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Hydroxyphenyltellurium(IV) Halides

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The preparation and properties of some hydroxyphenyltellurium(IV) halides are described. Conductivity and cryoscopic measurements show that materials of the type $RTeBr_3$, $RTeI_3$ *and* R_3TeX *(X = Cl, Br, I) behave as 1:1 electrolytes in dilute solution, whereas compounds with compositions* R_2TeX_2 *exhibit molecular properties and tend to polymerise at higher concentration. The* ^1H *NMR spectra are discussed.*

Introduction

Although aryltellurium(IV) halides have been known for many years, only three hydroxyphenyltellurium(IV) halides appear to have been identified [1–3]. We report here the preparation of new hydroxyphenyltellurium(IV) halides by the reaction of tellurium tetrachloride with phenol (hydroxybenzene), catechol (1,2-dihydroxybenzene), and resorcinol (1,3-dihydroxybenzene) and the subsequent reaction of these chlorides with potassium halides. Some of the physical and spectroscopic properties of the materials are described.

Experimental

The chlorides were prepared from the stoichiometrically required proportions of tellurium tetrachloride and appropriate hydroxybenzene compound in chloroform solution.

p-Hydroxyphenyltellurium(IV) trichloride, bis 1,2-dihydroxyphenyltellurium(IV) dichloride and tris 1,3-dihydroxyphenyltelluronium(IV) chloride were prepared by boiling the mixtures under reflux in an atmosphere of nitrogen until the evolution of hydrogen chloride ceased. Bis-*p*-hydroxyphenyltellurium(IV) dichloride was prepared from an excess of the organic compound under prolonged heating (47 h). The deposited solids were removed by filtration and recrystallised from either acetone/CCl_4 or ether and dried *in vacuo.*

1,2-dihydroxyphenyltellurium(IV) trichloride and bis 1,3-dihydroxyphenyltellurium(IV) dichloride were prepared by addition of the cold reactants. The precipitated products were removed by filtration, washed in benzene and dried *in vacuo.*

The hydroxyphenyltellurium(IV) -trichlorides and -dichlorides were converted to -bromides and -iodides by halogen exchange using potassium -bromide or -iodide in dry methanol.

Analytical data are recorded in Table I.

Conductance measurements were performed under dry conditions in nitrobenzene, acetone and acetonitrile solution at 22 ± 2 °C using a conductance bridge and dip type cell with smooth platinum electrodes. Molecular weights were determined cryoscopically in nitrobenzene. (Tables deposited with the Editor).

^1H NMR spectra were recorded in *d*-acetone using tetramethylsilane as an internal reference. Chemical isomer shift data are recorded in Table II.

Results and Discussion

Although many aryltellurium(IV) halides have been reported the only derivatives of hydroxybenzene type compounds appear to be the hydroxyphenyltellurium(IV) -trichloride [2] and -triiodide [3] and the bis 1,3-dihydroxyphenyltellurium(IV) dichloride [1]. These results were confirmed during these investigations and it therefore seems that the reported [1] interaction of tellurium tetrachloride with phenol to give a yellow crystalline addition compound is erroneous.

The ^1H NMR spectrum of hydroxyphenyltellurium(IV) trichloride shows a four line AA'BB' signal characteristic of a 1,4 disubstituted benzene derivative. It seems therefore that, despite the acidic nature of the hydroxyl proton, phenol undergoes a Friedel-

TABLE I. Analytical Data.

Compound	m.p. °C	Yield %	Found (%)				Molecular formula	Calcd. (%)			
			C	H	Te	Hal		C	H	Te	Hal
(p-HOC_6H_4)$TeCl_3$	224	85	21.85	1.64	38.88	32.07	$C_6H_5Cl_3OTe$	22.03	1.53	38.95	32.56
(p-HOC_6H_4)$TeBr_3$	220–222	86	16.38	1.10	26.99	52.76	$C_6H_5Br_3OTe$	15.62	1.08	27.70	52.11
(p-HOC_6H_4)TeI_3	158–160	96	11.70	0.80	20.87	63.10	$C_6H_5I_3OTe$	11.99	0.83	21.22	63.31
(p-HOC_6H_4)$_2TeCl_2$	200–203	70	37.50	2.40	33.35	18.68	$C_{12}H_{10}Cl_2O_2Te$	37.40	2.59	33.18	18.47
(p-HOC_6H_4)$_2TeBr_2$	197–199	90	30.70	2.11	26.72	33.97	$C_{12}H_{10}Br_2O_2Te$	30.38	2.11	26.94	33.78
(p-HOC_6H_4)$_2TeI_2$	130–132	90	25.92	1.80	22.08	44.20	$C_{12}H_{10}I_2O_2Te$	25.39	1.76	22.49	44.73
$(1,2(OH)_2C_6H_3)TeCl_3$	194	64	20.95	1.50	37.36	31.04	$C_6H_5Cl_3O_2Te$	21.01	1.75	37.19	31.05
$(1,2(OH)_2C_6H_3)TeBr_3$	175–178	95	15.10	1.00	25.95	51.08	$C_6H_5Br_3O_2Te$	15.13	1.05	26.77	50.32
$(1,2(OH)_2C_6H_3)TeI_3$	107–110	95	11.7	0.75	20.14	62.13	$C_6H_5I_3O_2Te$	11.67	0.81	20.67	61.67
$(1,2(OH)_2C_6H_3)_2TeCl_2$	145–147	39	33.38	2.30	30.42	16.87	$C_{12}H_{10}Cl_2O_4Te$	34.59	2.40	30.63	17.02
$(1,2(OH)_2C_6H_3)_2TeBr_2$	184–186	95	28.36	2.06	24.86	32.10	$C_{12}H_{10}Br_2O_4Te$	28.51	1.98	25.24	31.62
$(1,2(OH)_2C_6H_3)_2TeI_2$	175–178	90	24.56	1.75	20.93	42.86	$C_{12}H_{10}I_2O_4Te$	24.04	1.67	21.29	42.34
$(1,3(OH)_2C_6H_3)_2TeCl_2$	190	70	33.87	2.26	30.21	17.61	$C_{12}H_{10}Cl_2O_4Te$	34.59	2.40	30.63	17.02
$(1,3(OH)_2C_6H_3)_2TeBr_2$	150–153	96	28.30	2.10	24.89	32.16	$C_{12}H_{10}Br_2O_4Te$	28.51	1.98	25.24	31.62
$(1,3(OH)_2C_6H_3)_2TeI_2$	179–182	93	24.10	2.00	20.93	42.95	$C_{12}H_{10}I_2O_4Te$	24.04	1.67	21.29	42.34
$(1,3(OH)_2C_6H_3)_3TeCl$	129–131	33			26.06	7.63	$C_{18}H_{15}ClO_6Te$			26.04	7.25
$(1,3(OH)_2C_6H_3)_3TeBr$		85			24.34	15.41	$C_{18}H_{15}BrO_6Te$			23.87	14.96
$(1,3(OH)_2C_6H_3)_3TeI$		80			21.28	22.31	$C_{18}H_{15}IO_6Te$			21.94	21.86

Crafts type condensation reaction with tellurium tetrachloride involving the attack by the $TeCl_3^+$ unit of the position *para* to the hydroxyl group in the aromatic ring. No *ortho* or *meta* substituted products were isolated and thin layer chromatography gave no indication of mixures. The mechanism of electrophilic attack is presumably similar to that which occurs during the reaction of aromatic ethers with tellurium tetrachloride [4–6]. It is interesting that phenol, like anisole, phenetole and diphenyl ether [4–6], react with tellurium tetrachloride under relatively mild refluxing conditions to give insoluble trichlorides even when a twofold quantity of the aromatic compound is present, and that the formation of the tellurium(IV) dichloride derivative requires a large excess of the organic compound under more vigorous conditions.

Resorcinol reacted with tellurium tetrachloride to give the tellurium(IV) dichloride as opposed to the expected -trichloride which was obtained from the analogous reaction with catechol. Presumably the tellurium(IV) trichoride of resorcinol is soluble in the chloroform reaction solvent and further attack by unreacted aromatic molecules gives the tellurium(IV) dichloride. In this respect it is interesting to note that when boiled under reflux resorcinol reacts with tellurium tetrachloride to give the hygroscopic tellurium(IV) chloride. Compounds of the type R_3TeCl could not be prepared from phenol or catechol. It is possible that the position *para* to a hydroxyl group in resorcinol is activated to electrophilic attack to a greater extent because that position is *ortho* to the other hydroxyl group.

It is interesting that pure organotellurium products were not obtained from reactions of tellurium tetrachloride with hydroquinone (1,4-dihydroxybenzene) and that similar reactions with *para* substituted derivatives of anisole also gave the formation of either a tellurium oxide or elemental tellurium.

The rate of hydrogen chloride liberation during the reaction of the hydroxyaryl compounds with tellurium tetrachloride and the extent of reduction of $TeCl_4$ to elemental tellurium decreased in the order catechol > resorcinol > phenol. The trend reflects the yields of the hydroxyphenyltellurium(IV) chlorides under the milder conditions which lie in the order phenol > resorcinol > catechol.

p-Hydroxyphenyltellurium(IV) trichloride was not reduced by cold aqueous potassium metabisulphite to a low melting point ditelluride, as occurs with other organotellurium(IV) trichlorides [4–6]. The yellow *p*-hydroxyphenyltellurium(IV) trichloride decomposed under these conditions to elemental tellurium.

The crystalline hydroxyphenyltellurium(IV) -trihalides and -dihalides are stable in dry air. The trihalides are hydrolysed more readily than the dihalides with the ease of hydrolysis decreasing in the order Cl > Br > I. The compounds are insoluble in cold non polar organic solvents but are soluble in more polar solvents such as nitrobenzene, acetone, aceto-

TABLE II. ^1H NMR Chemical Shifts for Aryl Protons.

Compound	δ_A ppm	δ_B ppm	$\delta_A-\delta_B$ ppm	$^3J_{AB}$ Hz
$(p\text{-}HOC_6H_4)TeCl_3$	7.99	6.99	1.00	9
$(p\text{-}HOC_6H_4)_2TeCl_2$	7.87	6.96	0.91	9
$(p\text{-}HOC_6H_4)TeBr_3$	7.95	6.91	1.04	9
$(p\text{-}HOC_6H_4)_2TeBr_2$	7.94	6.96	0.98	9
$(p\text{-}HOC_6H_4)TeI_3$	7.98	6.90	1.08	9
$(p\text{-}HOC_6H_4)_2TeI_2$	7.96	6.89	1.07	9

nitrile and methanol. The solubility decreases in the order $R_2TeX_2 > RTeX_3 > R_3TeX$ and decreases within a given series in the order $Cl > Br \geqslant I$.

The molar conductance data for R_3TeX, $RTeBr_3$ and $RTeI_3$ are similar to those expected [7] for 1:1 electrolytes containing *ca.* 10^{-3} *M* of solute. The results indicate the dissociation of R_3TeX into R_3Te^+ and X^- species and the formation of $RTeX_2^+$ and X^- from $RTeBr_3$ and $RTeI_3$. The conductivity measurements for the chlorides $RTeCl_3$ suggest that these materials are less dissociated and the general behaviour of compounds of composition $RTeX_3$ is similar to that observed in aminoaryltellurium(IV) trihalides [8]. All compounds of the type R_2TeX_2 show covalent behaviour with a lower tendency to dissociation in solution and in this respect resemble the bis phenyltellurium(IV) dihalides [9].

The molecular weights of the materials R_3TeX, $RTeBr_3$ and $RTeI_3$ at concentrations below 10^{-2} mol l^{-1} are lower than the formula weights as would be expected in compounds undergoing 1:1 dissociation. Compounds of the type $RTeCl_3$ and R_2TeX_2 have molecular weights which are only slightly lower than formula weights at lower concentrations and, as suggested by the conductance measurements, appear to dissociate to a lesser extent than the 1:1 electrolytes. The increasing molecular weights of these latter compounds with increasing concentration may reflect some polymerisation at higher concentration.

The AA′BB′ ^1H NMR signals from the *p*-hydroxyphenyltellurium(IV) halides are consistent with compounds containing two pairs of chemically equivalent nuclei with different chemical shifts. The protons in positions *ortho* to tellurium appear at lower field and are designated as δ_A.

The values of $\delta_A-\delta_B$ for the dihalides increase with decreasing electronegativity of the halides and reflect a movement of the signals from the protons *ortho* to tellurium to lower field and a corresponding movement of the signals from the protons *meta* to tellurium to higher field. These movements in opposite directions show that shielding of the *ortho* protons and simultaneous deshielding of the *meta* protons occur with halides of high electronegativity. The values of $\delta_A-\delta_B$ for the trihalides are larger than those of the corresponding dihalides and the increase in $\delta_A-\delta_B$ with decreasing electronegativity of halide is a consequence of the protons *meta* to tellurium moving to higher field with decreasing electronegativity. The ^1H NMR spectra of the other hydroxyphenyltellurium(IV) halides showed complex multiplet signals from the aryl protons which could not be resolved.

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