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# The Chemistry of Pentavalent Organobismuth Reagents. Part 14.<sup>†</sup> Recent Advances in the Copper-Catalyzed Phenylation of Amines.

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**Abstract:** A reinvestigation of the copper-mediated phenylation of amines by  $Bi^{v}$  reagents is reported. The influence of the ligands bound to bismuth and the basicity of the amines have been examined. These results, combined with our previous observations, led to the development of a new system for the quantitative phenylation of selected hindered aliphatic and aromatic amines. © 1997 Elsevier Science Ltd.

# INTRODUCTION

The arylation of organic substrates by pentavalent bismuth reagents<sup>1</sup> has been known since 1980.<sup>2</sup> Systematic studies showed that  $\beta$ -dicarbonyl compounds, phenols, enolizable ketones and related compounds could be arylated with ease and often in good yield.<sup>3</sup> However, the facile arylation of amines and, less effectively, of alcohols requires the presence of a copper-based catalyst.<sup>4</sup> Recently the selective arylation of the immunosuppressive drug FK-506 by Merck research laboratories<sup>5,8</sup> has given products of biological interest. For this purpose, Bi<sup>v</sup> and copper catalysis were essential.

The objective of the present article is to examine the factors that could give improved yields in amine arylation. All these reactions involve ligand coupling.<sup>1.6</sup> This mechanism may permit the formation of hindered compounds in good yield under mild conditions.

Similar chemistry has also been developed using aryllead compounds.<sup>7</sup> However, whilst the latter are easy to prepare and efficient, they are environmentally unfriendly. Thus the bismuth derivatives are the reagents of choice in industrial laboratories. We now report our latest results on the arylation of a variety of aliphatic and aromatic amines with Bi<sup>V</sup> derivatives under copper catalysis (Scheme 1). Several new mechanistic aspects have been considered. These include, amongst others, the influence of the ligands bound to the Bi atom and the basicity of the different amines involved in the reaction.

$$Ar_{3}BiX_{2} + R_{1}R_{2}NH + "Cu" \xrightarrow{CH_{2}Cl_{2}} R_{1}R_{2}N-Ar$$

Scheme 1

+

#### **RESULTS AND DISCUSSION**

For the purpose of this study, numerous bismuth<sup>v</sup> compounds were readily prepared by (i) direct oxidation of  $Ph_3Bi$ ,<sup>8</sup> (ii) addition of the appropriate acid to  $Ph_3BiCO_3$ ,<sup>3a)</sup> and (iii) by a novel method developed in our laboratories that involves ligand exchange on  $Ph_3Bi(OAc)_2$ .<sup>9</sup> The yields are in most cases excellent and the syntheses facilitate the preparation of the desired bismuth<sup>v</sup> derivatives on a multigram scale (Table 1).

Entry	Bismuth Derivative	Method of Preparation	Yield <sup>a</sup> (%)
1	Ph <sub>3</sub> Bi(OPiv) <sub>2</sub>	Ph <sub>3</sub> BiCO <sub>3</sub> + PivOH	76
2	Ph <sub>3</sub> Bi(OC(O)-C <sub>6</sub> H <sub>4</sub> - <i>p</i> N(Me) <sub>2</sub> ) <sub>2</sub>	$Ph_3BiCO_3 + HOC(O)-C_6H_4-pN(Me)_2$	68
3	Ph <sub>3</sub> Bi(OAc) <sub>2</sub>	$Ph_3Bi + CH_3CO_3H / CH_3CO_2H$	77
4	Ph <sub>3</sub> BiCO <sub>3</sub>	$Ph_3BiCl_2 + K_2CO_3$	98
5	Ph <sub>3</sub> Bi(OC(O)CF <sub>3</sub> ) <sub>2</sub>	Ph <sub>3</sub> Bi(OAc) <sub>2</sub> + TFA	87
6	Ph <sub>3</sub> Bi(OSO <sub>2</sub> CH <sub>3</sub> ) <sub>2</sub>	Ph <sub>3</sub> Bi(OAc) <sub>2</sub> + MesOH	82
7	$Ph_3Bi(OSO_2-C_6H_4-pCH_3)_2$	$Ph_3Bi(OAc)_2 + TosOH$	75

Table 1: Summary of Preparative Methods of Bismuth<sup>v</sup> Species.

a: Isolated yields.

The relative phenylating aptitudes of the above bismuth compounds were established using a copper<sup>fl</sup> pivalate catalyzed arylation of mesidine (2,4,6-trimethyl aniline) (Table 2). A typical reaction required a mixture of one equivalent of the starting mesitylamine in the presence of a small excess of the Bi<sup>V</sup> derivative (1.1 eq.) and 0.1 eq. of copper<sup>fl</sup> pivalate in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The choice of Cu(OPiv)<sub>2</sub><sup>10</sup> as catalyst was governed by its high solubility in common organic solvents. This permitted a homogeneous reaction.

The first interesting observation is related to efficiency:  $Cu(OPiv)_2$  surpassed both  $Cu(OAc)_2^{11}$  and metallic copper<sup>4a)</sup> in terms of reaction time and yield. Furthermore, the induction period characteristic of metallic copper was absent, thus increasing the overall efficacy of the system.

The second observation apparent from this data is that, contrary to common belief, electronwithdrawing groups attached to bismuth do not improve the yield of phenylated product. This can be ascribed to the acidity of the expelled ligand compared to the basicity of the amine. These mechanistic aspects will be discussed further (*vide infra*). The extended reaction time required with  $Ph_3BiCO_3$  (Table 2, entry 4) may be attributed to the poor solubility of this phenylating agent in dichloromethane. Nevertheless, the reaction produced a quantitative yield of arylated product.

$ NH_2$ + $Bi^V$ $\xrightarrow{Cu^{II} (OPiv)_2 cat.}$ $ NH-Ph$				
Entry	<b>Bismuth Derivative</b>	React. Time	Yield <sup>a</sup> (%)	
1	Ph <sub>3</sub> Bi(OPiv) <sub>2</sub>	5 min.	100	
2	Ph <sub>3</sub> Bi(OC(O)-C <sub>6</sub> H <sub>4</sub> - <i>p</i> N(Me) <sub>2</sub> ) <sub>2</sub>	5 min.	100	
3	Ph <sub>3</sub> Bi(OAc) <sub>2</sub>	5 min.	100	
4	Ph <sub>3</sub> BiCO <sub>3</sub>	3 hours	100	
5		∫ 5 min.	80	
		24 hours	90	
6	$Ph_{3}Bi(OSO_{2}CH_{3})_{2}$	5 min.	50	
7	Ph <sub>3</sub> Bi(OSO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> - <i>p</i> CH <sub>3</sub> ) <sub>2</sub>	5 min.	47	

Table 2: Examples of Mesidine Phenylation by Various Bi<sup>V</sup> Reagents.

a: Gas Chromatographic yields. For yields under 100%, the mass balance was accounted for as the unreacted starting material.

During the course of the phenylation process (presumably involving a transient high-valent copper species that results from an *in situ* oxidation by  $Bi^{V}$ ), the concomitant liberation of the acid salt originally bound to bismuth is observed (Scheme 2). Depending on the pKa values of these ligands (XH / X<sup>-</sup>), the remaining starting amine may be protonated, thus inhibiting further reaction (Table 3). In accordance with these mechanistic considerations, the utilization of an appropriate base would therefore allow the efficient phenylation of more basic amines.

$$R_{1}R_{2}NH + Ar_{3}BiX_{2} + CuY_{m} - \frac{CH_{2}Cl_{2}}{r.t.} \begin{bmatrix} R_{1}R_{2}NH & Ar \\ R_{1}R_{2}NH & In \\ X & Y_{m} \end{bmatrix}$$

$$R_{1}R_{2}N-Ar + Ar_{2}BiX + CuY_{m} + XH$$

Scheme 2

To confirm the above hypothesis, phenylation experiments were conducted using aniline as a model substrate. Whereas the yield obtained in entry 3 (Table 3) is quantitative, the large difference between the pKa values of aniline and tosic acid (expelled from  $Ph_3Bi(OTos)_2$ ) (entry 1) does not permit more than 50% conversion. The addition of one equivalent of *N-tert*-butyl-*N'-N''*-tetramethylguanidine (BTMG)<sup>12</sup> (entry 2) increased the yield of the arylation to 80%. The same holds true for the more basic dibutylamine (entries 4 and 5), except that a stronger base (*e.g.* KH) was necessary to ensure a quantitative yield of phenylated product. When the reaction does not go quantitatively (*cf.* entry 1), we were able to detect the formation of by-products (*e.g.* Ph-OPiv and Ph-OTos) which may arise from a reductive ligand coupling from the transient high-valent copper.

A blank experiment, involving  $Ph_3Bi(OTos)_2$  and  $Cu(OPiv)_2$  without amine, led to the exclusive formation of these by-products in high yield. The remaining copper was identified by titration<sup>13</sup> as a cuprous salt. Furthermore, when the same blank experiment was performed under an oxygen atmosphere, the degradation of both reagents (Bi and Cu) was totally curtailed. From these observations, it appears reasonable that the well-established Cu<sup>1</sup> / Cu<sup>III</sup> transition<sup>14</sup> is participating in this process.

The latter notwithstanding, only trace amounts of  $Cu^{I}$  were detected in the experiment reported in entry 1 and no significant efficiency changes were detected when bubbling  $O_2$  through the reaction mixture. The system apparently behaves differently in the presence of an amine - a manifold other than the aforementioned  $Cu^{I}/Cu^{II}$  is probably active.

Entry	Amine (pKa)	<b>Bismuth Derivative</b>	Base	Ligand (pKa)	Products	Yield <sup>a</sup> (%)
1	Ph-NH <sub>2</sub> (4.7)	Ph <sub>3</sub> Bi(OTos) <sub>2</sub>		TsOH (-6.5)	$Ph_2$ -NH + $Ph$ -NH <sub>3</sub> <sup>+</sup>	50
2	Ph-NH <sub>2</sub> (4.7)	Ph <sub>3</sub> Bi(OTos) <sub>2</sub>	BTMG	TsOH (-6.5)	Ph <sub>2</sub> -NH + BTMGH⁺	80
3	Ph-NH <sub>2</sub> (4.7)	Ph <sub>3</sub> Bi(OAc) <sub>2</sub>		AcOH (4.8)	Ph <sub>2</sub> -NH + AcOH	100
4	<i>n</i> -Bu₂NH (11)	Ph <sub>3</sub> Bi(OAc) <sub>2</sub>		AcOH (4.8)	<i>n-</i> Bu <sub>2</sub> N-Ph + <i>n</i> -Bu <sub>2</sub> NH <sub>2</sub>	+ 45
5	<i>п</i> -Ви <sub>2</sub> NH (11)	Ph <sub>3</sub> Bi(OAc) <sub>2</sub>	кн	AcOH (4.8)	n-Bu₂N-Ph + H₂	100

Table 3: Comparative pKa Values of Amines and Ligands Involved in the Cu<sup>II</sup> Catalyzed Phenylation Process.

a: Gas Chromatographic yields of phenylated product.

With these results in hand, we examined (Table 4) the reaction of various amines with  $Ph_3Bi(OAc)_2$  /  $Cu(OPiv)_2$  in the presence of an appropriate base (when required). The phenylation of aromatic amines, including the hindered examples, is particularly efficient (entries 1, 2, 3) and does not require the use of a base. The diphenylation of these amines works equally well (*cf. N*-phenyl phenethylamine, entry 6). However, with diphenylamine itself, the transformation was less effective (entry 8). The use of KH in this particular case did not increase the phenylation yield.

For the aliphatic amines, potassium hydride is in most cases necessary to effect a complete reaction (entries 4, 5, 7). A blank experiment performed under the same conditions, but without copper (entry 7\*), did not give satisfactory yields of the expected product. This shows the superiority of the copper-catalyzed system over the anionic chemistry that can be associated with bismuth<sup>V</sup>. The reaction could even be extended to the highly hindered aliphatic *t*-butyl amine in 100% yield (entry 9). A previous attempt failed.<sup>4a)</sup>

	R₁R₂NH +	Ph <sub>3</sub> Bi(OAc) <sub>2</sub>	Cu <sup>ll</sup> (OPiv)₂ cat. ►	- R₁R₂N-Ph	
Entry	Amine	Base	React. Time	Product <sup>a</sup>	Yield <sup>b</sup> (%)
1	Ph-NH <sub>2</sub>		5 min.	Ph <sub>2</sub> -NH	100
2			5 min.		100
3			5 min.		9h 100
4		{ { кн	{ 12 hours 3 hours		Ph { 66 100
5		{ кн	12 hours 3 hours		100 Ph 100
6			1 hour		100 Ph <sub>2</sub>
7	ռBu₂NH	{ {кн кн	{ 12 hours 3 hours 3 hours	<i>n</i> -Bu₂NPh	{ 45 63* 100
8	Ph <sub>2</sub> NH		1 hour	Ph <sub>3</sub> N	45
9		кн	3 hours		100

**Table 4:** Examples of Phenylation of Amines under Various Conditions.

a: For data of known compounds, see ref.19. b: Gas Chromatographic yields. \*: This experiment was conducted without copper<sup>II</sup> pivalate.

When working with a stoichiometric amount of cupric pivalate and more than one equivalent of amine, we sometimes obtained yields in excess of the theoretical amount with respect to the Bi<sup>V</sup> species assuming the transfer of only one phenyl group per mole of reagents. Therefore, the second phenylation must result from trivalent bismuth. As dismutation of Ph<sub>2</sub>Bi(OAc) yields Ph<sub>3</sub>Bi,<sup>15</sup> the increased yields may be vindicated by invoking Ph<sub>3</sub>Bi as the active species in the presence of cupric salts. Indeed, we have already noted that Ph<sub>3</sub>Bi was an efficient reagent for the phenylation of amines using stoichiometric amounts of cupric acetate.<sup>16</sup> Furthermore, trialkylbismuth and diphenylalkylbismuth reagents can readily alkylate amines with Cu(OAc)<sub>2</sub><sup>17</sup> catalysis. Also, Cu<sup>II</sup> catalyzes the ethylation of amines in the presence of diethylaluminum chloride.<sup>10</sup>

In conclusion, we have shown that bismuth reagents arylate aliphatic and aromatic amines with cupric pivalate and a suitable base with high efficiency.

### **EXPERIMENTAL**

General : Melting points were determined on a Thomas-Hoover microscope and are uncorrected. Infrared (IR) spectra were recorded on an ATI Mattson Genesis series FT-IR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian XL-200E spectrometer at frequencies of 200 and 50 MHz, respectively. Chemical shifts are reported in parts per million (ppm) and coupling constants are in Hz. <sup>1</sup>H NMR spectra were referenced to tetramethylsilane ( $\delta = 0.0$  ppm), whereas the residual solvent peak was used as an internal reference for <sup>13</sup>C NMR spectra. Microanalyses were performed by Atlantic Microlab, Inc. of Norcross, Georgia. Flash column chromatography was performed on Baxter S/P brand silica gel (60Å, 230-400 mesh). Gas Chromatographic analysis was performed on a Hewlett Packard 5890 series II instrument equipped with flame ionization detector and with a Hewlett Packard 3396A integrator. N<sub>2</sub> was used as the carrier gas. The columns used were either a DB-WAX (30 m × 0.32 mm × 0.25 µm) or a DB-1 (15 m × 0.32 mm × 0.25 µm) from J&W Scientific. All reactions were performed in a flame-dried flask using anhydrous solvents: CH<sub>2</sub>Cl<sub>2</sub> and THF were dried by distillation over calcium hydride and over sodium, respectively. In selected cases the phenylated amines were isolated by SiO<sub>2</sub> flash chromatography.

Preparation of  $Ph_3Bi(OAc)_2$ . This compound was prepared by a procedure that was modified from that published by Sinclair.<sup>8</sup> To a solution of Ph<sub>3</sub>Bi (15 g, 34 mmol, 1 eq.) in 100 mL CH<sub>2</sub>Cl<sub>2</sub> / THF (7/3) at 0°C was added dropwise CH<sub>3</sub>CO<sub>3</sub>H (8.6 mL of a 32% soln. in CH<sub>3</sub>CO<sub>2</sub>H, 1.2 eq.). The mixture was stirred at r.t. for 1 hour. Et<sub>2</sub>O (100 mL) was then added and the precipitate was filtered, washed with Et<sub>2</sub>O, collected, and recrystallized from CH<sub>2</sub>Cl<sub>2</sub> to give Ph<sub>3</sub>Bi(OAc)<sub>2</sub> (14.6 g, 77%) (m.p. 192-194°C, pale yellow crystals). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.82 (s, 6H), 7.45-7.59 (m, 9H), 8.15 (d, J = 8.1 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$ 

21.9, 130.6, 131.1, 133.9, 160.9, 178.0. IR (KBr): cm<sup>-1</sup> 1588, 1470, 1437, 1331, 984, 731.

Preparation of  $Ph_3Bi(OC(O)-C_6H_4-pNMe_2)_2$ : To a suspension of  $Ph_3BiCO_3^{3a}$  (1 g, 2 mmol, 1 eq.) in 20 mL THF was added 4-dimethylaminobenzoic acid (0.68 g, 2.05 eq.). The suspension was stirred overnight at room temperature, filtered, washed with THF, collected, and recrystallized from  $CH_2Cl_2$  / pentane to give  $Ph_3Bi(OC(O)-C_6H_4-pNMe_2)_2$  (1 g, 68%) (m.p. 171°C, yellow crystals).

<sup>1</sup>**H** NMR (CDCl<sub>3</sub>):  $\delta$  2.95 (s, 12H), 6.57 (d, J = 9 Hz, 4H), 7.37 (m, 3H), 7.51 (m, 6H), 7.87 (d, J = 9 Hz, 4H), 8.29 (d, J = 8.3 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  40.1, 110.5, 120.3, 130.2, 130.9, 131.6, 133.9,

152.6, 161.9, 173.0. **IR** (**KBr**): cm<sup>-1</sup> 1559, 1549, 1521, 1437, 1302, 1186, 781. **Anal:** Calcd for C<sub>36</sub>H<sub>35</sub>BiN<sub>2</sub>O<sub>4</sub>: C, 56.25; H, 4.59; N, 3.64. Found: C, 55.69; H, 4.68; N, 3.49.

Preparation of  $Ph_3Bi(OPiv)_2$ : To a suspension of  $Ph_3BiCO_3$  (2 g, 4 mmol, 1 eq.) in 40 mL CH<sub>2</sub>Cl<sub>2</sub> was added pivalic acid (0.96 mL, 2.1 eq.). The solution was stirred at r.t. for 1 hour and the solvent was removed *in vacuo*. The residue was recrystallized from CH<sub>2</sub>Cl<sub>2</sub> (2.1 g, 76%) (m.p. 130°C, colorless crystals).

<sup>1</sup>**H** NMR (CDCl<sub>3</sub>):  $\delta$  0.95 (s, 18H), 7.39-7.58 (m, 9H), 8.13 (d, J = 8.2 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  27.6, 38.8, 130.3, 130.7, 133.8, 161.3, 184.6. IR (KBr): cm<sup>-1</sup> 2952, 1594, 1474, 1438, 1341, 732. Anal: Calcd for C<sub>28</sub>H<sub>33</sub>BiO<sub>4</sub>: C, 52.34; H, 5.18. Found: C, 52.44; H, 5.17.

A general procedure for the preparation of  $Ph_3Bi(OC(O)CF_3)_2$ ,<sup>18</sup>  $Ph_3Bi(OTos)_2$ ,<sup>3a)</sup> and  $Ph_3Bi(OMes)_2$ is given for the latter: To a solution of  $Ph_3Bi(OAc)_2$  (1 g, 1.79 mmoles, 1 eq.) in 18 mL anhydrous  $CH_2Cl_2$ was added  $CH_3SO_3H$  (0.26 mL, 2.2 eq.) at room temperature. The reaction was stirred overnight and the volatiles were removed *in vacuo*. The crude product was then recrystallized from  $CH_2Cl_2$ , over which hexanes had been layered, to afford  $Ph_3Bi(OSO_2CH_3)_2$  (0.92 g, 82%) (m.p. 166-170°C, colorless crystals).

<sup>1</sup>**H** NMR (CDCl<sub>3</sub>):  $\delta$  2.41 (s, 6H), 7.60 (t, J = 7.3 Hz, 3H), 7.78 (dd, J = 7.3 Hz and 8.5 Hz, 6H), 8.23 (d, J = 8.5 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  39.8, 132.4, 132.7, 134.7, 157.1. IR (KBr): cm<sup>-1</sup> 1468, 1438, 1282, 984, 930, 725. Anal: Calcd for C<sub>20</sub>H<sub>21</sub>BiO<sub>6</sub>S<sub>2</sub>: C, 38.10; H, 3.36; S, 10.17. Found: C, 38.00; H, 3.34; S, 10.10.

A general procedure for the arylation of weakly basic amines is given for the phenylation of 2,6-diisopropyl aniline: To a solution of 2,6-diisopropyl aniline (0.1 g, 1 mmol, 1 eq.) and  $Cu(OPiv)_2$  (0.03 g, 0.1 eq.) in 10 mL CH<sub>2</sub>Cl<sub>2</sub> was added in one portion Ph<sub>3</sub>Bi(OAc)<sub>2</sub> (0.62 g, 1.1 eq.). The reaction was stirred at r.t. for 5 min. An aliquot was then taken from the reaction mixture and poured into a 3N HCl soln. After basification (3N NaOH soln.) and extraction (AcOEt), the sample was analyzed by GC in the presence of an appropriate standard (naphthalene).

Colorless crystals, m.p. 45°C. **HRMS(FAB)** calcd. for  $C_{18}H_{23}N$  (M<sup>+</sup>): 253.1830, found; 253.1840. <sup>1</sup>**H NMR** (**CDCl**<sub>3</sub>):  $\delta$  1.12 (d, J = 6.9 Hz, 12H), 3.19 (m, 2H), 5.09 (br.s, 1H), 6.46 (d, J = 7.4 Hz, 2H), 6.69 (m, 1H), 7.08-7.27 (m, 5H). <sup>13</sup>**C NMR** (**CDCl**<sub>3</sub>):  $\delta$  23.8, 28.2, 112.9, 117.6, 123.8, 127.2, 129.1, 135.1, 147.5, 148.1. **IR** (**KBr**): cm<sup>-1</sup> 3397, 2961, 1602, 1497, 1305, 746.

A general procedure for the arylation of stongly basic amines is given for the phenylation of tert-butylamine: To a solution of oil-free KH (0.1 g, 2.5 eq.) in 8 mL THF was added a solution of tert-butylamine (0.073 g, 1 mmol, 1 eq.) in 2 mL THF. After 5 min.,  $Cu(OPiv)_2$  (0.03 g, 0.1 eq.) was added to the reaction mixture followed by  $Ph_3Bi(OAc)_2$  (0.62 g, 1.1 eq.). The reaction was stirred for 3 hours at r.t. An aliquot was then taken from the reaction mixture and poured into a 3N HCl soln. After basification (3N NaOH soln.) and extraction (AcOEt), the sample was analyzed by GC in the presence of an appropriate standard (naphthalene). **HRMS(FAB)** calcd. for  $C_{10}H_{16}N$  (M + H<sup>+</sup>): 150.1283, found; 150.1278. <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.33 (s, 9H), 3.22 (br.s, 1H), 6.72-6.76 (m, 3H), 7.11-7.19 (m, 2H). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  30.0, 51.4, 117.4, 118.3, 128.8, 146.8. **IR (neat):** cm<sup>-1</sup> 3406, 2932, 1601, 1497, 1320, 694. Acknowledgments: We thank Schering-Plough, Unilever, and Merck Research Labs. for their timely support of this work. We also thank Dr. R. N. Young for his interest in this work.

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