

## Direct Electrochemical Synthesis of Organobismuth Compounds and their coordination compounds

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### ABSTRACT

Organobismuth and organobismuth halides have been synthesized by electrolyzing the solutions of alkyl/aryl halides (bromoethane, 1-bromopropane, 1-chlorobutane and chlorobenzene) in acetonitrile at sacrificial bismuth anode. These organobismuth halides do not form coordination compounds when refluxed with ligands such as 1,10-phenanthroline and 2,2'-bipyridyl. However, coordination compounds of these organobismuth compounds have been synthesized by electrolyzing the solution of the above substrate in the presence of ligands in acetonitrile at sacrificial bismuth anode. All these products have been characterized by infrared spectral data, elemental analysis and various physical properties. Current efficiencies of all these systems are quite high.

**Keywords:** Coordination compounds, current efficiencies, electrosynthesis, H-type cell, organobismuth halides.

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### I. INTRODUCTION

Electrochemical technique is the direct route to carry out oxidation or reduction without introducing any foreign oxidizing or reducing agents. The most important advantage of this technique is the simplicity and high product yield. Electrochemical technique has widely been used in synthetic inorganic [1-5] and organic chemistry [6-10]. Organobismuth reagents are useful for the controlled arylation of enolic systems [11-12] and for organic synthesis [13-14]. So, in the present communication, we have extended the application of electrochemical methods to the synthesis of Organobismuth Compounds and their coordination compounds in high yield and in a one-step route.

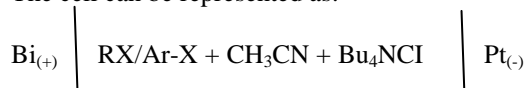
### II. EXPERIMENTAL

A H-type cell made of pyrex glass in which the cathode and anode compartments were separated from each other by a sintered glass disc of G-3 porosity, was used as the reaction vessel. Both compartments were provided with two openings; one for guard tube and the other for electrode. Platinum gauze (2.0x1.0x1.0 cm<sup>3</sup>) was used as cathode and bismuth rod (2.0x10.0x0.2 cm<sup>3</sup>) as anode. Direct current was obtained with the help of Toshniwal electrophoresis power supply. Acetonitrile was kept over phosphorus pentoxide for 24 h and then double distilled. Freshly distilled acetonitrile was used as solvent in all these reactions. Tetrabutylammonium chloride (Reidal pure) was

crystallized from conductivity water and dried under reduced pressure at 100°C. It was then used as supporting electrolyte in all these reactions.

The electrolytic solution in the anode compartment was stirred efficiently using magnetic stirrer. 2.0 mL of alkyl/aryl halide, 1.0 g of tetrabutylammonium chloride and 250 mL of freshly distilled acetonitrile were taken in the H-type cell. Bismuth metal electrode was dipped in anode compartment and platinum gauze in the cathode compartment and outlets were sealed after fitting the guard tubes. Necessary connections were made with power supply and potential across the electrodes was then adjusted so that a current of 20 mA passed through the solution.

The cell can be represented as:



Where:

RX/Ar-X is alkyl halide/aryl halide

Bi<sub>(+)</sub> is Bismuth anode.

Pt<sub>(-)</sub> is Platinum cathode.

Bu<sub>4</sub>NCl is supporting electrolyte.

The electrolysis was carried out with continuous stirring in the anode compartment. After conducting electrolysis for twelve hours, the product was filtered, washed with hot acetonitrile and dry ether and finally dried under vacuum. The current efficiencies (gram equivalents of metal dissolved

per faraday of electricity passed) of all these reactions were determined by electrolyzing the above systems for exactly two hours at a constant current of 20 mA as reported earlier[15]. Melting point of all these products was recorded using electrical device with heating rate of 5°C per minute. Infrared spectra of the products were recorded on Perkin-Elmer spectrophotometer (RXI) in the region of 4000-450 cm<sup>-1</sup> using potassium bromide pellets. The products were analyzed for bismuth contents. Weighed amount of the product was heated to dry mass with fuming nitric acid six times. The dry mass was dissolved in few drops of dilute nitric acid and 100 mL solution was made. The contents of bismuth in solution were estimated volumetrically by oxine method [16]. The microanalyses of C, H and X of these compounds have also been carried out.

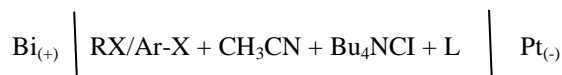
### II.I The coordination compounds of bismuth with alkyl/aryl halides

Electrochemically prepared organobismuth compounds have been refluxed with the ligand (1,10-phenanthroline or 2,2'-bipyridyl) in various solvents for 48 h in order to prepare coordination compounds of these organobismuth compounds. Analytical data and infrared spectral data of these products show that no coordination products have been formed. Therefore, in addition to the alkyl/aryl halide and supporting electrolyte, 1.0 g of the ligand was also added to these systems and the solution was then electrolysed at bismuth anode. The solid product separated in anode compartment was filtered, washed with dry ether and dried under vacuum. The analytical data (bismuth, carbon, hydrogen and halogen contents in all these products)

along with their electrolytic characteristics of these systems are summarized in Table 2 and Table 3.

The data conform to molecular formula (R)<sub>2</sub>BiX.L. The products obtained are insoluble in commonly used organic solvents. Melting point of all these products has also been determined. All these compounds do not melt up to 300°C, however, colour of these compounds changes around 240°C thereby indicating that these products decompose around this temperature.

The cell can be represented as:



Where:

RX/Ar-X is alkyl halide/aryl halide

Bi<sub>(+)</sub> is Bismuth anode.

Pt<sub>(-)</sub> is Platinum cathode.

Bu<sub>4</sub>NCl is supporting electrolyte.

L is 1,10-phenanthroline or 2,2'-bipyridyl

### III. RESULTS AND DISCUSSION

The products obtained are insoluble in commonly used organic solvents like chloroform, benzene, methanol, acetone, dimethyl sulphoxide, *N,N*-dimethyl formamide *etc.* All these compounds do not melt up to 300°C, however, colour of these compounds changes around 240°C thereby indicating that these products decompose around this temperature. The analytical data (bismuth, carbon, hydrogen and halogen contents in all these products) along with their electrolytic characteristics of these systems are summarized in Table I. Perusal of Table I reveals that the analytical data conform to the molecular formula (R)<sub>2</sub> BiX.

**Table - I: Electrolysis Characteristics, Analytical and other Related Data of Electrolytic Products of Alkylhalides/ Aryl halide Systems at Bismuth Anode**

System	Potential	Electricity Passed (Coulomb)	Product	Colour	Elemental Analysis Found/(Calc.)%				Current Efficiencies (Gram Equivalent/ Faraday)
					Bi	C	H	X	
Bromoethane	30	864	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> BiBr	Light brown	59.2 (60.2)	9.7 (13.8)	1.9 (2.7)	19.6 (22.4)	1.86
1- Bromopropane	40	864	(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> BiBr	Dark brown	54.5 (55.3)	16.5 (19.2)	3.1 (3.7)	21.3 (21.1)	1.45
1-Chlorobutane	50	864	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> BiCl	Light brown	57.3 (58.3)	22.8 (26.8)	3.4 (5.1)	6.9 (9.7)	0.97
Chlorobenzene	30	864	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> BiCl	Dark brown	51.4 (52.5)	34.8 (36.2)	2.7 (2.5)	4.2 (8.7)	0.84

Infrared spectra of the products have been recorded using potassium bromide pellets in the region of 4000 – 400 cm<sup>-1</sup>. The characteristic bands appear in the regions of 432 – 428 cm<sup>-1</sup> and 461 – 452 cm<sup>-1</sup>. Literature reveals [17-18] that ν(M – C)

absorption bands appear in the region of 460 – 429 cm<sup>-1</sup>. Thus the bands appearing in the region of 432 – 428 cm<sup>-1</sup> in the present products can be assigned to ν(Bi – C) stretching vibrations [19-20].

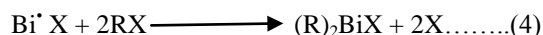
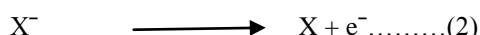
Current efficiencies of all these systems have been determined and are found to be unusually high, i.e. more than one. High current efficiencies of all these systems can be explained on the basis the following reaction mechanism.

**At inert cathode:**



The halide ions formed at cathode migrate to the anode compartment under the influence of applied potential and undergo the following sequence of reactions:

**At sacrificial anode:**



The reactions (3) and (4) constitute a chain process and proceed without the consumption of any current from the source and thus explain the high current efficiencies of these systems.

**III.I Coordination Compounds of Organobismuth Compounds:**

The products isolated from the electrochemical reactions of alkyl/aryl halide and ligands separated in the anode compartment were isolated and identified by elemental analysis and infrared spectral studies. Infrared spectra of the products have been recorded on Perkin –elmer spectrophotometer (RXI) in the region of 4000 – 450 cm<sup>-1</sup> using potassium bromide pellets and the important absorption bands are listed in Table –II and Table - III.

**Table-II: Electrolysis Characteristics, Analytical and other Related Data of Electrolytic product of various alkyl/aryl halide Systems + 1, 10-phenanthroline at Bismuth Anode**

System	Potential	Electricity Passed (Coulomb)	Product	Colour	Elemental Analysis Found/(Calc.)%				Current Efficiencies (Gram Equivalent/ Faraday)
					Bi	C	H	X	
Bromoethane +1,10-phenanthroline	40	864	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> BiBr C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	Dark Brown	36.3 (35.4)	31.2 (35.2)	1.3 (3.3)	11.4 (14.5)	0.94
1-Bromopropane +1,10-phenanthroline	50	864	(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> BiBr C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	Light Brown	35.2 (36.4)	33.9 (37.6)	1.1 (3.8)	9.4 (13.7)	0.84
1-Chlorobutane +1,10-phenanthroline	30	864	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> BiCl C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	Dark Brown	36.4 (37.5)	31.1 (43.1)	2.4 (4.6)	1.4 (6.3)	0.91
Chlorobenzene+1,10-phenanthroline	30	864	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> BiCl C <sub>12</sub> H <sub>8</sub> N <sub>2</sub>	Light Brown	34.4 (35.0)	47.6 (48.3)	1.2 (3.0)	4.0 (5.8)	0.97

**Table-III: Electrolysis Characteristics, Analytical and other Related Data of Electrolytic product of various alkyl/aryl halide Systems + 2, 2' - bipyridyl at Bismuth Anode**

System	Potential	Electricity Passed (Coulomb)	Product	Colour	Elemental Analysis Found/(Calc.)%				Current Efficiencies (Gram Equivalent/ Faraday)
					Bi	C	H	X	
Bromoethane + 2, 2' - bipyridyl	50	864	(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> BiBr C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	Dark Brown	41.9 (41.5)	33.0 (33.3)	3.2 (3.5)	15.1 (15.7)	0.97
1-Bromopropane + 2, 2' - bipyridyl	30	864	(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> BiBr C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	Light Brown	39.8 (39.4)	36.1 (36.2)	4.2 (4.1)	14.5 (14.9)	0.94
1-Chlorobutane + 2, 2' - bipyridyl	40	864	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> BiCl C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	Dark Brown	40.3 (40.6)	42.2 (42.0)	5.2 (5.0)	6.2 (6.8)	0.91
Chlorobenzene+ 2, 2' - bipyridyl	30	864	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> BiCl C <sub>10</sub> H <sub>8</sub> N <sub>2</sub>	Light Brown	37.4 (37.7)	47.9 (47.6)	3.2 (3.2)	6.2 (6.3)	0.93

Current efficiencies of some of these systems have also determined which are quite close to 100%, thereby indicating that the reactions leading to formation of coordination compounds are the predominant reactions of these systems. Infrared spectral data reveal that characteristic bands appear in

the regions of 436 – 433 cm<sup>-1</sup> and 1605 – 1595 cm<sup>-1</sup>. The bands appearing in the regions of 436 – 433 cm<sup>-1</sup> in the present products can be assigned to ν(Bi – C) [21] stretching vibrations . Comparison of the present infrared data to those of the parent products shows a shift of these bands towards the higher regions. The additional bands appearing in the region

of 1605 – 1595  $\text{cm}^{-1}$  in these products may be due to  $\nu$  (C  $\equiv$  C) and  $\nu$  (C  $\equiv$  N) stretching vibrations of the ligand molecules. However, these bands appear at slightly higher region as compared to those reported in the pure ligand molecules. The shift of stretching vibration  $\nu$  (Bi – C) bands towards higher region than those of the parent organobismuth compounds and presence of bands due to ligand molecules confirm the coordination of the ligand.

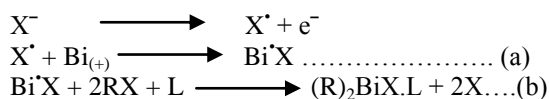
Current efficiencies of all these systems were determined (Enlisted in Table – II and Table – III) which are found to be very high. High current efficiencies indicate that the reactions leading to the formation of coordination compounds of organobismuth are the predominant reactions of the systems. The reaction scheme is given below:

**At inert cathode:**



The halide ions formed at cathode migrate to the anode compartment under the influence of applied potential and undergo there following sequence of reactions:

**At sacrificial anode:**



The reactions (a) and (b) constitute a chain process and proceed without the consumption of any current from the source and thus explain the quite high current efficiencies.

**IV. CONCLUSION**

The project studies thus reveals that the present technique provides a new synthetic method for the laboratory preparation of organobismuth halides. The method is associated with high current efficiencies.

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