

Synthesis and Characterisation of Some New Tris (α -Naphthyl) Bismuth (V) Carboxylates; (α -C₁₀H₇)₃BiX₂

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Abstract—A series of tris (α -naphthyl) bismuth (V) carboxylates (α -C₁₀H₇)₃Bi(OCOR)₂ where OCOR = p-trifluoromethyl mandelate, p-methoxy mandelate, salicylate, 2pyrazine carboxylate, mandelate have been synthesised and characterised by solid state infrared, ¹H and ¹³C NMR spectroscopy, molecular weight and conductance measurements. The newly synthesized derivatives are monomeric in benzene and non ionic in acetonitrile. In the solid state a penta coordinate dispensation around bismuth having monodentate OCOR group indicated on the basis of spectroscopic and physic chemical datas.

Keywords— Tris (α -naphthyl) bismuth carboxylates, IR, ¹H NMR, ¹³CNMR spectra, monomeric, non ionic

1 INTRODUCTION

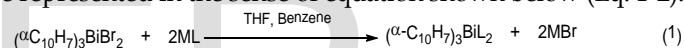
Despite a considerable amount of work done on the synthesis, reactivity and characterization on organoantimony and organoarsenic carboxylates, corresponding studies on organobismuth compounds are strikingly lacking. It is probably due to the difficulties encountered in the preparation of parent organobismuth compounds which requires strict anhydrous conditions otherwise tend to decompose or are susceptible to hydrolysis. However, the introduction of bulkier cyclohexyl and naphthyl group on to the bismuth atom render hydrolytic and thermal stability and therefore easy to handle and characterize. Apart from this sterically congested organobismuth compounds have been little studied vis-à-vis aryl and alkyl group substituted organobismuth compounds and also hold good promise to be biologically potential due to the presence of bismuth-carbon bond which is biodegradable and bismuth as such is non toxic [1-14].


The present investigation focused on the synthesis of hitherto unreported tris(α -naphthyl) bismuth (V) carboxylate with a view to establish the nature and mode of bonding of carboxylate group. The newly synthesized compounds were characterised by solid state infrared (IR), ¹H, ¹³C NMR spectra. Solution phase studies complementary these have been carried out to establish their behaviour in solution [15, 16].

2 Results and Discussion

The 1:1 and 1:2 molar ratio reactions of triorganobismuth (V) dibromide with silver salt of corresponding carboxylic acid offered a series of triorganobismuth (V) dicarboxylates and –

halocarboxylates. All the reactions were carried out in an oxygen free atmosphere in anhydrous organic solvent at room temperature and under dark condition. These reactions may be represented in the sense of equation shown below (Eq. 1-2):



[Where ML; M = Ag; L = o-OHC₆H₄COO, RCH(OH)COO (R = C₆H₅-, p-CH₃O-C₆H₄-, p-CF₃-C₆H₄-, 

In case of pyrazine carboxylic acid (9, 10), and all the α -hydroxy carboxylic acids moieties both 1:2 and 1:1 molar ratio reactions proceed smoothly and afforded different products (Eq 1-2). The mandelic acid and its derivatives forms, cyclometallates with triphenylbismuth (V) dichloride but the same was not observed here. There observation indicates that sterically hindered α -naphthyl group prohibit the cyclisation. The newly synthesized compounds do not decompose on storage for several days and are quite stable toward air and moisture. The yields of products were nearly quantitative except for the losses during workup process. The complexes are freely soluble in most of the organic solvent. They are off white crystalline solid, and have sharp melting points. The complexes have been characterized by elemental analysis, IR and NMR (¹H, ¹³C) techniques. They have been found non-electrolyte in acetonitrile (10⁻³M) and shown monomeric constitution in freezing benzene [35].

2.1 INFRARED SPECTRA

Infrared spectra of all the compounds (1-10) were recorded in the 4000-400 cm⁻¹ region on FT IR spectrophotometer (Shimadzu 8201 PC) IR absorptions corresponding to α -naphthyl group bound to bismuth are in dose conformity with the reported values of analogous tris (α -naphthyl) bismuth and – antimony [17,18]. The diagnostic IR absorption bonds of the

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newly synthesized compounds have been identified and are listed in Table. The infrared spectra of all the compounds show almost identical absorption due to α -naphthyl group. The Bi-C stretching frequency corresponding to γ -mode was observed in the range 430-410 cm^{-1} as a medium to weak band [19, 20, 21]. The Bismuth – halogen, stretching frequency in spectra of the halocarboxylates are not observed in the range of 4000-400 cm^{-1} . IR spectra provide a method of assessing carboxylates co-ordination made from the position and separation ($\Delta\nu = \nu_{\text{asym}} - \nu_{\text{sym}}$) between the asymmetric and symmetric OCO stretching modes [22-24]. In the IR spectra of these compounds the carboxylate bonds are observed in the characteristic region: ν_{asym} (OCO) between 1606 and 1630 cm^{-1} , ν_{sym} (OCO) between 1385 and 1310 cm^{-1} . On the basis of $\Delta\nu$ (OCO) values (335 – 275 cm^{-1}) these compounds belong to the same class [21]: there are no interaction between the carbonyl oxygen atom of the carboxylate group and the bismuth atom, which indicate the presence of monodentate 'ester type' – OCO group.

2.2 ^1H NMR SPECTRA

^1H NMR Spectra of the representative compounds were recorded on Bruker DRX – 300 (300 MHz FT NMR) spectrometer using CDCl_3 as solvent with chemical shift being reported as δ (ppm) from tetramethyl silane (TMS) as reference. The integration of the spectra is in good agreement with the expected values in the complex molecule. The proton Magnetic resonance spectra of newly synthesized compounds are listed in Table-4. The chemical shifts of the Protons of naphthyl group appear in the range δ (7.50 – 8.20) ppm in the form of multiplet. The appearance of signals of protons of naphthyl group as multiplet is due to low to long-range coupling. In this way, the signals for naphthyl protons were found in good agreement with those reported earlier [10, 11]. The α -hydroxy acids containing α -hydrogen (comp. no. 3-8), shows the proton signal for α -hydrogen in the range δ (4.96 – 5.13) ppm. In case of compound (7, 8) containing the methoxy protons was observed at δ (3.78, 3.81) ppm respectively as singlet. The phenyl ring proton appears in the range δ (6.55 – 7.95) ppm as multiplet, the details are summarized in the table 4. The three magnetically non equivalent protons (H_2 , H_3 , H_4) of 2-pyrazine carboxylate (9, 10) were observed at δ 9.05 (s), 8.78(d) and 8.85 (d) ppm, respectively. The peaks of ligands (carboxylates) with free carboxylic acid and with those of similar organometallic compounds reported earlier [16, 31].

2.3 ^{13}C NMR SPECTRA

The ^{13}C NMR spectra of some representative compounds were recorded on 300 MHz FT NMR (Bruker DRX – 300) spectrometer operating at ~ 75 MHz using CDCl_3 as solvent and reference (δ 77.0 ppm) with chemical shifts being reported as δ (ppm). The peaks are compared identified and are listed in Table-5. The chemical shift of some magnetically non-equivalent carbon of naphthyl ring were observed at different δ -values in the C_1 – 129, C_2 , - C_3 , - C_6 , - C_7 = 126.5; C_4 , C_5 , C_8 , at 128.5 ppm and C_9 – C_{10} at 133.9 and 133.7 ppm respectively. The position of the carbon centre of carboxylate group in all complexes shifts toward lower field due to deshielding as

compared to the free acid moieties, which indicates the participation of carboxylate group in co-ordination to Bismuth [32]. The positions of the carbon of ligands are recognized and have the chemical shift values in range. In case of all the sterically congested Organo-bismuth(V) carboxylates, the chemical shift of ligands shows effective difference from the chemical shift of carbon of free acid for carbon centers C_1 and C_{12} , but other carbons are almost not affected. The effect of sterically congested naphthyl group on chemical shift of Carbon centers of ligand and acid is remarkable when compared to those of triphenyl bismuth (V) carboxylates [16, 31]. The presence of all peaks of carbons of naphthyl group and ligand acid on one hand and the change in chemical shift of different carbon centers of ligand and acid compared to those of free acid on the other hand confirms the formation of Bi-O-C(O) bond. Thus on the basis of spectral data in combination with molecular weight and conductance data, it may be concluded that the newly synthesized compounds possess a monomeric, bismuth. The three α -naphthyl group (s) occupy the equatorial position and the electronegative group (s) ligand or chlorine occupies axial positions (Fig. 1) [31-42].

3 EXPERIMENTAL

The preparation of $(\alpha\text{-C}_{10}\text{H}_7)_3\text{BiBr}_2$ was prepared by reported method [5]. The carboxylic acids were used in the form of silver salts which were obtained by reacting sodium salt of corresponding acid with silver nitrate. Tetrahydrofuran (THF) was distilled under an atmosphere of nitrogen from sodium-benzophenone. Special precautions were taken to exclude moisture and oxygen. The reactions of silver salts were done under dark condition to avoid decomposition. Typical Examples of $(\alpha\text{-C}_{10}\text{H}_7)_3\text{BiBr}_2$ and its mono and di carboxylate derivative $(\alpha\text{-C}_{10}\text{H}_7)_2\text{BiBr}(\text{OCOR})$, $(\alpha\text{-C}_{10}\text{H}_7)_3\text{Bi}(\text{OCOR})_2$ respectively are described below in detail and the conditions for the other reaction are summarized in Table-1. Analytical data are given in Table-2 to 5.

3.1 1:2 Molar Ratio Reaction of Tris (α -naphthyl) bismuth (V) bromide with silver salt of Salicylic acid

The heterogeneous solution of tris (α -naphthyl) Bismuth (v) dibromide (0.75g, 1.0 mmol) and silver salt of salicylic acid (0.49 g, 2.0 mmol) in THF (25 ml) was stirred at room temperature for 24 h. The AgCl thus formed was filtered off, the filtrate was concentrated in vacuo (3-4 ml) followed by addition of n-hexane (5 ml) afforded white crystalline solid which was characterized as tris (α -naphthyl) bismuth (V) disalicylate (2). Similarly 1:1 molar ratio reaction of tris (α -naphthyl) bismuth (V) dibromide (0.75g, 1.0 mmol) with silver salt of salicylic acid (0.245 g, 1.0 mmol) in THF (25 ml) afforded white crystalline solid characterized as tris (α -naphthyl) bismuth (V) Bromo Salicylate (2).

3.2 1:2 molar Ratio Reactions of Tris (α -naphthyl) bismuth (V) Dibromide with silver salt of (RS) Mandelic Acid

In an atmosphere of dry nitrogen a solution of tris (α -naphthyl) bismuth (V) dibromide (0.750 g, 1.0 mmol) and silver salt of (RS) mandelic acid (0.518 g, 2.0 mmol) in THF (25 ml) was stirred at room temperature for 24h. The heterogeneous

ous solution containing precipitate of AgCl was filtered. The filtrate on concentration in vacuo followed by addition of Petroleum ether (60-80°C) afforded white crystalline solid. The compound was crystallized from a mixture of THF and petroleum ether (60-80°C) in the ratio 1:4 and was characterized as (Rs) – tris (α -naphthyl) bismuth (v) di mandelate (3). In the same manner, 1:1 molar ratio reaction of tris (α -naphthyl) bismuth (V) dibromide (0.75 g, 1.0 m mol) with silver salt of (Rs) – mandelic acid (0.259 g, 1.0 m mol) in THF (20 ml) offered the white crystalline compound characterized as (RS) tris (α -naphthyl) bismuth (V) (bromo) (mandelate) (4).

3.3 1:2 Molar Ratio Reaction of Tris (α -naphthyl) bismuth (V) dibromide with silver salt of 2-Pyrazine carboxylic acid (9)

In an inert atmosphere, a heterogeneous solution of tris (α -naphthyl) bismuth (V) dibromide (0.75g, 1.0 mmol) and silver salt of 2-pyrazine carboxylic acid (0.462 g, 2.0m mol) in dry benzene (20 ml) was stirred at room temperature for 24h. The silver nitrate, thus formed was filtered off completely and solvent was evaporated under vacuum to afford off white crystalline solid. The compound was recrystallized from a mixture of benzene and petroleum ether (60-80°C) in the ratio 1:3 and was characterized as tris (α -naphthyl) bismuth (V) di (2-pyrazine carboxylate) (9). In the same manner, 1:1 molar ratio reaction of tris (α -naphthyl) bismuth (V) dibromide (0.75g, 1.0 m mol) with silver salt of 2-pyrazine carboxylic acid (0.388 g, 1.0 m mol) in THF (15 ml) afforded the off white crystalline compound characterized as tris (α -naphthyl) bismuth (V) (Bromo) (2-pyrazine carboxylate) (10).

4 FIGURES

Figure 1 Showing TBPY Structure of Compounds

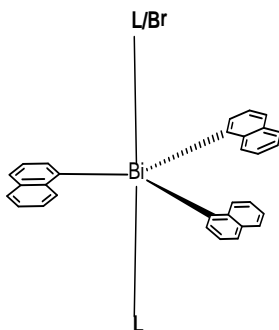


Fig:1Showing TBPY arrangement of tris(α -naphthyl)bismuth(V) halo-carboxylates and dicarboxylates; where L = o-OHC₆H₄COO, C₆H₅CH(OH)COO, p-CF₃-C₆H₄CH(OH)COO, p-MeOC₆H₄CH(OH)-COO, 2-pyrazine carboxylate

5 TABLES

Table – 1 Preparation and Properties of Tris (α -naphthyl) bismuth (V) halo carboxylates and dicarboxylates

Comp. No.	Complex	Organometallic Halides (g)	Ligand (g)	Molar Ratio/ Solvent mL	M.P. (°C)
1	(α -C ₁₀ H ₇) ₃ Bi(Br)(OCOC ₆ H ₄ OH-o)	(α -C ₁₀ H ₇) ₃ BiBr ₂ (0.75)	[o-OHC ₆ H ₄ COOAg] (0.245)	1:1 THF (25)	105
2	(α -C ₁₀ H ₇) ₃ Bi(OCOC ₆ H ₄ OH-o) ₂	(α -C ₁₀ H ₇) ₃ BiBr ₂ (0.75)	[o-OHC ₆ H ₄ COOAg] (0.490)	1:2 THF (25)	138
3	(α -C ₁₀ H ₇) ₃ Bi[OCOCH(OH)C ₆ H ₅] ₂	(α -C ₁₀ H ₇) ₃ BiBr ₂ (0.75)	[C ₆ H ₅ CH(OH)COOAg] (0.518)	1:2 THF (25)	118
4	(α -C ₁₀ H ₇) ₃ Bi(Br)[OCOCH(OH)C ₆ H ₅]	(α -C ₁₀ H ₇) ₃ BiBr ₂ (0.75)	[C ₆ H ₅ CH(OH)COOAg] (0.250)	1:2 THF (20)	85
5	(α -C ₁₀ H ₇) ₃ Bi[OCOCH(OH)C ₆ H ₄ CF ₃ -p] ₂	(α -C ₁₀ H ₇) ₃ BiBr ₂ (0.75)	[p-CF ₃ -C ₆ H ₄ CH(OH)COOAg] (0.654)	1:2 THF (25)	144
6	(α -C ₁₀ H ₇) ₃ Bi(Br)[OCOCH(OH)C ₆ H ₄ CF ₃ -p]	(α -C ₁₀ H ₇) ₃ BiBr ₂ (0.75)	[p-CF ₃ -C ₆ H ₄ CH(OH)COOAg] (0.327)	1:1 THF (20)	136
7	(α -C ₁₀ H ₇) ₃ Bi[OCOCH(OH)C ₆ H ₄ OCH ₃ -p] ₂	(α -C ₁₀ H ₇) ₃ BiBr ₂ (0.75)	[p-CH ₃ OC ₆ H ₄ CH(OH)COOAg] (0.578)	1:2 THF (25)	148
8	(α -C ₁₀ H ₇) ₃ Bi(Br)[OCOCH(OH)C ₆ H ₄ OCH ₃ -p]	(α -C ₁₀ H ₇) ₃ BiBr ₂ (0.75)	[p-CH ₃ OC ₆ H ₄ CH(OH)COOAg] (0.462)	1:2 THF (15)	129
9	(α -C ₁₀ H ₇) ₃ Bi[OCOC ₄ N ₂ -2] ₂ *	(α -C ₁₀ H ₇) ₃ BiBr ₂ (0.75)	[C ₄ N ₂ COOAg] (0.462)	1:2 THF (25)	110
10	(α -C ₁₀ H ₇) ₃ Bi(Br)[OCOC ₄ N ₂ -2] ₂ *	(α -C ₁₀ H ₇) ₃ BiBr ₂ (0.75)	[C ₄ N ₂ COOAg] (0.388)	1:2 THF (15)	98

*OCOC₄N₂-2 is 2-pyrazine carboxylate

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CONCLUSION

The replacement of phenyl group (C_6H_5-) by bulkier organic moiety (i.e. α -naphthyl) enhances the hydrolytic stability thus it can also expect that it can affect the biological activity. The carboxylates group acts as monodentate group. The compounds are monomeric and non electrolyte in solution having pentacoordinate dispensation around bismuth atom.

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