave a mixture of 2-(phenylamino)ethanol, 2-(diphenylamino)ethanol, and 2-(phenylamino)ethyl phenyl ether. Other compounds readily O-phenylated included benzoin and 2-mercaptoethanol. The latter compound yielded a mixture of bis(2-phenoxyethyl) disulfide and 2-hydroxyethyl 2-phenoxyethyl disulfide. It was also shown in competitive reactions between ethylene glycol, 2-methoxyethanol, and 2-phenoxyethanol that the effect of the OH, OMe, and OPh groups on the rates of reaction was in the order 8:4:1, respectively.

In order to learn more about the O-phenylation of glycols, the reaction between $Ph_3Bi(OAc)_2$ and 2,2-dimethylpropane-1,3-diol was studied in greater detail. This glycol was readily mono-phenylated in refluxing CH_2Cl_2 in nearly quantitative yield; further reaction to yield the di-ether was considerably slower. No reaction occured in acetone, benzene, chloroform, bromochloromethane, or tetrahydrofuran, and only a poor yield was obtained in 1,2-dichloroethane. In dichloromethane, a poor yield was obtained at room temperature, but a 91% yield was obtained when the reaction mixture was refluxed for 4 hours in the light. There was, in this case, an induction period of 2 hours and no reaction occured under reflux in the dark. It was found, however, that the addition of small amounts of copper(II) acetate had a marked effect on the reaction. Thus, in refluxing CH_2Cl_2 with the addition of 0.001 equivalent of $Cu(OAc)_2$, the induction period was eliminated and the reaction was completed in 0.25 hours.

Furthermore, the reaction occured as well in the dark as in the light, and it could be carried out in a variety of solvents (MeCl, PhH, etc.) at 60°C. This use of $Cu(OAc)_2$ as a catalyst was based on the discovery of Dodonov and coworkers [41], that $Ph_3Bi(OAc)_2$ effectively phenylated simple alcohols (EtOH, Me_2CHOH, BuOH, and $Me_2CHCH_2CH_2OH$) to the alkyl phenyl ethers in the presence of $Cu(OAc)_2$, whereas in the absence of the catalyst, only oxidation of the alcohols to the corresponding aldehyde or ketone occurred. Barton and coworkers found, however, that $Cu(OAc)_2$ was not an effective catalyst for the O-phenylation of all monhydric alcohols. Thus there was only a negligible increase in the O-phenylation of β-cholestanol when $Cu(OAc)_2$ was used. They also found that $Co(OAc)_2$, $Ni(OAc)_2$, and $FeCl_3$ were without effect on the reaction, and they suggested that a copper complex was involved in the reaction with the possible transfer of a phenyl group from bismuth to copper.

In two preceding papers [37,38] in this series, Barton and his coworkers demonstrated rather conclusively that C-phenylation of a variety of organic substrates (phenols, enols, etc.) by organobismuth(V) reagents, under basic conditions, involved the formation of a Bi-O intermediate (*e.g.*II) which on heating gave the final C-phenylated product. They considered two mechanisms for this reductive elimination, a concerted and a radical mechanism. Although the fact that only *ortho* C-phenylation occurred favored the concerted mechanism, the phenylation of some highly hindered substrates might be better explained by a radical mechanism.

In order to obtain further information on the mechanism of the reductive elimination reaction, Barton and coworkers [42] have prepared a series of triarylbismuth carbonates, both symmetrical and unsymmetrical, of the following types, Ar_3BiCO_3, where Ar was Ph, p-MeC_6H_4, p-$MeOC_6H_4$, or p-$O_2NC_6H_4$, and $Ar_2Ar'BiCO_3$ and $ArAr'_2BiCO_3$, where Ar was p-MeC_6H_4, and Ar' was Ph, p-$MeOC_6H_4$, or p-$O_2NC_6H_4$. The synthesis of these compounds involved the preparation of several triarylbismuthines, Ar_3Bi, where Ar was p-MeC_6H_4, p-$MeOC_6H_4$, or p-$O_2NC_6H_4$. The p-tolyl and p-anisyl compounds were known and were obtained by the reaction of the corresponding Grignard reagent with $BiCl_3$. The authors were enabled, however, to increase the yield of the p-anisyl compound from the previously reported 10% to 65%. The p-nitro compound could not be obtained by the Grignard reaction. A number of other reactions were then tried unsuccessfully. Finally, $(p\text{-}O_2NC_6H_4)_3Bi$ was obtained, together with $(p\text{-}O_2NC_6H_4)_2(p\text{-}MeC_6H_4)Bi$ and $(p\text{-}O_2NC_6H_4)(p\text{-}MeC_6H_4)_2Bi$ by a radical-type aryl exchange reaction:

$$[p\text{-}O_2NC_6H_4N_2]BF_4 + (p\text{-}MeC_6H_4)_3Bi \xrightarrow[\text{PhH}]{\text{Cu, DMF}} (p\text{-}O_2NC_6H_4)_3Bi\ (16\%) +$$

$$(p\text{-}O_2NC_6H_4)_2(p\text{-}MeC_6H_4)Bi\ (15\%) + (p\text{-}O_2NC_6H_4)(p\text{-}MeC_6H_4)_2Bi\ (12\%)$$

In addition to these three triarylbismuthines a number of *p,p'*-disubstituted biphenyl compounds were formed in this radical-type reaction.

Two diarylchlorobismuthines were obtained by disproportionation:

$$2Ar_3Bi + BiCl_3 \xrightarrow[0°]{Et_2O} 3Ar_2BiCl$$

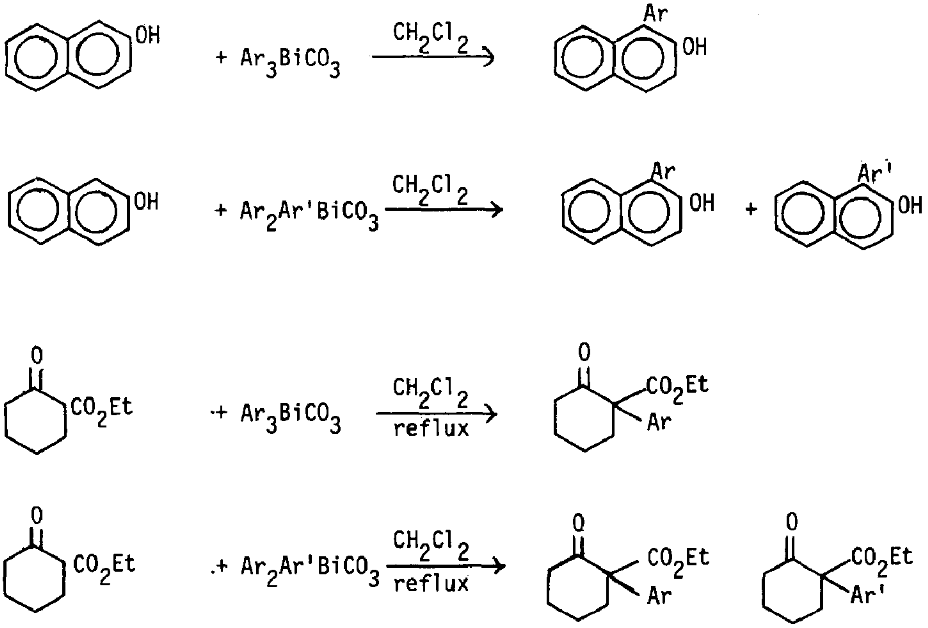
(where Ar was Ph or $p\text{-}MeC_6H_4$)

For these reactions the $BiCl_3$ was slowly added to an ether solution of the triarylbismuthine. By the reverse addition (bismuthine to $BiCl_3$) chlorodi-*p*-tolylbismuthine was obtained in a pure state:

$$(p\text{-}MeC_6H_4)_3Bi + 2\ BiCl_3 \longrightarrow 3\ p\text{-}MeC_6H_4BiCl_2$$

From these diarylchloro- and aryldichlorobismuthines and the appropriate Grignard reagent, the following unsymmetrial triarylbismuthines were prepared: $Ar_2Ar'Bi$ and $ArAr'_2Bi$ (where Ar was $p\text{-}MeC_6H_4$, and Ar' was Ph or $p\text{-}MeOC_6H_4$). Since unsymmetrical triarylbismuthines are known to undergo dismutation reactions, it was necessary to check the purity of these unsymmetrical triarylbismuthines. This was done by mass spectrometry. Since the symmetrical triarylbismuthines gave stable molecular ions, their presence could have been readily detected had they been present. The triarylbismuthines, both symmetrical and unsymmetrical, were then converted to the corresponding triarylbismuth dichlorides with sulfuryl chloride. Several of the dichlorides were unstable and were not characterized as such but converted immediately to the corresponding triarylbismuth carbonates. Most of the dichlorides, however, were stable and were characterized before being converted to the carbonates. Except for the unstable dichlorides, the new compounds were characterized by elemental analyses, PMR, and mass spectrometry.

Having obtained the above described symmetrical and unsymmetrical triarylbismuth carbonates, the authors then studied the C-phenylation of two substrates, β-naphthol and 2-carbethoxycyclohexanone. β-Napththol was treated with the bismuth compound for 24 hours at room temperature in methylene dichloride. 2-Carbethoxycyclohexanone was refluxed in methylene dichloride with the bismuth compound for 6 hours. The resulting mono C-phenylated products were isolated as pure compounds when symmetrical triarylbismuth carbonates were used, or as mixtures when unsymmetrical triarylbismuth carbonates were used:



With β-naphthol, 1-phenyl- or 1-*p*-substituted phenyl-β-naphthols were obtained. With 2-carbethoxycyclohexanone, 2-phenyl- or 2-*p*-substituted phenyl cyclohexanones were similarly produced. The yields of C-phenylated products were large (69 - 99%) in all cases. Apparently no O-phenylated products were formed. The products obtained from the symmetrical triarylbismuth carbonates were characterized unequivocally by ^{13}C NMR for the β-naphthol compounds and by ^{1}H NMR for the cyclohexanone compounds.

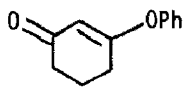
Since the yields of phenylated products obtained from either β-naphthol or 2-carbethoxycyclohexanone and symmetrical triarylbismuth carbonates did not differ significantly from each other, under the reaction conditions employed, no differences in migratory aptitudes of the phenyl group or the three substituted phenyl groups (*p*-Me, *p*-OMe, or *p*-NO_2) attached to the Bi atoms, were apparent. However, when unsymmetrical triarylbismuth carbonates were employed, marked differences in migratory aptitudes were found. Mixtures, which could not be separated, were obtained from both β-naphthol and 2-carbethoxycyclohexanone, when these compounds were treated with any of the following organobismuth(V) reagents,

$Ph_2(p\text{-}MeC_6H_4)BiCO_3$, $Ph(p\text{-}MeC_6H_4)_2BiCO_3$, $(p\text{-}MeOC_6H_4)_2(p\text{-}MeC_6H_4)BiCO_3$, and $(p\text{-}MeOC_6H_4)(p\text{-}MeC_6H_4)_2BiCO_3$. However, the ratio between the amounts of the two products obtained in each case could be determined. In the case of β-naphthol and either $Ph_2(p\text{-}MeC_6H_4)BiCO_3$ or $Ph(p\text{-}MeC_6H_4)_2BiCO_3$, the ratio was obtained by comparing glc data with that obtained from glc data of the known pure compounds. With β-naphthol and either $(p\text{-}MeOC_6H_4)_2(p\text{-}MeC_6H_4)BiCO_3$ or $(p\text{-}MeOC_6H_4)(p\text{-}MeC_6H_4)_2BiCO_3$, or with 2-carbethoxycyclohexanone and any of the above four reagents, the ratio was calculated from the integration values obtained from the PMR spectra of the mixtures. The reaction between β-naphthol and either $(p\text{-}MeC_6H_4)_2(p\text{-}O_2NC_6H_4)BiCO_3$ or $(p\text{-}MeC_6H_4)(p\text{-}O_2NC_6H_4)_2BiCO_3$ gave products in which 1-*p*-nitrophenyl-2-naphthol predominated, and it was possible to obtain this compound in a pure state by means of preparative tlc. The ratios of the amounts of the two products obtained from 2-carbethoxycyclohexanone and either $(p\text{-}MeC_6H_4)_2(p\text{-}O_2NC_6H_4)BiCO_3$ or $(p\text{-}MeC_6H_4)(p\text{-}O_2NC_6H_4)_2BiCO_3$, were again determined from the integrated PMR data. Knowing the ratios between the amounts of products obtained in each case, the relative migratory aptitudes of the four different groups were readily calculated. Thus, from β-naphthol the ratios were p-NO_2, 3.55; H, 1 ; *p*-Me, 0.45; *p*-OMe, 0.22. From 2-carbethoxycyclohexanone, the ratios were p-NO_2, 3.55; H, 1; *p*-Me,0.60; *p*-OMe, 0.25. A plot of the log of these values vs. Hammett values did not give a straight line. The authors compared their migratory values with those obtained from other laboratories in which the same substituted phenyl groups were involved in free radical reactions or with a reaction which involved a cationic mechanism (the pinacol rearrangement). They concluded that a free radical mechanism could not be ruled out, but that the results were better explained by associating migratory aptitude with the electron density at the carbon atom attached to bismuth and hence to the Bi-C bond energy. The authors further stated that ESR data, to be reported later, ruled out a free radical mechanism.

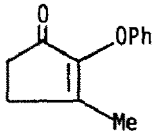
It should be noted that Barton and coworkers [43] had previously reported that β-naphthol and triphenylbismuth carbonate, in the presence of a base 1,1,3,3-tetramethylguanidine, gave a 76% yield of 1-phenyl-2-naphthol. In the present paper [42], however, a 76% yield of the same product was obtained when no base was added. In fact, in none of the phenylation reactions described in the present paper was a base present.

Having found that $Cu(OAc)_2$ was an effective catalyst for the O-phenylation of at least one glycol, *viz.* 2,2-dimethylpropane-1,3-diol, Barton and coworkers [44] studied the effect of $Cu(OAc)_2$ on the O-phenylation of phenols and enols. Phenol and $Ph_3Bi(OAc)_2$ in CH_2Cl_2 under reflux for 23 hours in an argon atmosphere gave an 86% yield of diphenyl ether. Under essentially the same reaction conditions, but with the addition of 1.2 equivalents of the base 2-*tert*-butyl-1,1,3,3-tetramethylguanidine, a 20% yield of 2-hydroxybiphenyl and a trace of diphenyl ether were obtained. When $Cu(OAc)_2$ (0.1 equivalent) was added (but without base) the reaction could be run at room temperature with almost the same yields of diphenyl ether (80% after 24 hours, 77% after 1 hour). The effect of $Cu(OAc)_2$ on the reaction in the presence of the base was surprising. A 53% yield of diphenyl ether and only a 6% yield of 2-hydroxybiphenyl were obtained. The authors then found that copper powder was an even more effective catalyst than $Cu(OAc)_2$. Thus, a 90% yield of diphenyl ether was obtained from phenol in CH_2Cl_2 in an argon atmosphere at room temperature in the presence of 0.1 equivalent of Cu powder after 4 hours. The authors then used this catalyst to effect O-phenylation of a variety of phenol derivatives. In most cases the yields were excellent (80-90% for most phenols). There was a marked steric effect. Thus, 2,4-di-*tert*-butylphenol gave only a 26% yield of the corresponding ether, and 2,4,6-tri-*tert*-butylphenol did not react. Both 4-carbomethoxyphenol and 4-nitrophenol gave large yields (90 and 97%, respectively) of the corresponding ethers. In addition to $Ph_3Bi(OAc)_2$, the authors tried $Ph_4BiOCOCF_3$ as a phenylating agent (in benzene under argon for 24 hours at room temperature). With 3,5-di-*tert*-butylphenol the yields of ether increased from 27 to 85%, and with β-naphthol from 50 to 80%, by the addition of $Cu(OAc)_2$.

The authors also studied the phenylation of several enols with three organobismuth(V) reagents ($Ph_3Bi(OAc)_2$, $Ph_3Bi(OCOCF_3)_2$ and $Ph_4BiOCOCF_3$). The solvents employed were CH_2Cl_2 (at room temperature) and benzene (at 50°C) and the catalysts were either Cu or $Cu(OAc)_2$. 2-Carbethoxycyclohexanone gave the 2-phenyl derivative in 27% yield (after 20 hours) without a catalyst and a 40% yield with the addition of 0.1 equivalent of $Cu(OAc)_2$ (after 40 hours). Dimedone and 2-hydroxy-3-methylcyclopent-2-ene-1-one gave increased yields of the O-phenylated products (VIII and IX) when Cu powder was used as a catalyst. The authors mentioned that thiols were oxidized to disulfides with $Ph_3Bi(OAc)_2$, and the yields were unaffected by the addition of Cu powder.



VIII



IX

Russian workers [45] had previously shown that primary and secondary aliphatic amines, as well as aniline, underwent N-phenylation with $Ph_3Bi(OAc)_2$ in the presence of $Cu(OAc)_2$, but that with diphenylamine, phenylation occured only to the extent of 3% under forcing conditions (50°C for 74 hours). No phenylation of the amines occurred in the absence of the copper compound. Barton and coworkers [39] had previously noted that phenylation of ethanolamine occurred preferentially on the nitrogen atom. They also noted [44] that copper powder was a superior catalyst to $Cu(OAc)_2$ for the O-phenylation of phenols. Accordingly, Barton and coworkers [46] tried copper powder as a catalyst for the N-phenylation of simple amines. This proved to be a very effective reaction. Thus, aniline and a variety of substituted anilines, were phenylated in almost quantitative yields by the use of $Ph_3Bi(OAc)_2$ in the presence of 0.1 equivalent of Cu powder. The substituted anilines, $ArNH_2$, where Ar = $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $2\text{-}O_2NC_6H_4$, $4\text{-}O_2NC_6H_4$, or $2,4,6\text{-}Me_3C_6H_2$ were used; the reaction mixtures were stirred at room temperature for periods that varied from 0.25 to 24 hours. The yields of N-monophenylated products varied from 74 to 97%. It was also possible to obtain diphenylation by increasing the reaction time. Thus, aniline gave a 23% yield of triphenylamine when the reaction was carried out for 48 hours, while *p*-anisidine gave a mixture of *N*-phenyl-*p*-anisidine (28%) and *N,N*-diphenyl-*p*-anisidine (68%) when the reaction was run for 24 hours with 1.1 equivalents of Cu powder and then for a second 24 hour period with the further addition of 1.1 equivalents of Cu powder. The yield of *N*-(4-nitrophenyl)aniline was only 15% when the reaction was carried out for 2 hours using 1.02 equivalents of Cu powder, but increased to 90% by increasing the reaction time to 16 hours and increasing the Cu powder to 2.2 equivalents.

In addition to $Ph_3Bi(OAc)_2$, the authors tried various other organobismuth(V) reagents. Thus, $Ph_3Bi(OCOCF_3)_2$ was a more effective phenylating agent, giving a 99% yield of Ph_2NH from $PhNH_2$ after stirring for only 0.5 hours, while $Ph_3Bi(O_3SC_6H_4Me\text{-}p)_2$ was less effective (38% yield) and Ph_3BiCO_3 gave no diphenylamine (after 24 hours stirring). Also effective was $Ph_4BiOCOCF_3$, but $Ph_4BiO_3SC_6H_4Me\text{-}p$ was less effective and Ph_5Bi gave no diphenylamine. The reaction of $(4\text{-}MeC_6H_4)_3Bi(OAc)_2$ and aniline gave a 98% yield of $4\text{-}MeC_6H_4NHPh$ after stirring for 11 hours.

Aliphatic amines were also phenylated with organobismuth(V) reagents with the addition of Cu powder. Thus, butylamine gave a mixture of *N*-butylaniline (60%) and butyldiphenylamine (20%) after 4 hours stirring and a 70% yield of butyldiphenylamine by increasing the amount of Cu powder from 1.1 to 2.2 equivalents. Cyclohexylamine gave a 90% yield of *N*-cyclohexylaniline. Morpholine gave a 32% yield of the N-phenyl derivative (when $Ph_3Bi(OCOCF_3)_2$ was used as the phenylating agent). Ethyl 2-amino-3-phenylpropionate gave a mixture of the *N*-phenyl (70%) and *N,N*-diphenyl derivatives (18%). *tert*-Butylamine, however, did not react. Diethylamine gave a 32% yield of *N,N*-diethylaniline after 24 hours. In contradiction to this latter result and also the result with morpholine, the authors stated that aliphatic and heterocyclic secondary amines were not phenylated by $Ph_3Bi(OAc)_2$ or $Ph_3Bi(OCOCF_3)_2$ in the presence of metallic copper. Benzophenone hydrazone gave a 90% yield of the *N*-monophenylated product after stirring for 24 hours, but imines, enamines, oximes, amides, 1,1,3,3-tetramethylguanidine, and semicarbazones did not react with $Ph_3Bi(OAc)_2$ and Cu powder.

In a paper devoted to the chemistry of biradicals produced by the photochemical decarbonylation of α-perphenylated cyclohexanones, Barton and coworkers [47] have described the preparation of 2,2,6,6-tetraphenylcyclohexanone from cyclohexanone and Ph_3BiCO_3 (93%) or $Ph_3Bi(O_3SC_6H_4Me\text{-}p)_2$ (80%), and of 2,2,5,5-tetraphenylcyclopentanone from 2,2-diphenylcyclopentanone and $Ph_3Bi(OCOCF_3)_2$ (74%). The new compounds were characterized by IR, NMR, and mass spectroscopy and by elemental analyses.

Three previous papers [39,44,46] in the present survey have described the catalytic effect of copper or copper salts on the phenylation of glycols, phenols, enols, and amines by organobismuth(V) reagents. The catalytic effect had been originally described by Dodonov and coworkers [45] who reported that primary and secondary alcohols were phenylated to the corresponding ethers with $Ph_3Bi(OAc)_2$ in the presence of $Cu(OAc)_2$, but were oxidized to aldehydes or ketones by $Ph_3Bi(OAc)_2$ in the absence of $Cu(OAc)_2$. Dodonov and coworkers [48] have also reported that the compounds $Ph_3Bi(O_2CR)_2$ (where R was Me, Ph, or $C_{11}H_{23}$) decomposed when heated in organic solvents to yield the esters RCO_2Ph in approximately quantitative yields, and that this reaction was markedly catalysed by copper salts. A mechanism for this reaction was proposed by the Russian authors. This work has now been expanded and somewhat modified by further investigations by the Russian workers [49]. They found that the nature of the solvent and the valency of the copper had a significant effect on the decomposition of $Ph_3Bi(OAc)_2$. When $Ph_3Bi(OAc)_2$ was heated in toluene at 100° C or was stirred in toluene at 20° in the presence of 0.50 molar equivalent of CuCl, PhOAc was the principal product (86% and 65%, respectively) together with benzene (8 and 20%, respectively) and (in the latter case only) small amounts of biphenyl. By contrast, when THF was the solvent, again in the presence of 0.50 molar equivalent of CuCl at 20° C, only 2% PhOAc was formed and the principal product was PhCl (32%). Chlorobenzene was also the principal product when $CuCl_2$ was used as the catalyst at 20° C in either toluene or THF (0.42 and 1.19 moles of PhCl per mole of $Ph_3Bi(OAc)_2$ employed). The authors stated that the Bi(III) compounds formed in the above reactions were isolated as Ph_3Bi and acetate derivatives, but the yields of Bi(III) compounds were not stated.

The authors [49] also reported the O-phenylation of primary and secondary alcohols by means of $Ph_3Bi(OAc)_2$ and $CuCl_2$:

$$Ph_3Bi(OAc)_2 + ROH \xrightarrow{CuCl_2} PhOR + AcOH + Ph_2BiOAc$$

(where R = Et, Bu, Me_2CH, or $Me_2CHCH_2CH_2$)

In addition to the ether and acetic acid, small amounts of benzene and chlorobenzene were found in each case, and the yields of ethers varied from 62 to 79%. The phenylation of isopropyl alcohol was also carried out with catalysts other than $CuCl_2$ (yield with $CuCl_2$, 77%) with the following results: CuCl, 87%; metallic Cu, 92%; $Cu(OAc)_2$ (0.01 molar equivalent), 86%. When the amount of $Cu(OAc)_2$ was increased from 0.01 molar equivalent to 1.0 molar equivalent the yield of $PhOCHMe_2$ increased from 86% to 97%. *tert*-Butyl alcohol was phenylated only to a small extent (9%) even when heated to 50° for 40 hours in the presence of CuCl. In addition to the above alcohols, phenol and $Ph_3Bi(OAc)_2$ in THF and with the addition of $Cu(OAc)_2$ gave 39% Ph_2O. Phenol itself was formed from water, $Ph_3Bi(OAc)_2$, and $Cu(OAc)_2$ (1.03 molar equivalents per mole of $Ph_3Bi(OAc)_2$).

The copper-catalyzed reaction of $Ph_3Bi(OAc)_2$ and amines, both primary and secondary, was also studied. In the case of primary amines, a large excess of the amine was used in order to obtain only the secondary amine as the product. With the following amines, and with $Cu(OAc)_2$ as the catalyst, the following yields of alkylanilines or diarylamines were obtained: Me_2CHNH_2, 82%; $Me_2CHCH_2NH_2$, 69%; Me_3CNH_2, 79%; $PhNH_2$, 82%. The secondary amines Et_2NH and Bu_2NH gave similar yields of dialkylanilines (65% and 85%, respectively), but Ph_2NH gave only a 3% yield of Ph_3N even after heating for 74 hours at 50° C. In this case large amounts of benzene and PhOAc were formed. These two substances were also the only products formed when Et_3N, $CO(NH_2)_2$ or $MeCONH_2$ was used as the substrate.

The authors now proposed a radical mechanism to explain their results:

$$Ph_3Bi(OAc)_2 + CuCl \longrightarrow Ph_3\dot{B}iOAc + CuClOAc$$

$$Ph_3\dot{B}iOAc \longrightarrow Ph_2BiOAc + Ph^{\cdot}$$

$$Ph^{\cdot} + CuClOAc + ROH \longrightarrow PhOR + CuCl + AcOH$$

They further stated that with either copper metal or Cu(II) compounds, catalytic amounts of Cu(I) compounds were first formed by reaction of the copper species and the organic or organometallic compound. They further stated that the presence of phenyl radicals in the above reactions was confirmed by the spin label technique in reactions of $Cu(OAc)_2$ or $CuCl_2$ (in toluene or THF) and Me_2CHOH in the presence of Me_3CNO or $2,4,6-Br_3C_6H_2NO$. It should be noted that Barton and coworkers [37,42] have claimed that phenylation reactions between organbismuth(V) reagents and organic substrates did not involve free radicals. However, the mechanisms suggested by Barton and coworkers were in reactions not employing copper catalysts, and they referred only briefly to the mechanism of copper catalysis in these reactions.

Dodonov and coworkers now compared the reactivity of alcohols in the phenylation reaction by reacting equimolar amounts of two different alcohols with $Ph_3Bi(OAc)_2$ in the presence of 0.1 molar equivalent of $CuCl_2$. The reactivity of the alcohols was in the order $MeOH > BuOH > Me_2CHOH >$ cyclo-$C_6H_{11}OH$. When Me_2CHOH was compared with H_2O, PhOH, or Me_2CHNH_2, the sole products of these reactions were PhOH, Ph_2O, or $Me_2CHNHPh$, respectively. In the reaction of Me_2CHOH with $Ph_3Bi(OAc)_2$ with $CuCl_2$ as the catalyst, the authors noted that the yield of Me_2CHOPh decreased markedly while the yield of PhCl correspondingly increased as increasing amounts of $CuCl_2$ were used in the reaction. By contrast, increasing the amount of $Cu(OAc)_2$ had very little effect on the yields of phenylation products from alcohols or amines. They then carried out reactions in which Me_2CHOH, $Ph_3Bi(OAc)_2$ and either $CaCl_2$ or $CaBr_2$ were stirred together in the presence of $Cu(OAc)_2$. Chlorobenzene or bromobenzene, with only traces of Me_2CHOPh, were formed. Similarly, Et_2NH, $Ph_3Bi(OAc)_2$, $Et_2NH{\cdot}HCl$, and $Cu(OAc)_2$ gave PhCl as the sole phenylated product. When any of these reactions were attempted without the addition of $Cu(OAc)_2$, no reaction occurred.

In addition to organobismuth(V) reagents the Russian workers [50] have found that alcohols were phenylated to the corresponding alkyl phenyl ethers by Ph_3Bi in the presence of $Cu(OAc)_2$. The reaction was slow and large amounts of benzene and acetic acid were also formed in the reaction. Thus, when Me_2CHOH was allowed to react with Ph_3Bi and $Cu(OAc)_2$ (1 and 2 molar equivalents, respectively) in an evacuated sealed ampoule for several days, 2.29, 0.52, and 0.46 molar equivalents of PhH, Me_2CHOPh, and AcOH were formed, respectively. If the same reaction was carried out in the air, the yields of these three products were 0.28, 1.96, and 0.16 molar equivalents, respectively. Similar results to the above with the primary alcohols, EtOH, BuOH, and $Me_2CHCH_2CH_2OH$, were observed. The reaction of Me_2CHOH with Ph_3Bi and $Cu(OAc)_2$ in a sealed ampoule was also carried out at 50° C for 6 hours with similar results.

It has been shown by previous authors that one hydroxyl group of a glycol could be phenylated by the use of triphenylbismuth diacetate, both in the presence and in the absence of a copper catalyst. Brunner and coworkers [51] have now investigated the stereochemistry of this reaction. They chose for this purpose the mono-phenylation of *cis*-cyclohexane-1,2-diol and of *meso*-butane-2,3-diol. The plane of symmetry of these *meso* compounds, however, is destroyed when on hydroxyl group is phenylated. In the absence of an optically active substance, the product would be in each case a racemic mixture. Accordingly, the authors carried out the reaction in the presence of a number of chiral pyridine oxazolines. Copper(II) acetate was also used as a catalyst. In the presence of the chiral substance the overall yield of the reaction was reduced from 87% to 35-45%. The reactions were carried out in CH_2Cl_2 solution at room temperature for 6 hours, and the products were purified by column chromatography and vacuum distillation. In order to determine the enantiomeric excess formed in the reaction, the phenoxy compounds were converted to the corresponding urethanes with methyl isocyanate, and the enantiomeric excess was determined by gas chromatography. With *cis*-cyclohexane-1,2-diol, 8 different chiral pyridine oxazolines were used. The optical induction with these optical catalysts varied between 13.0 and 30.2%. With *meso*-butane-2,3-diol only one of the pyridine oxazolines was used, and the optical induction was 17%.

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