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NEW ANIONIC SPECIES OF TELLURIUM(IV)

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SUMMARY

Tetrahaloaryltellurates(IV) were prepared by refluxing aryltellurium trihalides with phosphonium, tropylium and telluronium halides in $CHCl_3$. These compounds, which contain the $ArTeX_4^-$ anion, may be also prepared from aryltellurium trihalides and aqueous halogen hydride solutions. The phosphonium derivatives can be considered as potential precursors of tellurophosphoranes for Wittig reactions. Halogen exchange reactions allow the interconversion of the complex anions. The ionic nature of the compounds is supported by ion exchange reactions utilizing ion exchange resins, and by conductance measurements. Far infrared and Raman spectral data suggest a square pyramidal configuration for the $ArTeX_4^-$ anions.

Although hexa- and pentahalotellurates(IV) are well known[1–9], similar anionic species but containing a tellurium–carbon bond have received little attention. The compound $[(CH_3)_3Te^+][CH_3TeX_4^-]$ is the only reported example of this type[10]. In this paper tetrahaloaryltellurates(IV), compounds which are characterized by the pentacoordinate $ArTeX_4^-$ anion, are described.

RESULTS AND DISCUSSION

Synthesis

Phosphonium, tropylium, and telluronium tetrahaloaryltellurates(IV) were prepared by treating aryltellurium trihalides with phosphonium, tropylium, and telluronium halides in organic solvents. Tetrachloro- and tetrabromoaryltellurates(IV) may also be prepared utilizing the respective aryltellurium trihalide and aqueous halogen hydride (eqns. 1 and 2).

$$ArTeX_3 + [Y^+]X'^- \xrightarrow{\text{Solv.}} [Y^+][ArTeX_3X'^-] \qquad (1)$$

$$ArTeX_3 \overset{HX}{\rightleftharpoons} [H^+ArTeX_4^-] \xrightarrow{Y^+X^-} [Y^+][ArTeX_4^-] \qquad (2)$$

$$(Y = Ph_3PR;\ C_7H_7;\ Ph_3Te;\ X = Cl, Br;\ X' = Cl, Br)$$

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TABLE 1

$[ArTeX_3X'^-]$ SALTS PREPARED FROM $ArTeX_3$ AND PHOSPHONIUM, TROPYLIUM, AND TELLURONIUM HALIDES

$ArTeX_3$	*$[Y^+]X'^-$* [a]	*$[Y^+][ArTeX_3X'^-]$* [a]	*M.p. (°C)*	*Appearance* [b]	*Te analysis*	
					Found (%)	*Calc. (%)*
p-$EtOC_6H_4TeCl_3$	$[Ph_3PCH_2Ph]Cl$	$[Ph_3PCH_2Ph][p\text{-}EtOC_6H_4TeCl_4]$	177–180	Colorless plates	17.00	17.00
p-$EtOC_6H_4TeCl_3$	$[Ph_3PCH_3]Br$	$[Ph_3PCH_3][p\text{-}EtOC_6H_4TeCl_3Br]$	169–172	Colorless plates	18.13	17.91
p-$EtOC_6H_4TeCl_3$	$[Ph_3CH_2R']Br$	$[Ph_3PCH_2R'][p\text{-}EtOC_6H_4TeCl_3Br]$	177–181	Pale yellow crystals	16.21	16.27
p-$EtOC_6H_4TeCl_3$	$[Ph_4P]Cl$	$[Ph_4P][p\text{-}EtOC_6H_4TeCl_4]$	210–212	Colorless plates	17.39	17.48
$PhTeCl_3$	$[Ph_3PCH_2Ph]Cl$	$[Ph_3PCH_2Ph][PhTeCl_4]$	187–190	Colorless plates	18.34	18.23
$PhTeCl_3$	$[Ph_3PCH_3]Br$	$[Ph_3PCH_3][PhTeCl_3Br]$	133–135	Pale yellow crystals	19.20	19.09
$PhTeCl_3$	$[Ph_3PCH_2R']Br$	$[Ph_3PCH_2R'][PhTeCl_3Br]$	169–172	Colorless crystals	17.64	17.37
$PhTeCl_3$	$[Ph_4P]Cl$	$[Ph_4P][PhTeCl_4]$	220–223	Cream colored needles	18.70	18.60
p-$EtOC_6H_4TeBr_3$	$[Ph_3PCH_2Ph]Cl$	$[Ph_3PCH_2Ph][p\text{-}EtOC_6H_4TeBr_3Cl]$	122–124	Yellow needles	14.67	14.52
p-$EtOC_6H_4TeBr_3$	$[Ph_3PCH_3]Br$	$[Ph_3PCH_3][p\text{-}EtOC_6H_4TeBr_4]$	200–203	Yellow plates	15.00	15.09
p-$EtOC_6H_4TeBr_3$	$[Ph_3PCH_2R']Br$	$[Ph_3PCH_2R'][p\text{-}EtOC_6H_4TeBr_4]$	113–115	Yellow-orange crystals	13.64	13.90
p-$EtOC_6H_4TeBr_3$	$[Ph_4P]Br$	$[Ph_4P][p\text{-}EtOC_6H_4TeBr_4]$	228–232	Pale green crystals	13.76	14.05
$PhTeBr_3$	$[Ph_3PCH_3]Br$	$[Ph_3PCH_3][PhTeBr_4]$	166–170	Yellow needles	15.68	15.91
$PhTeBr_3$	$[Ph_3PCH_2R']Br$	$[Ph_3PCH_2R'][PhTeBr_4]$	147–150	Pale green crystals	14.36	14.60
$PhTeBr_3$	$[Ph_4P]Br$	$[Ph_4P][PhTeBr_4]$	224–226	Yellow needles	14.57	14.77
p-$EtOC_6H_4TeI_3$	$[Ph_3PCH_2Ph]Cl$	$[Ph_3PCH_2Ph][p\text{-}EtOPhTeI_3Cl]$	140–142	Red-brown crystals	12.44	12.53
$PhTeI_3$	$[Ph_3PCH_2Ph]Cl$	$[Ph_3PCH_2Ph][PhTeI_3Cl]$	138–141	Red-brown needles	12.86	13.09
p-$EtOC_6H_4TeCl_3$	$[C_7H_7]Br$	$[C_7H_7][p\text{-}EtOC_6H_4TeCl_3Br]$	218–221	Green crystals[c]	23.97	24.25
$PhTeCl_3$	$[C_7H_7]Br$	$[C_7H_7][PhTeCl_3Br]$	220–223	White needles[c]	26.31	26.47
p-$EtOC_6H_4TeBr_3$	$[C_7H_7]Br$	$[C_7H_7][p\text{-}EtOC_6H_4TeBr_4]$	205–208	Yellow needles[c]	19.23	19.30
$PhTeBr_3$	$[C_7H_7]Br$	$[C_7H_7][PhTeBr_4]$	275–277	Yellow crystals[c]	20.77	20.73
p-$EtOC_6H_4TeI_3$	$[C_7H_7]Br$	$[C_7H_7][p\text{-}EtOC_6H_4TeI_3Br]$	142–145	Red-brown crystals	15.90	15.95
$PhTeI_3$	$[C_7H_7]Br$	$[C_7H_7][PhTeI_3Br]$	230–232	Red-brown crystals[c]	16.93	16.87
$PhTeCl_3$	Ph_3TeBr	$[Ph_3Te][PhTeCl_3Br]$	192–194	Yellow crystals	33.90	34.03

[a] $R' = CO_2Et$. [b] From CH_2Cl_2 and AcOEt. [c] From CH_3CN and AcOEt.

TABLE 2

$[ArTeX_4^-]$ SALTS PREPARED FROM $ArTeX_3$, HX, AND PHOSPHONIUM, TROPYLIUM, AND TELLURONIUM HALIDES

$ArTeX_3$	*HX*	*Y^+X^-*	*$[Y^+][ArTeX_4^-]$*[a]	*M.p. (°C)*	*Appearance*[b]	*Te analysis*	
						Found (%)	*Calcd. (%)*
p-$EtOC_6H_4TeCl_3$	HCl	$[Ph_3PCH_3]Br$	$[Ph_3PCH_3][p$-$EtOC_6H_4TeCl_4]$[c]	156–157			
p-$EtOC_6H_4TeBr_3$	HBr	$[Ph_3PCH_2R']Br$	$[Ph_3PCH_2R'][p$-$EtOC_6H_4TeBr_4]$[d]	113–115			
p-$EtOC_6H_4TeCl_3$	HCl	$[C_7H_7]Br$	$[C_7H_7][p$-$EtOC_6H_4TeCl_4]$	218–221	Yellow needles	26.32	26.43
$PhTeCl_3$	HCl	$[C_7H_7]Br$	$[C_7H_7][PhTeCl_4]$	223–226	Yellow needles	29.18	29.13
p-$EtOC_6H_4TeCl_3$	HCl	$[Ph_3Te]Br$	$[Ph_3Te][p$-$EtOC_6H_4TeCl_4]$	142–143	White needles	33.96	34.07

[a] $R' = CO_2Et$. [b] From CH_3CN and AcOEt. [c] See Table 1.

The compounds prepared in organic solvents can contain either the same or different halogens depending on the starting materials, while those prepared in acidic medium can only contain the same halogens as the acids employed, due to rapid halogen exchange. Tables 1 and 2 show the compounds obtained. A large number of triphenylalkylphosphonium derivatives were prepared; these compounds could serve as precursors of tellurophosphoranes via the Wittig reaction (eqn. 3).

$$\begin{tikzcd}[\mathrm{Ph_3\overset{+}{P}\text{-}CH_2R}][\mathrm{ArTeX_4^-}] \arrow[r, "\text{Base}", "-\mathrm{HX}"'] & [\mathrm{ArTeX_2\text{-}CHR\text{-}\overset{+}{P}Ph_3}]\mathrm{X^-} \arrow[r, "\text{Base}", "-\mathrm{HX}"'] & \mathrm{ArTeX_2\text{-}CR{=}PPh_3} \arrow[d, "-\mathrm{Ph_3PO}"', "\mathrm{R'CHO}"] \\ & & \mathrm{ArTeX_2\text{-}CR{=}CHR'}\end{tikzcd} \quad (3)$$

Preliminary experiments are under investigation to test this scheme.

The tropylium tetrahaloaryltellurates(IV) were prepared with the purpose of enlarging the limited number of tropylium salts containing complex anions[11-16]. These derivatives may be prepared according to eqn. (1) or by treating the aryltellurium trihalides directly with cycloheptatriene in the presence of trityl perchlorate as hydride acceptor. The latter method does not require the laborious preparation of tropylium bromide (eqn. 4).

$$\begin{tikzcd}\mathrm{ArTeCl_3 + C_7H_8 + [Ph_3\overset{+}{C}]ClO_4^-} \arrow[r] & \{[\mathrm{C_7H_7^+}][\mathrm{ArTeCl_3ClO_4^-}]\} + \mathrm{Ph_3CH} \arrow[d, "-\mathrm{ClO_4^-}"', "+\mathrm{Br}"] \\ (\mathrm{Ar}{=}p\text{-}\mathrm{C_2H_5OC_6H_4}) & [\mathrm{C_7H_7^+}][\mathrm{ArTeBr_4^-}]\end{tikzcd} \quad (4)$$

The tetrachloro- and tetrabromoaryltellurates(IV) are fairly soluble in water. Their solutions are stable for a few hours, but after 16–20 h the aryltellurium oxohalides begin to separate (eqn. 5).

$$\begin{tikzcd}[\mathrm{Y^+}][\mathrm{ArTeX_4^-}] \arrow[r, shift left=0.5ex] & \mathrm{ArTeX_3 + Y^+X^-} \arrow[l, shift left=0.5ex] \arrow[d, "\mathrm{H_2O}"] \\ & \mathrm{ArTe(O)X + 2HX}\end{tikzcd} \quad (5)$$

$(\mathrm{X{=}Cl, Br; Y{=}Ph_3PR; C_7H_7; Ph_3Te})$

Halogen exchange reactions may be used to prepare several new compounds not accessible by the preceding methods. When THF solutions of the tetrachloro- or trichlorobromoaryltellurates(IV) were treated with excess dilute HBr at room temperature the tetrabromo derivatives were obtained. The transformation of the bromo compounds to the chloro derivatives required treatment of the former with concentrated HCl for several hours. The substitution of chlorine and bromine by iodide is easily performed in these compounds using excess KI in dilute HCl. The iodo derivatives could not be transformed into the corresponding chloro or bromo derivatives. These results were expected, as the nucleophilic character of the halides increases from chloride to iodide while the solvation decreases in the same order. The halogen interchange reaction and the corresponding new products are summarized in Tables 3A and 3B.

The ionic nature of the tetrahaloaryltellurates(IV) was confirmed in reactions with ion exchange resins and by conductance measurements. Two phosphonium derivatives dissolved in THF/ethanol (1/1) were allowed to interact with the anion exchange resins, IRA·400·BDh·Cl^-. The $ArTeX_4^-$ anions were exchanged for Cl^-; the phosphonium chlorides were isolated and identified as the corresponding perchlorates. Elution of the resin with excess $Et_4N^+Br^-$ solution gave the soluble

TABLE 3

A. TETRAHALOARYLTELLURATE(IV) HALOGEN EXCHANGE REACTIONS

Reactions			*Ar*	*R*[a]	*X*
$[Ph_3P{-}R][ArTeCl_4]$	$\underset{Cl}{\overset{Br}{\rightleftarrows}}$	$[Ph_3PR]$	p-EtO–C_6H_4[b]	CH_2Ph, CH_2R', Ph	
			Ph	CH_2Ph, CH_2R', Ph, CH_3	
$[Ph_3P{-}R][ArTeX_4]$	$\xrightarrow{I}$	$[Ph_3PR][ArTeI_4]$	p-EtO–C_6H_4, Ph	CH_2Ph	Cl
			Ph	CH_3	Br
$[Ph_3P{-}R][ArTeCl_3Br]$	$\xrightarrow{X}$	$[Ph_3PR][ArTeX_4]$	p-EtO–C_6H_4, Ph	CH_3, CH_2R'	Cl
			p-EtO–C_6H_4, Ph	CH_3, CH_2R'	Br
$[C_7H_7][ArTeCl_4]$	$\underset{Cl}{\overset{Br}{\rightleftarrows}}$	$[C_7H_7][ArTeBr_4]$	p-EtP–C_6H_4, Ph		
$[C_7H_7][ArTeCl_3Br]$	$\xrightarrow{X}$	$[C_7H_7][ArTeX_4]$	p-EtO–C_6H_4, Ph		Cl
			p-EtO–C_6H_4, Ph		Br
			Ph		I
$[Ph_3Te][PhTeCl_4]$	$\underset{Cl}{\overset{Br}{\rightleftarrows}}$	$[Ph_3Te][PhTeBr_4]$			
$[Ph_3Te][PhTeCl_3Br]$	$\xrightarrow{Cl}$	$[Ph_3Te][PhTeCl_4]$			

[a] $R'=CO_2Et$. [b]

TABLE 3

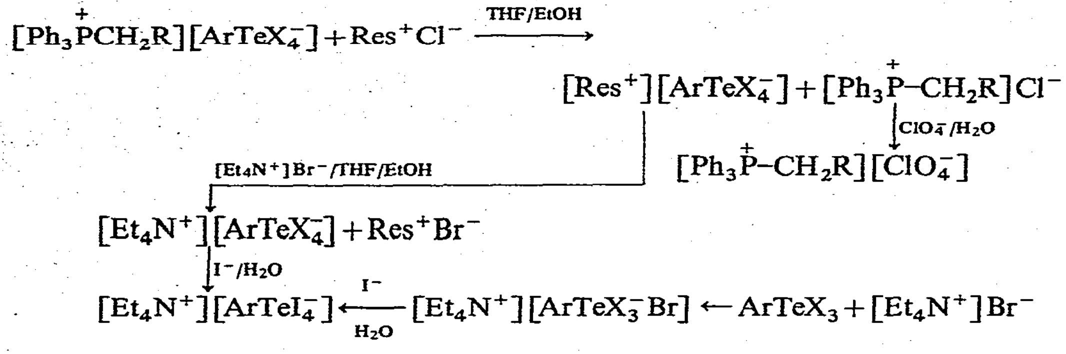
B. TETRAHALOARYLTELLURATES(IV) VIA HALOGEN EXCHANGE REACTION[a]
$[Y^+][ArTeX_4^-]+4X'^- \rightarrow [Y^+][ArTeX_4'^-]+4X^-$

Y^+[b]	$ArTeX_4^-$	X'	$[Y^+][ArTeX_4'^-]$			
			M.p. (°C)	*Appearance*[c]	*Te Found (%)*	*Te Calcd. (%)*
Ph_3PCH_2R'	p-$EtOC_6H_4TeBr_4$	Cl	128–131	White crystals	15.88	15.80
Ph_3PCH_3	$PhTeBr_4$	Cl	142–143	White crystals	20.21	20.46
Ph_3PCH_2R'	$PhTeBr_4$	Cl	186–188	White crystals	18.20	18.33
Ph_3PCH_2Ph	p-$EtOC_6H_4TeCl_4$	Br	185–187	Yellow needles	13.68	13.82
Ph_3PCH_2Ph	$PhTeCl_4$	Br	190–192	Yellow plates	14.45	14.53
Ph_3PCH_2Ph	p-$EtOC_6H_4TeCl_4$	I	138–141	Red-brown crystals	11.46	11.49
Ph_3PCH_2Ph	$PhTeCl_4$	I	141–143	Brown crystals	11.98	11.97
Ph_3PCH_3	$PhTeBr_4$	I	169–171	Red crystals	13.05	12.89
Ph_3PCH_3	p-$EtOC_6H_4TeCl_3Br$	Cl	156–157	White plates	18.92	19.10
C_7H_7	p-$EtOC_6H_4TeCl_4$	Br	218–221	Yellow needles	26.32	26.43
C_7H_7	$PhTeCl_3Br$	I	169–172	Brown-black crystals	15.85	15.87
Ph_3Te	$PhTeCl_4$	Br	191–192	Yellow needles	28.81	28.89
Ph_3Te	$PhTeBr_4$	Cl	197–199	White crystals	36.10	36.12

[a] This table shows only compounds not presented in Tables 1 and 2. [b] $R'=CO_2Et$. [c] From CH_2Cl_2/AcOEt.

tetraethylammonium tetrahaloaryltellurates(IV). On treatment with aqueous potassium iodide the corresponding tetraiodo derivatives were precipitated (Scheme 1).

SCHEME 1



$$[Ph_3\overset{+}{P}CH_2R][ArTeX_4^-] + Res^+Cl^- \xrightarrow{THF/EtOH} [Res^+][ArTeX_4^-] + [Ph_3\overset{+}{P}{-}CH_2R]Cl^-$$

$$[Ph_3\overset{+}{P}{-}CH_2R]Cl^- \xrightarrow{ClO_4^-/H_2O} [Ph_3\overset{+}{P}{-}CH_2R][ClO_4^-]$$

$$[Res^+][ArTeX_4^-] \xrightarrow{[Et_4N^+]Br^-/THF/EtOH} [Et_4N^+][ArTeX_4^-] + Res^+Br^-$$

$$[Et_4N^+][ArTeX_4^-] \xrightarrow{I^-/H_2O} [Et_4N^+][ArTeI_4^-]$$

$$[Et_4N^+][ArTeI_4^-] \xleftarrow[H_2O]{I^-} [Et_4N^+][ArTeX_3^-Br] \leftarrow ArTeX_3 + [Et_4N^+]Br^-$$

[(*a*) $Ar=C_6H_5; R=C_6H_5; X=Cl$; (*b*) $Ar=p\text{-}EtOC_6H_4; R=COOEt; X=Br$]

Conductance measurements were performed in nitrobenzene and nitromethane. Values of 20.8–25.0 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ and 62–83 $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$ were obtained for the respective solvent systems. The comparison of our conductance data (Table 4) with the known values for several types of electrolytes[17], confirms the behavior of the tetrahaloaryltellurates(IV) as 1/1 electrolytes.

TABLE 4

CONDUCTANCE DATA FOR TETRAHALOARYLTELLURATES

Compound	*In nitrobenzene* $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$	*In nitromethane* $\Omega^{-1}\cdot cm^2\cdot mol^{-1}$
$[Ph_3\overset{+}{P}{-}CH_2Ph]\,[p\text{-}EtOC_6H_4TeCl_4^-]$	20.8	64.0
$[Ph_3\overset{+}{P}{-}CH_3]\,[p\text{-}EtOC_6H_4TeBr_4^-]$	21.0	
$[Ph_3\overset{+}{P}{-}CH_3]\,[p\text{-}EtOC_6H_4TeCl_3Br^-]$	21.0	62.0
$[Ph_3\overset{+}{P}{-}CH_2Ph]\,[p\text{-}EtOC_6H_4TeBr_3Cl^-]$	22.0	
$[Ph_3\overset{+}{P}{-}CH_2Ph]\,[p\text{-}EtOC_6H_4TeI_3Cl^-]$	22.5	
$[C_7H_7^+]\,[p\text{-}EtOC_6H_4TeCl_4^-]$	24.0	83.0
$[C_7H_7^+]\,[p\text{-}EtOC_6H_4TeBr_4^-]$	25.0	81.0

Our investigation led us to the preparation of a number of previously unreported phosphonium, tropylium, and telluronium hexahalotellurate(IV) salts

$$TeX_4 + 2Y^+X^- \xrightarrow{Solv.} [Y^+]_2[TeX_6^{2-}] \qquad (6)$$

$$(Y = Ph_3PR;\ C_7H_7;\ Ph_3Te)$$

(eqn. 6). Depending on the halides used, TeX_6^{2-} anions could contain the same or different halogens. Some hexachlorotellurates(IV) were also prepared by treating solutions of tellurium tetrachloride in aqueous hydrochloric acid with phosphonium, tropylium or telluronium halides (eqn. 7). Tables 5 and 6 show the hexahalotellurates(IV) which were prepared. The phosphonium derivatives may assume importance as tellurophosphorane precursors (eqn. 8). In contrast to the tetrahaloaryltellurates(IV), the hexahalotellurates(IV) are unstable in water. On addition of water to their THF or ethanol solutions the corresponding tellurium oxohalides immediately separate (eqn. 9). As with the tetrahaloaryltellurates(IV), the conversion of

$$\mathrm{TeCl_4} \overset{\mathrm{HCl}}{\rightleftharpoons} [\mathrm{H_2TeCl_6}] \xrightarrow{[\mathrm{Y^+}]\mathrm{X^-}} [\mathrm{Y^+}]_2[\mathrm{TeCl_6^{2-}}] \qquad (7)$$

$$(\mathrm{Y} = \mathrm{Ph_3PCH_2Ph};\ \mathrm{C_7H_7};\ \mathrm{Ph_3Te})$$

$$\begin{tikzcd} {[\mathrm{Ph_3\overset{+}{P}{-}CH_2R}]_2[\mathrm{TeX_6^{2-}}]} \arrow[r, "\mathrm{Base}", "-2\mathrm{HX}"'] & {[\mathrm{Ph_3P{=}CR{-}TeX_2{-}CR{=}PPh_3}]} \arrow[d, "-2\mathrm{Ph_3PO}"', "2\mathrm{R'CHO}"] \\ & \mathrm{X_2Te(CR{=}CHR')_2} \end{tikzcd} \qquad (8)$$

TABLE 5

$[TeX_4X'_2{}^{2-}]$ SALTS PREPARED FROM TeX_4 AND PHOSPHONIUM, TROPYLIUM, AND TELLURONIUM HALIDES

Y^{+a}	X^-	X'^-	$[Y^+]_2[TeX_4X'_2{}^{2-}]$ M.p. (°C)	Appearance[b]	Te Found (%)	Te Calcd. (%)
Ph_3PCH_2Ph	Cl	Cl	228–230	Yellow plates	12.42	12.18
Ph_3PCH_3	Br	Br	272–275	Red crystals	10.81	10.99
Ph_3PCH_2R'	Br	Br	216–218	Yellow crystals	9.69	9.77
Ph_3PCH_2Ph	I	Cl	155–158	Brown crystals	8.96	8.74
Ph_3PCH_3	I	Br	180–183	Green-black crystals	9.67	9.46
Ph_4P	I	Cl	236–240	Brown crystals	9.19	9.21
C_7H_7	Cl	Br	258–260	Green powder	20.95	20.86
C_7H_7	Br	Br	319–322	Brown powder	16.06	16.29
C_7H_7	I	Br	272–275	Red-black needles	18.74	18.80
Ph_3Te	Br	Br	226–228	Yellow crystals[c]	9.63	9.71

[a] $R' = CO_2Et$. [b] From CH_3CN/AcOEt. [c] From DMF/AcOEt.

TABLE 6

HEXACHLOROTELLURATE(IV) SALTS FROM THE REACTION OF $TeCl_4$, HCl, AND PHOSPHONIUM, TROPYLIUM, AND TELLURONIUM HALIDES ($Y^+X'^-$)

Y^+	X'^-	$[Y^+]_2[TeCl_6^{2-}]$ M.p. (°C)	Appearance[a]	Te Found (%)	Te Calcd. (%)
Ph_3PCH_2Ph	Cl	228–230[b]			
C_7H_7	Br	291–294	Yellow powder	24.23	24.40
Ph_3Te	Br	213–215	White needles	27.34	27.44

[a] From DMF/AcOEt. [b] See Table 5.

$$\begin{array}{l} [\mathrm{Y}^+]_2[\mathrm{TeX}_6^{2-}] \rightleftharpoons [\mathrm{TeX}_4] + 2\mathrm{Y}^+\mathrm{X}^- \\ \qquad\qquad\qquad\quad \big\downarrow{\scriptstyle \mathrm{H_2O}} \\ \qquad\qquad\qquad\quad \mathrm{Te(O)X}_2 + 2\mathrm{HX} \end{array} \tag{9}$$

$(\mathrm{X} = \mathrm{Cl}, \mathrm{Br}; \mathrm{Y} = \mathrm{Ph_3PR}; \mathrm{C_7H_7}; \mathrm{Ph_3Te})$

chlorides to bromides, and of chlorides and bromides to iodides was possible; Table 7 shows these reactions and lists the new compounds obtained.

TABLE 7

$[\mathrm{TeX'}_6{}^{2-}]$ SALTS VIA HALOGEN EXCHANGE WITH HALOGEN HYDRIDES (HX′)

Y^+	*X^-*	*X'^-*	*$[Y^+]_2[TeX'_6{}^{2-}]$*			
			M.p. (°C)	*Appearance*	*Te Found (%)*	*Te Calcd. (%)*
$\mathrm{Ph_3PCH_2Ph}$	Cl	Br[a]	237–240	Orange crystals[b]	9.60	9.71
$\mathrm{Ph_3PCH_3}$	Br	Cl[a]	248–252	Yellow needles[b]	13.94	14.26
$\mathrm{Ph_3PCH_2Ph}$	Cl	I	228–230	Brown crystals[c]	7.91	8.00
$\mathrm{Ph_3PCH_3}$	Br	I	184–186	Black needles[c]	8.68	8.83
$\mathrm{C_7H_7}$	Br[d]	I	232–235	Black crystals[e]	11.88	11.91
$\mathrm{Ph_3Te}$	Br	I	208–210	Black powder[e]	24.10	23.82

[a] The reverse halogen exchange is also possible. [b] From DMF/AcOEt. [c] From $\mathrm{CH_2Cl_2}$/AcOEt. [d] $[\mathrm{C_7H_7}]_2[\mathrm{TeCl_4Br_2}]$ was also utilized as a starting material. [e] From $\mathrm{CH_3CN}$/AcOEt.

Infrared and Raman spectra

The compounds reported form the basis of a potentially rich area for vibrational spectroscopic investigations. While RTeX_4^- species presumably display C_{4v} symmetry[18], molecules of this type containing two different halogen atoms may possess lower symmetry depending on the extent and manner of substitution.

The vibrational spectroscopic data which have been collected thus far may be found in Table 8. The data for PhTeCl_4^- are most complete and will be discussed first.

Experience has shown that low frequency M–X vibrations generally give rise to much more intense absorptions or scatterings than do phenyl modes, thus greatly simplifying data interpretation. In the interpretation of the spectrum of ArTeX_4^- we assume local C_{4v} symmetry about the central atom despite the lower overall symmetry imposed by the phenyl group and possibly the crystal lattice. Nine normal modes (three are doubly degenerate) are expected for a square pyramidal $\mathrm{TeX_4Z}$ molecule if Z is in the apical position. The modes which may approximately be described as Te–C stretching $\nu_1(A_1)$ and bending $\nu_8(E)$ are not expected to be observed in a straightforward manner. Rather, these will be incorporated into phenyl modes as described by Mackay[19]. Seven remaining modes mainly associated with the $\mathrm{TeX_4}$ group should be observed: $2A_1$, $2B_1$, B_2, and $2E$. All are Raman active while only four are infrared active.

For PhTeCl_4^- the symmetric Te–Cl stretch $\nu_2(A_1)$ is observed as a strong polarized Raman band at 282 cm^{-1} (Table 8). This mode is observed as a very weak

TABLE 8

INFRARED AND RAMAN SPECTRAL DATA (cm^{-1})[a]

$[Ph_3\overset{+}{P}CH_3][PhTeCl_4^-]$			$[Ph_3\overset{+}{P}CH_2Ph][p\text{-}EtOC_6H_4TeCl_4^-]$	
Infrared (Nujol mull)	*Raman*		*Raman (Nujol mull)*	*Assignment; approximate description; activity*
	Solid	*CH_3CN*		
282 vw (sh)	282 s	282 s, p	277 s[b]	ν_2 (A_1); sym. stretch; IR and Raman
	273 w (sh)		260 vw (sh)	ν_4 (B_1); (?); Raman
256 s	250 s	251 ms, dp	249 m[c]	ν_7 (E); antisym. stretch; IR and Raman
			240 vw (sh)	
226 vs	220 w (sh)		227 w	$\nu_3(A_1)$; sym. out of plane bend; IR and Raman
	198 vw		220 vw (sh)	
			290 w	
178 m	174 m	172 wm, dp	148 m	$\nu_9(E)$; antisym. in plane bend; IR and Raman
	162 vw			
	150 vw			
	127 w		127 m	
			91 m	

$[Ph_3\overset{+}{P}CH_3][PhTeBr_4^-]$		$[Ph_3\overset{+}{P}CH_2Ph][p\text{-}EtOC_6H_4TeBr_4^-]$	
Raman (Nujol mull)	*Raman (CH_3CN)*	*Raman (Nujol mull)*	*Assignment; approximate description; activity*
181 wm	177 w (sh), dp	179 wm	ν_7 (E); antisym. stretch; IR and Raman
167 s	167 s, p	163 s[d]	$\nu_2(A_1)$; sym. stretch; IR and Raman
148 m	152 m, dp	148 m[e]	$\nu_4(B_1)$; antisym. stretch; Raman
112 w		99 w	$\nu_3(A_1)$?
82 m		82 m	

[a] Abbreviations: s, strong; m, medium; w, weak; (sh), shoulder; p, polarized; dp, depolarized. [b] CH_3CN, 282 s, p. [c] CH_3CN, 252 m, dp. [d] CH_3CN, 162 s, p. [e] CH_3CN, 147 m, dp.

shoulder in the IR spectrum. The antisymmetric stretch $\nu_7(E)$ appears as a moderately strong absorption both in the Raman (251 cm^{-1}) and IR (256 cm^{-1}) spectrum. The strong IR peak at 226 cm^{-1} is best assigned to $\nu_3(A_1)$; a corresponding Raman absorption is seen at 220 cm^{-1}. This mode for square pyramidal $InCl_5^{2-}$ is found at substantially lower frequency (142 cm^{-1})[20], although frequencies for ν_2 and ν_7 in $PhTeCl_4^-$ are in good agreement with those for $InCl_5^{2-}$. A number of weak low frequency absorptions are seen in the Raman spectrum of solid $[Ph_3\overset{+}{P}CH_3][PhTeCl_4^-]$. These are apparently due to "*B*" modes which for the most part cannot be individually assigned with presently available data. The weak peak at 273 cm^{-1} may be due to $\nu_4(B_1)$ of $PhTeCl_4^-$ as the related mode in ICl_4^- (D_{4h}) occurs at 261 cm^{-1}[21].

Only Raman spectral data are available for $[Ph_3\overset{+}{P}CH_2Ph][p\text{-}EtOC_6H_4TeCl_4^-]$. The observed frequencies are close to those observed for $[Ph_3\overset{+}{P}CH_3][PhTeCl_4^-]$ and are similarly assigned (Table 8).

Raman data for two $ArTeBr_4^-$ salts may also be found in Table 8. The symmetric Te–Br stretch $\nu_2(A_1)$ clearly stands out as a strong polarized peak at ca. 165 cm^{-1}. In contrast to $ArTeCl_4^-$, $\nu_7(E)$ which is found at ca. 180 cm^{-1} lies higher in frequency than ν_2 in $ArTeBr_4^-$. This crossover of A and E modes has been well established for compounds containing linear X–M–X systems (M = Se, Te; X = Cl, Br)[22,23]. It is interesting that the interchange persists in a molecule containing two such systems. The third high frequency Raman band is assigned to $\nu_4(B_1)$ mainly by analogy with the corresponding mode in $PtBr_4^{2-}$[24].

Taken as a whole, available Raman and infrared data are fully consonant with the presence of square pyramidal $ArTeX_4^-$ anions in the compounds studied.

The far infrared spectra of certain TeX_6^{2-} salts were investigated in order to check for the presence of appropriate absorptions. In $[Ph_3\overset{+}{P}CH_2Ph]_2[TeCl_6^{2-}]$ $\nu_3(T_{1u})$ of $TeCl_6^{2-}$ was observed as a strong, broad peak at 224 cm^{-1}. For $[Ph_3Te]_2[TeBr_6^{2-}]$ the corresponding mode was found as a very strong peak at 172 cm^{-1}. Both these observations are in agreement with the literature[25].

For $[Ph_3\overset{+}{P}CH_3]_2[TeI_4Br_2^{2-}]$ a *trans* arrangement of halide ligands is suggested by the observation of two absorptions; a weak shoulder at 194 cm^{-1} is assigned to the Te–Br antisymmetric stretch (A_{2u}), while a strong broad peak at 141 cm^{-1} is assigned to the Te–I antisymmetric stretch (E_u).

EXPERIMENTAL

The following starting materials were prepared by described procedures: *p*-ethoxyphenyltellurium trichloride[26]; *p*-ethoxyphenyltellurium tribromide; *p*-ethoxyphenyltellurium triiodide[27]; phenyltellurium trichloride[28]; phenyltellurium tribromide[29]; phenyltellurium triiodide[29]; triphenylmethylphosphonium bromide[30]; triphenylbenzylphosphonium chloride[31]; triphenylcarbethoxymethylphosphonium bromide[32]; tetraphenylphosphonium chloride[33]; tetraphenylphosphonium bromide[33]; tropylium bromide[34]; triphenyltelluronium bromide[35].

Phosphonium, tropylium and telluronium tetrahaloaryltellurates(IV)

General Procedures

(*a*). The aryltellurium trihalide (0.003 mol) was mixed with a chloroform solution (25 ml) of the phosphonium, tropylium, or telluronium halides (0.003 mol). The solution (phosphonium or telluronium derivative) or the suspension (tropylium derivative) was refluxed for 4 h. On evaporation, the complex was generally obtained as a crystalline solid. Some phosphonium derivatives were obtained as pasty masses which, however, were easily crystallized by trituration with AcOEt. The phosphonium and telluronium derivatives were recrystallized from CH_2Cl_2–AcOEt, and the tropylium derivatives from CH_3CN–AcOEt. The yields for all the purified products were higher than 85%.

(*b*). The aryltellurium trichloride or tribromide (0.001 mol) was dissolved in 6*N* HCl or 3*N* HBr respectively. A solution of the phosphonium, tropylium or telluronium halide (0.001 mol) in 20 ml water was added dropwise with magnetic stirring. The complex precipitated immediately and quantitatively and was removed by filtration.

(*c*). Tropylium tetrabromo-*p*-ethoxyphenyltellurate(IV) was prepared by treating a mixture of *p*-ethoxyphenyltellurium trichloride (0.72 g, 0.002 mol) and trityl perchlorate (0.68 g, 0.002 mol) in 25 ml CH_3CN, with cycloheptatriene (0.19 g, 0.002 mol). After the reaction mixture had stood for 2 h at room temperature the crystalline solid was separated by filtration giving 0.75 g (63% yield). The product was recrystallized from CH_3CN/AcOEt, m.p. 212–213. (Analysis: Found: Te, 23.31. $[C_7H_7^+][p\text{-}C_2H_5OC_6H_4TeCl_3ClO_4^-]$ calcd.: Te, 23.40%.)

The filtrate was evaporated and the residue extracted with ether. The ethereal solution on evaporation gave 0.48 g of triphenylmethane (100% yield). The above tropylium derivative (0.54 g, 0.001 mol) was dissolved in a few ml of THF and then treated with 15 ml 10% HBr. The tetrabromo derivative precipitated in (99% yield) (0.65 g); it was identical to the compound obtained in (*a*).

Phosphonium, tropylium and telluronium hexahalotellurates(IV)

General procedure

(*a*). A mixture of tellurium tetrahalide (0.005 mol) and the phosphonium, tropylium or telluronium halide (0.01 mol) in 50 ml $CHCl_3$ was magnetically stirred and refluxed for 6 h. The crystalline hexahalotellurate was separated by filtration in quantitative yield.

(*b*). To a stirred solution of tellurium tetrachloride (0.27 g, 0.001 mol) in 10 ml 6*N* HCl, a solution of the phosphonium, tropylium or telluronium halide (0.002 mol) in 20 ml water was added dropwise. The hexahalotellurate precipitated and was removed by filtration in quantitative yield. Most of the tropylium derivatives were virtually insoluble in common organic solvents. In some cases analytical samples were obtained by washing the crude crystalline compounds with CH_2Cl_2.

Halogen exchange reactions of tetrahaloaryltellurates(IV) and hexahalotellurates(IV)

(*a*). *Conversion of chloro derivatives into bromo derivatives.* A solution of the phosphonium or telluronium derivative (0.002 mol) or a suspension of the tropylium derivative in 20–30 ml THF was treated dropwise with magnetic stirring with 15 ml 10% HBr. The tropylium tetrabromoaryl derivatives and all the hexabromotellurates(IV) separated, while the more soluble phosphonium and telluronium tetrabromoaryltellurates(IV) were obtained after evaporation of excess THF in a rotatory evaporator.

(*b*). *Conversion of bromo derivatives into chloro derivatives.* A solution of the phosphonium or telluronium derivative (0.002 mol) or a suspension of the tropylium derivative in 20–30 ml THF was treated with 15 ml conc. HCl with magnetic stirring for 6 h. The tropylium tetrachloroaryl derivative and all the hexahalotellurates(IV) separated as crystalline solids and were removed by filtration. For phosphonium and telluronium tetrachloroaryltellurates(IV) evaporation of excess THF was necessary. Tropylium and telluronium hexabromotellurates(IV) did not react under these conditions and were recovered unchanged.

(*c*). *Conversion of chloro and bromo derivatives into iodo derivatives.* A suspension of the chloro and bromo derivative (0.002 mol) in 1*N* HCl was treated with excess aqueous KI solution with magnetic stirring. The iodo derivative precipitated immediately and was removed by filtration in quantitative yield.

(*d*). *Attempted conversion of iodo derivatives into chloro and bromo derivatives.* All the attempted transformations of the iodo derivatives into the corresponding chloro or bromo derivatives, using aqueous HCl or HBr, failed. The starting materials were unchanged.

Treatment with anion exchange resin

Through a column containing 20 g IRA·400·BDh resin, covered with THF, was slowly passed a solution of 0.001 mol phosphonium tetrahaloaryltellurate(IV) in 30 ml 1/1 THF/ethanol followed by 200 ml of the same solvent mixture. The eluate was evaporated, the residue disolved in water and treated with excess saturated aqueous $NaClO_4$ solution. The phosphonium perchlorates precipitated as colorless crystalline solids and were removed by filtration in quantitative yields. $[Ph_3\overset{+}{P}-CH_2Ph]ClO_4^-$ m.p. 237–238°; $[Ph_3\overset{+}{P}-CH_2COOEt]ClO_4^-$ m.p. 143–147°. These same perchlorates were prepared by reacting $NaClO_4$ with triphenylbenzylphosphonium chloride or triphenylcarbethoxymethylphosphonium bromide in aqueous solution. (The m.p.'s were identical and the IR spectra superimposable.) The column was slowly eluted with 15 times its volumes of 2% $Et_4N^+Br^-$ solution in THF/ethanol. The eluate was concentrated to 50 ml and then treated with excess KI in aqueous 2% HCl. The tetraethylammonium tetraiodoaryltellurates(IV) precipitated and were separated by filtration. Yield for $[Et_4N^+][PhTeI_4^-]$ was 85%, m.p. 176–178°. Analysis: Found: Te, 14.87. Calcd.: Te, 15.14%. Yield for $[Et_4N^+][p\text{-}EtOC_6H_4TeI_4^-]$ was 90%, m.p. 130–133°. Analysis: Found: Te, 14.33. Calcd.: Te, 14.37%.

These same derivatives were prepared by the reactions of the corresponding aryltellurium trichlorides with tetraethylammonium bromide in refluxing $CHCl_3$ followed by treatment with aqueous KI. (The m.p.'s were identical and the IR, spectra superimposable.)

Conductance measurements

The measurements were made with 10^{-3} *M* solutions of the tetrahaloaryltellurates(IV) at 25.00±0.02°C in nitrobenzene and nitromethane. An Industrial Instrument Model RC-16 B conductivity bridge and a Leeds and Northrup cell ($K=0.1070_8$ cm^{-1}) was used.

Infrared and Raman spectra

Infrared and Raman spectra were obtained as described previously[22].

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