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ORGANOTELLURIUM DERIVATIVES

IV *. SYNTHESIS OF SOME DIARYLTELLURIUM DIHALIDES AND PSEUDOHALIDES

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Summary

Iodine monohalides (ICl, IBr), cyanogen halides (CNBr, CNI) and thiocyanogen $(SCN)_2$ add oxidatively to diaryltellurium(II), R_2Te (R = Ph, p-$CH_3OC_6H_4$) under mild conditions (~5°C). The resulting organotellurium(IV) derivatives react metathetically with silver pseudohalides to yield several new diaryltellurium(IV) pseudohalide derivatives.

Introduction

Diorganotellurium(II) are known to combine with molecular halogens (Cl_2, Br_2 or I_2) [1] to yield diorganotellurium dihalides (eq. 1). The dichlorides,

$$R_2Te + X_2 \rightarrow R_2TeX_2 \qquad (1)$$

R_2TeCl_2, are also formed by the oxidation of diaryltellurium(II) with sulfuryl and thionyl chlorides [1] or some metal chlorides such as $FeCl_3$, $CuCl_2$ and $HgCl_2$ [1]. However, there is no report of an interhalogen, pseudohalogen or halopseudohalogen, oxidising a diorganotellurium(II).

Except for $Me_2Te(CN)_2$ [2] organotellurium pseudohalides are of recent origin [3,4]. We recently prepared and characterised a number of tetrahalo- and tetrapseudohalocyclopentanetellurates(IV) [5]. In this paper, synthesis of several diaryltellurium dipseudohalides, mixed dihalides, mixed dipseudohalides and mixed halide/pseudohalides is described.

Results and discussion

Iodine monohalides and cyanogen halides add oxidatively to diaryltellurium(II) at ~5°C to produce diaryltellurium mixed dihalides and halide/pseudohalides,

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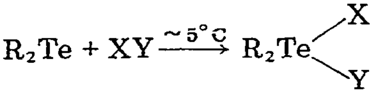
* For part III see ref. 5.

respectively (eq. 2). The fact that aryltellurium(II) halides and aryl halides are not formed under these conditions indicates that oxidative addition is preferred to Te—Ar bond cleavage.

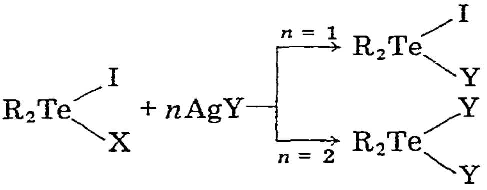


$$R_2Te + XY \xrightarrow{\sim 5^\circ C} R_2Te\begin{matrix}X\\Y\end{matrix} \qquad (2)$$

(where R = C_6H_5, p-$CH_3OC_6H_4$; XY = ICl, IBr, ICN, BrCN)

A freshly prepared solution of thiocyanogen in carbon tetrachloride also reacts in the sense of eq. 2 to provide the corresponding diisothiocyanate at room temperature in the dark.

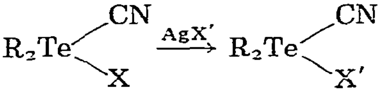
The metathetical reactions of mixed dihalides, R_2TeIX (X = Cl, Br), with silver pseudohalides in chloroform yield diaryltellurium mixed halidepseudohalides (when Cl^- or Br^- is displaced in preference to I^-) or dipseudohalide (eq. 3),



$$R_2Te\begin{matrix}I\\X\end{matrix} + nAgY \begin{cases} \xrightarrow{n\,=\,1} R_2Te\begin{matrix}I\\Y\end{matrix} \\ \xrightarrow[n\,=\,2]{} R_2Te\begin{matrix}Y\\Y\end{matrix} \end{cases} \qquad (3)$$

(X = Cl, Br; Y = CN, CNO, SCN, SeCN)

Interaction of $R_2Te(CN)X$ with silver salts not only yields the corresponding dicyanides but also mixed dipseudohalides (eq. 4).



$$R_2Te\begin{matrix}CN\\X\end{matrix} \xrightarrow{AgX'} R_2Te\begin{matrix}CN\\X'\end{matrix} \qquad (4)$$

(R = C_6H_5; p-$CH_3OC_6H_4$; X = Br, I; X' = CN, CNO, SCN)

The diorganotellurium mixed dihalides and halide/pseudohalides reported herein are coloured crystalline solids with sharp melting points. They are generally soluble in common organic solvents. Except for diphenyltellurium cyanate derivatives which decompose slowly on standing even at low temperature, the pseudohalide derivatives are thermally stable and can be stored unchanged for several weeks. The molar conductances of 10^{-3} M solutions in acetonitrile and methanol are in the range 28—40 Ω^{-1} mol^{-1} cm^2 and 15—72 Ω^{-1} mol^{-1} cm^2, respectively, indicating that they are nonelectrolytes [6]. Molecular weight measurements in freezing benzene show that they are monomeric.

Infrared spectra

Infrared absorptions associated with the vibrational modes of the pseudohalide groups are listed in Table 3. The thiocyanate and selenocyanate groups (XCN; X = S or Se) give rise to three fundamental modes of vibration due to ν(C—N), ν(C—X) and δ(NCX); of these the ν(C—X) mode of vibration has been used for distinguishing between the iso (at 870—850 cm^{-1} when X = S, and 630 ± 20 cm^{-1} when X = Se) and the normal (at 760—720 cm^{-1} when X = S and

TABLE 1

OXIDATIVE ADDITION REACTIONS OF DIARYLTELLURIUM(II) (eq. 2)

Products [a] (R_2TeXY)		M.p. (°C)	Analysis (found (calcd.) (%))			Molecular weight (found (calcd.))	Conductance (Ω^{-1} mol^{-1} cm^2)	
X	Y		Te	(X + Y) [b]	I		CH_3CN	CH_3OH
For R = Ph								
I	Cl	204—205	28.50 (28.72)	36.08 (36.55)	27.89 (28.57)	440.0 (444.1)	28.5	45.0
I	Br	212—213	26.00 (26.11)	43.08 (42.32)	26.00 (25.97)	480.9 (488.6)	[e]	39.0
I	CN	142—143	30.05 (29.95)	—	28.69 (29.18)	[e]	30.0	60.8
Br	CN	225	33.00 (32.90)	—	[c]	395.0 (387.7)	[e]	71.4
SCN	SCN	127—128	31.99 (32.04)	28.09 (29.22)	—	[e]	[e]	60.8
For R = MeOPh								
I	Cl	145	25.20 (25.30)	33.00 (32.19)	—	495.9 (504.2)	30.5	50.8
I	Br	160	23.58 (24.68)	25.00 (24.54)	39.20 (40.00)	520.0 (516.9)	[e]	66.6
I	CN	176	28.08 (27.55)	—	26.98 (27.41)	470.0 (463.0)	38.4	45.8
Br	CN	230	31.05 (30.66)	—	[d]	415.1 (416.0)	[e]	50.0
SCN	SCN	138—140	28.99 (29.92)	26.92 (27.24)	—	440.0 (426.3)	[e]	64.0

[a] Yields were between 80—100%. [b] (X + Y) = total halide or pseudohalide (%). [c] Found C, 41.02; H, 2.53 and calcd. C, 40.27; H, 2.57%. [d] Found N, 3.82 and calcd. N, 3.38%. [e] Insufficient solubility.

550—520 cm^{-1} when X = Se) forms [7]. The IR spectra of the compounds examined show ν(C—X) at 830 ± 8 cm^{-1} (when X = S) and 598 cm^{-1} (when X = Se) which suggests Te—NCX bonding.

Similarly, in the case of cyanate group, out of the three fundamental modes viz., ν(C—N), ν(C—O), δ(NCO); the ν(C—O) band is distinctly apart for the iso (1350—1320 cm^{-1}) and the normal (1320—1250 cm^{-1}) forms [7]. In the infrared spectra of $R_2Te(I)NCO$ and $R_2Te(NCO)_2$ this mode of vibration has been identified at 1350 ± 20 cm^{-1}, which is indicative of Te—NCO bonding in these compounds.

The organic isonitriles R—NC absorb at 2160—2120 cm^{-1} which is distinctly lower than the corresponding organic nitriles R—CN, 2260—2220 cm^{-1} [8,9]. The spectra of $R_2Te(CN)_2$ and $R_2TeI(CN)$ show ν(C—N) at ~2110 cm^{-1} and ~2020 cm^{-1}, respectively (the lowering may be attributed to the mass effect between C and Te), which may be taken as an evidence for the iso structure (Te—NC). It is noteworthy that while organotin cyanides are mixtures of iso and normal forms [10], the organoantimony cyanides exist only in the iso form [11], and thus the Te—NC structure is consistent with trends in the periodic table. Three bands at 1985, 2020, 2148 cm^{-1} and a single band at 2140 cm^{-1} are observed in the spectra of mixed pseudohalides $R_2TeCN(CNS)$ and $R_2TeCN(CNO)$, respectively, and are assigned to the ν(C—N) stretching frequency of the pseudo-

TABLE 2

METATHETICAL REACTIONS OF DIORGANOTELLURIUM MIXED DIHALIDES WITH SILVER SALTS (eq. 3 and 4)

Reactants $R_2TeIX + nAgY$		Products[a] $R_2TeX'Y$		M.p. (°C)	Analysis (Found (calcd.) (%))			Conductance (Ω^{-1} cm^2 mol^{-1}) CH$_3$OH	Molecular weight (Found (calcd.))
X[b]	nY	X′	Y		Te	I	N		
For R = C_6H_5									
Cl	NCS	I	NCS	170	26.92 (27.33)	27.05 (27.14)	—	58.0	465.0 (466.8)
Cl	NCO	I	NCO	78—80	28.90 (28.30)	27.95 (28.15)	—	c	c
Cl	CN	I	CN	142	—	—	—	—	—
Cl	2NCS	NCS	NCS	127—128	—	—	—	—	—
Cl	2NCO	NCO	NCO	85—90 (dec.)	34.09 (34.91)	—	7.66 (7.65)	70.0	370.0 (366.0)
CN	CN	CN	CN	70	38.25 (38.19)	—	8.41 (8.38)	17.8	320.0 (333.6)
CN	NCS	CN	NCS	142 (dec.)	34.80 (34.87)	—	7.89 (7.62)	18.9	c
CN	NCO	CN	NCO	174—175 (dec.)	36.80 (36.47)	—	8.08 (8.00)	15.2	c
Cl	2NCSe	NCSe	NCSe	110—112	25.99 (25.73)	—	—	c	c
For R = p-$CH_3OC_6H_4$									
Cl	NCS	I	NCS	110	24.80 (25.76)	25.59 (25.62)	—	50.0	488.0 (495.1)
Cl	NCO	I	NCO	138—140	26.60 (26.63)	26.84 (26.48)	—	48.9	480.0 (479.0)
Cl	CN	I	CN	176	—	—	—	—	—
Cl	2NCS	NCS	NCS	138—140	—	—	—	—	—
CN	CN	CN	CN	74—75	34.98 (35.22)	—	7.77 (7.73)	20.0	360.0 (362.2)
Cl	2NCSe	NCSe	NCSe	220	24.99 (23.81)	—	5.33 (5.38)	c	c

[a] Yields 95—100%. [b] Bromides in place of chloride may also be used. [c] Insufficient solubility.

TABLE 3

IR FREQUENCIES ASSOCIATED WITH PSEUDOHALIDE GROUPS

R_2TeXY			Absorption frequencies (cm^{-1})		
R	X	Y	ν(C—N)	ν(C—X)	δ(NCX)
C_6H_5	I	CN	2020w	—	—
C_6H_5	Br	CN	2030w	—	—
C_6H_5	I	NCS	2030vs	835w	460m
C_6H_5	I	NCO	2150vs	1322w	620w
C_6H_5	NCS	NCS	1980vs	838w	472m
C_6H_5	NCO	NCO	2150s	1320w	610w
C_6H_5	CN	CN	2100w(br)	—	—
C_6H_5	CN	NCS	2148w. 2020s 1985(sh)	830w	461m, 445m
C_6H_5	CN	NCO	2140s	1380m	—
C_6H_5	NCSe	NCSe	2050vs	598w	445m
$CH_3OC_6H_4$	I	CN	2030w	—	—
$CH_3OC_6H_4$	Br	CN	2020w	—	—
$CH_3OC_6H_4$	I	NCS	2030vs	821s	475m
$CH_3OC_6H_4$	I	NCO	2180s	1370w	630m(br)
$CH_3OC_6H_4$	NCS	NCS	2022vs	821s	470m
$CH_3OC_6H_4$	CN	CN	2110w(br)	—	—
$CH_3OC_6H_4$	NCSe	NCSe	2040vs	598w	447m

halide groups (i.e., CN, CNO or CNS). Bands at 830 and 1380 cm^{-1} in the spectra of $R_2TeCN(CNS)$ and $R_2TeCN(CNO)$ are ν(C—X) (where X = S or O) stretching and clearly indicate N-bonded thiocyanate and cyanate groups, respectively.

Experimental

Diphenyl- and bis(*p*-methoxyphenyl)tellurium(II) [12,13], IBr [14] and BrCN [15] were prepared by reported methods. ICN and ICl were obtained from B.D.H. Freshly prepared solutions of thiocyanogen [16] in carbon tetrachloride were used in the dark. Molar conductance of 10^{-3} *M* solutions in acetonitrile and methanol was measured with a PR-9500 conductivity assembly at room temperature. Molecular weights were determined cryoscopically by use of a Beckmann thermometer. Infrared spectra were recorded (4000—400 cm^{-1}) as Nujol mulls with Perkin—Elmer 337 infracord spectrophotometer.

Some typical experiments are described, and details of others are given in Tables 1 and 2.

(a) Oxidative addition reactions

(i) Reaction of diphenyltellurium(II) with iodine monochloride. Iodine monochloride (0.650 g; 4 mmol) in ether (5 ml) was slowly added to a stirred solution of diphenyltellurium(II) (1.121 g; 4 mmol) in the same solvent (50 ml) at ~5°C. After stirring for 1 h the orange red solid, diphenyltellurium chloride iodide, was filtered off and dried in vacuum.

Reactions with IBr, ICN and BrCN were carried out similarly.

(ii) Reaction of bis(p-methoxyphenyl)tellurium(II) with thiocyanogen. A freshly prepared solution of thiocyanogen (0.464 g; 4 mmol) in CCl_4 was stirred

for 5 h at ~20°C in the dark (to prevent polymerisation of thiocyanogen) with bis(*p*-methoxyphenyl)tellurium(II) (1.36 g; 4 mmol) in the same solvent (50 ml). The mixture was concentrated under reduced pressure. Yellow bis(*p*-methoxyphenyl)tellurium dithiocyanate separated on addition of ether. It was filtered off, washed with ether, and dried in vacuum.

Diphenyltellurium dithiocyanate was prepared similarly.

Metathetical reactions

(a) Reaction of diphenyltellurium chloride iodide with silver cyanate. Silver cyanate (0.300 g, 2 mmol) and diphenyltellurium chloride iodide (0.888 g; 2 mmol) were stirred together in chloroform (30 ml) at room temperature. The precipitated silver chloride was filtered off and the filtrate on concentration yielded yellow needles of diphenyltellurium iodide cyanate.

Compounds of the formula R_2TeIX (R = Ph; X = SCN and R = p-$CH_3OC_6H_4$; X = CNO or SCN) were obtained similarly. The diaryltellurium dipseudohalides, R_2TeX_2 (R = Ph, p-CH_3OCH_4; X = CN, SCN, CNO) were obtained when two moles of the silver salt was used.

(b) Reaction of diphenyltellurium iodide cyanide with silver thiocyanate

A mixture of the diphenyltellurium iodide cyanide (0.870 g; 2 mmol) and silver thiocyanate (0.33 g; 2 mmol) in $CHCl_3$ (30 ml) was stirred for 4 h at room temperature. The silver iodide was filtered off, and the filtrate was concentrated to give diphenyltellurium cyanide thiocyanate.

$R_2Te(CN)(NCO)$ was similarly synthesised.

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