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Electrochemistry of hypervalent compounds—V. Anodic oxidation of trivalent organoantimony and organobismuth compounds

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Abstract—Anodic oxidation of triphenylantimony in the presence of various oxygen nucleophiles or halide ions provided the corresponding hypervalent compounds having Sb—Y bonds (Y = RCOO, F, Cl, Br) in good yields. On the contrary, anodic oxidation of triphenylbismuth gave only carbon–bismuth bond cleavage products. Cathodic reduction of anodically synthesized hypervalent organoantimony compounds was also investigated by cyclic voltammetry. © 1997 Elsevier Science Ltd.

Key words: Anodic acyloxylation, anodic fluorination, hypervalent compound, triphenylantimony, triphenylbismuth.

INTRODUCTION

Hypervalent compounds have unique molecular structures and they exhibit quite interesting reactivities [1–3]. Recently, hypervalent organoantimony and organobismuth compounds have been shown to be useful reagents for organic synthesis [4, 5]. Although the chemistry of hypervalent compounds has been intensively studied, only a few examples of electrosynthesis of hypervalent compounds have been reported to date [6].

From these viewpoints, we have recently studied anodic oxidation of organotellurium and organoiodine compounds in the presence of fluoride ions and we have found that hypervalent fluorinated tellurium and iodine products are formed in good yields [7–10]. These findings prompted us to study anodic oxidation of trivalent organoantimony and organobismuth in the presence of various nucleophiles. In contrast to organonitrogen and organophosphorous compounds, anodic oxidation of trivalent organoantimony and organobismuth compounds has been scarcely studied so far [11].

In this paper, we wish to report our attempts to electrosynthesize hypervalent antimony and bismuth compounds with M-halogen or M—O (M = Sb, Bi) bonds in one step under mild conditions. Triphenylantimony **1** and triphenylbismuth **2** were selected as model compounds in this study.

EXPERIMENTAL

Materials

Supporting electrolytes. $Et_3N\cdot3HF$, Et_4NCl, Et_4NBr, CH_3COOLi, CF_3COONa, and $HCOOLi\cdot H_2O$ were commercially available. $HCOOLi\cdot H_2O$ was dried under heating to remove crystalline water. PhCOOLi was prepared from PhCOOH and LiOH and dried under heating.

Substrates. Triphenylantimony **1** and triphenylbismuth **2** were purchased from Tokyo Kasei Co.

Solvents. Acetonitrile was refluxed in the presence of CaH_2 and then distilled in a stream of nitrogen. Methanol was refluxed in the presence of metallic sodium and then distilled. Acetic acid was commercially available and was used for the electrolysis without purification.

Electrolysis

An H-type glass cell with a glass frit disk diaphragm was used for the electrolysis. Anodic oxidation was carried out by the following procedure. The anolyte (17 ml) containing 2 mmol of **1** or **2** and a supporting electrolyte (0.6 M). A platinum plate ($5 \times 5\ cm^2$) and wire (0.8 mm × 10 cm) were used as

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an anode and cathode, respectively. Constant current electrolysis was carried out at ambient temperature in an atmosphere of nitrogen until the starting substrate **1** or **2** was consumed completely (monitored by TLC).

Separation and analysis of products.

After electrolysis, the anolyte was evaporated under reduced pressure and then mixed with water. Only when $Et_3N \cdot 3HF$ was used as a supporting electrolyte, the anolyte was neutralized with NH_4OH. The resulting mixture was extracted repeatedly with ether (**3a** and **3b**) or ethyl acetate and the combined extracts were washed with water and brine, and then dried over anhydrous $MgSO_4$. After removal of solvent, the remaining solid was recrystallized from ethanol. In the cases of **3c** and **4c**, after recrystallization as above, the residual ethanol solution was evaporated and the remaining residue was dissolved in hot hexane. The insoluble material was removed by filtration and the filtrate was evaporated under reduced pressure to provide additional pure **3c** and **4c**.

Triphenylantimony difluoride (**3a**) [12], dichloride (**3b**) [13], dibromide (**3c**) [13], diacetate (**4a**) [14], bis(trifluoroacetate) (**4b**) [14] were identical with authentic samples by comparison of their melting points and spectroscopic data.

Triphenylantimony diformate (**4d**). mp 140–141°C (Lit[15] 157–162°C). ^1H NMR($CDCl_3$), $\delta = 7.51–7.55$ (m, 9H, aromatic H), 7.98–8.05 (m, 6H, aromatic H), 8.10 (s, 2H, OCO*H*). MS, *m/e* 397 (M^+-OCOH).

Triphenylantimony dibenzoate (**4c**). mp 169–170°C. ^1H NMR($CDCl_3$), $\delta = 7.31–7.37$ [m, 5H, $Sb(C_6H_5)$], 7.42–7.50 [m, 10H, $Sb(C_6H_5)_2$], 7.92–7.95 [m, 4H, $(C_6H_5COO)_2Sb$], 8.1–8.15 [m, 6H, $(C_6H_5COO)_2Sb$]. MS, *m/e* 517 (M^+-Ph), 473 (M^+-OCOPh). Anal. Found: C, 64.53; H, 3.93%. Calcd for $C_{32}H_{25}O_4Sb$: C, 64.57; H, 4.23%.

RESULTS AND DISCUSSION

Oxidation potentials of group-15-compounds

The oxidation potentials of triphenylantimony **1** and triphenylbismuth **2** together with other triphenyl derivatives of group-15-compounds were measured by cyclic voltammetry using a platinum anode in 0.1 M $Et_4NOTs/MeCN$ containing 1 mM of the substrates at room temperature at 100 mV s^{-1} scan rate. Except for triphenylamine, these substrates showed irreversible anodic waves. The anodic peak potentials (E_p^{ox}) are summarized in Table 1. The oxidation potential increases in the order of $N < P < Sb < Bi \le As$ as shown in Table 1. The order of the oxidation potential is not the same as that of the ionization potentials of these elements [16]. This is in sharp contrast to the cases of group-14- and group-16-compounds [17, 18].

Table 1.
Oxidation potentials (peak potentials, E_p^{ox}) of Ph_3M[a]

M	E_p^{ox} (V vs *ssce*)	IP of M (eV)[b]
N	1.06	14.53
P	1.31	10.49
As	1.63	9.81
Sb	1.50	8.64
Bi	1.60	7.29

[a] Platinum anode; 0.1 M $Et_4NOTs/MeCN$; 1 mM Substrate; Scan rate: 100 mV s^{-1}.
[b] The first ionization potentials of elements M.

Table 2.
Anodic oxidation of triphenylantimony in the presence of halide ions

Run	Y	Charge passed (F mol^{-1})	Yield (%)
1	F[a]	1.9	**3a** 90
2	F[b]	2.6	**3a** 58
3	Cl[c]	2.6	**3b** 71
4	Br[d]	2.0	**3c** 72

[a] 0.6 M $Et_3N \cdot 3HF/MeCN$ was used.
[b] 0.6 M $Et_4NBF_4/MeCN$ was used.
[c] 0.6 M $Et_4NCl/MeCN$ was used.
[d] 0.6 M $Et_4NBr/MeCN$ was used.

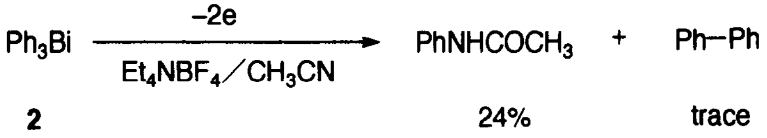
Macro-scale electrolysis of triphenylantimony 1 and triphenylbismuth 2

Next, anodic oxidation of **1** and **2** was carried out at a constant current in acetonitrile in the presence of halide ions. It was found that dihalogenation took place at the antimony atom selectively to provide the hypervalent antimony compounds **3** in good yields. In these cases, aromatic halogenation did not take place at all.

Previously, Nikitin *et al.* reported that constant current anodic oxidation of **1** in acetonitrile containing high concentration (1.2 M) of Et_4NBF_4 provided **3a** in almost quantitative yield [12]. In this case, however, a large amount of supporting electrolyte is necessary. When the lower concentration (0.6 M of Et_4NBF_4 was used, the yield of **3a** decreased to 58% (Table 2, run 2). On the contrary, the electrolysis using 0.6 M $Et_3N \cdot 3HF$ provided **3a** in much higher yield and with better current efficiency (run 1) compared with the case of Et_4NBF_4.

In sharp contrast to the case of **1**, triphenylbismuth **2** did not give any halogenated product regardless of the kind of halide ion. Instead of the desired hypervalent products, only carbon–bismuth bond cleavage products such as acetanilide and biphenyl were detected. Particularly when $Et_4NBF_4/MeCN$ was used as an electrolytic solution, appreciable amounts of acetanilide were formed from **2** as shown in Scheme 1.

Next, anodic oxidation of **1** was carried out in



Scheme 1.

Table 3.
Anodic oxidation of triphenylantimony in the presence of oxygen nucleophiles

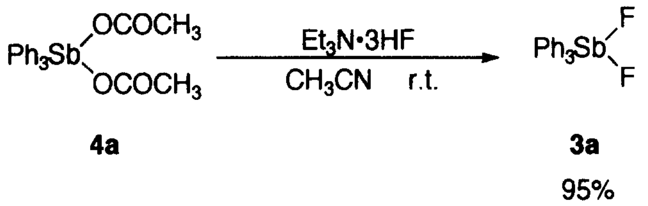
Run	R	M	Charge passed (F mol^{-1})	Yield (%)
1	CH_3	Li	3.1	**4a** 81
2[a]	CF_3	Na	2.2	**4b** 67
3	Ph	Li	5.5	**4c** 92
4	H	Li	4.0	**4d** 82

[a] CH_3OH/CH_3CN (9:1) was used as a solvent.

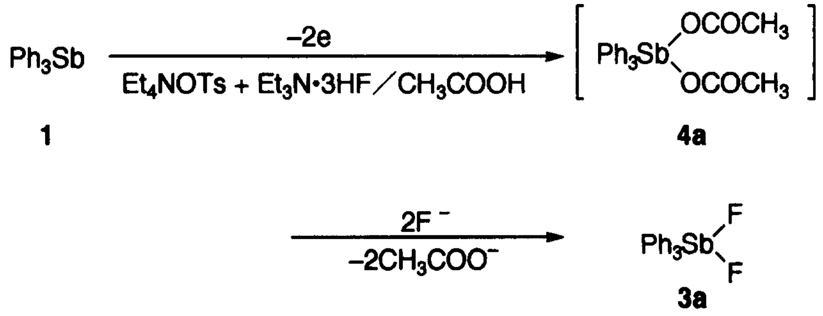
methanol containing various lithium or sodium carboxylates. Regardless of the kind of carboxylate, dicarboxylation took place selectively at the antimony atom to provide the corresponding hypervalent products in moderate to excellent yields as shown in Table 3. When benzoate and formate salts were used, a considerable amount of the products **4c** (*ca.* 40%) and **4d** (*ca.* 14%) was precipitated during the electrolysis. No aromatic carboxylation was observed in all cases. Therefore, this anodic carboxylation is highly selective as observed in the case of anodic dihalogenation of **1**. It is noted that methoxylation did not take place at all although methanol was used as a solvent. This is reasonable in consideration that electronegative ligands stabilize well hypervalent compounds [1].

It is known that the nucleophilicity of fluoride ions is extremely low compared to acetic acid. However, anodic oxidation of **1** in $Et_3N{\cdot}3HF/AcOH$ gave difluorinated product **3a** solely and no acetoxylated product **4a** was formed. When **4a** was treated with $Et_3N{\cdot}3HF$, the fluorinated product **3a** was formed almost quantitatively (Scheme 2). Such a ligand exchange reaction is characteristic of hypervalent compounds. Therefore, it is reasonable to assume that in acetic acid in the presence of fluoride ions, anodic acetoxylation takes place first at the antimony atom, and then exchange of the oxygen-ligands with fluoride ligands occurs in the course of the electrolysis to provide difluoro product **3a**, as shown in Scheme 3, since in general the more electronegative the ligand, fluorine stabilizes hypervalent compounds more strongly. A similar phenomenom was observed in the formation of hypervalent difluorinated organotellurium compounds by the anodic oxidation of tellurides in acetic acid containing $Et_3N{\cdot}3HF$ [7].

In contrast to the case of **1**, anodic oxidation of **2** in the presence of carboxylate ions did not give any isolated products. In this case, only polymerized products were formed and neither expected hypervalent products nor phenyl carboxylate was detected.



Scheme 2.



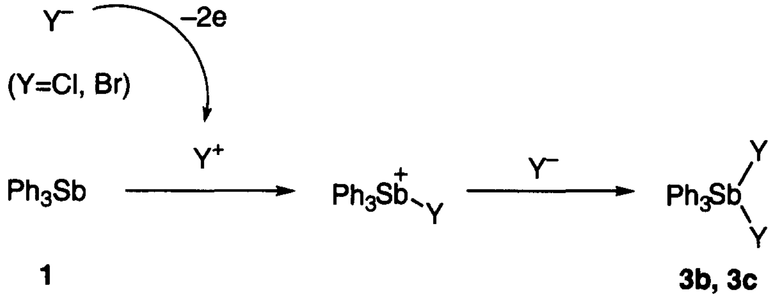
Scheme 3.

Reaction mechanism for the formation of hypervalent compounds.

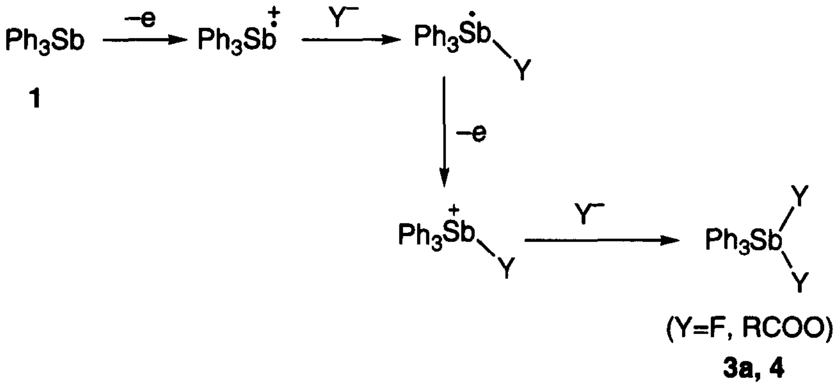
In consideration of the oxidation potentials of substrates (**1** and **2**) and nucleophiles, the formation of **3b** and **3c** should be initiated by discharge of chloride and bromide ions, respectively (Scheme 4). On the other hand, direct electron transfer from **1** should be an initial step in the formation of **3a** and **4** (Scheme 5) since the oxidation potentials of fluoride and carboxylate ions are higher than that of **1**.

The formation of acetanilide and biphenyl from **2** seems to proceed as illustrated in Scheme 6. After generation of a radical cation of **2**, carbon–bismuth bond cleavage should take place to form a phenyl radical, which provides biphenyl and acetanilide as the final products. In addition to this mechanism, in analogy to the reaction of triarylamines [19], one could also assume another mechanism like Scheme 7. However, the fate of the intermediate containing bismuth is unclear at the present time because unidentified polymerized products were always formed as major products and no isolable product containing bismuth was obtained in the anodic oxidation of **2**.

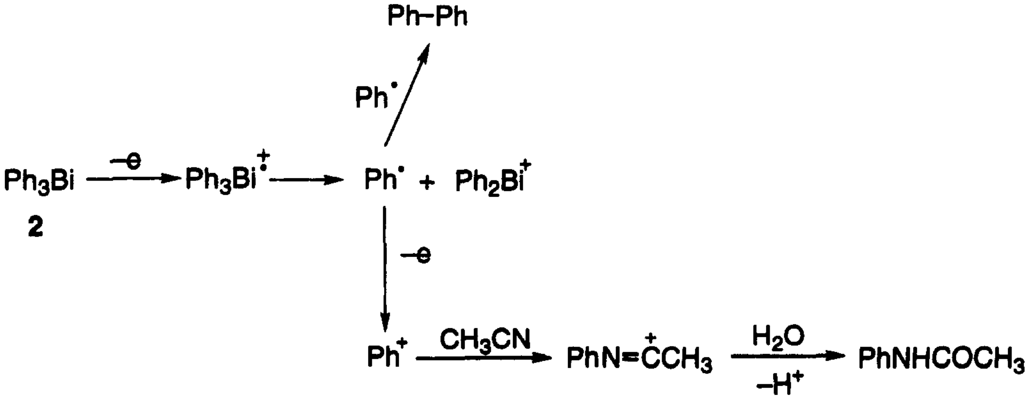
Triphenylantimony **1** gave the corresponding hypervalent products in good yields while triphenylbismuth **2** provided carbon–bismuth bond cleavage products regardless of nucleophiles. This seems to be



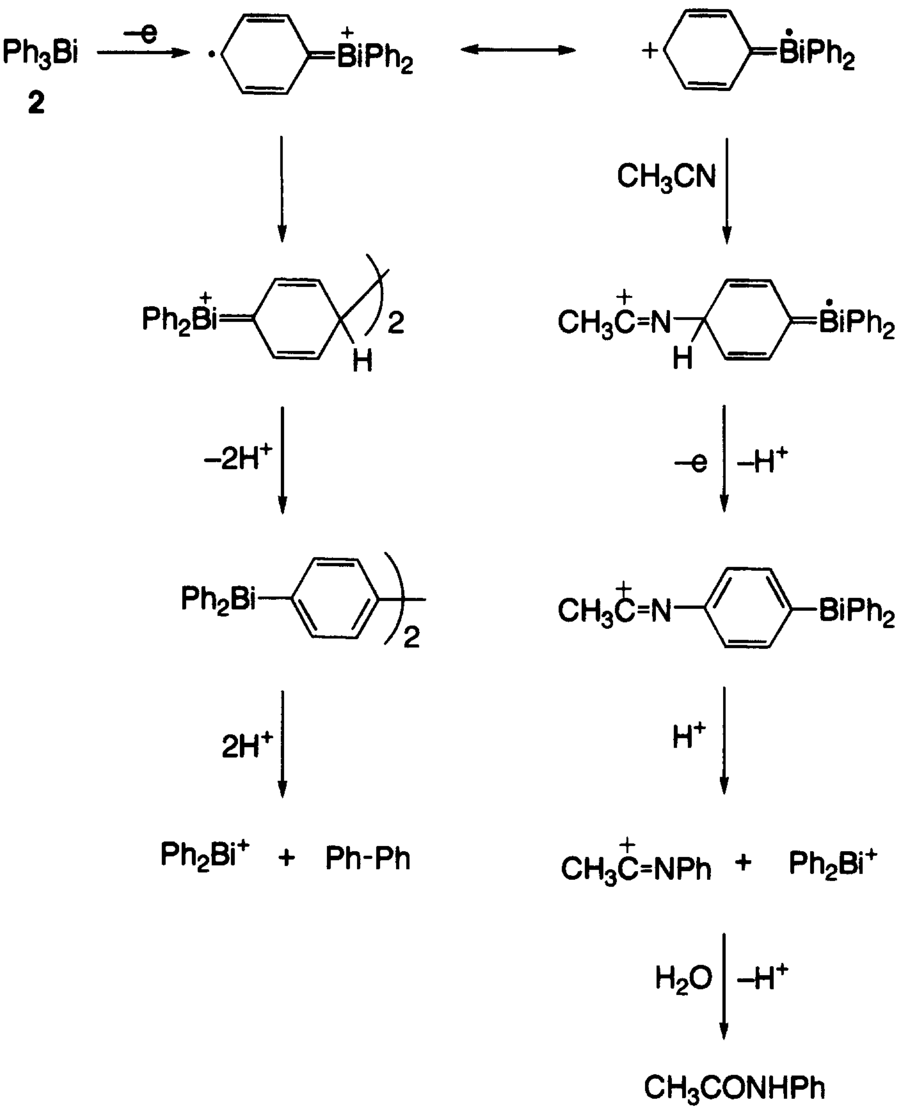
Scheme 4.



Scheme 5.



Scheme 6.



Scheme 7.

mainly attributable to the large different bond energies of C—Sb and C—Bi bonds (267 kJ mol^{-1} vs 200 kJ mol^{-1}).

Reduction potentials of hypervalent antimony compounds

Since electrochemical reduction of hypervalent compounds has been rarely studied [6, 7, 20], reduction potentials of **3** and **4** were measured by cyclic voltammetry. The cathodic peak potentials (E_p^{red}) are summarized in Table 4. In the case of halogenated hypervalent compounds **3**, the order of the reduction potential is Br < Cl < F and this is the same as that of electronegativities of halogen ligands. This order reflects the order of the stability of halogenated hypervalent compounds. A similar trend

Table 4.
Reduction potentials (peak potentials, E_p^{red}) of hypervalent antimony compounds [Ph_3SbY_2]

	Compound	
No.	Y	E_p^{red} (V vs *ssce*)
3a	F	− 2.26
3b	Cl	− 1.79
3c	Br	− 1.57
4a	CH_3COO	− 1.45
4b	CF_3COO	− 1.65
4c	PhCOO	− 2.28
4d	HCOO	− 2.29

Platinum cathode; 0.1 M Bu_4NClO_4/MeCN; 2 mM substrate; scan rate: 100 mV s^{-1}.

was observed in the case of fluorinated hypervalent tellurium compounds [6]. On the other hand, in the case of hypervalent compounds **4** bearing carboxylate ligands, the order of E_p^{red} is as follows: $CH_3COO < CF_3COO < PhCOO < HCOO$. The order of acidities of these ligands is as follows: $CH_3COO < PhCOO < HCOO < CF_3COO$. Since the latter order should reflect the order of the electron-withdrawing ability, *ie* electronegativity of carboxylate ligands, it is expected that hypervalent compound **4b** bearing trifluoroacetate ligands should be the most stable and should have the most negative reduction potential. However, the reduction potential of **4b** was less negative than expected. The reason is unclear at present.

CONCLUSIONS

It was found that anodic behaviour of organobismuth compound was quite different from that of organoantimony compound. We have demonstrated that the electrochemical method was useful for the preparation of hypervalent antimony compounds, similar to the case of organotellurium and organoiodine compounds as reported previously [7–10]. The chemical preparation of **3** and **4** requires hazardous halogen and a multisteps procedure [12–15], respectively, while electrochemical preparation does not require any hazardous reagents and can be performed in one step under mild conditions. Therefore, the electrochemical method seems to be superior to the conventional chemical method.

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