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TETRAORGANYLPHOSPHONIUM SALTS OF DIHALOORGANYLTELLURATES(II) AND DIHALOORGANYLSELENATES(II)

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Summary

Salts containing $[ArTeI_2]^-$ and $[ArTeBrI]^-$ are obtained by the reaction of Ar_2Te_2 with I_2 followed by treatment of the resulting solution with a tetraorganylphosphonium halide. Only certain cations yield the desired salts as crystalline materials. Tetraorganylphosphonium salts of $[C_6H_5SeBr_2]^-$ are also reported.

Introduction

Compounds of the type ArTeX (X = uninegative anion) are relatively unstabl and few have been reported. The first member of this class to be prepared was *p*-methoxyphenyltellurenyl methanethiosulfonate [1]. For many years the only known tellurenyl halide was 2-naphthyltellurenyl iodide [2]. Isolation of the latter compound was unexpected because the reaction of iodine with other diaryl ditellurides gave aryltellurium triiodides. Recently Piette et al. [3, 4] have prepared a number of *o*-formyl- and *o*-acetylphenyltellurenyl halides. The stability of these compounds is due to the *ortho* substituent on the benzene ring.

We have recently published methods for the preparation of a variety of tetrahaloaryltellurates(IV) [5], and report now the synthesis of dihaloaryltellurates(II) from aryltellurenyl halides and phosphonium halides.

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Results and discussion

The stable 2-naphthyltellurenyl iodide reacts readily with triphenylmethylphosphonium iodide to yield triphenylmethylphosphonium diiodo(2-naphthyl)tellurate(II) (I, eqn. 1), an air stable red crystalline compound. It is of greater

$$2\text{-}C_{10}H_7TeI + [(C_6H_5)_3PCH_3]I \rightarrow \underset{(I)}{[(C_6H_5)_3PCH_3][2\text{-}C_{10}H_7TeI_2]} \qquad (1)$$

interest, however that a number of unstable and normally non-isolable tellurenyl halides may be prepared in situ and then treated with tetraorganylphosphonium halides to yield dihalo(aryl)tellurates(II) (eqn. 2a, b). Compounds II—V (Table 1)

$$ArTeTeAr + X_2 \rightarrow 2\,ArTeX \qquad (2a)$$
$$ArTeX + [(C_6H_5)_3PR]X' \rightarrow [(C_6H_5)_3PR][ArTeXX'] \qquad (2b)$$

were obtained via eqns. 2a, b as stable crystalline solids. This reaction sequence did not yield crystalline materials in all cases. Attempts to prepare $[(C_6H_5)_3PCH_2C_6H_5][p\text{-}EtOC_6H_4TeICl]$ and methyltriphenylphosphonium salts of $[C_6H_5TeI_2]^-$, $[p\text{-}CH_3C_6H_4TeI_2]^-$ and $[C_6H_5TeBrI]^-$ gave intractable oils.

An unexpected result was obtained when we tried to prepare the compound $[C_6H_5)_3PCH_3][p\text{-}EtOC_6H_4TeBr_2]$. The tetrabromo(*p*-ethoxyphenyl)tellurate(IV) was obtained in 33% yield, and 65% of the starting ditelluride was recovered. This result, together with the isolation of oily mixtures in some cases, suggests that the equilibria (all rapid) represented by eqns. 3a—d exist. Whether one obtains a pure

$$Br_2 + Ar_2Te_2 \rightleftharpoons 2\,ArTeBr \qquad (3a)$$
$$ArTeBr + R_4PBr \rightleftharpoons [R_4P][ArTeBr_2(\text{cryst})] \qquad (3b)$$
$$ArTeBr + Br_2 \rightleftharpoons ArTeBr_3 \qquad (3c)$$
$$ArTeBr_3 + R_4PBr \rightleftharpoons [R_4P][ArTeBr_4(\text{cryst})] \qquad (3d)$$

tellurate(II) or tellurate(IV), or a mixture, apparently depends on a delicate balance involving the relative stability and solubility of the Te^{II} vs. the Te^{IV} containing salt in a particular system.

Alkylammonium dibromoarylselenates(II) have been prepared by Wynne, et al. [6]. We now report an extension of this work to the preparation of the tetraorganophosphonium dihaloarylselenates(II) listed in Table 2. Of particular

TABLE 1

ANALYTICAL DATA AND PROPERTIES OF DIHALO(ARYL)TELLURATE(II) SALTS

Compound	Number	Yield (%)	M.p. (°C)	Appearance or crystals	E [a]	Te, found (calcd.)(%)
$[(C_6H_5)_3PCH_3]$-$[2\text{-}C_{10}H_7TeI_2]$	I	98	160—162	Brilliant red	59	16.00 (16.23)
$[(C_6H_5)_3PCH_3]$-$[p\text{-}CH_3OC_6H_4TeI_2]$	II	85	104—106	Brown reddish	80	16.69 (16.68)
$[(C_6H_5)_3PCH_3]$-$[p\text{-}EtOC_6H_4TeI_2]$	III	95	142—143	Red-violet	69	16.27 (16.36)
$[(C_6H_5)_3PCH_3]$-$[p\text{-}EtOC_6H_4TeIBr]$	IV	90	127—128	Red	80	17.67 (17.54)
$[(C_6H_5)_3PCH_3]$-$[p\text{-}CH_3OC_6H_4TeBr_2]$	V	96	144—145	Red	87	19.13 (18.98)

[a] Equivalent conductivity in nitromethane ($ohm^{-1}\ cm^2$) at 10^{-3} M, 25°C.

TABLE 2

ANALYTICAL DATA AND PROPERTIES OF DIHALO(ARYL)SELENATE(II) SALTS

Compound	Number	Yield (%)	M.p.	Appearance of crystals	E [a]	Se, found (calcd.)(%)
$[(C_6H_5)_3PCH_3]$-$[C_6H_5SeBr_2]$	VI	100	105—106	Orange [b]	79	13.45 (13.30)
$[(C_6H_5)_3PHC(CH_3)CO_2CH_3]$-$[C_6H_5SeBr_2]$	VII	95	145—146	Red-violet [c]	90	11.85 (11.86)
$[(C_6H_5)_4P]$-$[C_6H_5SeBr_2]$	VIII	95	176—178	Orange [d]	81	11.91 (12.05)
$[(C_6H_5)_3PCH_2C_6H_5]$-$[C_6H_5SeBrCl]$	IX	100	165—166	Red [d]	77	12.64 (12.63)
$[(C_6H_5)_3PCH_2C_6H_5]$-$[C_6H_5SeBr_2]$	X	90	156—157	Orange [c]	86	11.55 (11.79)

[a] Equivalent conductivity in nitromethane (ohm^{-1} cm^2) at 10^{-3} *M*, 25°C. [b] Recrystallized from CH_3CN. [c] Recrystallized from EtOH. [d] Recrystallized from CH_2Cl_2/EtOAc.

interest is the unique preparation of the "mixed" dihalo derivative triphenylbenzylphosphonium bromochlorophenylselenate(II) (IX). No difficulties such as oil formation or production of Se^{IV} species were encountered in the preparation of compounds VI—X. This may be due to the greater resistance of selenium to oxidation and the lesser importance of an equilibrium paralleling eqn. 3c. Also of interest was the finding that 2,4-dinitrophenylselenenyl bromide was unreactive towards tetraorganylphosphonium halides. Direct evidence for intramolecular coordination of the *o*-nitro group has recently been obtained through an X-ray crystal structure determination of *o*-nitrophenyl(thiourea)selenium(II) thiocyanate [7]. It is therefore likely that our inability to isolate a dibromo(2,4-dinitrophenyl)selenate(II) is due to the presence of a coordinated *o*-nitro group and the instability of any higher coordinated species.

The conversion of IX to X (eqn. 4) by treatment with ethanolic/aqueous

$$[C_6H_5SeBrCl]^- + HBr(EtOH/H_2O) \rightarrow [C_6H_5SeBr_2]^- + HCl \qquad (4)$$

HBr and the crystallization of III from the same medium demonstrate a high stability of the anions in acidic medium, which parallels the similar stability of tetrahaloaryltellurate(IV) and hexahalotellurate (IV) anions [5].

Raman spectroscopic data

Raman spectral data for compounds I—IV are summarized in Table 3. The observation of an intense polarized absorption near 100 cm^{-1} together with a weak higher frequency absorption closely parallels the results for $(CH_3)_2TeI_2$ [8]. The presence of a linear I—Te—I group in the diiodoaryltellurate(II) anions is thus strongly indicated and is consistent with the expected T-shaped molecule resulting from the disposition of three bonding and two nonbonding electron pairs.

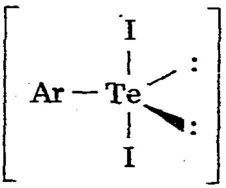

TABLE 3

RAMAN SPECTROSCOPIC DATA (cm^{-1})

I	II	III	IV	Assignment
47 w		53 m	71 m	
67 s	74 a	69 m		
80 w				
90 w	89 w		85 w (sh)	
100 w				
124 m	105 vs [a]	96 s [b]	103 s	ν_{sym} (X—Te—X′)
	133 vw	126 w		
	144 vw	139 vw	149 vw	ν_{asym} (X—Te—X′)
	155 vw			
176 vw	177 vw		183 w	
199 m	217 vw			

[a] Polarized in CH_3CN solution (106). [b] Polarized in CH_3CN solution (105).

The Raman spectrum of IV which presumably contains an unsymmetric Br—Te—I group is similar to that for I—III. It is surprising that the symmetric X—Te—X′ mode for this compound is not altered substantially relative to I—III.

As was observed previously [5], salts containing $C_6H_5SeBr_2^-$ exhibit a strong polarized absorption assigned to ν_{sym} (Br—Se—Br) in the vicinity of 170 cm^{-1} (VI, 185; VII, 157 s; IX, 178 s cm^{-1}). Compound IX gave rise to a strong Raman absorption at 180 cm^{-1} assigned to ν_{sym} (Br—Se—Cl).

Experimental section

Raman spectroscopic and conductivity data were obtained as previously described [5]. 2-Naphthyltellurenyl iodide [2], bis(*p*-methoxyphenyl) ditelluride [9], bis(*p*-ethoxyphenyl) ditelluride [9], di-*p*-tolyl ditelluride [10], diphenyl ditelluride, phenylselenenyl bromide [11], triphenylmethylphosphonium iodide [12], and bromide [13], triphenylbenzylphosphonium chloride [14], triphenyl-α-carbomethoxyethylphosphonium bromide [15], and tetraphenylphosphonium bromide [16] were prepared by standard literature methods.

Typical preparative procedures are outlined below for aryltellurenyl and arylselenenyl salts. Melting points, analytical and conductivity data and yields may be found in Tables 1 ($ArTeX_2^-$) and 2 ($ArSeX_2^-$).

Triphenylmethylphosphonium diiodo(2-naphthyl)tellurate(II) (I)

A solution of 2-naphthyltellurenyl iodide (1.14 g, 3.0 mmole) and triphenylmethylphosphonium iodide (1.21 g, 3.0 mmole) in 25 ml $CHCl_3$ was refluxed for 2 h. Evaporation of solvent gave a dark oil which was taken up in a few ml of CH_2Cl_2. Upon addition of ethyl acetate the title compound separated as dark red crystals (2.30 g, 98% yield).

Tetraorganylphosphonium dihalo(aryl)tellurates(II) (Table 1)

Aryltellurenyl halides were prepared in situ by the addition of the appropriate halogen (ca. 2 mmoles in 20 ml benzene) to 2 mmoles of diaryl ditelluride also in 20 ml benzene at 0°. A solution of tetraorganophosphonium halide (4 mmoles, 20 ml $CHCl_3$) was then added and the mixture was stirred for 12 h.

The desired compounds separated and were filtered and recrystallized from CH_2Cl_2/EtOAc.

Compound IV was prepared by generating *p*-$EtOC_6H_4TeI$ in situ and adding $[(C_6H_5)_3PCH_3]Br$ or by preparing *p*-$EtOC_6H_4TeBr$ in situ and adding $[(C_6H_5)_3PCH_3]I$.

Attempted preparation of triphenylmethylphosphonium dibromo(p-ethoxyphenyl)tellurate(II)

Bis(*p*-ethoxyphenyl) ditelluride (0.49 g, 1.0 mmole) in 25 ml benzene was treated, successively, with bromine (0.16 g, 1.0 mmole) and triphenylmethylphosphonium bromide (0.17 g, 2.0 mmole) in 20 ml $CHCl_3$. The crystals which formed after stirring for 12 h were collected and washed with cold ethanol. The product was triphenylmethylphosphonium tetrabromo(*p*-ethoxyphenyl)tellurate(IV) [5], (0.56 g, 33% yield, m.p. 205—206°). The mixed m.p. with an authentic sample was not depressed. Upon concentration the filtrate gave 0.32 g bis(*p*-ethoxyphenyl) ditelluride (65.3% of the initial amount), m.p. 106°. Repeated attempts changing solvent and temperature gave the same result.

Attempts to prepare other tetraorganylphosphonium dihalo(aryl)tellurates(II)

Attempts to prepare $[(C_6H_5)_3PCH_3]$ [*p*-$CH_3C_6H_4TeI_2$] gave impure oils. Unidentified products were also obtained in the attempted preparation of $[(C_6H_5)_3PCH_2C_6H_5]$ [*p*-$EtOC_6H_4TeICl$] and $[(C_6H_5)_3PCH_3]$ $[C_6H_5TeIBr]$ starting from the appropriate ditellurides, iodine, and tetraorganylphosphonium halide.

Tetraorganylphosphonium dihalo(aryl)selenates(II)

A solution of C_6H_5SeBr (3.0 mmoles) and tetraorganylphosphonium halide (3.0 mmoles) in 30 ml $CHCl_3$ was refluxed for 4 h. On evaporation of solvent the crude products were obtained as pasty oils. Compounds VI, VIII and IX crystallized on treatment with AcOEt. Compound VII crystallized upon treatment of an ethanol solution with 10% aqueous HBr at 0°. Compound X was obtained by treating an ethanol solution of IX with 10% HBr at 0°. The product separated as a crystalline solid in quantitative yield.

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References

1 O. Foss, Acta Chem. Scand., 6 (1952) 306.
2 G. Vicentini, E. Giesbrecht and L. Pitombo, Chem. Ber., 92 (1959) 40.
3 J.L. Piette and M. Renson, Bull. Soc. Chim. Belges, 80 (1971) 699.
4 J.L. Piette, R. Lysy and M. Renson, Bull. Soc. Chim. France, (1972) 3559.
5 N. Petragnani, L. Torres, K.J. Wynne and W. Maxwell, J. Organometal. Chem., 55 (1973) 295.
6 K.J. Wynne and P.S. Pearson, Inorg. Chem., 11 (1972) 1196.
7 R. Erikson and S. Hauge, Acta Chem. Scand., 26 (1972) 3153.
8 G.C. Hayward and P.J. Hendra, J. Chem. Soc. (A), (1969) 1760.
9 L. Reichel and E. Kirschbaum, Chem. Ber., 76 (1943) 1105.
10 W. Farrar, Research, 4 (1951) 177.

11 O. Behaghel and H. Seibert, Ber., 65 (1932) 815.
12 A. Michaelis and L. Gleichman, Ber., 15 (1882) 801.
13 G. Wittig and V. Schöllkopf, Org. Synth., 40 (1960) 66.
14 K. Friedrich and H.G. Henning, Chem. Ber., 92 (1959) 2756.
15 O. Isler, H. Gutmann, M. Montavan, R. Ruegy, G. Ryser and P. Zeller, Helv. Chim. Acta, 40 (1957) 1242.
16 L. Horner and H. Hoffmann, Chem. Ber., 91 (1958) 45.