

Characterization and Synthesis of triphenyl bismuth V Compounds

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ABSTRACT

Organometallic compounds can be defined as any member of a class of substance containing at least one metal to carbon bond in which carbon is a part of organic group. In these compounds metal act as main group compound or transitional metal compound. The main group metals of organometallic compounds are typically considered to be those of S-block (gp 1 and 2) and heavier elements of p block (gp 13, 14, 15) respectively of the periodic table.

The properties of organometallic compounds depends upon the type of carbon-metal bonds involved. Some are ordinary covalent bond (in which pairs of electrons is shared between atoms). Some are ionic bond (in which pair of bonded electron is donated by only one atom) making the bond polarized where one bond is more negative than the other. Thus in organometallic compounds the metal atom is less electro negative than the carbon atom [1]. The polarity of M-C bond makes the organometallic compound a good substrate for studying electrophilic substitution at the metal atom. Due to this polarity. Organometallic compounds are susceptible to be attacked by a wide variety of reagents, which opens a vast area for the synthesis of various type of new organometallic compounds.

Introduction:-

Organometallic compounds are chemical compounds which contain at least one bond between a metallic element and a carbon atom belonging to an organic molecule. The bond between the metal atom and the carbon belonging to the organic compound is covalent in nature. Generally organometallic like compounds exist in solid state, especially the compounds in which the hydro-carbon groups are aromatic or have a ring structure. Mainly organometallic compounds are found to be toxic to human.

From past studies it has been observed that organometallic chemistry plays important role in other branch of chemistry such as biological, analytical and medicinal chemistry. Vitamin

B_{12} (cabalamin) is essential cofactor for every human being. Its unique reactivity is due to the presence of direct metal-carbon bond, making it a truly organometallic compound. As researchers worked deeper into organometallic chemistry, they realized that this field is quite compatible with biology, giving birth to a new field bio organometallic chemistry. The biological aspects of organometallic compounds especially arsenic [2] and antimony [3] compounds were used extensively in medicines till today. Group 15 organometallic compounds are considered important for medicinal use, industrial aspects, biocides and chemotherapeutic agents in past years [4, 5]

The corresponding pentafluorophenyl derivatives of bismuth in either of its oxidation state +3 or +5 has been paid no attention. Surprising group 15 element As and Sb has been extensively studied by various workers. In reference with group 15 metal like As and Sb we have considered Bi in +5 oxidation state. We have considered pentafluorophenyl with Bi metal which not only render hydrolytic stability but they are also lipid soluble. The coupled advantage with Bismuth compounds is they are non toxic in nature, when formation of Bi – C (Bismuth – carbon) bond these compound on further decomposition they become toxic compounds in nature. Moreover, recent studies have shown that bismuth compounds specially thiolates and other nitrogen containing derivates are better antifungal and antitumor agents respectively [6,7,8]

Several organobismuth (v) compounds of the type $R_3 Bix_2$ (R=aryl group) x=halides acetate, nitrate etc) we have basically emphasized on halide in our literature. Although structural aspects of triphenylbismuth dihalides have been studied by several workers [9,10,11,12] very little is known about the structural feature and chemical constitution of organobismuth (v) acid derivates in general. On the basis of dipole moment studies, Jensen posed a trigonal bipyramidal structure of dichloride. In our investigation several triphenyl bismuth (v) compounds are studied, we have also examined the infra red spectra, electrical conductance, molecular weight of these compounds.

Starting material:-

$BiCl_3$ Bismuth chloride is the most common starting material of organobismuth compounds $BiCl_3$ is a white powder, refluxing with thionyl chloride ($SOCl_2$), especially used for Grignard reaction.

Anhydrous $BiCl_3$ is also obtained by distilling commercial dehydrate $BiCl_3 \cdot 2H_2O$, which is a white to pale yellow, deliquescent crystalline solid soluble in aromatic hydrocarbons and donating organic solvents such as diethyl ether and tetrahydrofuran (THF).

BiF_3 bismuth fluoride is found in form of white or grey dimorphic crystal practically insoluble in water but soluble in concentrated hydrofluoric acid.

BiI_3 is black fine crystalline solid. Insoluble in water, but slowly decomposed in hot water it dissolve in liquid ammonia and aqueous potassium iodide.

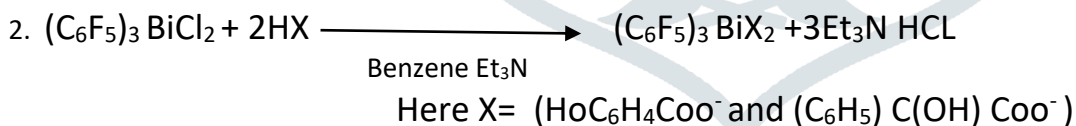
BiOCl_2 Bismuth oxychloride is colourless fine powder. Insoluble in water and alcohol, but ready soluble in HCl and HNO_3 . Oxihalides are prepared by partially hydrolysis of trivalent bismuth ($\text{BiO}(\text{NO}_3)$) with corresponding NaX (x is halide) in aqueous solution. Bismuth Sulphide (Bi_2S_3) is a dark brown to grayish black solid readily formed by heating Bi with S. The sulphide are insoluble in water but soluble in con HNO_3 and hot HCL . Concentration aqueous potassium Sulphide dissolve bismuth sulphide to form bismuth thio bismutate KBiS_2 . Bi_2Se_3 and Bi_2Te_3 are both gray to black crystalline powder.

Tris (pentafluorophenyl) Bismuth (v) Dicarboxylate

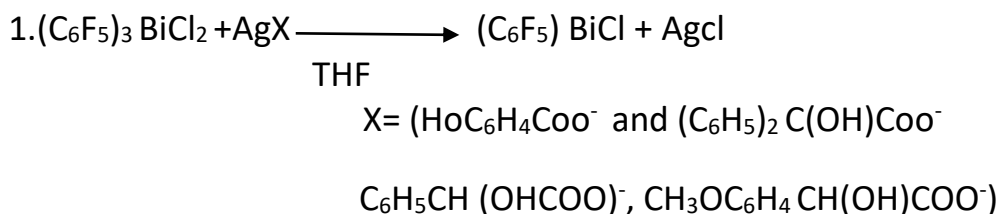
Result and discussion:-

In an anhydrous oxygen free atmosphere tris (pentafluorophenyl) Bismuth (v) carboxylate can be prepared by the intraction of tris (pentafluorophenyl) bismuth dichloride $(\text{C}_6\text{F}_5)_3 \text{BiCl}_2$ with carboxylic acid in 1:2 and 1:1 molar ratio in presence of lewis base, triethylamine (Et_3N) as hydrogen halide acceptor.

These reactions can also be obtained by simple metathesis of $(\text{C}_6\text{F}_5)_3 \text{BiCl}_2$ with an appropriate silver salt of carboxylic acid.



By Metathesis Process



All the reaction were carried at room temperature with contant steaming for almost 24Hr. All the newly synthesized tris(pentafluorophenyl)bismuth(v) dicaboxylate were crystalline solid, and soluble in organic solvent. The compound were further characterized by their melting point and

analytical technique such as elemental analysis, infrared and NMR spectroscopy to ascertain their structure and Biological property.

Measurements:-

The electrical conductances were measured at 25^o c with a Beckman Model RC – 18 A Conductivity Bridge using a glass cell with platinized platinum electrodes. The conductance of the solvent was measured in each case. Molecular weight were determined in benzene solutions (concentration range 10⁻² to 10⁻³ mole/kg) with a Hitachi-Perkin Elmer model 115 vapor osmometer. Melting point were determined with a Fisher Johns melting point apparatus. The analytical and molecular weight data and MP of the investigated compounds are given in table 1

Comp	Found		Calculated		Molecular Weight.		Melting Point.
	C	H	C	H	F	C	
Ph ₃ Bi(CH ₃ Coo) ₂	47.34	3.69	47.32	3.79	549	558	173
Ph ₃ Bi6(CH ₂ clcoo) ₂	42.07	2.95	42.12	3.05	614	627	166
Ph ₃ Bi(ccl ₃ Coo) ₂	34.38	1.74	34.54	1.96	762	765	158
Ph ₃ Bi(CHCl ₂ Coo) ₂	37.61	2.24	37.95	2.46	687	696	118-119
Ph ₃ BiBr	37.36	2.89	36.02	2.51	593	600	139
Ph ₃ Bi Cl ₂	42.29	3.10	42.29	2.95	504	511	159-160
Ph ₃ Bi(CH ₂ CNCoo) ₂	47.06	3.03	47.37	3.14	608	608	123-124

Table 1

All the compounds are non-hygroscopic white crystalline solid and are soluble in common organic solvents like benzene, chloroform and acetone. The equivalent conductance of these compound in nitro methane at 25^o C in the concentration range 10⁻³ to 10⁻⁴M are recorded in table 2. The conductivity data shows that these compound behave as molecular species in nitro methane, and show negligible conductivities [13]

Conductance data of Ph₃Bix₂

Concentration compounds in nitro methane at 25^oc

Compounds	M	C(ohm ⁻¹) Cm ² eq ⁻¹
Ph ₃ BiCl ₂	2x10 ⁻³	0.06
	1x10 ⁻³	0.14
	5x10 ⁻⁴	0.29
	2x10 ⁻⁴	.068
	1x10 ⁻⁴	1.38
Ph ₃ Bi(CHCl ₂ Coo) ₂	2x10 ⁻³	0.53
	1x10 ⁻³	0.42
	5x10 ⁻⁴	0.44
	2.5x10 ⁻⁴	0.33
	1.25x10 ⁻⁴	0.25
Ph ₃ Bi(CH ₂ ClCoo) ₂	2x10 ⁻³	0.08
	1x10 ⁻³	0.08
	5x10 ⁻⁴	0.10
	2x10 ⁻⁴	0.50
	1x10 ⁻⁴	0.40
Ph ₃ Bi(CH ₃ Coo) ₂	2x10 ⁻³	0.05
	1x10 ⁻³	0.13
	5x10 ⁻⁴	0.15
	2.5x10 ⁻⁴	0.20
	1.25x10 ⁻⁴	0.28
Ph ₃ Bi(CCl ₃ Coo) ₂	2x10 ⁻³	1.10
	1x10 ⁻³	1.18
	5x10 ⁻⁴	1.26
	2x10 ⁻⁴	1.40

Table 2

IR AND MMR SPECTRAL ANALYSIS:-

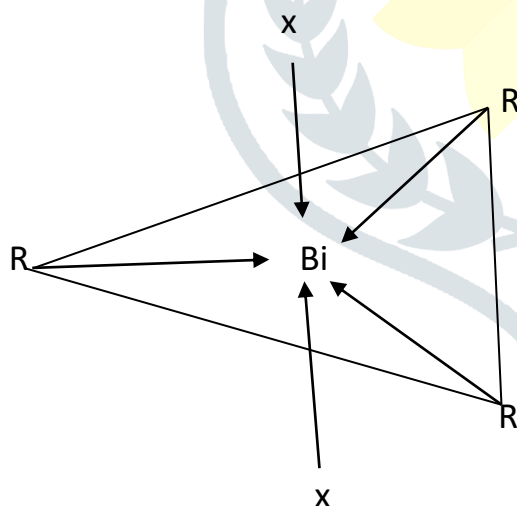
The IR spectra of new tris(pentafluorophenyl)bismuth(v) dicarboxylates were recorded in perkin Elmur spectrophotometer in 4000 – 300/cm range. The IR spectra of these compounds show absorption bands due to pentafluorophenyl group. The absorption frequencies have fully assigned. The Bi – C vibration in case of pentafluorophenyl derivation appear in the range of 440 – 468/cm. The IR data suggest a monodentate coordination mode of carboxylate ligands.

The IR absorption frequencies of carboxylate derivatives are given in table 3. The ν_{asy} (OCO) frequency appears in the range 1670 to 1625 cm^{-1} and the corresponding ν_{sym} (OCO) frequency appears in the range 1365-1235 cm^{-1} . The difference b/w these 2 frequencies ν_{asy} (OCO) - ν_{sym} (OCO) has reported in past (15, 16) indicates the carboxylate moiety behaves as unidentate ligand or carboxylate group.

The H-NMR spectra of the representative tris(pentafluorophenyl)bismuth (V) dicarboxylate showed a multiplet in the range of 8.72 – 8.12 ppm which indicate aromatic proton.

The H NMR spectra of all the compounds were recorded in CDCl_3 at on 300 MHz instrument. The observation is same as in the case of triphenyl bismuth (V) dihalides, where the electron density decreases at i-centre with the decrease of electronegativity of carboxylate oxygen attached to metal. In most cases the chemical shift value of carboxylate were showing the marginal difference with the chemical shift value of carbon of free carboxylate acid.

Thus, from the IR, NMR spectra data aided by molecular weight and conductance measurement, it is evident that carboxylate group behaves as monodentate ligand. This may be attribute the presence of pentafluoro phenyl ring resulting in the donation of electrons density from unshared electrons fluorine to the system ring and thus increase the lewis acid character of central metal atom bismuth and decrease the tendency to accept the electrons from the ligands. In the newly synthesized carboxylate derivatives the bismuth metal is in penta coordinated state imparting trigonal bipyramidal structure. In which carboxylate group occupy optical position whereas the three pentafluoro group at equatorial positions. [15, 16, 17, 18, 19]



Structure of tris (pentafluoro) bismuth(V) dicarboxylate

Experiment:-

1. Tris(pentafluorophenyl)bismuth dichloride was prepared by direction chlorination in laboratory.

Tris (pentafluorophenyl bismuth dichloride (0.02Mole) carboxylic acid (0.04) and carboxylic acid (2ml) were stirred together in (2.MM) benzene solution (50 ml) in the presence of triethylamine at room temperature for 3 hours and the refluxed for 2 hr the off white colour $\text{Et}_3\text{N.HCl}$ was formed of (M.P 240°C) which was further filtered off and the filtrate on evaporation in vacuum gives an off white colour crystalline solid. These crystalline solid compound recrystallized further in petroleum ether.

Tris (pentafluorophenyl bismuth dichloride (0.02Mole) 4-chlorobenzoic (0.04) and 4-nitrobenzene (2ml) were stirred together in (2.MM) benzene solution (50 ml) in the presence of triethylamine at room temperature for 3 hours and the refluxed for 2 hr the off white colour $\text{Et}_3\text{N.HCl}$ was formed of (M.P 240°C) which was further filtered off and the filtrate on evaporation in vacuum gives an off white colour crystalline solid. These crystalline solid compound recrystallized further in petroleum ether.

IR data of tris(pentafluoro) bismuth dicarboxylate

S.No	Compound	Coocm Asym	Coosym	Δ Asy- Δ syn
1	$\text{Ph}_3\text{Bi}(\text{CH}_3\text{Coo})_2$	1648	1235	413
2.	$\text{Ph}_3\text{Bi}(\text{CH}_2\text{ClCoo})_2$	1666	1330	336
3.	$\text{Ph}_3\text{Bi}(\text{Ccl}_3\text{Coo})_2$	1670	1326	344
4.	$\text{Ph}_3\text{Bi}(\text{CHCL}_2\text{Coo})_2$	1635	1358	277
5.	$\text{Ph}_3\text{Bi}(\text{CH}_2\text{CNCoo})_2$	1625	1345	280

Table 3

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