

ANIONIC COMPLEXES OF ORGANOBISMUTH(III)

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(Received July 14th, 1969)

SUMMARY

The preparation and properties of some new compounds containing organobismuth anions are reported. Salts of the type $M[(C_6H_5)_2BiX_2]$ [$M = (CH_3)_4N$, $(C_6H_5)_4As$; $X = Cl, Br, I, SCN$] and $[(C_6H_5)_4As][C_6H_5BiX_3]$ ($X = Cl, Br, I$) have been obtained from nonaqueous media and studied by conductivity, molecular weight and UV spectra measurements. The anionic species are present in acetone and in methylene chloride; they decompose in methanol.

INTRODUCTION

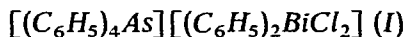
As a part of our investigations of anionic complexes of organometallic compounds, with particular reference to their salt formation^{1,2}, some organobismuth(III) compounds have been analyzed. No information was found in literature on any $(C_6H_5)_2Bi^{III}$ complex; a few $C_6H_5Bi^{III}$ complexes are known, *viz.* $Bipy \cdot H[C_6H_5BiBr_3]$ and $C_6H_5BiBr_2 \cdot Bipy^3$, $C_6H_5BiX_2 \cdot 2 Py$ ($X = Cl, Br$)⁴ and $C_6H_5Bi(S_2CNR_2)_2$ (Ref. 5).

This paper reports the preparation of salts of $(C_6H_5)_2Bi^{III}$ and $C_6H_5Bi^{III}$ complex anions. Informations about the behaviour of these compounds in various solvents have been obtained through conductivity, molecular weight and UV spectra measurements.

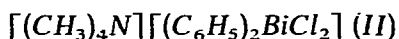
EXPERIMENTAL

The materials used were as follows: $(C_6H_5)_4AsCl$ (Fluka); $(CH_3)_4NCl$ (C. Erba) was recrystallized from methanol; $(C_6H_5)_4AsX$ ($X = Br, I$) were obtained through precipitation from aqueous tetraphenylarsonium chloride and the corresponding sodium halide, and recrystallized from water/ethanol; $(C_6H_5)_4AsCl \cdot HCl$ was prepared as in ref. 6; $(C_6H_5)_3Bi$ (Fluka) was purified by dissolving it into anhydrous ethyl ether and evaporating the solvent under vacuum after filtration; $(C_6H_5)_2BiX$ ($X = Cl, Br$) and $C_6H_5BiBr_2$ were prepared from triphenylbismuthine and BiX_3 ($X = Cl, Br$) as reported in ref. 7; $(C_6H_5)_2BiI$ was obtained according to ref. 8; $C_6H_5BiI_2$ according to ref. 9. The solvents were purified under nitrogen: methanol, with magnesium methoxide; acetone, through successive distillations from $KMnO_4/K_2CO_3$; ethyl ether, over Na/K ; methylene chloride, by acid-base washing and distillation from CaH_2 .

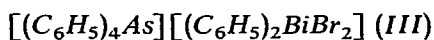
The salts of anionic organobismuth complexes were prepared in anhydrous solvents using the following methods:



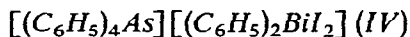
Equimolecular quantities of diphenylchlorobismuthine and tetraphenylarsonium chloride were dissolved into warm acetone; by adding ethyl ether the white compound was obtained in quantitative yield, and was recrystallized from acetone or ethanol. It was also prepared by use of the acid cleavage of phenyl groups from triphenylbismuthine: an acetic solution of $(C_6H_5)_3Bi$ and $(C_6H_5)_4AsCl \cdot HCl$ (molar ratio 1/1) was boiled for a few minutes; alternatively, a stoichiometric amount of ethanolic HCl was added to ethanolic $(C_6H_5)_3Bi$ and $(C_6H_5)_4AsCl$ (molar ratio 1/1) and the solution was boiled off. In both cases the product was obtained by adding ether. Under similar conditions and in absence of HCl, $(C_6H_5)_3Bi$ does not react with tetraphenylarsonium chloride. M.p.: 165–167°. (Found: C, 52.68; H, 3.64; Cl, 8.81. $C_{36}H_{30}AsBiCl_2$ calcd.: C, 52.89; H, 3.70; Cl, 8.67%.)



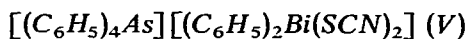
Diphenylchlorobismuthine and tetramethylammonium chloride (molar ratio 1/1) were dissolved in boiling acetone; the solution was evaporated to a small volume and the white compound was precipitated with pentane. M.p.: 155–156°. (Found: C, 37.35; H, 4.29; Cl, 13.57; N, 2.67. $C_{16}H_{22}BiCl_2N$ calcd.: C, 37.81; H, 4.36; Cl, 13.95; N, 2.75%.)



Diphenylbromobismuthine and tetraphenylarsonium bromide (molar ratio 1/1) were dissolved in boiling acetone; white-yellowish needles were obtained from the gradually evaporated solution, and were recrystallized from acetone. Alternatively, methanolic KBr was added to a methanolic solution of the compound (I) (molar ratio 2/1); the solvent was distilled under vacuum and the bromide complex was extracted with acetone. M.p.: 179–182°. (Found: C, 47.65; H, 3.32; Br, 17.63. $C_{36}H_{30}AsBiBr_2$ calcd.: C, 47.70; H, 3.33; Br, 17.63%.)



Diphenyliodobismuthine and tetraphenylarsonium iodide were dissolved in cold acetone. Small yellow-orange crystals were obtained by adding ether to the yellow solution. The compound precipitated also from a cold methanolic solution of (I) and KI (molar ratio 1/2). It was recrystallized from acetone/ether or methanol. M.p.: 201–203°. (Found: C, 43.27; H, 3.13; I, 25.46. $C_{36}H_{30}AsBiI_2$ calcd.: C, 43.22; H, 3.02; I, 25.37%.)



An acetic solution of (I) was treated with NaSCN in acetone (molar ratio 1/2) and an equal volume of ether was added. NaCl was filtered off, and the complex was precipitated with a larger volume of ether. The white solid was recrystallized from ethanol or acetone/ether. M.p.: 115–117°. (Found: C, 52.59; H, 3.36; N, 3.20. $C_{38}H_{30}AsBiN_2S_2$ calcd.: C, 52.90; H, 3.50; N, 3.25%.)

$[(C_6H_5)_4As][C_6H_5BiCl_3]$ (VI)

An acetic solution of triphenylbismuthine was added to a methanolic solution of tetraphenylarsonium chloride (molar ratio 1/1) and HCl (molar ratio 1/2). After boiling for a few minutes white crystals were obtained and recrystallized from acetone. The compound also precipitated from an hot acetone solution containing equimolecular quantities of diphenylchlorobismuthine and $(C_6H_5)_4AsCl \cdot HCl$. M.p.: 229–231°. (Found: C, 46.06; H, 3.25; Cl, 13.47. $C_{30}H_{25}AsBiCl_3$ calcd.: C, 46.43; H, 3.26; Cl, 13.71%.)

 $[(C_6H_5)_4As][C_6H_5BiBr_3]$ (VII)

The compound precipitated as pale-yellow crystals from a boiling acetic solution of phenyldibromobismuthine and tetraphenylarsonium bromide. It was also obtained by dissolving compound (VI) and NaBr (molar ratio 1/3) in hot methanol. The complex was recrystallized from acetone. M.p.: 228–230°. (Found: C, 39.92; H, 2.74; Br, 26.80. $C_{30}H_{25}AsBiBr_3$ calcd.: C, 39.63; H, 2.77; Br, 26.36%.)

 $[(C_6H_5)_4As][C_6H_5BiI_3]$ (VIII)

Red-orange crystals were obtained by adding phenyldiiodobismuthine in cold acetone to acetic tetraphenylarsonium iodide; alternatively, by adding methanolic NaI to a methanolic solution of (VI). Subsequent recrystallizations from acetone lowered progressively the melting point. M.p.: 225–228°. (Found: C, 34.40; H, 2.29; I, 36.14. $C_{30}H_{25}AsBiI_3$ calcd.: C, 34.30; H, 2.40; I, 36.25%.)

Attempts to prepare $[(C_6H_5)_4As][C_6H_5Bi(SCN)_3]$ by similar methods always led to yellowish impure solids with a strong smell of phenyl thiocyanate.

The compounds (I), (III)–(V) and (VI) are generally soluble in cold acetone, acetonitrile, methylene chloride, chloroform and in hot alcohols; (VII) and (VIII) are slightly soluble in cold methylene chloride, chloroform and in hot acetone, acetonitrile and alcohols. All the compounds are insoluble in ethyl ether, hydrocarbons and carbon tetrachloride. All the compounds are stable in the solid state and are not affected by air and moisture. The bromide and iodide complexes must be stored in dark bottles.

Molecular weight measurements were carried out with a Mechrolab osmometer Model 302. Benzil was used as calibrating substance. The i values were calculated as usual^{1,2}. The measurements in acetone and methanol were carried out at 37°, those in methylene chloride at 25° (Tables 1 and 2).

Conductivity measurements were carried out in acetone and methylene chloride at 25° using a LKB bridge and operating within 10 min from solution preparation. Data are reported in Table 3 along with some measurements conducted on arsonium salts for comparison.

Spectrophotometric measurements were carried out on a Beckman DK-2A spectrophotometer. Solution spectra were measured in anhydrous methylene chloride at 25°, using 1 cm silica cells. Wavelengths of the absorption maxima and extinction coefficients (average for concns. in the range $0.5\text{--}1.5 \cdot 10^{-4}$ mole \cdot l⁻¹) are reported in Table 3. Spectra of solid samples finely grinded in nujol and adsorbed on Whatman Nr. 1 paper were recorded. The maxima are reported in parenthesis in Table 3.

TABLE 1

OSMOMETRIC MEASUREMENTS OF ORGANOBISMUTH(III) COMPLEXES IN ANHYDROUS SOLVENTS

Compound	Molar concn. ($\times 10^2$)	<i>i</i>		
		In CH_3COCH_3 at 37°	In CH_3OH at 37°	In CH_2Cl_2 at 25°
(I) $[(\text{C}_6\text{H}_5)_3\text{As}][(\text{C}_6\text{H}_5)_2\text{BiCl}_2]$	0.75	1.57	2.92	1.19
	0.50	1.62	2.98	1.22
	0.25	1.67	2.95	1.39
(II) $[(\text{CH}_3)_4\text{N}][(\text{C}_6\text{H}_5)_2\text{BiCl}_2]$	0.75	1.46		
	0.50	1.51		
	0.25	1.62		
(III) $[(\text{C}_6\text{H}_5)_4\text{As}][(\text{C}_6\text{H}_5)_2\text{BiBr}_2]$	1.00	1.57	2.73	1.18
	0.50	1.67	2.81	1.30
	0.25	1.72	2.84	1.35
(IV) $[(\text{C}_6\text{H}_5)_4\text{As}][(\text{C}_6\text{H}_5)_2\text{BiI}_2]$	0.75	1.57	^a	1.22
	0.50	1.65		1.32
	0.25	1.75		1.38
(V) $[(\text{C}_6\text{H}_5)_3\text{As}][(\text{C}_6\text{H}_5)_2\text{Bi}(\text{SCN})_2]$	0.75	1.67	2.81	1.29
	0.50	1.76	2.95	1.37
	0.25	1.96	3.06	1.45
(VI) $[(\text{C}_6\text{H}_5)_4\text{As}][\text{C}_6\text{H}_5\text{BiCl}_3]$	0.50	1.57	3.20	^{b,c}
	0.25	1.72	3.39	
	0.125	1.83	3.62	
(VII) $[(\text{C}_6\text{H}_5)_4\text{As}][\text{C}_6\text{H}_5\text{BiBr}_3]$	0.50	^a	3.06	^{b,d}
	0.25		3.27	
	0.125		3.45	
(VIII) $[(\text{C}_6\text{H}_5)_4\text{As}][\text{C}_6\text{H}_5\text{BiI}_3]$		^a	^a	^{b,e}

^a The solubility is not sufficient for osmometric measurements. ^b Molecular weight is reported (see below) instead of *i* owing to the small dissociation of the complex (concn. between $0.1\text{--}0.5 \times 10^{-2}$ mole/l). ^c Mol. wt. found: 745 (calcd.: 776). ^d Mol. wt. found: 820 (calcd.: 909). ^e Mol. wt. found: 810 (calcd.: 1050).

TABLE 2

MOLECULAR WEIGHTS OF MONO- AND DIPHENYLBISMUTHINES IN ANHYDROUS SOLVENTS^a

Compound	Mol. wt. calcd.	Mol. wt. found	
		In CH_3COCH_3 at 37°	In CH_2Cl_2 at 25°
$(\text{C}_6\text{H}_5)_2\text{BiCl}$	398	400	409
$(\text{C}_6\text{H}_5)_2\text{BiBr}$	443	450	447
$(\text{C}_6\text{H}_5)_2\text{BiI}$	490	472	493
$\text{C}_6\text{H}_5\text{BiBr}_2$	446	444	^b
$\text{C}_6\text{H}_5\text{BiI}_2$	540	521	^b

^a Osmometric measurements in methanol could not be carried out owing to the continuous variation of *i* with time, indicating a reaction with the solvent. ^b The solubility is too low for mol. wt. measurements.

DISCUSSION

The compounds prepared are salts of organobismuth(III) complex anions, as it can be stated on the base of analytical data and of the values for both *i* and molar

conductivities in acetone (Tables 1 and 3). In this solvent the anions $(C_6H_5)_2BiX_2^-$ ($X=Cl, Br, I, SCN$) and $C_6H_5BiCl_3^-$ seem in fact to be present as monomeric species, together with the arsonium (or ammonium) cations. If the anionic complexes were completely dissociated in this solvent, the osmometric measurements should give $i \rightarrow 3$, corresponding with the presence of arsonium (or ammonium) cation, X^- and $(C_6H_5)_2BiX$ (or $C_6H_5BiCl_2$). The last compounds act as monomeric species, slightly dissociated in some cases, in acetone, according to molecular weights and molar conductivities (Tables 2 and 3). Complexes not sufficiently soluble in acetone for osmometric measurements gave similar conductance values; this would seem to indicate that the anionic species $C_6H_5BiX_3^-$ ($X=Br, I$) are again present. The possibility of solvent coordination is not taken into account. The molar conductivities for all the complexes in acetone are in the range $105-125 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$, while the value for tetraphenylarsonium salts at the same concentration ($1 \times 10^{-3} \text{ mole} \cdot \text{l}^{-1}$) is about $150 \text{ ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$. (Arsonium salts yield $i \rightarrow 2$ in the same solvent). The difference may be due to both the considerable anion size of the complexes and their incomplete dissociation. $[C_6H_{13}N_2][BiCl_4]$ resembles the organobismuth complexes here described in behaving as a 1/1 electrolyte in acetone¹⁰.

In methanol the halogenobismuthines decompose completely. The diphenylbismuth(III) complex anions are dissociated ($i \rightarrow 3$, Table 1), but the free halogenobismuthines do not react with the solvent when arsonium (or ammonium) salts are present. In fact the complexes can be recrystallized from methanol. The dissociation of phenylbismuth(III) complexes leads to a partial decomposition of free phenylbismuthines ($i > 3$, Table 1).

TABLE 3

MOLAR CONDUCTIVITIES AND UV DATA

Molar conductivities ($\text{ohm}^{-1} \cdot \text{cm}^2 \cdot \text{mole}^{-1}$) in anhydrous acetone (concn. $1 \times 10^{-3} \text{ mole/l}$) and methylene chloride (concn. $0.5 \times 10^{-3} \text{ mole/l}$); maxima ($m\mu$) and extinction coefficients ϵ of electronic absorption spectra in methylene chloride (values in parentheses refer to spectra in *nujol*); temp.: 25° .

Compound	Molar conductivity		λ_{max} ($m\mu$)	$\epsilon \times 10^{-3}^a$
	In CH_3COCH_3	In CH_2Cl_2		
$(C_6H_5)_4AsCl$	152	58		
$(C_6H_5)_4AsBr$	149	55		
$(C_6H_5)_4AsSCN$	155	60		
$(C_6H_5)_2BiCl$	2	0	316	2.2 ^b
$(C_6H_5)_2BiBr$	2	0	325	2.3 ^b
$(C_6H_5)_2BiI$	5	0		
$C_6H_5BiBr_2$	2	0	341	2.8
(I)	108	54	295 (298)	4.8
(II)	125		295	
(III)	112	56	309 (313)	6.8
(IV)	114	55	294, 342 (350)	12.5, 10.0
(V)	123	55	(sh ~ 305)	
(VI)	106	50	326 (318)	3.0
(VII)	110	51	362 (353)	4.0
(VIII)	108	53	308, 425 (425)	24.5, 5.2

^a ϵ values are slightly variable; average values are listed (concn. in the range $0.5-1.5 \times 10^{-4} \text{ mole/l}$).

^b In anhydrous benzene the same λ_{max} and ϵ are obtained.

Measurements in methylene chloride were carried out in order to investigate the behaviour of complexes in the solvent used for spectrophotometric studies. The compounds $(C_6H_5)_2BiX$ ($X=Cl, Br, I$) are monomeric in this solvent (Table 2) and the solutions, like those of $C_6H_5BiX_2$ ($X=Br, I$), do not conduct (Table 3). The salts of the organobismuth complexes are much more associated than in acetone, especially for $C_6H_5Bi^{III}$ derivatives (Table 1). The conductivities are similar to those found for arsonium salts, which are again considerably associated; for $(C_6H_5)_4AsSCN$ $i=1.4$ (concn. = $1.5 \times 10^{-3} M$) has in fact been found.

The absorption spectra maxima in methylene chloride of $(C_6H_5)_2BiX$ ($X=Cl, Br$), $C_6H_5BiBr_2$ and the complexes prepared are shown in Table 3. For $(C_6H_5)_2Bi^{III}$ the complex formation causes a shift of the bismuth-halogen band towards lower wave-lengths; phenyldibromobismuthine behaves in the opposite way, the band at $341 m\mu$ shifting to $362 m\mu$ in the corresponding bromide complex.

The maxima for solid samples in nujol (Table 3, in parenthesis) do not coincide with the values in solution. They are shifted towards increasing wave-lengths for $(C_6H_5)_2Bi^{III}$ complexes; the contrary is observed for $C_6H_5Bi^{III}$ complexes. For the compounds $[(C_6H_5)_4As][C_6H_5)_nBiCl_{4-n}]$ ($n=0, 1, 2$) the band is present at higher energies as the number of chlorine atoms bonded to bismuth decreases; the values of λ_{max} for the complex $[(C_6H_5)_4As][BiCl_4]$ are 326 in methylene chloride and 332 in nujol. The structure of the organobismuth anions is probably similar to that of bismuth tetrahalide anions. Raman and IR spectral studies^{10,11} indicate a distorted tetrahedral geometry for the anions BiX_4^- ($X=Cl, Br, I$) both in solution and in the solid state. IR studies on the prepared complexes are in progress.

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