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N- and *O*-arylation with triphenylantimony *ortho*-phenylenedioxides

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2,2,2-Triphenyl-1,3,2-benzodioxastibolanes react with alcohols, phenols, and amines in the presence of copper salts to give the corresponding *O*- and *N*-phenyl derivatives. Cyclic Sb^V dialkoxide containing an electron-withdrawing nitro group in the dioxastibolane fragment is most reactive in *N*-phenylation of primary and secondary amines. Organoantimony analogs containing electron-donating groups are more efficient in *O*-phenylation of primary and secondary alcohols and phenols.

Key words: *N*-arylation, *O*-arylation, dioxastibolanes, triphenylantimony, copper diacetate, amines, alcohols, phenols.

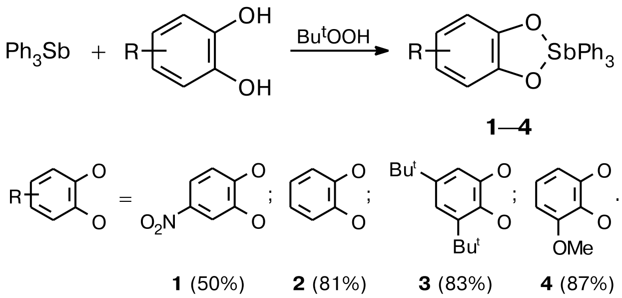
Reductive coupling reactions involving organic derivatives of Subgroups IIIa—VIIa *p*-elements of the Periodic Table has found wide use in organic synthesis for *C*-, *O*-, *N*- and S-alkylation, vinylation, alkynylation and arylation.[1] A broad spectrum of synthetic potentialities of this method, high regioselectivity of reactions, and mild reaction conditions made reductive coupling attractive for functionalization of some physiologically active molecules.[2] Moreover, using non-transition element derivatives for arylation makes it possible to introduce into organic substrates both aromatic fragments containing neutral and electron-withdrawing substituents and donating aryl groups; this significantly extends the range of arylation methods based on cross-coupling in the coordination sphere of transition metals.[3]

Among non-transition elements, antimony compounds as arylating agents are less known. To date, these derivatives have been involved only in *O*-arylation reactions. It was shown[4] that triphenylantimony reacts with primary and secondary alcohols in the presence of copper diacetate or dipelargonate in air to give alkyl phenyl ethers in good yields. Reactions of alcohols with triphenylantimony diacetate and an excess of copper diacetate afford alkyl phenyl ethers in 65% yields.[5] In addition, pentaphenylantimony can serve as *O*-phenylating agent in the presence of copper salts.[6]

The goal of the present work was to study the effect of the dialkoxide fragment in triphenyldioxastibolanes on *N*-phenylation of amines and *O*-phenylation of alcohols and phenols.

We synthesized four dioxastibolanes **1—4** from triphenylantimony and the corresponding 1,2-dihydroxybenzenes in the presence of *tert*-butyl hydroperoxide (Scheme 1).[7] Nonsubstituted pyrocatechol and its derivatives containing either electron-donating (methoxy and *tert*-butyl) or electron-withdrawing (4-nitro) groups were used as aromatic diols.

Scheme 1



The dioxastibolanes synthesized were tested in *N*- and *O*-phenylation of amines and alcohols, respectively (Scheme 2; Tables 1, 2).

The substrates in *N*-phenylation were isopropylamine, isobutylamine, diethylamine, and dibutylamine (see Table 1). In almost all the reactions, triphenylantimony dioxastibolanes proved to be less reactive than the diacyl derivatives of triphenylantimony and triphenylbismuth.[1,5] Nitrobenzodioxastibolane revealed itself the most reac-

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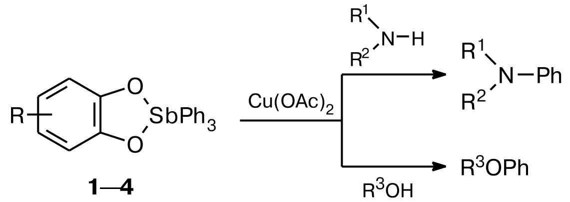
Scheme 2



$R^1 = H$, $R^2 = Pr^i$; $R^1 = H$; $R^2 = Bu^i$; $R^1 = R^2 = Et$, Bu
$R^3 = Me$, Et, Pr^i, Bu^t, Ph

tive, while dioxastibolanes **3** and **4** containing electron-donating *tert*-butyl and methoxy groups were the least reactive.

Primary amines were found to be more reactive than secondary ones, which is probably due to steric effects. The higher yields of arylation products from isobutylamine compared to isopropylamine (see Table 1) can be explained by a higher reaction temperature for the former (60 °C), while the reaction with isopropylamine (b.p. 34 °C) was carried out at 30 °C.

Methanol, ethanol, propan-2-ol, *tert*-butyl alcohol, and phenol were used as substrates for *O*-phenylation. In these reactions, stibolanes were found to be inversely reactive (see Table 2) with reference to *N*-phenylation of amines. Thus, Sb^V derivatives with donating methoxy and *tert*-butyl groups in the dialkoxide fragment were the most reactive in *O*-phenylation.

Table 1. Yields of the products for *N*-phenylation of amines with a triphenylantimony dioxastibolane—Py—$Cu(OAc)_2$ system (1 : 2 : 1) with amines as solvents (60 °C, 15 h)

Substrate	Product	Yield (%)			
		1	**2**	**3**	**4**
Pr^iNH_2*	Pr^iNHPh	42	22	31	24
Bu^iNH_2	Bu^iNHPh	87	64	33	20
Et_2NH	Et_2NPh	43	22	16	12
Bu_2NH	Bu_2NPh	26	8	9	5

* The reaction was carried out at 30 °C.

Table 2. Yields of the products for *O*-phenylation of hydroxy-containing substrates with a triphenylantimony dioxastibolane—Py—$Cu(OAc)_2$ system (1 : 2 : 1) with alcohols as solvents (60 °C, 15 h)

Substrate	Product	Yield (%)			
		1	**2**	**3**	**4**
MeOH	MeOPh	17	30	57	40
EtOH	EtOPh	38	29	48	51
Pr^iOH	Pr^iOPh	14	19	36	30
Bu^tOH	Bu^tOPh	—	—	Traces	5
MeOH*	MeOPh	3	4	6	5
EtOH*	EtOPh	6	10	7	13
PhOH*	PhOPh	25	25	38	35

* The reaction was carried out in THF with 4 equiv. of the corresponding alcohol or phenol.

Primary alcohols (methanol and ethanol) were *O*-phenylated more easily than secondary and tertiary analogs. In the latter case, *tert*-butyl phenyl ether as a reaction product was detected only in trace amounts (see Table 2).

The yields of the phenylation products from methanol, ethanol, and phenol taken in stoichiometric amounts strongly depend on the substrate acidity (see Table 2).

Note that in the absence of copper diacetate, neither *N*- nor *O*-phenylation products were detected in reaction mixtures. Therefore, *N*- and *O*-arylation involving cyclic Sb^V dialkoxides should include a transmetalation step at which the aryl fragment is transferred from the antimony atom to the copper atom.[8] Reactivity inversion in *N*- and *O*-arylation for stibolanes containing electron-donating and -withdrawing groups in the dialkoxide fragment suggests that transmetalation is preceded by the formation of different organoantimony intermediates.

An intermediate in *N*-phenylation is a donor—acceptor hexacoordinated antimony complex with an amine to be arylated. This assumption is consistent with literature data.[9] In this case, transmetalation can be facilitated by a nitrogen—antimony coordination bond; the strongest N→Sb bond will be formed by a stibolane containing an electron-withdrawing group in the dialkoxide fragment.

In *O*-phenylation with triphenylantimony *ortho*-phenylenedioxides, cyclic dialkoxides can undergo reversible opening into acyclic dialkoxides by analogy with hydrolysis[10] or solvolysis of substituted pentaarylantimony.[11] Obviously, this equilibrium will be shifted to acyclic dialkoxides for 3-methoxy- and 3,5-di-*tert*-butylbenzodioxastibolanes because the corresponding pyrocatechols are less acidic than nonsubstituted pyrocatechol and its 4-nitro derivative. This is indicated by reduced yields of phenylation products when an alcohol is taken in a stoichiometric amount. Moreover, this assumption is confirmed by thermal decomposition data for acyclic Sb^V dialkoxides.[11a,b] These compounds decompose into ethers at 200—220 °C.[11a,b] Thermal decomposition is substantially facilitated by copper salts.[1c]

Thus, we showed for the first time that antimony derivatives can be used for *N*-arylation. Primary and secondary amines are most easily *N*-phenylated with the dioxastibolane containing a nitro group in the dialkoxide fragment. In contrast, cyclic Sb^V dialkoxides bearing electron-donating groups are most reactive in *O*-phenylation of primary and secondary alcohols, as well as phenol.

Experimental

^{1}H and ^{13}C NMR spectra were recorded on a Bruker DPX-200 spectrometer; chemical shifts are given on the δ scale (ppm) relative to Me$_4$Si. IR spectra were recorded on a Specord 75IR spectrometer (Vaseline oil in thin film). Chromatographical analysis was carried out on a Tsvet 2-65 instrument with an internal standard. The reaction products Pr^{i}NHPh, Bu^{i}NHPh, Et$_2$NPh, Bu$_2$NPh, and PhOPh were identified on a column 240×0.2 cm (Chromaton *N*-AW with 15% Apiezon L) at a thermostat temperature of 160, 160, 165, 230, and 220 °C, respectively. The reaction products MeOPh, EtOPh, Pr^{i}OPh, and Bu^{t}OPh were identified on a column 240×0.2 cm (Inerton with 5% OV-17) at a thermostat temperature of 80, 100, 125, and 150 °C, respectively. Commercially available Pr^{i}NHPh, Bu^{i}NHPh, Et$_2$NPh, Bu$_2$NPh, MeOPh, EtOPh, Pr^{i}OPh, Bu^{t}OPh, and PhOPh were used as reference compounds for GLC.

Triphenylantimony 4-nitrophenylene-1,2-dioxide (1). *tert*-Butyl hydroperoxide (0.42 g, 4.7 mmol) in 10 mL of benzene was slowly added for 40 min to a stirred and ice-cooled mixture of triphenylantimony (1.48 g, 4.2 mmol) and 1,2-dihydroxy-4-nitrobenzene (0.65 g, 4.2 mmol) in 30 mL of benzene. After the reaction was completed, highly volatile products were collected in a trap under reduced pressure. The solid residue was recrystallized from a benzene—hexane mixture to give compound **1** (1.06 g, 50%), m.p. 145 °C (*cf.* Ref. 12: m.p. 144—146 °C).

Triphenylantimony *o*-phenylenedioxide (2) was synthesized as described above. The yield of **2** was 81%, m.p. 144 °C (*cf.* Ref. 7: m.p. 144 °C).

Triphenylantimony 3,5-di-*tert*-butylphenylene-1,2-dioxide (3)^{13} was synthesized as described above. The yield of compound **3** was 83%, m.p. 77 °C. Found (%): C, 67.35; H, 5.98; Sb, 21.51. C$_{32}$H$_{35}$O$_2$Sb. Calculated (%): C, 67.03; H, 6.15; Sb, 21.23. ^{1}H NMR (CDCl$_3$), δ: 1.28 (s, 9 H, Me); 1.57 (s, 9 H, Me); 6.71 (s, 1 H, H(4)); 6.95 (s, 1 H, H(6)); 7.40—7.51 (m, 9 H, H(3´), H(4´) and H(5´)); 7.71—7.81 (m, 6 H, H(2´) and H(6´)). ^{13}C NMR (CDCl$_3$), δ: 29.7 and 31.8 (C($\underline{\text{C}}\underline{\text{H}}_3$)$_3$); 34.4 and 34.7 ($\underline{\text{C}}Me_3$); 107.8 and 112.5 (C(3) and C(5)); 129.2 (C(3´) and C(5´)); 131.1 (C(4´)); 133.2 (C(4)); 135.1 (C(2´) and C(6´)); 137.9 (C(1´)); 139.5 (C(6)); 143.0 and 146.6 (C(1) and C(2)).

Triphenylantimony 3-methoxyphenylene-1,2-dioxide (4) was synthesized as described above. The yield of compound **4** was 87%, m.p. 101 °C. Found (%): C, 61.32; H, 4.51; Sb, 24.42. C$_{25}$H$_{21}$O$_3$Sb. Calculated (%): C, 61.13; H, 4.31; Sb, 24.79. ^{1}H NMR (CDCl$_3$), δ: 3.89 (s, 3 H, Me); 6.40 (dd, 1 H, H(4), J_1 = 7.8 Hz, J_2 = 1.9 Hz); 6.53—6.69 (m, 2 H, H(5) and H(6)); 7.30—7.56 (m, 9 H, H(3´), H(4´) and H(5´)); 7.68—7.81 (m, 6 H, H(2´) and H(6´)). ^{13}C NMR (CDCl$_3$), δ: 56.3 (OMe); 103.4 and 106.4 (C(4) and C(6)); 116.9 (C(5)); 129.3 (C(3´) and C(5´)); 131.3 (C(4´)); 135.0 (C(2´) and C(6´)); 137.3 (C(3)); 146.7 and 148.4 (C(1) and C(2)). IR, ν/cm^{-1}: 450, 460 (Sb—Ph); 605 (Sb—O); 1210 and 1230 (C—O).

***N*- and *O*-phenylation with amines and alcohols as solvents (general procedure).** An alcohol or an amine (3 mL), pyridine (0.9 mmol), Cu(OAc)$_2$ (0.45 mmol), and an appropriate dioxastibolane (0.45 mmol) were placed in a round-bottomed flask. The reaction mixture was stirred at 60 °C for 15 h. After the reaction was completed, the solution was filtered through a porous filter. Highly volatile products were distilled off the mixture under reduced pressure. The organic derivatives were identified by GLC.

***O*-Phenylation with stoichiometric amounts of alcohols and phenol (general procedure).** Ethanol or methanol (0.90 mmol), pyridine (0.90 mmol), Cu(OAc)$_2$ (0.45 mmol), and an appropriate dioxastibolane (0.45 mmol) were placed in a round-bottomed flask. The reaction mixture was stirred in THF (3 mL) at 60 °C for 15 h. After the reaction was completed, the solution was filtered through a porous filter. Highly volatile products were distilled off the mixture under reduced pressure. The organic derivatives were identified by GLC.

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