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The Chemistry of Organobismuth Reagents Part XIII
Ligand Coupling Induced by Pd(0)[†]

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Abstract

Palladium zero converts triphenylbismuth quantitatively to diphenyl and metallic bismuth. Many other derivatives of Bi (III) and Bi(V) are similarly transformed to diaryls in excellent yield. Similar reactions with triphenylantimony and with perphenyl lead derivatives suggest that a number of non-transition metal elements should show similar behaviour.

Acid chlorides also react under mild conditions with triphenylbismuth under catalysis by palladium (0) to furnish phenylketones in excellent yield (with respect to the triphenylbismuth). All three phenyls are transferred when a suitable excess of the acid chloride is used. Diaryl formation is a minor side reaction.

Three and five valent organo-bismuth reagents have been shown to arylate efficiently amines, phenols and enols and alcohols under copper catalysis[1,2]. The mechanism of this arylation process surely involves the formation of a copper aryl bond, which undergoes reductive elimination (ligand coupling[3]) to give product. It seemed to us that if two aryl groups could be induced to migrate onto a suitable metal, the coupling reaction might provide a synthesis of diaryls. The obvious metals for inducing the coupling reaction are nickel[4] and palladium[5]. The latter metal proved to be very efficient. There was some prior work on the reactions of triphenylbismuth with olefins catalysed by Pd°, but here diaryl formation was an undesired side reaction[6].

The reaction of triphenylbismuth **1** with a Pd(0) catalyst, prepared *in situ* from palladium diacetate and triethylamine in tetrahydrofuran (THF) at room temperature for 12 hrs. gave diphenyl **2** (97%), indicating that all three phenyl groups had coupled. The other products were Pd metal and Bi(0). Raising the temperature to 65° shortened the reaction time to 2.5 hrs. Changing the solvent to acetonitrile gave a similar result, but using hexamethylphosphoramide (HMPA) gave a very fast reaction (10 minutes at 65°) and a quantitative yield. Similarly (Table I) tri-*p*-anisylbismuth **3** gave di-*p*-anisyl **4** in very high yield and tri-*p*-tolylbismuth **5** afforded di-*p*-tolyl **6** in equally good yield.

This coupling reaction of aryl residues is not confined to aryl bismuth derivatives. Triphenylantimony **7** also gave excellent yields of diphenyl

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with Pd(0) catalysis and again, all three phenyls were coupled. In addition, hexaphenyldilead 8 as well as tetraphenyllead 9 gave a good yield of diphenyl. It would seem that many of the non-transition elements at the bottom of the Periodic Table will behave in the same way. The driving force for the reaction is clearly the formation of the aryl-aryl bond. This must be stronger than the sum of the two metalloid-carbon bonds that are broken.

The reactions so far discussed were carried out using a molar proportion of palladium acetate. Many other bismuth compounds also gave excellent yields of diaryl coupled products using only 0.05 mmol of palladium acetate. These included diphenylbismuth chloride 10, diphenylbismuth acetate 11, diphenylbismuth trifluoroacetate 12, triphenylbismuth dichloride 13, triphenylbismuth diacetate 14 and triphenylbismuth ditrifluoroacetate 15. Triphenylbismuth carbonate 16 gave an inferior yield of diphenyl, no doubt because of its insolubility. Tri-p-anisyl- 17 and tri-p-tolyl 18 bismuth dichlorides also gave respectively dianisyl 4 and di-p-tolyl 6 in excellent yield under the catalytic conditions.

Triphenylantimony dichloride 19 also gave a good yield of diphenyl under catalytic conditions using HMPA, but tetrahydrofuran was less efficient.

In a recent article[7] the alkylation of amines using alkyl bismuth^{III} reagents and copper catalysis has been reported. Since the bismuth-alkyl bond is weaker than the bismuth-aryl bond, we were confident that trivalent alkyl bismuth reagents would also couple under palladium catalysis. Indeed tris-β-phenylethylbismuth 20 gave a good yield of 1,4-diphenylbutane (20) on treatment with palladium acetate at room temperature. It is of interest that no styrene was formed.

The addition of triphenylphosphine decreased markedly the rate of diaryl formation both for 1 and for 13. We also examined a typical zerovalent nickel catalyst bis(1,5-cyclooctadiene)nickel. With both 1 and 13 coupling in THF at room temperature using either 1.0 or 0.1 equivalents of catalyst gave only traces of diphenyl.

All the reactions so far described produce a black ppt. which clearly contains metallic palladium. In the case of triphenylbismuth, the formation of diphenyl and metallic bismuth is also quantitative. The black ppt. was shown to be a mixture of palladium and bismuth.

The reactions presented above are convenient for the synthesis of symmetrical diaryls. We decided to see if the aryl group transfer to palladium could lead to coupling to another functional group. For the first study we decided to examine coupling to aroyl and acyl chlorides.

From the earlier work of Stille and his colleagues[5,8] we considered that acid chlorides 22 would react with palladium (0) (Scheme) to give an intermediate Pd^{II} complex 23. Ligand exchange of chloride for phenyl from triphenylbismuth 1 would afford the species 24 which by ligand coupling would furnish a phenyl ketone 25. From the ligand exchange, diphenyl bismuth chloride 10 would be formed. This is known[7] to disproportionate readily to triphenylbismuth 1 and bismuth trichloride. Alternately, the phenyls exchanged for chlorine one by one. In either case, the transfer of all three phenyls can be foreseen. Naturally, the competitive reaction of ligand coupling of phenyl with phenyl (see above) might also be observed.

In the event (Table II) a catalytic amount (5%) of palladium acetate coupled a variety of acid chlorides with bismuth derived phenyl ligands in excellent yield. The only other product of the reaction were traces of diphenyl. In order to minimise the latter, we used 5 equivalents of the acid chloride. All the three phenyl groups of the bismuth reagent 1 were utilised.

Ar_3Bi

1 Ar = Ph
3 Ar = p-Anisyl
5 Ar = p-Tolyl

Ar-Ar

2 Ar = Ph
4 Ar = p-Anisyl
6 Ar = p-Tolyl

7 Ph_3Sb
8 $(Ph_3Pb)_2$
9 Ph_4Pb

$Ph_2Bi\ X$

10 X = Cl
11 X = OAc
12 X = O_2CCF_3

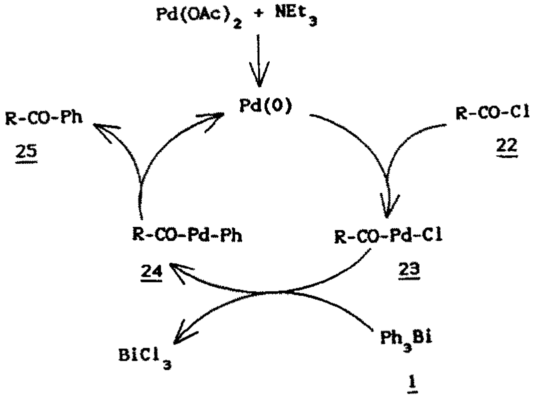
$Ph_3Bi\ X_2$

13 X = Cl
14 X = OAc
15 X = O_2CCF_3
16 X_2 = CO_3

$Ar_3Bi\ Cl_2$

17 Ar = p-Anisyl
18 Ar = p-Tolyl

19 Ph_3SbCl_2
20 $(PhCH_2CH_2)_3Bi$
21 $(PhCH_2CH_2)_2$



Scheme

Table I

$$Ar_3M/Ar_3MX_2/Ar_2MX \xrightarrow[\text{solvent}]{Pd(OAc)_2,\ Et_3N} Ar\text{-}Ar$$

Entry	Substrate 1 mmole	Product	Pd (0) (mmole)	Solvent	Temp., Time	Yield %
1	1	2	1	THF	rt, 12h	97
2	1	2	1	HMPA	65°, 10min.	100
3	1	2	1	CH_3CN	65°, 1.5h	96
4	1	2	1	THF	65°, 2.5h	94
5	3	4[a]	1	THF	rt, 12h	98
6	5	6	1	THF	rt, 12h	99
7	7	2	1	HMPA	65°, 10min.	93
8	7	2	1	CH_3CN	65°, 2h	94
9	7	2	1	THF	rt, 12h	87
10	7	2	1	THF	65°, 1.5h	97
11	8	2	1	THF	rt, 12h	72
12	9	2	1	HMPA	65°, 10min.	99
13	10	2	0.05	THF	rt, 30min.	99
14	11	2	0.05	THF	rt, 1h	98
15	12	2	0.05	THF	rt, 1h	98
16	13	2	0.05	THF	rt, 30min.	100
17	14	2	0.05	THF	rt, 1h	99
18	15	2	0.05	THF	rt, 1h	98
19	16	2	0.2	THF	rt, 12h	52
20	17	4	0.05	THF	rt, 30min.	98
21	18	6	0.05	THF	rt, 30min.	99
22	19	2	0.05	HMPA	65°, 10min.	86
23	19	2	0.05	THF	rt, 24h	25
24	20[b]	21[c]	1	THF	rt, 16h	74

a. See Ref. 9

b. See Ref. 7

c. See Ref. 10

Table II

$$\underset{21}{RCOCl} + \underset{1}{Ph_3Bi} \xrightarrow[\text{HMPA, 65°, 5h.}]{Pd(OAc)_2,\ NEt_3} \underset{25}{RCO\text{-}Ph} + BiCl_3$$

Entry	RCOCl 22 R=	RCOPh 25 R=	Yield 25 %
1	C_6H_5	C_6H_5	96
2	$C_6H_5\text{-}CH_2$	$C_6H_5\text{-}CH_2$	94
3	CH_3	CH_3	95
4	CH_3CH_2	CH_3CH_2	92
5	$CH_3(CH_2)_{14}$	$CH_3(CH_2)_{14}$[a]	94
6	Cyclohexyl	Cyclohexyl	91
7	$(CH_3)_3\text{-}C$	$(CH_3)_3\text{-}C$	89
8	1-Adamantyl	1-Adamantyl[b]	90

a. Ref. 11

b. Ref. 12

Experimental

Melting points were determined with a Kofler hot-stage apparatus and are uncorrected. ^{1}H-NMR spectra were determined for solutions in deuteriochloroform with TMS as internal standard on Varian XL-200E and Varian Gemini-200 instruments. I.R. spectra were recorded on a Perkin Elmer 881 spectrophotometer. All solvents and reagents were purified and dried by standard techniques. Chromatographic separations were performed using Analtech silica gel GF (1000 micron.) plates (Prep. t.l.c.) and Aldrich silica gel 130-270 mesh 60°A (column chromatography). Ether refers to diethyl ether.

Preparation of Organobismuth Reagents

A - Triarylbismuth (III) derivatives - Triphenylbismuth (1) (75%, mp. 78°C) tri-p-methoxyphenylbismuth (3) (63%, mp. 185°C) tri-p-tolylbismuth (5) (85%, mp. 119-120°C) and tris-β-phenylethylbismuth (20)[7] were prepared by reaction of bismuth trichloride with an appropriate Grignard reagent as previously reported[13].

B - Diarylbismuth (III) derivatives - Diphenylbismuth chloride (10)[13] (90%, mp. 185-87°C, lit.[13] 190°C), diphenylbismuth trifluoroacetate (12)[14] (65% mp. 216°C, lit.[14] 213-215°C) were prepared following the literature methods.

C - Pentavalent bismuth reagents - Triphenylbismuth dichloride (13)[13] was prepared by reaction of triphenylbismuth with sulfuryl chloride. Tri-p-methoxyphenylbismuth dichloride (17)[13] and tri-p-tolylbismuth dichloride (18)[13] were prepared in an analogous manner. Triphenylbismuth carbonate (16)[15], triphenylbismuth diacetate (13)[15] and triphenylbismuth ditrifluoroacetate (15)[15] were prepared by employing methods described in the literature.

D - Miscellaneous - Triphenyl antimony (7) and hexaphenyldilead (8) were purchased from Alfa Products. Tetraphenyl lead was obtained from Aldrich. Triphenylantimony dichloride (19)[16] was prepared by reacting triphenylantimony with sulfuryl chloride (94%, mp. 142-43°C, lit.[16] 143°C).

General Procedure for the Preparation of Diaryl from Triarylbismuth Derivatives

A - Using THF as solvent - To a well stirred suspension of palladium acetate (1 mmole) suspended in THF (2 ml) under argon at room temperature, was added NEt_3 (2 mmole). After 2-3 minutes stirring, a yellow coloured solution resulted. Triarylbismuth (1 mmole) in THF (4 ml) was added and the reaction mixture was stirred at room temperature for 12 hrs. A black precipitate was formed. The t.l.c. analysis indicated the complete consumption of triarylbismuth and the formation of a new product. The reaction mixture was diluted with ether (10 ml) and filtered through a short Celite bed. The column was washed (5x25 ml) with ether and the ether washings combined. Evaporation of the solvent furnished diaryl. For yields see Table I. All compounds synthesised had the correct N.M.R., Mass. Spec. and I.R. spectra and where appropriate, were compared with authentic specimens.

Employing this procedure, we prepared i) diphenyl (2) (97%, mp. 70-71°C, lit.[17] 69-71°C) from triphenylbismuth (1); ii) di-p-anisyl (4) (98%, mp. 175°C, lit.[9] mp. 175-76°C) from tri-p-methoxyphenylbismuth (3); iii) di-p-tolyl (6) (99%, mp. 120-21°C, lit.[9] 121-22°C) from tri-p-tolylbismuth (5) and iv) 1,4-diphenylbutane (21) (74%, mp. 51-52°C, lit.[10] 51-52°C) from tris-β-phenylethylbismuth (20).

B - Using HMPA as solvent - To a well stirred suspension of $Pd(OAc)_2$ (1 mmole) in hexamethylphosphoramide (HMPA) (2 ml) kept under argon at room temperature was added NEt_3 (2 mmole). After stirring for 2-3 minutes, a clear yellow solution resulted. To this was added the appropriate organometallic compound (1 mmole) in HMPA (4-5 ml). The solution turned dark immediately; it was then heated to 65° for 10 minutes. A fine black powder precipitated. The reaction mixture was cooled and filtered over celite. The celite column was washed with ether (5x25 ml) and ether washings combined and shaken with water to remove traces of HMPA. The organic phase was separated, dried over anhydrous $MgSO_4$, and evaporated to furnish the diaryl.

General Procedure for the Preparation of Diaryl from Diphenylbismuth (III) and Triphenylbismuth (V) Derivatives.

The Pd(0) catalyst was prepared from $Pd(OAc)_2$ (0.05 mmole) and NEt_3 (0.1 mmole) in THF (1 ml) as described before. To this yellow coloured solution was added the appropriate Bi(III) or Bi(V) derivative (1 mmole) in THF (5 ml). The solution turned black after stirring for 10 minutes at room temperature. The stirring was continued for a further period of 20 or 50 minutes (Table I). The t.l.c. analysis of the reaction mixture indicated complete consumption of starting material. The reaction mixture was then diluted with ether and filtered over Celite, the column washed with ether (5x25 ml) and the washings combined and evaporated to give the diaryl.

Reaction of Triphenylbismuth with a Ni(0) Catalyst

A solution of bis(1,5-cyclooctadiene)nickel (1 mmole) in THF (5 ml) was kept well stirred under argon at room temperature. To this was added a solution of triphenylbismuth (1 mmole) in THF (3 ml) and the reaction mixture was stirred at room temperature for 52 h. The solution was then filtered over Celite and the Celite column washed with ether. The combined washings after evaporation furnished a residue which when subjected to prep. t.l.c. (hexane as eluent) gave diphenyl (10 mg, 4%) and unreacted triphenylbismuth (97%).

Reaction of Triphenylbismuth Dichloride with Ni(0) Catalyst

To a solution of bis(1,5-cyclooctadiene)nickel (0.1 mmole) in THF (2 ml) was added triphenylbismuth dichloride (1 mmole) in THF (3 ml). The reaction mixture was stirred at room temperature, under argon for 62 h. After the usual work-up and chromatography of the resulting residue only traces of biphenyl were obtained.

General Procedure for the Arylation of Acylhalides

$Pd(OAc)_2$ (0.05 mmole) was suspended in HMPA (1 ml) and the solution was kept well stirred under argon at room temperature. To this was added NEt_3 (0.1 mmole). A yellow solution resulted after 2-3 minutes. A solution of an appropriate acid chloride (5 mmole) in HMPA (2 ml) was introduced slowly, followed by the addition of triphenylbismuth (1 mmole) in HMPA (5 ml). The reaction mixture was then heated to 65°C and stirred at that temperature for 5h. It was then cooled, diluted with ether (50 ml) and filtered through a short column of basic alumina. The column was washed with ether (4x25 ml) and the ether washings combined and shaken with water (3x250 ml). The organic phase was separated, dried over anhydrous magnesium sulfate and evaporated to give the ketone. This was further purified either by prep. t.l.c. or by recrystallisation. See Table II for the yields.

Analysis of the Black Precipitate Formed in the Diaryl Formation Reaction

Pd(0) catalyst was prepared from $Pd(OAc)_2$ (225 mg, 1 mmole), and NEt_3 (0.28 ml, 2 mmole) in HMPA (2 ml). Triphenylbismuth (440 mg, 1 mmole) in HMPA (4 ml) was added and the reaction mixture stirred at 65° for 10 min. The resulting black precipitate was filtered and washed with CH_2Cl_2 several times. It was then air-dried to constant weight, 322 mg. [theory for Pd(0) + Bi(0): 315 mg.]

A - Separation of Pd black - The black precipitate was suspended over ethanolic HCl (3%, 50 ml) and stirred at room temperature for 10 min. A portion of the precipitate dissolved to give a green to grey solution. The undissolved black powder was filtered, washed with ethanol and air-dried to constant weight, 124 mg. [theory for Pd(0) 106 mg.].

B - Conversion of the Palladium Black to $Pd(OAc)_2$ - The Pd black (124 mg) obtained above, was taken in acetic acid (3 ml) containing HNO_3 (0.072 ml) and heated at reflux for 6 hrs. The black precipitate dissolved completely to give a dark yellow solution which upon cooling provided $Pd(OAc)_2$ (193 mg. 86%; mp. 271°, lit.[5] 274). A dimethylglyoxime complex of $Pd(OAc)_2$ was also prepared by treating an ethanolic solution of the acetate with DMG, mp.>320.

C - Analysis of the Filtrate - The green to grey coloured filtrate obtained in Stage A was treated with H_2S gas to give a dark brown precipitate (170 mg.; 257 mg. expected as Bi_2S_3).

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