Arylation Reactions with Organobismuth Reagents

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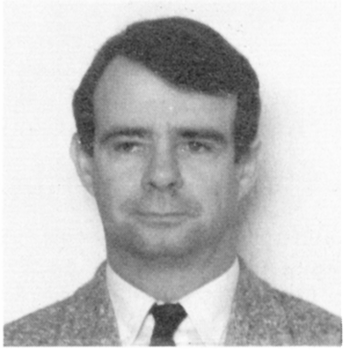
Contents

I. Introduction

The chemistry of organobismuth started in 1850 with the synthesis of triethylbismuthine by Löwig and Schweizer.[1] As this compound is spontaneously flammable in air, it is only with the synthesis of the air-stable triphenylbismuthine by Michaëlis and Polis in 1887[2] that the development of organobismuth chemistry began. A large number of derivatives of triphenylbismuthine have since been prepared. The first tetraaryl- and pentaarylbismuth compounds were only synthesized in 1952 by Wittig and Clauss.[3]



Jean-Pierre Finet was born in 1949. He received the pharmacist degree from the University of Tours and the Doctorat d'État ès Sciences from the University of Orléans (under Prof. Buzas). After a postdoctoral fellowship at the Research Institute for Medicine and Chemistry, Cambridge, MA (under Dr. R. H. Hesse and M. M. Pechet), he joined the C.N.R.S. He worked in Prof. Barton's group at the Institut de Chimie des Substances Naturelles du C.N.R.S. in Gif sur Yvette before moving to Marseille in 1987. He works now on the chemistry of group IV and V aromatic derivatives and their application to the synthesis of natural products and stable free radicals.

With an electronic configuration [Xe $4p^{14}5d^{10}6s^{2}6p^{3}$], bismuth has all its lower energy orbitals filled, leaving five electrons in nonequivalent outer orbitals. The participation of the two s electrons leads to two possible valencies: Bi(III) and Bi(V). Two series of organic compounds are known: the trivalent and the pentavalent derivatives. The possibility of reduction of Bi(V) to Bi(III) led to the conception of an oxidation reaction.[4] Moreover, the bismuth–carbon bond is one of the weakest among element–carbon bonds: the mean bond dissociation energy of triphenylbismuthine (Ph_3Bi) is 193.9 ± 10.8 kJ/mol compared to 321 ± 21 kJ/mol for triphenylphosphine (Ph_3P) and 373.7 ± 4.2 kJ/mol for triphenylamine (Ph_3N).[5] A unique reactivity was hence expected and demonstrated by the arylation reactions of a great array of substrates.

A number of reviews have been written on the various aspects of the chemistry of organobismuth compounds. Reviews devoted solely to the chemistry of organobismuth compounds are by Gilman and Yale,[6] Lisowski,[7] Harrison,[8] and Freedman and Doak.[9] Freedman and Doak have also reviewed organobismuth chemistry on an annual basis since 1967 in *Organometallic Chemistry Reviews*, later incorporated into the *Journal of Organometallic Chemistry*. A compilation of organobismuth derivatives was made by Wieber in the *Gmelin Handbuch* series.[10] The more recent developments in the application of organobismuth compounds have been partly reviewed by Barton et al.[11,12]

The present review focuses on the arylation reactions with trivalent and pentavalent organobismuth com-

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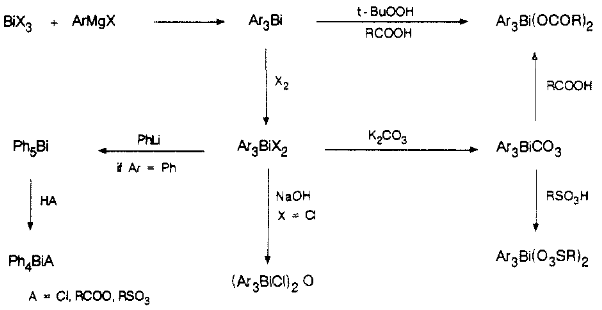
SCHEME 1. Synthesis of Organobismuth Compounds



pounds, most of which have been discovered in the past 10 years. A brief review of the oxidation reactions with pentavalent organobismuth is also warranted as oxidation sometimes competes with arylation reactions.

II. Synthesis of Organobismuth Reagents

The arylation reactions have been performed with four types of organobismuth reagents. Two of them are derived from trivalent bismuth: the diaryl- and the triarylbismuthine series. The other two derive from pentavalent bismuth: the tetraaryl- and the pentaarylbismuth series. The synthesis of these compounds has been extensively reviewed.[9,10] Therefore only a brief account of the best synthetically useful methods will be given, with a special emphasis on the more recently described compounds (Scheme 1).

A. Synthesis of Bismuth(III) Derivatives

The most general and usually high-yielding method for the synthesis of triarylbismuthines is the reaction of Grignard reagents with bismuth trihalide. Thus reaction of phenylmagnesium bromide with bismuth trichloride affords triphenylbismuthine in 84% yield.[13,14] Most of the useful triarylbismuthines are prepared in this way.[10] However, this method cannot be applied to the synthesis of (nitrophenyl)bismuthine derivatives. Tris(*m*-nitrophenyl)bismuthine was obtained from the product of nitration of the corresponding pentavalent triphenylbismuth dinitrate.[15] Tris(*p*-nitrophenyl)bismuthine is prepared by reaction of bis(*p*-nitrophenyl)iodonium chloride with bismuth trichloride[16] or by a radical-type exchange reaction between tri-*p*-tolylbismuthine and *p*-nitrobenzenediazonium tetrafluoroborate in the presence of metallic copper in dimethylformamide.[17] The trivalent diarylbismuthine compounds are generally made by disproportionation reaction between triarylbismuthine and bismuth trihalide[18-21] or by reaction of triarylbismuthine with the appropriate carboxylic or sulfonic acid.[22,23]

B. Synthesis of Bismuth(V) Derivatives

Although pentaphenylbismuth and tetraphenylbismuthonium derivatives were isolated for the first time by Wittig and Clauss,[3] pentavalent triarylbismuth compounds have been known since the work of Michaëlis and Polis.[2] Triarylbismuthine compounds are oxidized to their pentavalent derivatives by action of chlorine, bromine, and sulfuryl chloride as well as by lead tetraacetate, benzoyl peroxide, benzoyl nitrate, and *N*-halosuccinimide.[9,24] Treatment of triarylbismuth dihalides with sodium hydroxide leads to μ-oxobis(halotriarylbismuth),[25] whereas treatment with potassium carbonate leads to triarylbismuth carbonates.[17,24] The exact nature of these compounds has still not been established as no precise structural data are available. Triarylbismuth disulfonates and diacylates are prepared by addition of the appropriate sulfonic or carboxylic acid to triarylbismuth carbonates.[26,27] High yields of the diacylates can also be obtained by oxidation of triarylbismuthines by *tert*-butylhydroperoxide in the presence of the appropriate carboxylic acid.[28] Addition of phenyllithium to a solution of triphenylbismuth dichloride yields pentaphenylbismuth,[3,29] the structure of which was determined recently.[30] Pentaphenylbismuth reacts with various mineral and organic acids to give tetraphenylbismuthonium derivatives.[9,10,25,31,32]

TABLE 1

metal	reaction conditions	products	ref
Li	ether	C_6H_5Li (20%) + Bi	33
Na	NH_3	$C_6H_5Na + C_6H_6$ (90%) + Bi	34
K	THF	$Ph_2BiK + PhK$	35
Sb	300 °C	Ph_3Sb (89%)	36
Hg	250 °C	Ph_2Hg (24%) + Bi(amalgam)	37-39

TABLE 2

reactant	products	ref
$AlCl_3$	$PhAlCl_2 + C_6H_6 + BiCl_3$	41
$AsCl_3$	$Ph_2AsCl + PhAsCl_2 + Ph_2BiCl$	42, 43
$HgCl_2$	$Ph_2Hg + PhHgCl$	39
$HgCl_2, H_2O$	$PhHgCl + BiOCl + C_6H_6$	44
$Hg(O_2SAr)_2$	$PhHgO_2SAr + Bi(O_2SAr)_3$	45
PCl_3	$Ph_2PCl + PhPCl_2 + Ph_2BiCl$	42, 43
$SbCl_3$	$Ph_3SbCl_2 + Ph_2BiCl$	42, 43
$SbCl_3$	Ph_2SbCl	39
$SnCl_4$	$Ph_2SnCl_2 + BiCl_3$	39, 43
$TlCl_3$	$Ph_2TlCl + Ph_2BiCl + BiCl_3$	39, 42, 43, 46
$AgNO_3$	$(PhAg)_2, AgNO_3$	47

III. Arylation with Trivalent Organobismuth

Arylation reactions by trivalent bismuth compounds have a relatively limited scope although they have been known for many years. Two major types of arylation take place: (a) with metals, metalloids, and their derivatives; (b) by induced homolytic decomposition.

A. With Metals

The bismuth atom in triphenylbismuthine can be displaced by other metals (Table 1).

The exchange between mercury and bismuth acts reversibly. Indeed diphenylmercury and bismuth metal yield triphenylbismuthine (41%) under similar conditions.[37] Transmetalation occurred also between tris(pentafluorophenyl)bismuthine and a variety of metals and metalloids (As, Hg, In, S, Sn).[40]

B. With Metal Salts

Triarylbismuthine reacts with some metallic and metalloid halides to give either bismuth–carbon bond cleavage or arylation. Such an example is the disproportionation between triarylbismuthine and bismuth trihalide.[18-21] Other known examples are given in Table 2.

The reaction of triphenylbismuthine with antimony trichloride gives either a pentavalent triphenylantimony dihalide[42] or a trivalent diphenylantimony halide[39] when the reaction is performed in chloroform solution under a carbon dioxide atmosphere. Transmetalation also occurs between diphenylbismuthine chloride and mercury(II) chloride.[48]

$$Ph_2BiCl + HgCl_2 + H_2O \rightarrow PhHgCl + BiOCl + PhH + HCl$$

Diphenylmercury was not formed in this case. Many other inorganic halides cleave the bismuth–carbon bond but are not phenylated during the reaction; for example[39]

$$Ph_3Bi + CuCl_2 \rightarrow PhCl + Ph_2BiCl + BiCl_3 + Ph\text{-}Ph$$

C. With Metal Alkyls

n-Butyllithium and *n*-butylsodium react with triarylbismuthines with metal–metal exchange.

$$Ar_3Bi + 3n\text{-}BuM \rightarrow 3ArM + n\text{-}Bu_3Bi \quad (M = Li, Na)$$

This exchange is favored by electron-attracting substituents on the triarylbismuthine.[49] Steric effects present a significant influence as tris(*o*-chlorophenyl)bismuthine is not cleaved, whereas tris(*o*-ethoxyphenyl)bismuthine is cleaved.[50] Metal–metal exchange occurs also with aryllithium. *p*-Tolyllithium was reported to react slowly with triphenylbismuthine via an ate complex.[51]

$$(C_6H_5)_3Bi + p\text{-}CH_3C_6H_4Li \rightleftharpoons p\text{-}CH_3C_6H_4Bi(C_6H_5)_3Li \rightleftharpoons p\text{-}CH_3C_6H_4Bi(C_6H_5)_2 + C_6H_5Li$$

D. With Metal Hydrides

A partial reaction takes place when triphenylbismuthine is treated with triethyltin hydride to afford phenyltriethyltin.[52]

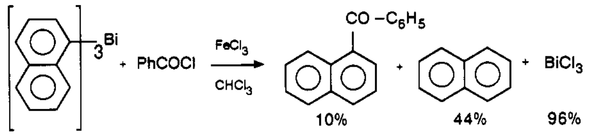
$$Ph_3Bi + Et_3SnH \rightarrow Et_3SnPh + H_2 + Bi$$

E. With Acid Chlorides and Miscellaneous Compounds

Low yields of ketones are obtained through interaction of triphenylbismuthine with acyl halides.[42]

$$Ph_3Bi + CH_3COCl \rightarrow PhCOCH_3 + Ph_2BiCl$$

In the case of tris(α-naphthyl)bismuthine, a modest yield of α-naphthyl phenyl ketone was formed only upon addition of aluminum chloride or iron(III) chloride.[53]



Triarylbismuthine derivatives react with selenium dioxide in benzene–ethanol solution to give arylseleninic acids in high yields,[54] although no reaction took place in benzene alone.[55]

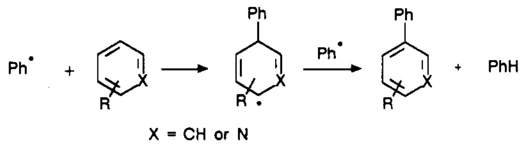
$$2Ar_3Bi + 9SeO_2 + 3H_2O \rightarrow 6ArSeO_2H + Bi_2(SeO_3)_3$$

By contrast, triarylbismuthine derivatives react with sulfur dioxide to give a mixture of arylbismuthine arenesulfinates.[56]

$$Ar_3Bi + SO_2 \rightarrow Ar_{3-n}Bi(O_2SAr)_n$$

F. Induced Homolytic Decomposition

Homolytic cleavage of the carbon–bismuth bond occurs upon ultraviolet light irradiation[57–60] or γ-irradiation from a cobalt source.[61,62] Metallic bismuth is formed together with a range of products derived from the reaction of the phenyl radical with the solvent: 2-, 3-, and 4-phenylpyridines in pyridine, and 2-, 3-, and 4-methyl- or *tert*-butylbiphenyl in toluene or *tert*-butylbenzene.



The aromatic solvent is phenylated in 45–55%. The formation of free phenyl radicals was proved by spin-trapping and ESR studies.[59,60]

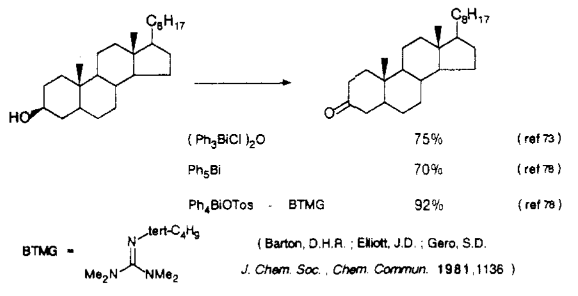
In the γ-radiation-induced decomposition, phenylcyclohexadiene, hydrogen, and a bismuth-containing compound were also isolated.[61,62] When the irradiation was performed in chloroform, triphenylbismuth dichloride was formed by radiolysis of the solvent with liberation of chlorine radicals.

IV. Oxidation Reactions with Pentavalent Organobismuth

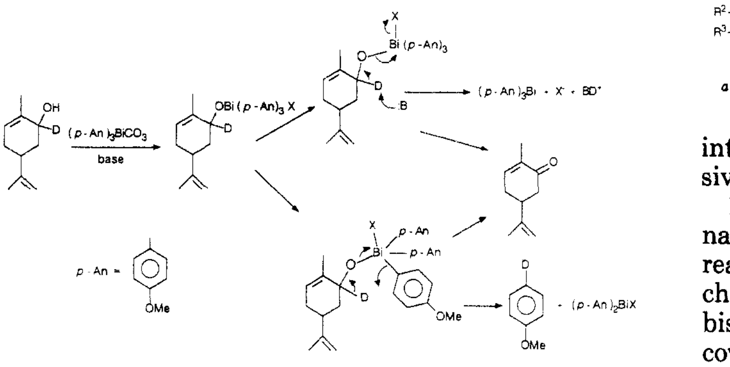
Although the oxidizing properties of pentavalent organobismuth compounds are not the topic of this review, they deserve a brief survey as the outcome of many arylation reactions is very dependent upon the nature of the organobismuth compound that is used and the reaction conditions, leading either to arylation or to oxidation. The oxidation reactions with triphenylbismuth carbonate have already been partly reviewed.[63,64]

Arylbismuth reagents of the type Ar_3BiX_2 are mild and efficient oxidizing agents toward a wide range of primary, secondary, allylic, and benzylic alcohols. The first reported oxidation was noted during attempts of recrystallization of triphenylbismuth dihydroxide in various hydroxylic solvents.[65] More recently, triphenylbismuth carbonate was shown to oxidize efficiently alcohols under neutral conditions.[66–68] A great selectivity was observed in the presence of other sensitive functions such as indole, pyrrole, selenides, and thiols, although thiols are readily oxidized by triphenylbismuth carbonate to disulfides. Oxidation of highly functionalized natural products was performed in high yields.[69–71] Complex oxidations of primary and secondary alcohols were observed in the reactions with triphenylbismuth diacetate under neutral conditions with formation of *O*-phenyl ethers, esters, and the oxidized products (aldehyde or ketone).[28,72] Oxidations with reagents of the Ar_3BiX_2 type are best performed under basic conditions. The use of various derivatives such as μ-oxobis(chlorotriphenylbismuth),[68,73] triphenylbismuth diacylates,[66,68] triphenylbismuth dibromide,[66,68] triphenylbismuth dichloride,[66,68,74] and triphenylbismuth dinitrate[66,68] under basic conditions as oxidants has been reported. It must be noted that the exact nature of the oxidant is not known. For example, oxidations with μ-oxobis(chlorotriphenylbismuth) are performed in the presence of potassium

SCHEME 2. Oxidation of 3β-Cholestanol by Pentavalent Organobismuth

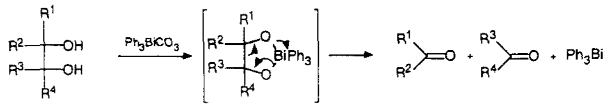


SCHEME 3. Mechanisms of Alcohol Oxidation: Oxidation of Carveol[a]



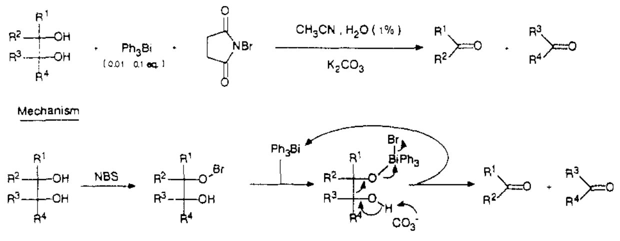
[a] References 66 and 67.

SCHEME 4. Stoichiometric 1,2-Glycol Cleavage[a]



[a] References 68 and 73.

SCHEME 5. Catalytic 1,2-Glycol Cleavage[a]



[a] References 82 and 83.

carbonate, and the effective oxidant could be either a polymeric or a cyclic carbonate derivative.

Aromatic thiolates and sodium organodithiocarbamates are oxidized by triphenylbismuth dichloride into the corresponding diaryl disulfides or tetraorganodithiuram disulfides in high yields.[75,76] The monoarylthionocarbamate derived from a protected carbohydrate was oxidized by triphenylbismuth carbonate to the disulfide although the thiocarbonyl groups of xanthates, *N,N*-dialkylthionocarbamates, and di-*tert*-butyl thioketone were unaffected.[67,68] Aliphatic and aromatic amines, indole, and enamines are not affected by triphenylbismuth carbonate. However, hydrazines are oxidized to the corresponding azines, and benzophenone hydrazone is quantitatively oxidized to diphenyldiazomethane. The oxime of 5-α-cholestan-3-one was cleaved by triphenylbismuth carbonate to the parent ketone.[66,68] Bis(*tert*-butylperoxy)triphenylbismuth oxidizes alcohols and aromatic hydrocarbons to the corresponding carbonyl. Thus benzaldehyde was obtained from either toluene or benzyl alcohol.[77]

Arylbismuth reagents of the type Ar_4BiX oxidize alcohols to the corresponding carbonyl compounds under basic conditions.[78] Aryl thiols react with tetraphenylbismuthonium trifluoroacetate ($Ph_4BiOCOCF_3$) to give only minor amounts of the disulfides, the major products being the unsymmetrical diaryl sulfides (see section V.D.). Similarly, pentaphenylbismuth (Ph_5Bi) acts as an oxidant for alcohols and as a phenylating agent for thiols[79] (Scheme 2).

The mechanism of these oxidations involves pentavalent covalent alkoxybismuth intermediates, which are prone to reductive elimination. In the reaction of D-deuteriocarveol with tri-*p*-anisylbismuth carbonate, two pathways were detected by the formation of *p*-deuterioanisole and of tri-*p*-anisylbismuthine[68] (Scheme 3). Mostly postulated, the existence of bismuth(V) intermediates with a covalent Bi–O bond was conclusively shown by a series of ^1H NMR experiments.[78]

1,2-Glycols are cleaved by triphenylbismuth carbonate and μ-oxobis(chlorotriphenylbismuth).[68,73,80] The reaction takes place at room temperature in methylene chloride under neutral conditions. In the triphenylbismuth carbonate–glycol cleavage reaction, the recovery of triphenylbismuthine is quantitative. Pinacol was cleaved by triphenylbismuth diacetate [$Ph_3Bi(OAc)_2$] under neutral and basic conditions, with a nonquantitative yield of triphenylbismuthine.[28] 1,2-Glycol stannylenes are cleaved by triphenylbismuth diacetate.[81] The oxidative cleavage of 1,2-glycols can be carried out catalytically, with *N*-bromosuccinimide as oxidant, in the presence of potassium carbonate and a trace of water in acetonitrile.[82] The mechanism of the triphenylbismuth carbonate stoichiometric reaction involves a cyclic pentavalent bismuth intermediate, whereas the catalytic reaction was explained by the formation of a glycol hypobromite which oxidizes triphenylbismuthine to a pentavalent bismuth species[83] (Schemes 4 and 5). A very mild oxidizing ability was observed with methyl diarylbismuthinates, as only activated 1,2-diaryl 1,2-glycols were affected.[84]

Some phenolic compounds have been oxidized by triphenylbismuth carbonate and triphenylbismuth dichloride under basic conditions. 2,6-Dimethylphenol is oxidized by triphenylbismuth carbonate under neutral or basic conditions to the 3,3′,5,5′-tetramethyldiphenoquinone.[79] 2,6-Di-*tert*-butylphenol reacts with triphenylbismuth dichloride or carbonate in the presence of a base favoring electron transfer such as *N*-*tert*-butyl-*N′,N′,N″,N″*-tetramethylguanidine (BTMG) to give the corresponding diphenoquinone.[85,86] Under similar conditions, the reaction of 2,6-di-*tert*-butyl-4-methylphenol with triphenylbismuth dichloride and BTMG affords the 4-methoxymethyl derivative when the reaction is performed in the presence of methanol.

V. Arylation with Pentavalent Organobismuth

Arylation by pentavalent bismuth compounds has been known for a number of years. However, it is only recently that its interest and importance as a mild and selective method for the arylation of a wide variety of substrates have been recognized. The arylation of inorganic substrates by pentavalent organobismuth or by trivalent organobismuthine involving an unstable pentavalent intermediate has been known since the 1920s. However, the development of this method for the arylation of organic substrates is more recent, and most of the results have been described in the past 10 years.

A. Arylation of Inorganic Substrates

The reaction of triarylbismuthine with halogens such as chlorine or bromine leads to the pentavalent derivatives dihalotriphenylbismuth, which are stable.[20,87-89] Under specific conditions, the decomposition of these compounds leads to carbon-bismuth bond cleavage with formation of the aryl halides, therefore formally realizing the arylation of the halogen. Reaction of triarylbismuthine with iodine leads directly to aryl iodides, the pentavalent intermediates being too unstable to be isolated.[87,90]

A similar type of carbon-bismuth bond cleavage occurs in the reaction of halogen halides and halogen cyanides with formation of Ar_2BiX and ArY compounds, where X is the more electronegative component of the halogen derivative XY.[20,87,90,91]

$$Ph_3Bi + ICl \rightarrow PhI + Ph_2BiCl$$

$$Ph_3Bi + BrCN \rightarrow PhBr + Ph_2BiCN$$

Triphenylbismuth dichloride reacts with moist mercury(II) chloride to give the unsymmetrical arylmercury chloride without formation of diphenylmercury.[48]

$$Ph_3BiCl_2 + HgCl_2 + H_2O \rightarrow PhHgCl + BiOCl + 2PhH + Cl_2$$

Reaction of triphenylbismuth dichloride with sodium azide and sodium cyanide affords triphenylbismuth diazide and dicyanide. Thermal decomposition of these compounds leads to phenyl azide and benzonitrile, respectively.[92]

$$Ph_3Bi(N_3)_2 \rightarrow PhN_3 + Ph_2BiN_3 + Ph_3Bi$$

$$Ph_3Bi(CN)_2 \rightarrow PhCN + Ph_3Bi$$

In the reaction of triphenylbismuth dichloride with sodium thiocyanate, no intermediate was isolated and phenyl thiocyanate was directly obtained.[88]

$$Ph_3BiCl_2 + NaSCN \rightarrow PhSCN + Ph_2BiSCN$$

A similar behavior was observed with tetraarylbismuthonium derivatives.[3]

$$Ph_4BiCl \xrightarrow{\text{room temp}} PhCl + Ph_3Bi$$

$$Ph_4BiCl + KCN \rightarrow PhCN + Ph_3Bi$$

$$Ph_4BiCl + KBr \rightarrow PhBr + Ph_3Bi$$

$$Ph_4BiCl + NaNO_2 \rightarrow PhNO_2$$

A phenyl transfer was realized between tetraphenylbismuthonium tetrafluoroborate and triphenylphosphine.[93]

$$Ph_4Bi^+BF_4^- + PPh_3 \rightarrow Ph_4P^+BF_4^- + Ph_3Bi$$

The reaction of bromine with pentaphenylbismuth leads also to aryl transfer to bromine.[3]

$$Ph_5Bi + Br_2 \rightarrow [PhBr + Ph_4BiBr] \rightarrow Ph_3Bi + 2PhBr$$

Pentaphenylbismuth reacts with sulfur dioxide to give diphenyl sulfone.[94]

$$Ph_5Bi + SO_2 \rightarrow Ph_2SO_2$$

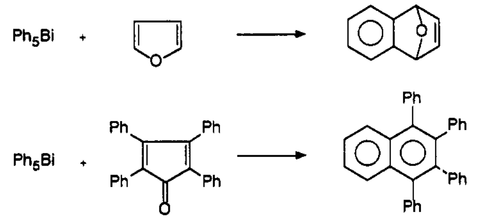
B. Reactions of Pentaphenylbismuth Involving Benzyne as an Intermediate

Decomposition of pentaphenylbismuth in pyridine, chloroform, or carbon tetrachloride involves benzyne as an intermediate. Benzyne can either polymerize into a resinous solid or react with various compounds. In moist pyridine, the products included phenol and diphenyl ether, diphenyl ether being formed by reaction of pentaphenylbismuth with phenol.[95] In the presence of *tert*-butyl alcohol, *tert*-butyl phenyl ether was obtained. Diels-Alder addition products were obtained with furan and with 2,3,4,5-tetraphenylcyclopentadienone.[78,96]

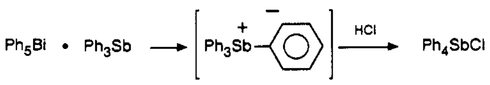
$$Ph_5Bi + H_2O \rightarrow PhOH$$

$$Ph_5Bi + PhOH \rightarrow PhOPh$$

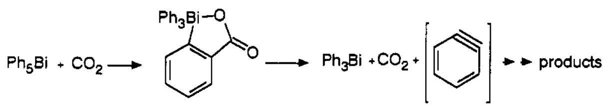
$$Ph_5Bi + t\text{-}BuOH \rightarrow t\text{-}BuOPh$$



An organoantimony betaine product was postulated to be formed when pentaphenylbismuth was reacted with triphenylantimony in carbon tetrachloride solution.[96] The betaine was neither isolated nor detected, the reaction mixture being treated with hydrogen chloride.

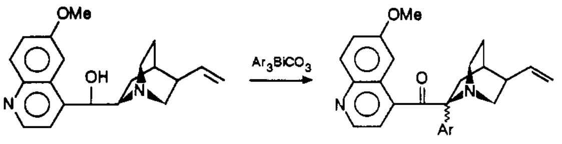


The reaction of pentaphenylbismuth with carbon dioxide yields 1,1,1-triphenyl-2,1λ^5-benzoxabismol-3-(1*H*)-one, which is decomposed via benzyne to give the same antimony betaine derivatives or *tert*-butyl phenyl ether.[97]



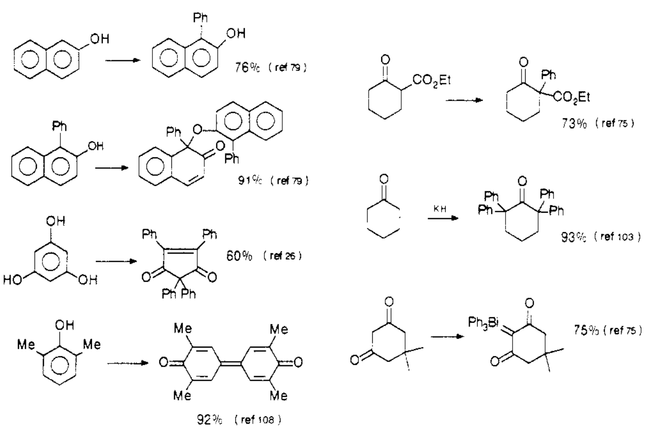
C. C-Arylation with Pentavalent Organobismuth

The seminal experiment for the development of the arylation reaction of a variety of organic substrates was the attempted oxidation of quinine by triphenylbismuth carbonate. A low yield of quininone (34%) was obtained. The final product was a mixture of diastereoisomeric α-arylated ketones (75%) when an excess of reagent was used.[67]

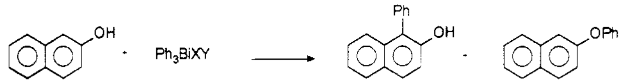


Subsequently, a variety of enolizable substrates were shown to be α-arylated by triarylbismuth carbonates (Scheme 6), as well as by other pentavalent triaryl-,

SCHEME 6. Reactions of Ph_3BiCO_3 with Phenols and Carbonyl Compounds



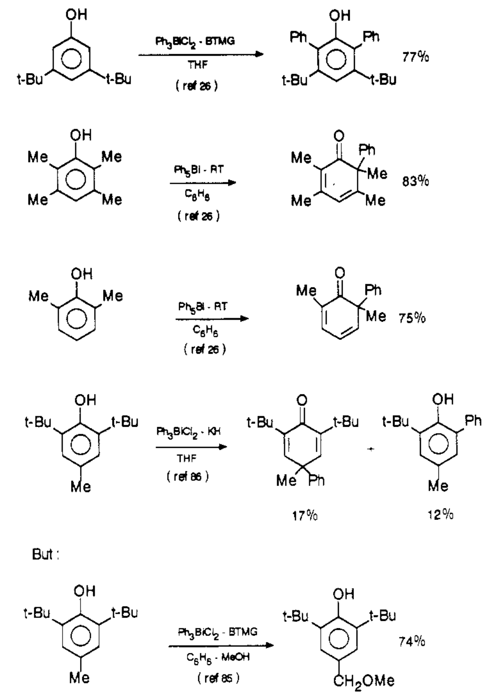
SCHEME 7. O- and C-Phenylation Reactions of 2-Naphthol



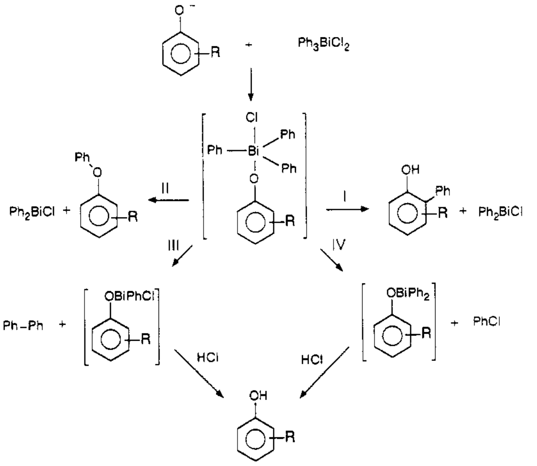
X	Y	pH	C-Phenyl %	O-Phenyl %	Ref
Ph	Ph	a	61	-	(79)
Ph	OCOCF$_3$	a	9	67	(26)
Ph	OCOCF$_3$	b	-	91	(26)
Ph	OCOCF$_3$	c	94	-	(26)
OCOCF$_3$	OCOCF$_3$	c	70	-	(26)
Cl	Cl	c	90	-	(26)

a : Neutral Conditions
b : Addition of Trichloroacetic Acid (0.6 eq.)
c : Preformed Anion using BTMG

SCHEME 8. C-Phenylation of Phenols



SCHEME 9. Decomposition Pathways Involved in the Reactions of Ph_3BiCl_2 with Phenolate Anions[a]



I: R = electron - donating , ortho C - phenylation
II: R = electron - withdrawing , O - phenylation
III: R = p - NO$_2$, Elimination of PhPh
IV: R = H , Elimination of PhCl

[a] Reference 85.

tetraphenyl-, and pentaphenylbismuth compounds.

1. C-Arylation of Phenols

The C-arylation of phenolic compounds can be performed by triphenylbismuth carbonate and also by a variety of triaryl- and tetraphenylbismuthonium derivatives in the presence of a base in various solvents (methylene chloride, benzene, toluene, tetrahydrofuran).[26,32,67,79] Similar C-phenylation is also realized with pentaphenylbismuth under neutral conditions.[79] The yield of the phenylated derivatives is not dependent upon the choice of the reagent. However, the tetraphenylbismuthonium series require generally milder reaction conditions with shorter reaction times.[98] They are also less prone to side reactions such as oxidation. However, only phenylation can be performed as the required tetraphenylbismuthonium reagents alone are available (Schemes 7 and 8).

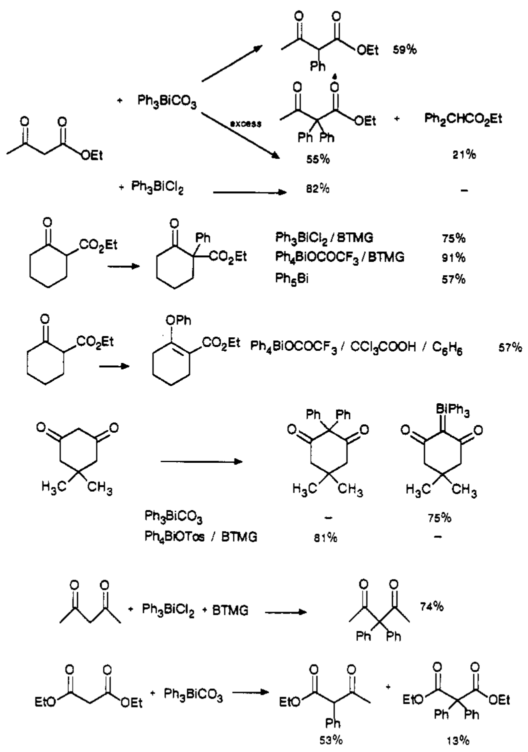
A variety of substituted pentavalent triarylbismuth derivatives are known and arylation can therefore be performed with electron-withdrawing or electron-donating substituted phenyl groups. The electronic properties of the substituents of the arylbismuth do not influence the overall yield of arylated products (*p*-nitro, 84% in the arylation of β-naphthol; *p*-methoxy, 69% in the arylation of β-naphthol).[17] On the other hand, the nature of the substituents on the phenolic moiety appeared to govern the regioselectivity of the arylation reactions, as shown by a study of the phenylation of a variety of substituted phenols by triphenylbismuth dichloride under basic conditions[85] (Scheme 9). Phenols bearing electron-donating substituents are essentially ortho C-phenylated. A small amount of the *O*-phenyl ether is found sometimes. Phenols bearing electron-withdrawing substituents are mostly or selectively O-phenylated. Phenol itself gave a complex mixture with formation of 2-phenylphenol, 2,6-diphenylphenol, diphenyl ether, and biphenyl. However, C-phenylation was ortho selective. Mono- or diarylation can be realized. No trace of the 3- and 4-phenyl isomers was found. This regioselectivity was observed for most of the phenols substituted with electron-donating groups. The steric influence of the ortho substituent does not interfere strongly with the overall yield, 2,4-di-*tert*-butylphenol yielding the 6-phenyl derivatives in 65% (pentaphenylbismuth) or 81% (triphenylbismuth bistrifluoroacetate/BTMG). In the case of 2,6-disubstituted phenols, the nature of the bismuth reagent, the nature of the alkyl substituents, and the reaction conditions determined the outcome of the reactions.[86]

Thus, in the case of 2,6-dimethylphenol, ortho C-phenylation yielded 6-phenylcyclohexadienone with pentaphenylbismuth and tetraphenylbismuthonium derivatives under basic conditions. With triphenylbismuth carbonate, oxidative dimerization took place[79] (see Section IV). 2-Methyl-6-phenylphenol can be phenylated to 2-methyl-2,6-diphenylcyclohexadienone under the conditions of the reaction of 2,4-dimethylphenol with pentaphenylbismuth, giving the corresponding 6-phenylcyclohexadienone.[26] 2,6-Diphenylphenol did not react with any organobismuth to form 2,2,6-triphenylcyclohexadienone. The behavior of the 2,6-di-*tert*-butylphenol derivatives was very dependent upon the reaction conditions.[85,86] In the presence of a base favoring electron transfer (such as BTMG), oxidation reactions took place with triphenylbismuth dichloride, whereas para phenylation was observed for the first time in the reaction of the potassium phenolates with triphenylbismuth dichloride. Even ortho and para phenylation with concomitant de-*tert*-butylation occurred in the reaction of 2,4,6-tri-*tert*-butylphenolate and triphenylbismuth dichloride. Better yields of the C-phenylated products were obtained in the reaction with tetraphenylbismuthonium reagents and a base. In the case of polyhydroxylic phenols, perphenylation occurred. Thus, phloroglucinol reacted with triphenylbismuth carbonate to form 2,4,6-triphenylphloroglucinol, which is then oxidized and further phenylated to 2,2,4,5-tetraphenylcyclopent-4-ene-1,3-dione.[26,79]

2. C-Arylation of Enols

α-C-Arylation of 1,3-dicarbonyl compounds such as β-diketones, β-keto esters, or malonic esters is easily performed with a variety of pentavalent organobismuth reagents under neutral or basic conditions[32,75,79] (Scheme 10). Monoarylation is difficult to obtain selectively in most cases. Good yields of the 2,2-diarylated 1,3-dicarbonyl compounds are generally obtained with triphenylbismuth dichloride and tetraphenylbismuthonium derivatives under basic conditions and with triphenylbismuth carbonate, triphenylbismuth diacetate, and pentaphenylbismuth under neutral conditions. Dimedone gave an ylide upon reaction with triphenylbismuth carbonate but the α,α-diphenyl derivative in the reaction with tetraphenylbismuthonium derivatives and BTMG.[75] Similarly, Meldrum's acid gave the corresponding ylide.[99] Such ylides can also be made by decomposition of the appropriate dicarbonyl diazonium derivative in the presence of triphenylbismuthine catalyzed by bis(hexafluoroacetylacetonato)copper(II).[100] These ylides react with aldehydes to give cyclopropanes, dihydrofurans, and α,β-unsaturated carbonyl compounds.[101] The arylation was extended to various triarylbismuth carbonates.[17] The reaction was also used as a new approach toward the synthesis of isoflavanones and 3-aryl-4-hydroxycoumarins.[102] Phenylation of activated chroman-4-one to isoflavanones was obtained in moderate to good yields. Selective monophenylation was performed in a low-temperature reaction with pentaphenylbismuth. Various 3-(3′- and 4′-substituted aryl)-4-hydroxycoumarins were accessible by reaction of 4-hydroxycoumarins with triarylbismuth dichloride and triarylbismuth dinitrate under basic conditions or with triarylbismuth diacetate under neutral conditions. In the latter reaction the best yields were realized in methylene chloride in the dark.

SCHEME 10. Phenylation of β-Dicarbonyl Compounds[a]



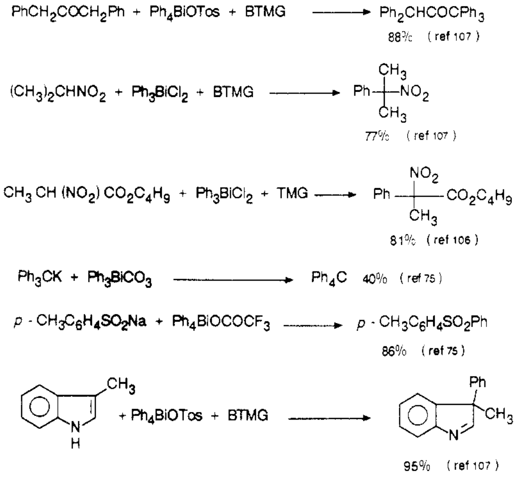
[a] Reference 75.

3. C-Arylation of Various Anions

Nonenolized substrates were not arylated by pentavalent organobismuth compounds under neutral conditions. However, their derived enolates reacted easily with triarylbismuth dichloride, triarylbismuth carbonate, or tetraphenylbismuthonium derivatives to give the corresponding α-aryl products. Generally, only polyarylated derivatives were isolated. Such is the case of ketones, whether aliphatic, acyclic or cyclic, or aromatic.[32,67,75,103,104] Thus acetophenone was converted by triphenylbismuth carbonate to phenyl triphenylmethyl ketone, 4,4-dimethylcholest-5-en-3-one to the 2,2-diphenyl analogue, and cyclohexanone to 2,2,6,6-tetraphenylcyclohexanone. The unknown hexaphenylacetone was not detected in the phenylation of 1,3-diphenylacetone: only pentaphenylacetone was obtained from the reaction of the potassium enolate of 1,3-diphenylacetone with triphenylbismuth carbonate or tetraphenylbismuthonium derivatives.[103,104] Similarly, arylation of chroman-4-one derivatives yielded the 3,3-diphenyl derivatives.[102] Attempted synthesis of 2,6-diphenylcycloalkanones from 2,6-dibromocycloalkanones by reaction with lithium diphenylcuprate (LiCuPh$_2$) followed by treatment with triphenylbismuth carbonate gave only low yields of 2-phenylcycloalkanones.[105]

Other stabilized anions that were successfully α-arylated include the anions of nitroalkanes, α-methyl-α-nitro carboxylic acid derivatives, esters, triphenylmethane, indole, and scatole[75,79,106,107] (Scheme 11). Nitroalkanes gave high yields of the α-*C*-aryl derivatives. In the case of indole, 3,3-diphenyl-3*H*-indole was

SCHEME 11. Phenylation of Anions



obtained by treatment of the sodium salt of indole with tetraphenylbismuthonium *p*-toluenesulfonate. 3-Phenylindole was formed in the reaction of indole with tetraphenylbismuthonium trifluoroacetate or tetraphenylbismuthonium *p*-toluenesulfonate in benzene under reflux under neutral conditions. A related example is the 2-phenylation of *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine with triphenylbismuth dichloride or tetraphenylbismuthonium *p*-toluenesulfonate/BTMG and with triphenylbismuth carbonate, whereas no phenylation occurred with tetraphenylbismuthonium tetrafluoroborate.[93]

D. O-Arylation

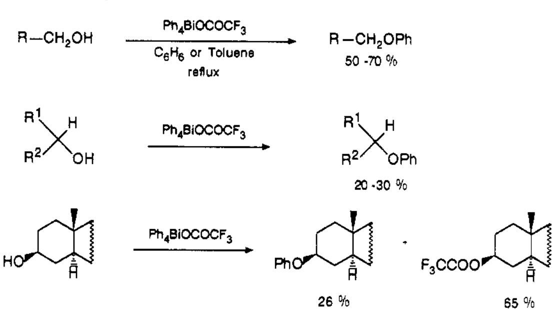
The second major type of arylation of organic substrates that can be successfully performed by pentavalent organobismuth reagents is the O-arylation of phenols, enols, and alcohols.

1. O-Arylation of Phenols and Enols

The first example was the formation of diphenyl ether during the decomposition of pentaphenylbismuth in the presence of phenol.[95,96] The major impetus came from the reaction of pentaphenylbismuth with 4-nitrophenol, leading exclusively to 4-nitrodiphenyl ether.[79] The selective O-phenylation of a phenol substituted with an electron-withdrawing group by pentaphenylbismuth developed into a study of the reaction of electron-rich phenols with pentavalent organobismuth reagents bearing electron-withdrawing groups under neutral conditions.[108] A variety of phenols were O-phenylated through reaction with tetraphenylbismuthonium acylate ($Ph_4BiOCOR$ with R = CH_3 or CF_3) or tetraphenylbismuthonium *p*-toluenesulfonate under neutral conditions. Good yields were obtained with tetraphenylbismuthonium trifluoroacetate in benzene under reflux, but acid catalysis (CCl_3COOH, 0.6 equiv) increased significantly the yields.[26,32] O-Phenylation of phenols was also obtained in the reaction of phenols with triphenylbismuth diacetate under neutral conditions.[109]

O-Phenylation of electron-depleted phenols was also realized by reaction of their enolates with triphenylbismuth dichloride.[85] The reaction is regioselective with 4-substituted phenols, but a mixture of O- and C-arylated products is formed in the case of the 3-substituted phenols.

SCHEME 12. O-Phenylation of Alcohols with $Ph_4BiOCOCF_3$[a]



[a] Reference 78.

The O-phenylation reaction with tetraphenylbismuthonium derivatives (Ph_4BiX with X = OCOR or OSO_2R) was extended to enols. A series of enolized dicarbonyl compounds were O-phenylated in modest to good yields with these reagents under neutral or acidic conditions.[32,75,108]

2. O-Arylation of Alcohols

As with phenols and enols, the reaction of alcoholic substrates with tetraphenylbismuthonium trifluoroacetate appeared to be pH dependent.[78] As previously noted, reactions of primary and secondary alcohols with tetraphenylbismuthonium trifluoroacetate or related tetraphenylbismuthonium reagents under basic conditions result in oxidation to the carbonyl derivatives. Under neutral or acidic conditions, the *O*-phenyl ethers of primary and secondary alcohols can be obtained in modest (secondary alcohols) to good (primary alcohols) yields by reaction of the alcohol with tetraphenylbismuthonium trifluoroacetate in benzene or toluene under reflux (Scheme 12). Tertiary alcohols gave intractable mixtures. However, O-arylation of tertiary alcohols can be realized through reaction with pentaphenylbismuth, involving benzyne as an intermediate.[96] *tert*-Butyl phenyl ether was also obtained in low yields in the reaction of triphenylbismuth diacetate with *tert*-butyl alcohol used as solvent and potassium carbonate or in the reaction of triphenylbismuth dichloride and lithium *tert*-butoxide.[28,74] The reaction of triphenylbismuth diacetate with secondary alcohols under neutral conditions results in poor to moderate yields of the corresponding *O*-phenyl ethers: 2-propanol (<20% with a large excess of alcohol), cyclohexanol (<3%), 3β-cholestanol (36%).[28,110-112]

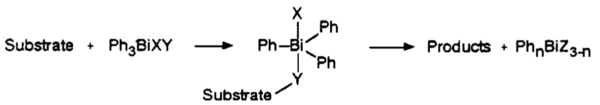
The reactivity of tetraphenylbismuthonium trifluoroacetate and triphenylbismuth diacetate toward hydroxylic functions was greatly improved by the presence of a neighboring group. Whereas reaction of cyclohexanol with tetraphenylbismuthonium trifluoroacetate in benzene under reflux afforded only 22% of the *O*-phenyl ether after 18 h, 52% of the monophenyl ether and 13% of the diphenyl ether of *cis*-cyclohexane-1,2-diol were formed under the same conditions.[110,111] A selective mono-O-phenylation of glycols was discovered by David and Thieffry during a comparative study of various oxidants toward α-glycols.[81,110,111] Good to excellent yields were obtained with various combinations of primary and secondary glycols and also for a secondary–tertiary glycol. Even ditertiary glycols afforded the monoether although in poor yields. The distance between the two hydroxyls is not determinant as only 1,5- and 1,6-glycols showed a decrease in the average yields. An axial preference was noted in conformationally rigid glycols. It was later found that this reaction is not restricted to glycols as ether alcohols and amino alcohols were also phenylated.[112]

E. S- and N-Arylations

A rather limited number of S- and N-arylations with organobismuth reagents have been described. Aryl thiols were converted to mixed arylphenyl thiols with pentaphenylbismuth or with tetraphenylbismuthonium trifluoroacetate.[79,108] Oxidation products were also formed in minor amounts (<15%). *p*-Toluenesulfinic acid reacts with pentaphenylbismuth and with tetraphenylbismuthonium trifluoroacetate under neutral or basic conditions to give phenyl *p*-tolyl sulfone in high yields. A similar result was obtained with triphenylbismuth carbonate.[108] Amides are not phenylated by triphenylbismuth carbonate and only in poor yields with tetraphenylbismuthonium derivatives.[78,79] Oximes were cleaved by tetraphenylbismuthonium trifluoroacetate under basic conditions to regenerate the ketone but the *O*-triphenylbismuth dioximates were obtained with triphenylbismuth dichloride under basic conditions.[113] Phenylhydroxylamine and triphenylbismuth carbonate under neutral or basic conditions gave diphenyl nitroxide and after reductive acetylation *N,N*-diphenylacetamide, but no reaction was observed between triphenylbismuth carbonate and nitrosobenzene.[67,107] Imides were phenylated in moderate yields by tetraphenylbismuthonium trifluoroacetate.[78] In the reaction of indole with tetraphenylbismuthonium trifluoroacetate under neutral conditions, 3,*N*-diphenylindole was formed as a minor product (2%).[75] Phenyl transfer to the amino functionality was first observed during an attempt of oxidation of the hydroxyl function of an amino alcohol by triphenylbismuth carbonate in chloroform.[114] High-yielding N-arylation was found in the reaction of amino alcohols with triarylbismuth diacetate in methylene chloride under reflux.[112]

F. Mechanistic Studies

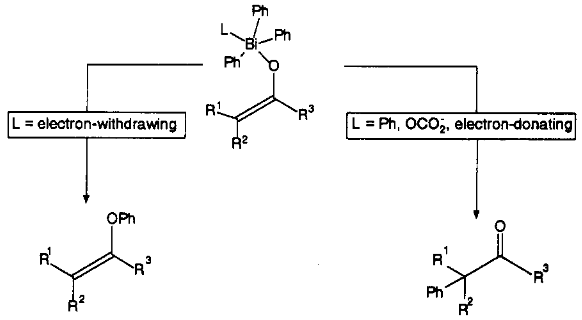
The variety in the types of arylation reaction and their regioselectivity are the main features of organobismuth-mediated arylation. Apart from the decomposition of pentaphenylbismuth involving benzyne (see Section V.B), the most obvious rationale was the formation of a covalent organobismuth intermediate whose decomposition is governed by the nature of the substrate, the nature of the substitutents on the organobismuth, and the reaction conditions.



1. Existence of a Covalent Intermediate in C- and O-Arylations

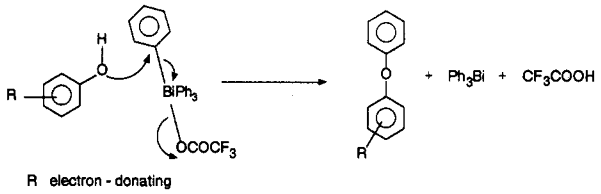
The occurrence of a covalent bismuth–substrate intermediate was invoked to explain the oxidation reactions (see section IV). A similar type of covalent intermediate was postulated in the case of C- and O-phenylations.[32,79] The duality of pathways during decomposition of these intermediates was supported by the already observed duality in the decomposition of alkoxytrianisylbismuth semicarbonates.

SCHEME 13. Postulated Influence of the Nature of the Substituents on the Regioselectivity of the Arylation[a]



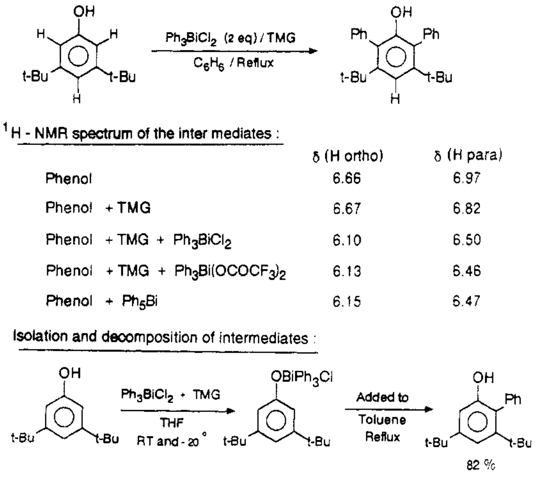
[a] References 32 and 108.

SCHEME 14. Mechanism of the O-Phenylation



An important observation was the isolation of (*p*-nitrophenoxy)tetraphenylbismuth in the reaction of pentaphenylbismuth with *p*-nitrophenol.[26] Thermal decomposition of this intermediate led to the *O*-phenyl ether. It was then postulated that the breakdown of the pentavalent bismuth intermediate was controlled by the nature of the fifth substituent[32,108] (Scheme 13). An electron-donating group would favor C-phenylation, and an electron-withdrawing group O-phenylation. The O-phenylation of phenols and enols by tetraphenylbismuthonium trifluoroacetate under neutral or acidic conditions lent some support to this proposal. However, synthesis of the postulated intermediate by a second route and study of its decomposition resulted only in *C*-phenyl products.[26,31] Therefore this proposal was disproved. Moreover, the C-phenylation is a fast reaction occurring at room temperature or even below, whereas the reaction under neutral or acidic conditions takes place slowly only in benzene under reflux. Similar results were obtained for the O-phenylation of alcohols by tetraphenylbismuthonium trifluoroacetate under neutral conditions.[78] These O-phenylation reactions were suggested to follow an aromatic S_N2 type pathway involving nucleophilic attack by the phenol on the bismuth-bearing aromatic carbon. The electron-withdrawing substituent ($OCOCF_3$) induces a partial positive charge on the ipso carbon, therefore facilitating the substitution (Scheme 14). Although unlikely, a 6- or 7-coordinated bismuth intermediate would be compatible with the observed bimolecular kinetics.[98] However, such an intermediate is more likely under basic conditions as already proposed in the reaction of pentaphenylbismuth with phenyllithium.[115] In the C-phenylation process the postulated covalent bismuth–substrate intermediates were first detected by physical methods and then isolated.[26] ^1H NMR monitoring of the reaction of 3,5-di-*tert*-butylphenol with pentaphenylbismuth and with triphenylbismuth bis(trifluoroacetate) or triphenylbismuth dichloride in the

SCHEME 15. Covalent (Aryloxy)bismuth Intermediates



^1H - NMR spectrum of the inter mediates :

	δ (H ortho)	δ (H para)
Phenol	6.66	6.97
Phenol + TMG	6.67	6.82
Phenol + TMG + Ph_3BiCl_2	6.10	6.50
Phenol + TMG + $Ph_3Bi(OCOCF_3)_2$	6.13	6.46
Phenol + Ph_5Bi	6.15	6.47

Isolation and decomposition of intermediates :

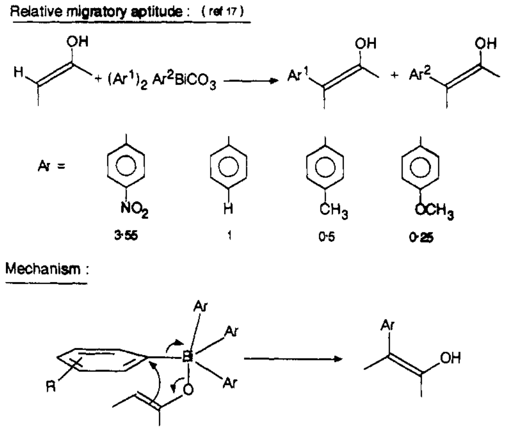
presence of *N,N,N′,N′*-tetramethylguanidine (TMG) has shown its occurrence. Two such intermediates were subsequently isolated, and their controlled thermal degradation led to the ortho *C*-phenyl derivatives (Scheme 15). Moreover, the synthesis and stability of the isomeric covalent carbon–bismuth compound in the case of acetone excluded this type of intermediate as an alternate pathway.[116] It must be noted that such a carbon–bismuth intermediate was likely to be involved in the ortho and para phenylation of sterically hindered 2,6-disubstituted phenols.[86] The reaction of triphenylbismuth dichloride with phenols gives a covalent (aryloxy)bismuth compound. The decomposition pathway followed by these intermediates is governed by the electronic nature of the substituents on the aryloxy substrate[85] (Scheme 9).

In the most stable conformation electronegative substituents in 5-coordinate complexes are apical. O-Phenylation of alcohols is thus disfavored. However, in the glycol case an apical–equatorial chelation was suggested to explain the facile mono-O-phenylation of glycols by triphenylbismuth diacetate under neutral conditions.[111]

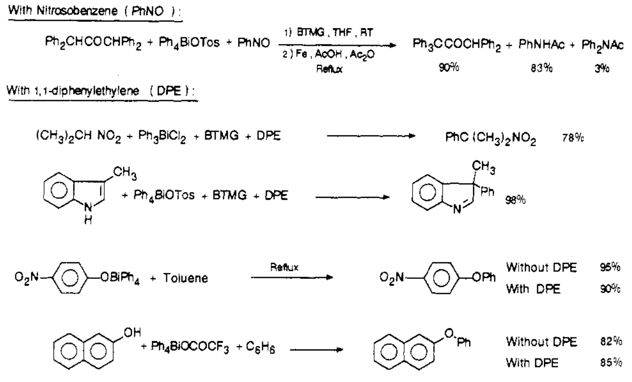
2. Mechanism of the Reductive Elimination Step

The second step of the arylation process involves a reductive elimination. Studies of the relative migratory aptitudes of aryl groups indicated that the C-phenylation reaction does not follow an ionic pathway.[17] Although these migratory aptitudes were of the same order as a free-radical type, the relative ratios are more consistent with a nonsynchronous concerted mechanism (Scheme 16). Qualitative ESR studies revealed the formation of phenyl radicals in the C-phenylation of phenols and enols.[107] They result from a decomposition pathway of the bismuth reagent, and the arylation reaction itself does not imply a free-radical pathway as demonstrated by quantitative chemical trapping experiments with a variety of substrates (Scheme 17). The possibility of a cage–radical mechanism was excluded on the basis of the reaction of pentaphenylbismuth with a phenol bearing an internal radical trap.[12]

SCHEME 16. Mechanism of the Reductive Elimination



SCHEME 17. Phenyl Radical Trapping Experiments[a]



[a] Reference 107.

3. Occurrence of Free Radicals

The quantitative chemical trapping method was also used in the study of other related reactions such as the C-phenylation of nitroalkanes and indoles and the thermal decomposition of (*p*-nitrophenoxy)triphenylbismuth derivatives. No free radicals were involved although qualitative ESR studies showed their presence.[107] Similarly, phenyl radicals were detected by ESR in the phenylation of *tert*-butyl alcohol. However, no chemical trapping has been performed.[74] A one-electron transfer was invoked in the reaction of tetraphenylbismuthonium tetrafluoroborate with *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine.[93]

Oxidative dimerization and oxidation of sterically hindered 2,6-substituted phenolic substrates by triphenylbismuth dichloride and triphenylbismuth carbonate in the presence of BTMG are likely to occur via aryloxyl radicals formed by electron transfer between BTMG and the bismuth reagent followed by reaction of the intermediate radical species with the phenol.[86] Dimerization of 2,6-dimethylphenol by reaction with triphenylbismuth carbonate was shown to be purely ionic with formation of a covalent bismuth–phenol intermediate.

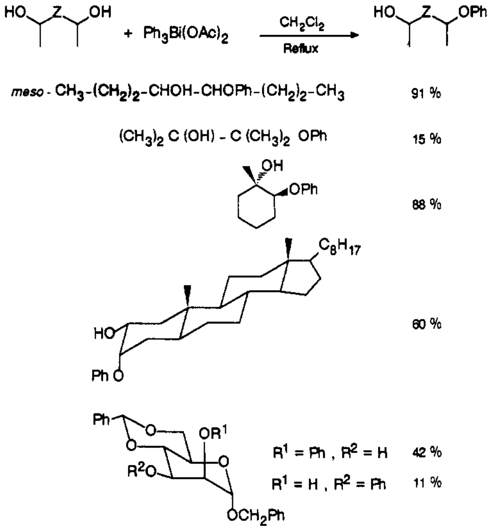
VI. Copper-Catalyzed Arylation

The observation of a catalytic effect of copper salts on the decomposition of triphenylbismuth diacylates led to the development of a copper-catalyzed arylation reaction by triarylbismuth diacylates in the presence of copper or its metallic salts.

A. With Alcohols, Glycols, Phenols, and Enols

Phenylation of lower aliphatic alcohols was observed when the copper-catalyzed decomposition of tri-

SCHEME 18. Glycol Mono-O-phenylation[a]



[a] Reference 111.

SCHEME 19. Effect of Copper Diacetate on the Phenylation of Glycols[a]

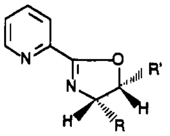
$$\text{HOCH}_2\text{-CMe}_2\text{-CH}_2\text{OH} + \text{Ph}_3\text{Bi(OAc)}_2 \xrightarrow{\text{CH}_2\text{Cl}_2} \text{HOCH}_2\text{–CMe}_2\text{–CH}_2\text{OPh}$$

$Cu(OAc)_2$	Reaction Conditions	Induction Time (h)	Reaction Time (h)	O-Phenyl (%)
0	Ref , a	2	4	91
10^{-4}	Ref , a	0	0.25	82
10^{-1}	Ref , b	0	0.25	78
10^{-1}	20°C, b	0	1	82

a : ambient light b : in the dark

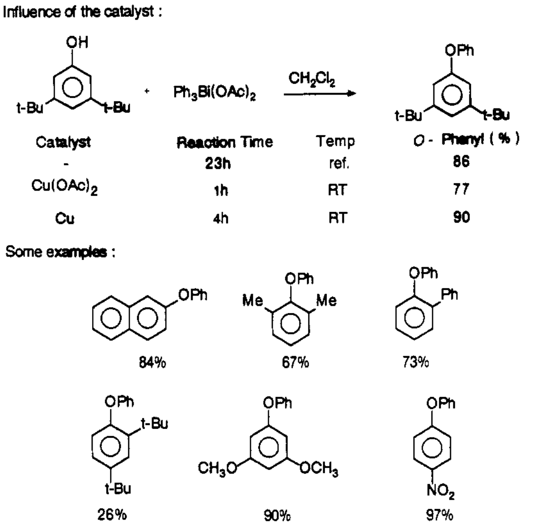
[a] Reference 112.

phenylbismuth diacetate was carried out in alcohols used as solvent (20 mL per mmol of bismuth reagent).[117,118] However, under stoichiometric conditions the O-phenylation of 3β-cholestanol by triphenylbismuth diacetate (1 equiv) was not significantly improved upon addition of copper diacetate.[112] The mono-O-phenylation reaction of glycols discovered by David and Thieffry presents characteristic features that are not compatible with the postulated covalent bismuth intermediate[111] (Scheme 18). The reaction is solvent selective (methylene chloride under reflux), is light catalyzed (no reaction in the dark), and presents an induction period (2 h in the case of the phenylation of 2,2-dimethylpropane-1,3-diol). Addition of small amounts of copper diacetate had a marked effect on the reaction (Scheme 19). The reaction became fast: reaction time can be as short as 0.25 h. Moreover, the copper-catalyzed reaction is not solvent selective or light catalyzed.[112] Optical inductions were observed in presence of a chiral pyridinooxazoline ligand.[119]



The highest e.e. (30.2%) was observed in the presence of the ligand [R = (S)-CHMeEt and R′ = H]. However, the yields were lower under these conditions: 35–45% instead of 87% in the absence of catalyst for the O-phenylation of *cis*-cyclohexane-1,2-diol.

SCHEME 20. Copper-Catalyzed O-Phenylation of Phenols[a]



Catalyst	Reaction Time	Temp	O-Phenyl (%)
-	23h	ref.	86
$Cu(OAc)_2$	1h	RT	77
Cu	4h	RT	90

[a] Reference 109.

This copper-catalyzed reaction was extended to the arylation of other hydroxylic substrates such as phenols and enols[109] (Scheme 20). A wide range of phenolic substrates can be selectively O-phenylated under very mild neutral conditions (1–24 h at room temperature in methylene chloride). The best yields were obtained with metallic copper catalysis. The electronic nature of the substituents of the phenol does not influence the yields (p-nitro, 97%; 3,5-dimethoxy, 90%). Only steric hindrance of the 2- and 6-substituents interferes with the reactivity. Thus only 26% of the O-phenyl ether was obtained with 2,4-di-*tert*-butylphenol, and no phenylation took place in the case of 2,4,6-tri-*tert*-butylphenol.

O-Phenylation of enolic compounds by tetraphenylbismuthonium trifluoroacetate was slightly improved by copper catalysis. Enolized diketones are O-phenylated by $Ph_3(BiOCOR)_2$ in moderate to good yields.[109]

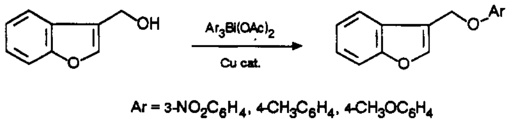
Triphenylbismuthine itself was reported to react with alcoholic solvents to form significant amounts of the O-phenyl ethers when treated with an excess of copper diacetate. The reaction is improved by the presence of atmospheric oxygen.[120,121]

$$\text{Alk–OH} + \text{Ph}_3\text{Bi} + \text{Cu(OAc)}_2 \rightarrow \text{Alk–OPh}$$

Phenols are also O-phenylated by triphenylbismuthine and copper diacetate but the reaction requires addition of a base such as triethylamine.[122]

$$\text{Ar–OH} + \text{Ph}_3\text{Bi} + \text{Cu(OAc)}_2 + \text{Et}_3\text{N} \rightarrow \text{Ar–OPh}$$

The analogous arylation of hydroxylic substrates can also be performed with various substituted triarylbismuth diacylates.[123]



B. With Amines

The reaction of amino alcohols with triphenylbismuth diacetate leads preferentially to N-phenylation.[112] This reaction is also strongly catalyzed by copper and its salts. The reaction of simple aliphatic amines with

SCHEME 21. N-Phenylation of Aliphatic Amines[a]

$$R{-}NH_2 + Ph_3Bi(OAc)_2 + Cu \xrightarrow{CH_2Cl_2} R{-}NHPh + R{-}NPh_2$$

Amine	Temp	Mono %	Di %
n - Butylamine	R.T.	60	20
Cyclohexylamine	R.T.	90	
Piperidine	R.T.	58	
Diethylamine	R.T.	15	
	Ref	42	
t - Butylamine	R.T.	15	
	Ref.	50	
$Ph_2N-NH-Ph$	R.T.	10 (Ph_3N)	

[a] Reference 125.

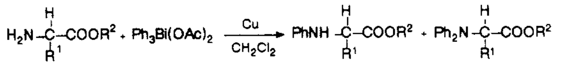
SCHEME 22. N-Phenylation of Aromatic Amines[a]

$$Ar{-}NHR' + Ph_3Bi(OAc)_2 + Cu^{\circ} \xrightarrow[R.T.]{CH_2Cl_2} Ar{-}NR'Ph$$

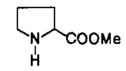
Ar	R'	Bi Reagent (eq)	Reaction Time (h)	*N* - Phenyl %
Phenyl	H	1·1	2	96
Phenyl	Phenyl	1·1	48	23
p -Tolyl	H	1	0·75	97
p -Anisyl	H	1	0·25	91
p -Anisyl	Phenyl	2·2	72	78
p -Nitrophenyl	H	2·2	16	90
Mesityl	H	2·2	24	92

[a] Reference 125.

SCHEME 23. N-Phenylation of α-Amino Esters[a]



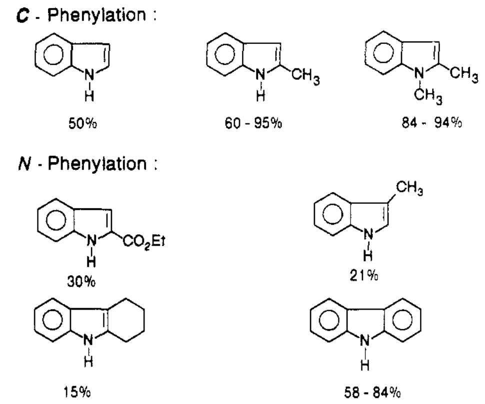
$$H_2N{-}\underset{R^1}{\overset{H}{C}}{-}COOR^2 + Ph_3Bi(OAc)_2 \xrightarrow[CH_2Cl_2]{Cu} PhNH{-}\underset{R^1}{\overset{H}{C}}{-}COOR^2 + Ph_2N{-}\underset{R^1}{\overset{H}{C}}{-}COOR^2$$

R¹	R²	%	%
H	Et	81	4
$PhCH_2$	Bzl	80	-
$BzlO_2C{-}CH_2$	Bzl	50	-
$BzlO_2C{-}(CH_2)_2$	Bzl	58	-
Indolylmethyl	Me	66	-
		61	

[a] References 126 and 128.

triphenylbismuth diacetate and copper diacetate (ratio: 10:1:0.02) in tetrahydrofuran led to good yields of the aryl amine (60–85% based on the bismuth reagent). Under these conditions diphenylamine afforded only up to 3% of triphenylamine.[124] However, when the reaction is performed in methylene chloride at room temperature with metallic copper as catalyst, preparatively useful yields of the monophenylamine derivatives are obtained[125] (Schemes 21 and 22). Thus phenylation of aliphatic and aromatic amines with triphenylbismuth diacetate and metallic copper (ratio: 1:1.1:0.1) in methylene chloride led to high yields of the derived aniline (up to 96% based on the amine). Among substituted anilines the electronic nature of the substituents plays a role only on the reaction rate but not on the overall yield (*p*-nitro, 90% after 16 h; *p*-methoxy, 91% after 15 min). The steric hindrance does not much affect the yield. Even triphenylamine was obtained in 23%. A variety of aliphatic, alicyclic, heterocyclic, and aromatic amines as well as hydrazines were N-arylated. No reaction took place with α-amino acids but their esters were mildly mono-N-phenylated[126] (Scheme 23). Faster and higher yielding reactions were realized with triphenylbismuth bis(trifluoroacetate) and metallic copper.[125] This reagent was efficient for the N- or C-3-phenylation of indole derivatives.[127] Preferential C-3-phenylation took place in high yields when the C-3 carbon of the substrate was not substituted. In this case even *N*,2-dimethylindole was phenylated in high yield (84%). With C-3-substituted indoles, modest yields of the *N*-phenyl derivatives were obtained (15–30%) (Scheme 24).

SCHEME 24. Copper-Catalyzed Phenylation of Indoles[a]

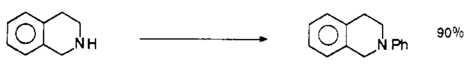


[a] Reference 127.

SCHEME 25. Phenylation with Triphenylbismuthine/Copper Diacetate[a]

$$R - NH_2 + Ph_3Bi + Cu(OAc)_2 \xrightarrow[RT\ /\ Argon]{CH_2Cl_2} R - NH - Ph$$

R = 4 - $MeOC_6H_4$ 82% ; C_6H_5 48% ; 4 - $O_2NC_6H_4$ 6%
cyclohexyl 76%



$$Ph_2N{-}NH_2 \longrightarrow Ph_2NNH{-}Ph \quad 66\%$$

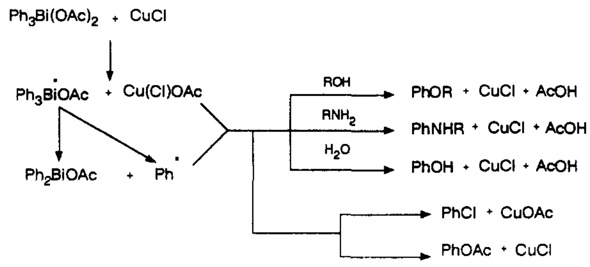
[a] Reference 122.

Triphenylbismuthine acts also as a phenylating agent toward a variety of amines in the presence of a stoichiometric amount of copper diacetate.[122] One example of hydrazine and hydrazones was also N-phenylated (Scheme 25).

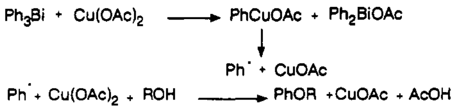
C. Mechanism

Two different types of mechanism have been postulated to rationalize the various copper-catalyzed arylation reactions. In view of the occurrence of phenyl radicals detected by ESR as their spin adducts with 2-methyl-2-nitrosopropane and 2,4,6-tribromonitrosobenzene, Dodonov et al. suggested a free-radical mechanism in both reaction types (triphenylbismuth diacetate–catalytic copper salt and triphenylbismuthine–stoichiometric copper diacetate).[118,121]

(a) $Ph_3Bi(OAc)_2$ + Cu (cat.):[118]



(b) $Ph_3Bi + Cu(OAc)_2$:[121]

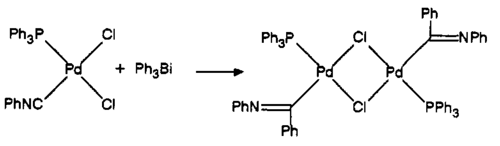


$$Ph_3Bi + Cu(OAc)_2 \longrightarrow PhCuOAc + Ph_2BiOAc$$
$$PhCuOAc \longrightarrow Ph^{\bullet} + CuOAc$$
$$Ph^{\bullet} + Cu(OAc)_2 + ROH \longrightarrow PhOR + CuOAc + AcOH$$

Barton et al. suggested a different mechanism involving an oxidative addition on a copper(I) species to give a copper(III) intermediate.[122,128] This would be prone to reductive elimination yielding the various products depending on the substrates. In the triphenylbismuthine reaction, copper diacetate would act as an oxidant of bismuth(III) to bismuth(V) followed by the same catalytic transfer as for the bismuth(V) reaction. Various types of copper substrates are involved in these pathways (Scheme 26).

VII. Palladium- and Platinum-Catalyzed Reactions

Among a range of phenyl derivatives of heavy metals, triphenylbismuthine reacted with isocyanides coordinated to palladium(II).[129]



Reaction of triphenylbismuthine or triphenylbismuth dichloride with olefins such as styrene, 1-octene, or ethyl acrylate in the presence of palladium(II) acetate or palladium(II) chloride in equimolecular amounts led essentially to biphenyl formation via the phenylpalladium intermediate.[130,131] A similar reactivity pattern was observed with platinum(IV) compounds.[132]

$$Ph_3Bi + PdX_2 \rightarrow Ph\text{-}Ph$$

However, 1-octene was converted to a mixture of octanones upon treatment with oxygen in the presence of triphenylbismuth dichloride–tetrachlorodilithiopalladium (Li_2PdCl_4)–lithium chloride.[133]

Biaryl formation is obtained quantitatively in the reaction of diarylbismuthine and triarylbismuth(III) and -(V) derivatives with a catalytic amount of palladium(0), prepared in situ from palladium(II) acetate and triethylamine.[134]

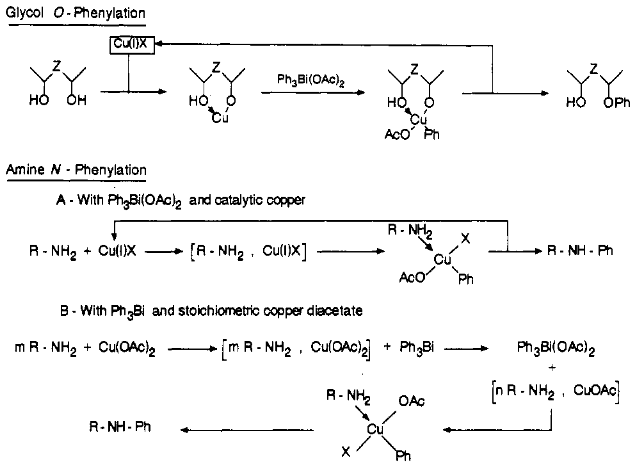
$$Ar_3Bi \text{ or } Ar_3BiX_2 + Pd(0) \rightarrow Ar\text{-}Ar\ (52\text{–}100\%)$$

When the reaction was performed in the presence of an acid chloride, excellent yields of phenyl ketones were obtained even with pivaloyl chloride and adamantanecarbonyl chloride (Scheme 27).

VIII. Conclusion

Organobismuth compounds as arylating agents in organic synthesis have shown a great selectivity toward a wide range of substrates. Thus C-, O-, N-, and S-arylations can be realized efficiently under generally mild conditions. Although in most cases two aryls are lost as byproducts, these reactions provide now a facile access to arylation of expensive substrates, and their utility as a new range of mild and selective reagents in organic synthesis should be demonstrated by the application of these reactions to the great variety of available organobismuth compounds.

SCHEME 26. Mechanisms Involved in the Copper-Catalyzed Phenylations

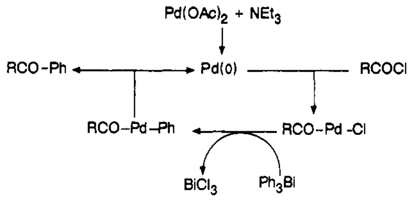


SCHEME 27. Palladium-Catalyzed Phenylation of Acid Chlorides[a]

$$RCOCl + Ph_3Bi \xrightarrow[HMPA,\ 65°]{Pd(OAc)_2,\ Et_3N} RCO\text{–}Ph + BiCl_3$$

R = CH_3	95 %
R = C_6H_5	96 %
R = $(CH_3)_3C$	89 %
R = 1-Adamantanyl	90 %

Mechanism :



[a] Reference 134.

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Registry No. Bismuth, 7440-69-9.

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