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Trihalotellurium Compounds of Hydroquinone Dimethyl Ether

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Tellurium(IV) chloride when reacted with hydroquinonedimethyl ether yield the aryltellurium trichloride, 1,4-$(MeO)_2C_6H_3]TeCl_3$. This trichloride undergoes halogen-exchange reactions to give corresponding tribromide and triiodide. Conductance and cryoscopic measurements reflect their electrolyte type behaviour in solution. ^1H NMR spectral study confirms the linkage of trichloro tellurium group to a carbon atom of aromatic ring which is *ortho* to one of the methoxy groups. Far IR spectra reflect their polymeric nature in the solid state.

INTRODUCTION

Tellurium(IV) chloride when reacted with aromatic ethers is known[1–8] to yield tellurium trichlorides and bis(aryl) tellurium dichlorides, where chlorotellurium group is linked to a carbon atom *para* to the —OR group. In view of this, a study of the reaction of $TeCl_4$ with an ether having *para* position already occupied (hydroquinone dimethyl ether), has been carried out to give new aryl tellurium trichloride.

EXPERIMENTAL

All experiments were carried out under dry conditions. Tellurium tetrachloride used was of E. Merck and was purified before use by a standard method[9]. Hydroquinone dimethyl ether was of SRL and was recrystallized before use. KBr and KI were of BDH, AnalaR quality. The solvents were purified and dried by standard methods[10, 11]

Preparations

[1,4-$(MeO)_2C_6H_3]TeCl_3$

Tellurium(IV) chloride (8.1 g, 30.0 mmol) and hydroquinone dimethyl ether (4.14 g, 30 mmol) in about 50 mL dry $CHCl_3$ were refluxed on an oil bath under an atmosphere of dry N_2 for about 40 h until the evolution of HCl ceased. The amount of HCl liberated corresponded to the loss of one equivalent of chlorine atoms per mole of $TeCl_4$. Then CCl_4 (*ca.* 50 mL) was added slowly and with constant shaking, which resulted in the separation of a brown coloured product. This was filtered, washed thoroughly with benzene to remove any reactant left and then dried over P_4O_{10} in *vacuo*. It was recrystallized from $CHCl_3$; yield: 60–70%.

$[1,4\text{-}(MeO)_2C_6H_3]TeBr_3$ and $[1,4\text{-}(MeO)_2C_6H_3]TeI_3$

The tribromide and triiodide were prepared from the aryltellurium trichloride by halogen-exchange process. A saturated solution of the trichloride in methanol was treated with excess of KBr/KI in the same solvent. An immediate darkening of colour followed by separation of KCl was observed. The addition of diethyl ether resulted in complete precipitation of KCl and excess KBr/KI from the solution. The clear solution upon concentration under vacuum yielded crystals of corresponding tribromide and triiodide, which were recrystallized from ether or acetone.

The purity of these compounds was checked by TLC. Tellurium and halogens were estimated volumetrically by standard methods[12]. Carbon and hydrogen contents were got estimated on a Coleman Model-33 C, H analyser. The analytical data and physical properties are given in Table 1.

RESULTS AND DISCUSSION

The results of elemental analysis show the compounds to be of $RTeX_3$ type. Hydroquinone dimethyl ether appears to undergo Friedel-Crafts type condensation reaction with $TeCl_4$ whereby the $TeCl_3^+$ unit attacks a position *ortho* to any —OCH_3 groups in the aromatic ring. It may also be mentioned that similar reaction with hydroquinone[13] does not give any aryltellurium chloride, rather reduces $TeCl_4$ to Te metal and gets converted into quinone. In other aromatic ethers where *para* position is vacant, the attack by $TeCl_3^+$ takes place at *para* position with respect to —OCH_3 group[1–8].

$$1,4\text{-}(MeO)_2C_6H_4 + TeCl_4 \rightarrow [1,4\text{-}(MeO)_2C_6H_3]TeCl_3 + HCl$$

This aryltellurium trichloride, when treated with KBr/KI, undergoes halogen-exchange reactions to give the corresponding tribromide and triiodide.

These compounds are fairly stable in dry air, but get hydrolysed in presence of moisture. They are soluble in polar organic solvents such as chloroform, ether, acetone, acetonitrile, methanol etc.

Molar conductance data in nitrobenzene, nitromethane and acetonitrile (Table 1) suggest their electrolytic behaviour. Λ_M values of these compounds (except $RTeCl_3$ in nitrobenzene and nitromethane and $RTeBr_3$ in nitrobenzene where the values are slightly lower) are within or close to the expected[14] ranges for 1 : 1 electrolytes containing *ca.* 10^{-3} M of solute and reflect the likely formation in solution of $RTeX_2^+$ and X^- ions. Lower values of Λ_M in some cases, especially in nitrobenzene, may be due to interaction of solvent molecules with solute ions or incomplete dissociation of the compound. This behaviour is very well supported by the molecular weight data in nitrobenzene which have been determined over a wide range of concentration upto the saturation point. The average molecular weights of $RTeBr_3$ and $RTeI_3$ are about one half of their formula weights, whereas that of $RTeCl_3$ is quite close to its formula weight.

TABLE 1

ANALYTICAL, CONDUCTANCE AND MOLECULAR WEIGHT DATA FOR TRIHALOTELLURIUM COMPOUNDS OF HYDROQUINONE DIMETHYL ETHER

Compound (Empirical formula) $R = 1,4\text{-}(OCH_3)_2C_6H_3^-$	Formula weight	Colour	m.p.* (°C)	Analysis % Found (Calc.)				†Λ_M ohm^{-1}cm^{2}mol^{-1}(*ca.* 10^{-3} M)			Conc. range mmol/ litre of solvent	Average molecular weight found
				Te	X	C	H	Nitrobenzene	Nitromethane	Acetonitrile		
$RTeCl_3(C_8H_9O_2TeCl_3)$	371.1	Brown	158–160	34.25 (34.38)	28.26 (28.70)	26.38 (25.78)	4.50 (4.83)	6.5	14.0	52.3	5.4–16.2	339.7
$RTeBr_3(C_8H_9O_2TeBr_3)$	504.5	Dark brown	125–127	24.73 (25.29)	46.12 (47.53)	18.82 (19.03)	1.53 (1.78)	8.5	63.4	104.2	3.9–11.9	249.6
$RTeI_3(C_8H_9O_2TeI_3)$	645.5	Reddish brown	110–112	19.40 (19.77)	58.71 (58.98)	16.27 (14.87)	1.73 (1.39)	20.5	105.1	152.4	3.1–9.3	330.2

*melt with decomposition.

†Value reported[14] for 1 : 1 electrolyte, Nitrobenzene = 20–30, Nitromethane = 60–115 and Acetonitrile = 120–160.

The ^1H NMR spectrum of $RTeCl_3$ type compound suggest the *ortho* substitution of trichlorotellurium moiety with respect to any of the —OCH_3 groups. One phenyl proton which is *ortho* to $TeCl_3$ group appears as a singlet and at relatively down field side (8.20δ ppm, 1H) reflecting the deshielding effect of electron withdrawing $TeCl_3$ group. The remaining two phenyl protons which are *ortho* to one another and have almost similar chemical environment appear at high field side (δ6.9–7.3 ppm, bp, 2H). The six methoxy protons resonate at 3.96 ppm as a broad singlet. Thus on the basis of the position of trichlorotellurium group, one may name this compound systematically as 2,5-dimethoxyphenyl tellurium(IV) trichloride.

The far IR spectra of these aryltellurium trihalides (Table 2) are quite similar to those of phenyl[15] and other aryltellurium trihalides and show the presence of bridged halogen atoms, thus reflecting their polymeric nature in the solid state. The $\nu_{Te\text{-}C}$ appears at *ca.* 250 cm^{-1} which is consistent with other phenyl derivatives of tellurium[15–18]

TABLE 2
FAR IR DATA (cm^{-1}) FOR TRIHALOTELLURIUM COMPOUNDS OF HYDROQUINONE DIMETHYL ETHER

$RTeCl_3$	$RTeBr_3$	$RTeI_3$	Assignments
253 s	258 s	256 s	$\nu_{Te\text{-}C}$
331 m	219 m	175 m	$\nu Te\text{-}X$(Terminal)
306 m	209 s	159 s	
	197 w	150 s	
173 s	131 s	106 s	$\nu Te\text{-}X$(bridge) + δTeX_2
159 s	122 s	94 s	
138 s	113 s		
134 m	106 s		

s = strong, m = medium, w = weak

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REFERENCES

1. K.J. Irgolic, The Organic Chemistry of Tellurium, Gorden and Breach, New York, p. 170 (1974).
2. E. Rust, *Berg.*, **30**, 2829 (1897).
3. G.T. Morgan and H.D.K. Drew, *J. Chem. Soc.*, **127**, 2307 (1925).
4. G.T. Morgan and R.E. Kellet, *J. Chem. Soc.*, 1080 (1926).
5. L. Reichel and E. Kirschbaum. *Ann. Chem.*, **523**, 211 (1936).
6. F.J. Berry, E.H. Kustan, M. Roshani and B.C. Smith, *J. Organometal. Chem.*, **99**, 115 (1975).
7. K. Raina and B.L. Khandelwal, *Indian J. Chem.*, **14A**, 63 (1976).
8. J. Bergman, *Tetrahedron*, **28**, 3323 (1972).

9. G. Brauer, Hand Book of Preparative Inorganic Chemistry, 2nd Edn., Academic Press, New York, Vol. 1, p. 442 (1967).
10. A.I. Vogel, A Text Book of Preparative Organic Chemistry, 3rd Edn., Longmans, London (1975).
11. Weissberger (Ed.), Technique of Organic Chemistry, Vol. 7, 2nd Edn., Interscience Publishers, Inc. (1967).
12. A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, 3rd Edn., ELBS and Longmans, London, pp. 324, 266–268 (1973).
13. B.L. Khandelwal, Krishan Kumar and F.J. Berry, *Inorg. Chim. Acta*, **47**, 135 (1981).
14. W.J. Geary, *Coord. Chem. Revs.*, **7**, 81 (1971).
15. W.R. McWhinnie and P. Thavornyutikarn, *J. Chem. Soc. (Dalton)*, 551 (1972).
16. N.S. Dance and C.H. W. Jones, *J. Organometal. Chem.*, **152**, 175 (1978).
17. W.R. McWhinnie and M.G. Patel, *J. Chem. Soc. (Dalton)*, 199 (1972).
18. N.S. Dance and W.R. McWhinnie, *J. Chem. Soc. (Dalton)*, 43 (1975).

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