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Monoorganyl derivatives of tellurium(IV)

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Abstract. Data on the synthesis, reactions and structures of monoorganyl derivatives of tellurium(IV) (σ-telluranes) $RTeX_3$ are systematised and generalised. The use of these compounds in preparative organic chemistry is considered. The bibliography includes 238 references.

I. Introduction

Derivatives of tetracoordinate tellurium $RTeX_3$ (X is an anionoid substituent) belong to the so-called σ-telluranes. Compounds R_2TeX_2 and tetraorganyltelluranes R_4Te are also σ-telluranes. σ-Telluranes $RTeX_3$ are important starting compounds in the synthesis of various organic derivatives of tellurium. Thus cyclisation of aryl- and arylvinyltellurium trichlorides is a method for the preparation of various tellurium-containing heterocycles, which is specific to the chemistry of organotellurium compounds. In addition, detelluration and halodetelluration of σ-telluranes $RTeX_3$ are used in organic synthesis. The two last-mentioned fields of application of monoorganyl derivatives of tellurium(IV) are based on the electrophilic properties of the trichlorotellurium group and a low (compared to other chalcogens) energy of the C—Te bond. σ-Telluranes are also characterised by higher stabilities compared to analogous sulfur and selenium derivatives because the higher energy levels of the *p* orbitals of tellurium are favourable for bonding.[1,2] Thus sulfur compounds $RSCl_3$ decompose to give RSCl and Cl_2 even at very low temperature, $RSeCl_3$ are stable at room temperature but decompose to RSeCl and Cl_2 on heating, whereas $RTeCl_3$ are stable up to their melting points.[3]

Previously, σ-telluranes $RTeX_3$ have been considered in a review (see Ref. 4) and in the corresponding sections of monographs (see Refs 3 and 5 – 7).

II. Methods of synthesis

Most compounds of the $RTeX_3$ type have been prepared from tellurium tetrachloride and diorganyl ditellurides as the starting compounds. Various derivatives of $RTeX_3$ can also be synthesised by anion exchange in organyltellurium trihalides. Approaches based on the use of hexahalotellurates, complexes of tellurium tetrachloride with aromatic amines, tellurinic acids and their anhydrides have been studied to a substantially lesser extent. The corresponding reactions were either examined for a few compounds or afforded a limited number of compounds.

1. Reactions of tellurium tetrahalides with heteroorganic compounds

The most important preparative procedures for the synthesis of organyltellurium trihalides involve exchange reactions of tellurium tetrahalides with heteroorganic compounds. These reactions were used primarily for the preparation of aryltellurium trichlorides and aryltellurium tribromides. Poor solubility of TeI_4 in nonpolar solvents and its decomposition in polar solvents prevent its use in the synthesis of tellurium triiodides.

In principle, a general procedure for the synthesis of organyltellurium trihalides could involve reactions of equimolar amounts of tellurium tetrahalides with organolithium or -magnesium compounds.

$$RM + TeX_4 \xrightarrow[-MX]{} RTeX_3$$

M = Li, MgX; X = Cl, Br.

However, these reactions afford complex mixtures of products due to a more profound exchange. Nevertheless, the reaction of 2-biphenylyllithium with $TeCl_4$ gave rise to 2-biphenylyltellurium trichloride, albeit in low yield (16%).[8]

(*N*,*N*-Dimethylcarbamoyl)tellurium trichloride **1** was prepared by the reaction of $TeCl_4$ with dimethylaminocarbonylsodium and isolated as a complex with DMF.[9]

$$Me_2NC(O)Na + TeCl_4 \xrightarrow[2)\ DMF]{1)\ CCl_4} Me_2NC(O)TeCl_3 \cdot DMF$$

1

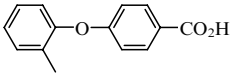
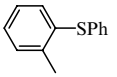
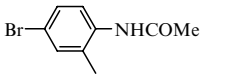
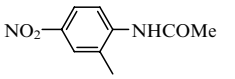
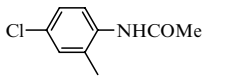
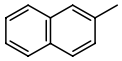
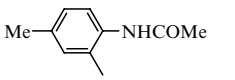
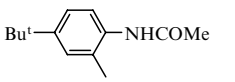
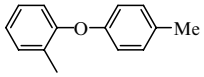
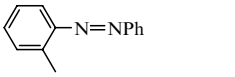
Organyltellurium trihalides can be synthesised by the reactions of tellurium tetrahalides with organic derivatives of Hg, Si, Sn or Pb. The procedure most generally employed involves the reaction of $TeCl_4$ with organomercury compounds. This procedure has been used for the synthesis of aryltellurium trichlorides **2**. Unlike telluration (see below) wich yields *p*-substituted aryltellurium trichlorides, this procedure is more versatile because it allows one to synthesise compounds with any substituents (including electron-withdrawing groups) at any position.[8,10–21]

$$ArHgCl + TeCl_4 \longrightarrow ArTeCl_3 + HgCl_2$$

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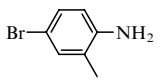
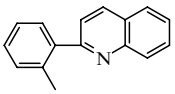
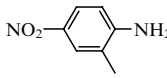
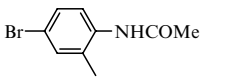
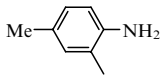
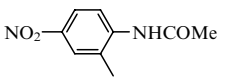
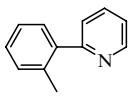
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Ar	Ref.	Ar	Ref.
	17		10
C_6F_5	14, 15		13
4-BrC_6H_4	16		
4-ClC_6H_4	16		
4-$NO_2C_6H_4$	16		21
3-FC_6H_4	16		
3-$NO_2C_6H_4$	16		
4-MeC_6H_4	11, 16		21
Ph	11,16		
	13		19
	12		19
2-PhC_6H_4	8		
4-$PhNHC_6H_4$	20		19
	10		18

The above-mentioned reaction is best carried out in anhydrous dioxane (sometimes $CHCl_3$ is used) because the resulting mercury(II) chloride forms a 1 : 1 complex with dioxane, which is poorly soluble at room temperature. Generally, the aryltellurium trichlorides formed in admixture with $HgCl_2$ and, hence, it is necessary to purify the reaction products by recrystallisation or to reduce them to diaryl ditellurides followed by chlorinolysis.

Arylmercury chlorides were used as the starting compounds in the synthesis of aryltellurium tribromides **3**. If molecules of the initial organic substrates contain amino groups [22] or the substrates represent pyridine [23, 24] or quinoline derivatives,[24] their reactions with $TeCl_4$ afford mixtures of unidentified compounds due apparently to side complexation reactions. In this case, $TeBr_4$ is more suitable.

$$ArHgCl + TeBr_4 \longrightarrow \underset{\mathbf{3}}{ArTeBr_3} + HgBr_2$$

Ar	Ref.	Ar	Ref.
	22		24
	22		21
	22		21
	23, 24		

Organyltellurium trihalides can also be synthesised from silicon or tin derivatives or, less often, lead or germanium derivatives. The reactivities of heteroorganic derivatives R_4E (E = Si, Ge, Sn or Pb) and R_3EX (X = Cl or Br) increase as the atomic weight of the element increases. The derivatives of the R_4E type are more reactive than R_3EX. Compounds R_2EX_2 and R_3EX do not react with tellurium tetrahalides. The Ar–E bond in mixed derivatives $ArEAlk_3$ is cleaved under the action of electrophilic tellurium tetrahalides. Thus aryltellurium trichlorides **2** were prepared in 65%–80% yields upon refluxing a mixture of equimolar amounts of aryltrimethylsilanes and $TeCl_4$ in toluene for 1 h.[25, 26]

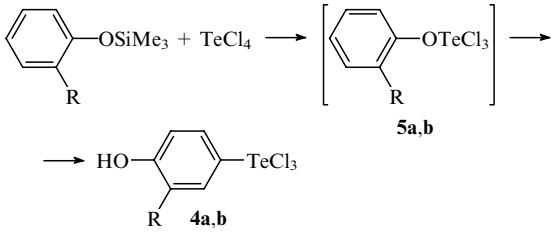
$$ArSiMe_3 + TeCl_4 \xrightarrow[-Me_3SiCl]{\Delta} \underset{\mathbf{2}}{ArTeCl_3}$$

Ar = 4-BrC_6H_4, Ph, 4-MeC_6H_4, 3-MeC_6H_4, 2-$C_6H_4CH_2Ph$.

In benzyltrimethylsilane, the C_{sp^3}–Si bond is inert with respect to $TeCl_4$. Refluxing of equimolar amounts of these compounds in toluene afforded a mixture of 4-$Me_3SiCH_2C_6H_4$–$TeCl_3$ and $(4\text{-}Me_3SiCH_2C_6H_4)_2TeCl_2$.[27]

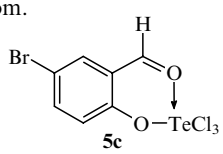
The corresponding aryltrimethylsilanes were used for the synthesis of bis(trichlorotelluro)benzenes. Thus 1,4-bis(trichlorotelluro)benzene [28] and 1,2-bis(trichlorotelluro)benzene [29] were prepared in ~ 50% yields upon refluxing equimolar amounts of $TeCl_4$ and 1,4-bis(trimethylsilyl)benzene or 1,2-bis(trimethylsilyl)benzene, respectively, in 1,2-dichlorobenzene.

4-Hydroxyaryltellurium trichlorides **4** were synthesised by the reactions of aryl trimethylsilyl ethers with $TeCl_4$ in boiling toluene in yields higher than 80%.[30]



R = H (**a**), Me (**b**).

It was assumed [30] that the reaction proceeded *via* intermediate aryloxytellurium trichlorides **5** followed by rearrangement into compounds **4**. This mechanism was supported by the synthesis of aryloxytellurium trichloride **5c** from $TeCl_4$ and the trimethylsilyl ether of 5-bromosalicylaldehyde.[30] Apparently, this compound is stabilised due to coordination of tellurium to the carbonyl oxygen atom.

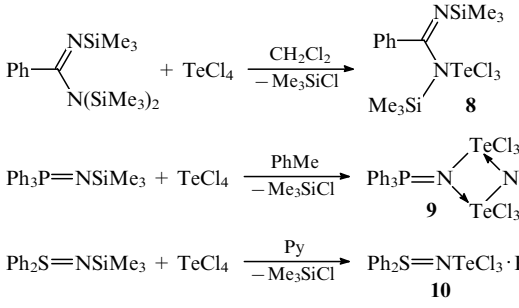


The reactions of TeF_4 with silylated perfluoroalkanols **6** afforded aryloxytellurium trifluorides **7** in 76%–82% yields.[31]

$$TeF_4 + \underset{\mathbf{6}}{Me_3SiOCH_2(CF_2)_nH} \xrightarrow[-Me_3SiF]{PhH,\ 50-60\ ^\circ C} \underset{\mathbf{7}}{F_3TeOCH_2(CF_2)_nH}$$

n = 2, 4, 6.

N-Trichlorotellurioamines **8**,[32] **9**[33] and **10**[34] were synthesised by the reactions of the corresponding *N*-trimethylsilyl derivatives with $TeCl_4$.



Organotin compounds react with tellurium tetrahalides at room temperature.[35–38] The yields of organyltellurium trihalides vary from moderate to very high.

$$R_4Sn + TeX_4 \xrightarrow{PhH \text{ or } PhMe} RTeX_3 + R_3SnX$$

X	R	Ref.	X	R	Ref.
Cl	Me	35	Br	Me	35
	Et	35		Et	35
	Pr	35		Pr	35
	Ph	35, 36		Ph	35
	4-MeC_6H_4	37			

$$R_3SnX + TeX_4 \xrightarrow{PhH \text{ or } CH_2Cl_2} RTeX_3 + R_2SnX_2$$

X	R	Ref.	X	R	Ref.
Cl	Et	38	Br	Et	38
	Ph	36		Ph	38

The reaction of tributylphenylstannane with $TeCl_4$ resulted in the cleavage of the C(Ar)—Sn bond to form phenyltellurium trichloride in 80% yield.[37]

Tetraarylgermanes react with tellurium tetrachloride like organotin derivatives.[37]

$$Ar_4Ge + TeCl_4 \longrightarrow \underset{\mathbf{2}}{ArTeCl_3} + Ar_3GeX$$

Ar = Ph, 4-MeC_6H_4.

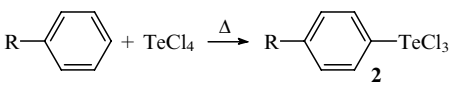
Germanium derivatives Ar_3GeCl do not react with $TeCl_4$.[37]

Tetraarylplumbanes react with $TeCl_4$ to form diaryltellurium dichlorides even under mild conditions.[39] Phenyltellurium trichloride was prepared with the use of Ph_3PbCl.[39]

$$Ph_3PbCl + TeCl_4 \xrightarrow{Dioxane} PhTeCl_3 + Ph_2PbCl_2$$

2. Reactions of $TeCl_4$ with activated arenes

The salt-like structure of tellurium tetrachloride, *viz.*, $[TeCl_3]^+Cl^-$ (see Refs 40–44) or $[TeCl_3]^+[TeCl_5]^-$ (see Ref. 45), both in the solid state and in solutions was confirmed by IR and Raman spectroscopy[40–45] and the data on conductivity.[41,42] This compound exhibits moderate electrophilicity and can be involved in electrophilic substitution (telluration) with arenes containing electron-donor substituents. The telluration is highly regioselective. The trichlorotellurio group enters exclusively into the *para* position with respect to the electron-donor substituent in the ring.[13,16,27,46–56] Heating of azobenzene with $TeCl_4$ afforded 2-trichlorotellurioazobenzene.[57] The yields of aryltellurium trichlorides **2** vary over a wide range.

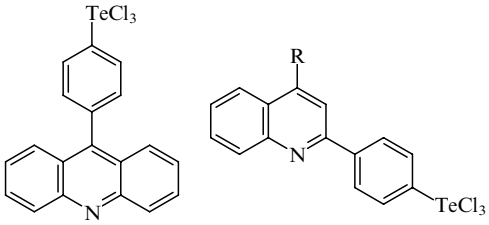


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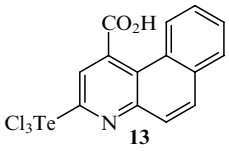
R	Ref.	R	Ref.
OH	46	OPr	16
Br	47	OBu	16
Me	48, 49	OPh	56
CH_2SiMe_3	27	OAc	16
OMe	16, 46, 50–52	SMe	16
OCH_2CO_2Me	53	SPh	13
OEt	16, 46, 51, 54, 55	NHAc	46

Morgan and Drew[55] were the first to demonstrate the high selectivity of telluration. He prepared bis(4-ethoxyphenyl) ditelluride by reduction of the product of the reaction of $TeCl_4$ with phenetole and demonstrated that the reaction of the ditelluride with nitric acid afforded exclusively 4-nitrophenetole. This selectivity was also proved by IR and ^1H NMR spectroscopy for a large number of compounds.

However, C-telluration does not occur if the benzene ring of compounds contains such a strong electron-donor substituent as the dimethylamino group; instead, the complex $2Me_2NPh \cdot TeCl_4$ is formed.[58,59] Analogous complexes were also obtained from other aromatic amines.[59–62] The corresponding tellurium trichlorides can be isolated from these complexes by subsequent treatment (see below). A decrease in the basicity of nitrogen prevents complexation with $TeCl_4$. For example, acetanilide underwent telluration in the *para* position.[46] Organyltellurium trichlorides **11**–**13** were synthesised from the corresponding derivatives of acridine or quinoline and $TeCl_4$ in CCl_4.[63]



11 **12** (R = NH_2, COOH)



13

However, other quinolines and acridines,[63] various pyridines,[42,45,60,63–65] indoles, carbazoles,[63] Schiff's bases[66–69] and hydrazones[70] react with tellurium tetrachloride to form only molecular complexes.

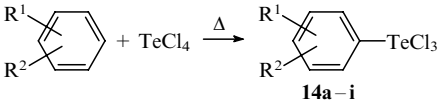
Aromatic compounds containing electron-withdrawing substituents (nitrobenzene or 4-nitroanisole) do not react with $TeCl_4$,[50] whereas refluxing of $TeCl_4$ with benzonitrile led to trimerisation of the latter yielding 2,4,6-triphenyltriazine.[47]

Under ordinary conditions, benzene does not react with $TeCl_4$ due to which it can be used in telluration as the solvent along with $CHCl_3$ and CCl_4. The introduction of one methyl group into the benzene ring leads to only weak activation of the ring with respect to telluration. Although prolonged boiling (20 h) of a solution of $TeCl_4$ in toluene afforded 4-methylphenyltellurium trichloride in 83% yield,[49] toluene can be used as the solvent in certain reactions of $TeCl_4$ with sufficiently reactive arenes.[16]

The $TeCl_3$ group possesses strong electron-withdrawing properties (see Section IV). Only one trichlorotellurium group can be introduced into the ring by telluration, unlike mercuration, which often gives rise to polymercurated compounds.

Polynuclear hydrocarbons, for example, naphthalene, react with $TeCl_4$ without additional activation of their nuclei by introducing electron-donor substituents. The reaction of $TeCl_4$ with naphthalene in toluene under conditions of kinetic control afforded 1-trichlorotellurionaphthalene in 24% yield,[16] which agrees with the usual direction of electrophilic substitution in naphthalene. However, prolonged heating of naphthalene with $TeCl_4$ at 110 °C without a solvent (under conditions of thermodynamic control) gave rise to 2-trichlorotellurionaphthalene in 54% yield.[71] The reaction of anthracene with $TeCl_4$ afforded a mixture of 9-chloro- and 9,10-dichloroanthracenes.[72]

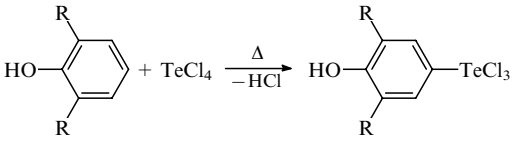
In the case of arenes containing two substituents, the $TeCl_3$ group is introduced in the *para* position with respect to the stronger electron-donor substituent.[16,48,50,55,73–75] If this position is occupied, the introduction occurs in the *ortho* position to this substituent.[50]



14a–**i**

Compound **14**	R^1	R^2	Ref.
a	4-Me	3-Me	48
b	4-OMe	3-Me	50
c	4-OMe	2-MeO	55
d	4-OMe	3-MeO	16
e	4-OMe	3-OH	55
f	4-OH	3-Me	73
g	4-OH	2-Cl	74
h	4-OH	3-Cl	74
i	2-OMe	5-Me	75

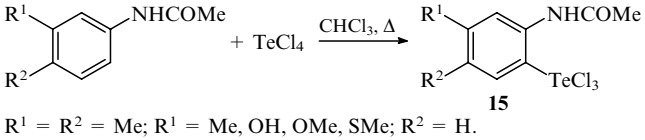
Telluration of dialkylphenols occurs in the *para* position with respect to the hydroxy group.[75]



R = Me, Bu^t.

The reactions of $TeCl_4$ with 4-bromoanisole and 3-methoxytoluene also gave rise to aryltellurium trichlorides.[50] However, the position of the introduction of the trichlorotellurium group into the ring was not established.[50]

Acetamidophenyltellurium trichlorides **15** were synthesised by telluration of 3-mono- and 3,4-disubstituted acetanilides.[19]



15

R^1 = R^2 = Me; R^1 = Me, OH, OMe, SMe; R^2 = H.

Aryltellurium tribromides and triiodides cannot be prepared by telluration of arenes with tellurium tetrabromide or tetraiodide, respectively, even in the case of such active compounds as anisole, phenetole or veratrole. Apparently, this is associated with a decrease in electrophilicity of tellurium tetrahalides TeX_4 on going from chlorine to iodine. The electrophilicity of tellurium tetrachloride can be increased by forming complexes of $TeCl_4$ with Lewis acids. In particular, the complex $[TeCl_3]^+[AlCl_4]^-$ was formed with $AlCl_3$.[43,76] Bergman[47] was the first to use this approach. However, prolonged boiling of the components in the presence of catalytic amounts of $AlCl_3$ afforded a mixture of aryltellurium trichlorides and diaryltellurium dichlorides. A more convenient procedure was proposed by Gunther *et al.*[77] The reactions are carried out with a two-to-threefold excess of $AlCl_3$. The course of the reaction is monitored by measuring the amount of hydrogen chloride evolved, and the reaction is stopped after evolution of one equivalent of HCl.

As mentioned above, direct telluration of arenes containing NR_2 substituents (R = H or Alk) cannot be performed because these compounds form 2 : 1 complexes with tellurium tetrahalides, which are poorly soluble in ordinary solvents (benzene, toluene or chloroform). Prolonged boiling of these complexes in anhydrous MeOH under an inert atmosphere did lead to electrophilic substitution at the *para* position with respect to the NR_2 group.[61]

$$2(R_2NPh)\cdot TeX_4 \xrightarrow[-Me_2NPh\cdot HX]{MeOH,\ \Delta} 4\text{-}R_2NC_6H_4TeX_3$$

R = H, Me; X = Cl, Br.

However, attempts to synthesise 4-dimethylaminophenyltellurium trichloride by this procedure failed.[59] It is believed[59] that 2 : 1 complexes of aromatic amines with $TeCl_4$ can have different structures depending on the nature of the amines. In the complexes with *N*- and *ortho*-substituted amines **16**, the tellurium-containing group is located at position 4 with respect to the NR^1R^2 group. Reduction of these complexes affords mixtures of 4-amino-substituted diaryl tellurides **17** and the corresponding diaryl ditellurides **18**. The ditellurides **18** can be converted into the tellurides **17** by treatment of the reaction mixture with a copper powder or Pd/C. The yields of the diaryl tellurides **17** vary over a wide range (8% – 72%).[59]

$$[R^1R^2N(ArH)]_2TeCl_4 \xrightarrow[2)\ NaHCO_3]{1)\ Na_2S_2O_5} \underset{\mathbf{16}}{}$$

$$\longrightarrow \underset{\mathbf{17}}{(R^1R^2NAr)_2Te} + \underset{\mathbf{18}}{(R^1R^2NAr)_2Te_2} \xrightarrow{Cu(0)\ or\ Pd/C} \mathbf{17}$$

R^1R^2NAr = 4-$Me_2NC_6H_4$, 4-$MeNHC_6H_4$, 4-$PhNHC_6H_4$, 4-$H_2NC_6H_4$, 4-H_2N-3-MeC_6H_3, 4-H_2N-3,5-$Me_2C_6H_2$, 4-H_2N-3-$EtOC_6H_3$, 4-H_2N-3-$CF_3C_6H_3$, 4-H_2N-3-$MeOCOC_6H_3$.

Reduction of 2 : 1 complexes of substituted anilines with $TeCl_4$ (**19**) gives rise to elemental tellurium and the corresponding anilines.[59]

$$\underset{\mathbf{19}}{(H_2NAr)_2TeCl_4} \xrightarrow[2)\ NaHCO_3]{1)\ Na_2S_2O_5} Te + H_2NAr$$

$ArNH_2$ = 4-$MeC_6H_4NH_2$, 3,5-$Me_2C_6H_3NH_2$, 3-$O_2NC_6H_4NH_2$, 2,4,6-$Br_3C_6H_2NH_2$.

The synthesis of *p*- or *o*-substituted aminophenyltellurium trihalides was carried out also with the use of hexahalotellurates of amines, which have been prepared in high yields from amines and solutions of tellurium tetrahalides in hydrohalic acids.[61,62] Refluxing of these salts in anhydrous methanol was accompanied by elimination of HX to form the corresponding aminoaryltellurium trihalide. It was believed[62] that hexahalotellurates in methanolic solutions exist in equilibrium with free amines and tellurium tetrahalides and the electrophilic substitution occurs at the nucleus of the free amine.

$$(R_2\overset{+}{N}HAr)_2TeX_6^{2-} \xrightarrow{MeOH,\ \Delta} R_2NArTeX_3$$

R_2NAr = 4-$H_2NC_6H_4$, 4-$MeNHC_6H_4$, 4-$Me_2NC_6H_4$, 4-H_2N-3-MeC_6H_3, 2-H_2N-5-MeC_6H_3, 2-H_2N-3,5-$Me_2C_6H_2$, 4-H_2N-3,5-$Me_2C_6H_2$; X = Cl, Br, I.

3. Reactions of $TeCl_4$ with compounds containing active methylene groups

The reactions of aliphatic compounds containing activated methyl or methylene groups with $TeCl_4$ can proceed as electrophilic substitution at the saturated carbon atom.

Generally, ketones containing at least one methylene group at the α position with respect to the carbonyl group react with $TeCl_4$ (a solution in $CHCl_3$) in a molar ratio of 2 : 1 to form mixtures of organyltellurium trichlorides **20** and diorganyltellurium dichlorides **21**. The trichlorides can be isolated provided that they are poorly soluble and form precipitates.[78–82] In some cases, the trichlorides were obtained as the only reaction products in high yields.[81,82] It was suggested[78] that the reaction proceeded through the addition of $TeCl_4$ at the double bond of the enol followed by elimination of HCl. Diisopropyl ketone did not react with $TeCl_4$.[78,79]

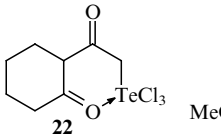
$$R^1COCH_2R^2 + TeCl_4 \xrightarrow{CHCl_3,\ \Delta}$$

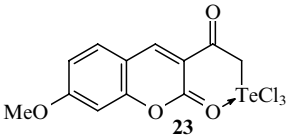
$$\longrightarrow \underset{\mathbf{20}}{R^1COCHR^2TeCl_3} + \underset{\mathbf{21}}{(R^1COCHR^2)_2TeCl_2}$$

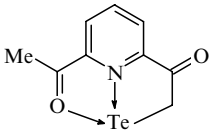
R^1	R^2	Ref.	R^1	R^2	Ref.
Me	Me	78–80	Ph	Ph	78
Et	Me	78	4-ClC_6H_4	H	82
Pr	H	80	2-HOC_6H_4	H	82

R^1	R^2	Ref.	R^1	R^2	Ref.
Pr	Et	78–80	3-$MeOC_6H_4$	H	82
Bu^t	H	78, 80	$(CH_2)_6$		81
Ph	Et	78	$(CH_2)_7$		81

The reactions of $TeCl_4$ with some polyfunctional ketones gave rise to organyltellurium trichlorides of the type **20** as the only products.[83] Thus telluration of 2-acetylcyclohexanone, 3-acetyl-7-methoxycoumarin and 2,6-diacetylpyridine afforded trichlorides **22**–**24**, respectively. Apparently, the trichlorotellurium group in the compounds **22**–**24** exhibits low electrophilicity due to the formation of intramolecular O → Te coordinate bonds, and the reaction stops at this stage. The presence of intramolecular coordinate bonds was confirmed by IR and NMR spectroscopy and X-ray diffraction study of the trichloride **24** (see Section IV). The ketones **22**–**24** are more stable to hydrolysis than other organyltellurium trichlorides, which was also attributed to intramolecular O → Te coordinate bonds.[83]

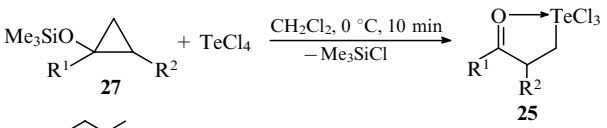

22


23

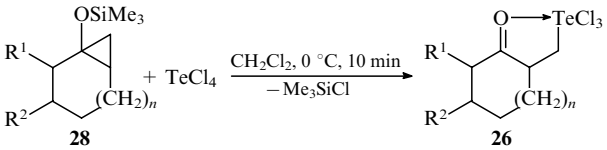

24

The compounds **22**–**24** have been used for the preparation of thermo- and photothermographic materials.[84]

Trichlorotellurio ketones **25** and **26** containing the trichlorotellurium group at the β position with respect to the carbonyl group were prepared by the reactions of trimethylsilyloxycyclopropanes **27** and **28**, respectively, with $TeCl_4$ (the yields were 71%–93%).[85] The compounds **25** and **26** were subjected to dehydrotelluration without isolation from the reaction mixture (see Section III). Based on the IR spectral data, Nakahira *et al.*[85] assumed the presence of intramolecular O—Te coordinate bonds in the ketones **25** and **26**.

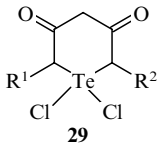

27 **25**

R^1 = Bu^t, , Ph; R^2 = H, Me.


28 **26**

$R^1 = R^2 = H$, $n = 2, 5$; $R^1 - R^2 = (CH=CH)_2$, $n = 1$.

In β-diketones, the most acidic hydrogen atoms of the methylene group are replaced by the $TeCl_3$ group only if the carbonyl groups bear aryl substituents. Thus the reaction of dibenzoylmethane with $TeCl_4$ afforded very unstable (dibenzoylmethyl)tellurium trichloride $(PhCO)_2CHTeCl_3$.[86] The reactions of $TeCl_4$ with β-diketones containing at least one hydrogen atom at each of the α- and α′-carbon atoms give rise to 1,1-dichloro-1-telluracyclohexane-3,5-diones **29** as the major products. Diorganyltellurium dichlorides and organyltellurium trichlorides **30** can be isolated in rare cases and only in reactions carried out in ethanol-free $CHCl_3$ as the solvent.[87–89]


29

$Cl_3TeCH(R^1)C(OH)=CHCOR^2$
30

R^1, R^2 = Alk.

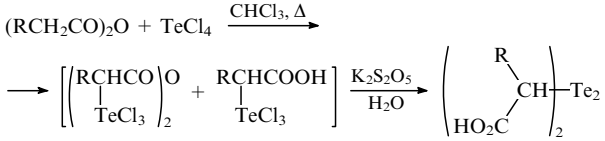
R^1	R^2	Ref.
H	C_6H_{13}	87
H	C_8H_{17}	88
Pr	Pr	89

The formation of organyltellurium trichlorides is favoured by the presence of two or three alkyl substituents at one of the α-carbon atoms and the presence of at least one hydrogen atom at the α′-carbon atom. If the organyltellurium trichlorides formed bear at least one hydrogen atom at position 3 and chloroform used as the solvent has not been freed from EtOH, the reactions yielded tellurium trichlorides of ethyl enolates **31**.[86–90] The position of the ethoxy group in these compounds has not been established unambiguously. However, taking into account the strong electron-withdrawing properties of the trichlorotellurium group, it can be assumed that the ethoxy group is located at the β position with respect to the $TeCl_3$ group.[22]

$R^1COCH=C(OEt)CR^2R^3TeCl_3$
31

R^1	R^2	R^3	Ref.
Me	H	H	90
Pr^n	H	H	87
Pr^n	H	Et	89
Pr^i	H	H	87
Pr^i	Me	Me	88
Bu^t	H	H	86
Pr^iCH_2	H	H	87
Ph	H	H	86
Et	H	Me	87

The reactions of tellurium tetrachloride with acetic or propionic anhydrides taken in a ratio of 1:2 in $CHCl_3$ afforded mixtures of the corresponding α-trichlorotellurocarboxylic acids and anhydrides.[50,91] However, these trichlorides were converted without isolation into ditellurides **32** under the action of an aqueous solution of $K_2S_2O_5$.


32

R = H, Me.

Methylenebis(tellurium trichloride) was isolated in low yield from the mixture obtained by the reaction of $TeCl_4$ with acetic anhydride.[91] Later, this compound was prepared by refluxing a mixture of $TeCl_4$ with Ac_2O (taken in a molar ratio of 3:1) in $CHCl_3$ in 52% yield.[92] The mechanism of formation of methylenebis(tellurium trichloride) was proposed.[92]

$(MeCO)_2O + TeCl_4 \longrightarrow (Cl_3TeCH_2CO)_2O + HCl,$

$(Cl_3TeCH_2CO)_2O + TeCl_4 \longrightarrow$

$\longrightarrow Cl_3TeCH_2CO_2TeCl_3 + Cl_3TeCH_2COCl,$

$Cl_3TeCH_2CO_2TeCl_3 \longrightarrow CH_2(TeCl_3)_2 + CO_2.$

Attempts to perform telluration of anhydrides of higher aliphatic acids resulted only in elimination of tellurium to form resinous products.

Of other compounds containing the active methylene group, nitromethane was subjected to telluration.[93]

$$MeNO_2 + TeCl_4 \xrightarrow{\Delta} O_2NCH_2TeCl_3$$

4. Addition of tellurium tetrachloride to multiple bonds

The major and, apparently, the only procedure for the preparation of alkanes and alkenes containing the $TeCl_3$ groups and the chlorine atoms at the vicinal positions involves the electrophilic addition of $TeCl_4$ to double or triple bonds.

a. Reactions of $TeCl_4$ with alkenes

Under mild conditions (0–60 °C), $TeCl_4$ adds to the double bond of acyclic or cyclic alkenes to form β-chloroalkyl- and β-chlorocycloalkyltellurium trichlorides **33**.[94–104] The reactions are generally performed in $CHCl_3$, CCl_4 or MeCN. In some cases, bis(β-chloroalkyl)- and bis(β-chlorocycloalkyl)tellurium dichlorides are formed along with the corresponding trichlorides. The addition of $TeCl_4$ proceeds regioselectively. Thus the reactions of $TeCl_4$ with terminal alkenes occur as a Markovnikoff addition.

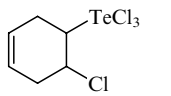
$$R^1CH=CHR^2 + TeCl_4 \longrightarrow Cl_3Te(R^1)CHCH(Cl)R^2$$

33

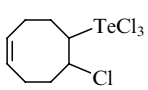
R^1	R^2	Ref.	R^1	R^2	Ref.
H	H	97	Me	Me	99, 100
H	Me	96, 98	$(CH_2)_3$		99, 100
H	Et	96	$(CH_2)_4$		94–96, 100, 102–104
H	Bn	101	$CH_2CH(Me)(CH_2)_2$		103, 104
H	C_8H_{17}	99, 100	$(CH_2)_6$		99, 100
D	C_8H_{17}	99, 100			

The direction of the reactions of $TeCl_4$ with alkenes and primarily with cycloalkenes depends substantially on the temperature. Thus the reactions of cyclohexene and 4-methylcyclohexene with $TeCl_4$ in $CHCl_3$, CCl_4 or MeCN at 25 °C gave rise to the adducts **33**, whereas the reactions carried out with boiling afforded benzene and toluene, respectively, as the major products.[103, 104]

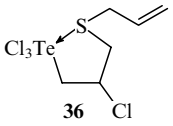
Dienes containing isolated double bonds, *viz*., 1,4-cyclohexadiene [104] and 1,5-cyclooctadiene,[104, 105] also react with tellurium tetrachloride. In these cases, $TeCl_4$ adds to only one double bond to form organyltellurium trichlorides **34** and **35** in 49% and 64% yields, respectively. Diallyl sulfide reacts analogously to give the trichloride **36**, which is stabilised by an intramolecular S–Te coordinate bond (2.763 Å).[106]



34



35



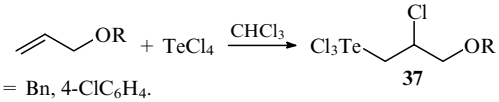
36

Unlike dienes containing isolated double bonds, cyclic dienes with conjugated double bonds (1,3-cyclohexadiene and 1,3-cyclooctadiene) react with $TeCl_4$ to form primarily dichlorocycloalkenes.[104]

The stereochemistry of the addition of $TeCl_4$ to alkenes has been studied.[100] Thus the reactions of (*Z*)- and (*E*)-but-2-enes generally give rise to mixtures of isomers due to competitive *syn*- and *anti*-addition. *p*-Benzoquinone as a substrate favours the formation of a *syn*-addition product. It is believed that the stereospecific *syn*-addition occurs more or less according to a concerted mechanism. The free-radical reaction competes with this addition.

The addition of aryltellurium trichlorides to alkenes, unlike that of $TeCl_4$, occurs nonstereoselectively.

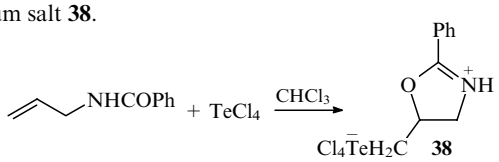
The reactions of allylic derivatives with $TeCl_4$ take different paths depending on the nature of the substituents at the sp^3 carbon atom.[107] The reactions of $TeCl_4$ with allylic alcohols are generally accompanied by resinification of the reaction mixtures and the reaction products cannot be isolated. The reactions of $TeCl_4$ with allyl ethers occur according to the Markovnikoff rule giving rise to trichlorides **37** in yields above 80%.



37

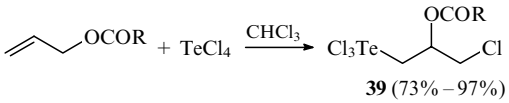
R = Bn, 4-ClC_6H_4.

The reaction of $TeCl_4$ with *N*-allylbenzamide,[107] like that with *N*-acetyldiallylamine,[108] afforded zwitterionic dihydrooxazolinium salt **38**.



38

The addition of $TeCl_4$ to allyl carboxylates proceeded anomalously. In this case, 1,3-addition products, *viz*., β-acyloxy-γ-chloropropyltellurium trichlorides **39**, rather than 1,2-addition products were obtained.[107]



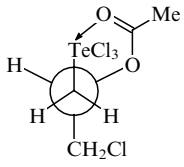
39 (73%–97%)

R = Me, Ph, 4-MeC_6H_4, 4-ClC_6H_4, 4-$O_2NC_6H_4$, (*E*)-CH=CHMe, (*E*)-CH=CHPh.

The reaction conditions depend on the nature of the substituent at the carbonyl carbon atom. Thus allyl benzoate and allyl 4-methylbenzoate reacted at room temperature, the reactions with allyl 4-chloro- and 4-nitrobenzoates proceeded only on boiling in chloroform, whereas allyl 2,4-dinitrophenylbenzoate did not react at all even on prolonged heating of the reaction mixture.

The reactions of $TeCl_4$ and $TeBr_4$ with allyl cinnamate in a mixture of Et_2O and H_2O at −30 °C occurred as 1,3-addition.[109]

According to the data from IR and ^1H NMR spectroscopy,[107] compound **39** (R = Me) in solution adopts the conformation **A** in which the $TeCl_3$ group is located in the *gauche* position with respect to the acetoxy group. This conformation is stabilised through the intramolecular O–Te coordinate bond.

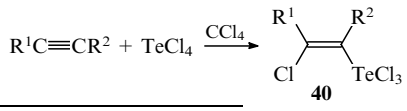


A

Tellurium tetrachloride reacts with α-methylallyl α,α-dimethylallyl and α-ethylallyl benzoates to give also 1,3-addition products.[109]

b. Reactions of $TeCl_4$ with alkynes

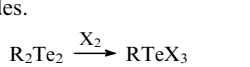
The reactions of $TeCl_4$ with alkynes have been studied to a substantially lesser extent than the reactions with alkenes. The reactions of $TeCl_4$ with alkynes in CCl_4 proceed regio- and stereospecifically giving rise to 2-chlorovinyltellurium chlorides **40** in yields of 75% and higher.[54, 110, 111] The *Z* configuration of the compounds **40** was established by halodetelluration yielding (*Z*)-chlorobromo(iodo)alkenes (see Section III).[111]

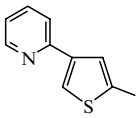
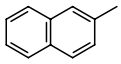
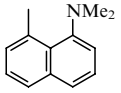
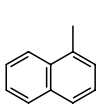
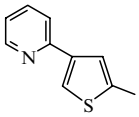
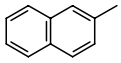


R^1	R^2	Ref.
H	CH_2OH	111
Ph	H	54, 110, 111
Ph	Me	111
Ph	Et	111
Ph	Ph	110, 111

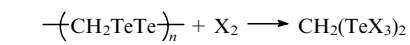
5. Oxidation of diorganyl ditellurides

A wide range of organyltellurium trihalides were prepared by oxidation of diorganyl ditellurides with chlorine,[22,26,91,112–120] bromine,[13,26,50,51,91,113,114,116,117,120–131] iodine[13,51,120,121,123,127,129–132] or fluorine diluted with an inert gas[133] at room or reduced temperature. Organyltellurium trichlorides can be prepared with the use of sulfuryl chloride[112,116] or thionyl chloride[114,115,117,120] instead of chlorine. These reactions are used primarily for the preparation of alkyltellurium trichlorides, aryltellurium tribromides and aryltellurium triiodides.



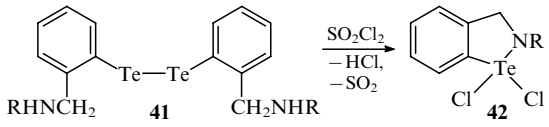
X	R	Ref.	X	R	Ref.
F	Ph	133	Br	4-$MeOC_6H_4$	13, 50, 51,
Cl	Me	118			123, 124, 127
Cl	Et	119	Br	4-$EtOC_6H_4$	13, 51,
Cl	HO_2CCH_2	91			121, 123,
Cl	3-FC_6H_4	114			124, 127
Cl	4-FC_6H_4	114			
Cl	Ph	112, 115	Br		13
Cl		120	Br		129
Cl	2-$OCHC_6H_4$	113	Br		128
Cl	2-NH_2-4-MeC_6H_3	22			
Cl	2-NH_2-4-BrC_6H_3	22			
Cl	2-NH_2-4-$NO_2C_6H_3$	22	Br	2-$PhCH_2C_6H_4$	26
Cl	2-$PhCH_2C_6H_4$	26	Br	4-$PhOC_6H_4$	13, 124, 127
Cl	2-$Me_2NCH_2C_6H_4$	116	Br	4-$PhSC_6H_4$	13
Cl	2-$Me_2NCH(Me)C_6H_4$	117	Br	2-PhC_6H_4	126, 131
Br	Me	122	Br	4-PhC_6H_4	131
Br	Et	130	I	Me	130
Br	HO_2CCH_2	91	I	Et	130
Br	$MeCH(CO_2H)$	50	I	Ph	127
Br	2-ClC_6H_4	125	I	4-MeC_6H_4	51, 127, 131
Br	3-FC_6H_4	114	I	4-$MeOC_6H_4$	13, 51, 121,
Br	4-FC_6H_4	114, 125			123, 127
Br	Ph	124, 127	I	4-$EtOC_6H_4$	13, 51, 123,
Br	2-MeC_6H_4	113, 125			127
Br	4-MeC_6H_4	51, 124, 127, 131	I		13
Br		120	I		129
			I	2-PhC_6H_4	131, 132
Br	2-$Me_2NCH_2C_6H_4$	116	I	4-PhC_6H_4	131
Br	2-$Me_2NCH(Me)C_6H_4$	117	I	4-$PhOC_6H_4$	13, 127
			I	4-$PhSC_6H_4$	13

Poly(ditellurides) are also oxidised with halogens. Thus treatment of poly(methylene ditelluride) with chlorine[91,93] or bromine[91] afforded bis(trihalogenotellurio)methanes.



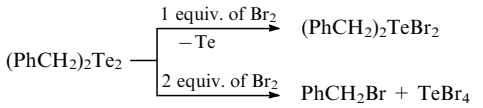
X = Cl, Br.

The reaction of bis{2-[*N*-(*p*-tolyl)benzylaminomethyl]phenyl} ditelluride (**41**) with SO_2Cl_2 yielded the telluracycle **42**.[134]

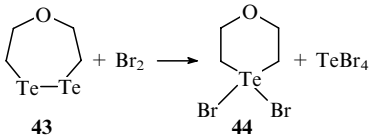


R = 4-MeC_6H_4.

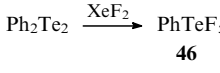
The behaviour of dibenzyl ditelluride in the reactions with halogens is anomalous compared to other ditellurides. Treatment of the former with bromine in CCl_4 led to the cleavage of both C–Te bonds giving rise to benzyl bromide and $TeBr_4$.[135] The reactions with the use of less than one equivalent of bromine afforded dibenzyltellurium dibromide as the major product.



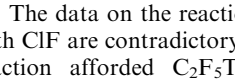
Ditelluride **43** also behaved anomalously. Thus the reaction with bromine yielded the telluracycle **44**.[136]



Organyltellurium trifluorides were synthesised not only with the use of fluorine but also using XeF_2 (see Refs 133, 137 and 138) or ClF.[138,139] Ditellurides containing perfluorinated organic groups were converted into organyltellurium trifluorides **45** under the action of XeF_2,[133,138] whereas diphenyl ditelluride under the same conditions was converted into phenylpentafluorotellurium **46**.[137]

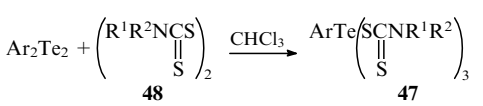


R = C_2F_5 (**a**), C_6F_5 (**b**).



The data on the reaction of bis(pentafluoroethyl) ditelluride with ClF are contradictory. Desjardins *et al.*[139] believed that the reaction afforded $C_2F_5TeF_3$ as the major product (*trans*-$C_2F_5TeClF_4$ and $TeClF_5$ were isolated as by-products in low yields), whereas Lau *et al.*[138] reported that a mixture of $C_2F_5TeCl_xF_{3-x}$, C_2F_5Cl and *trans*-$C_2F_5TeClF_4$ formed.

Some disulfides act as oxidising agents with respect to diaryl ditellurides. Thus thermochromic aryltellurium tris(dithiocarbamates) **47** were prepared by the reactions of diaryl ditellurides with thiuram disulfides **48** in almost quantitative yields.[140]



Ar = Ph, 4-$MeOC_6H_4$; R^1 = R^2 = Me, Et; R^1-R^2 = $(CH_2)_5$.

Oxidation of diaryl ditellurides with lead tetraacetate afforded the corresponding aryltellurium triacetates.[141–143] The presence of these compounds in solutions was established by ^1H NMR spectroscopy. However, attempts to isolate these compounds were unsuccessful due to rapid hydrolysis.

6. Exchange reactions of anionoid substituents

σ-Telluranes $RTeX_3$ containing different anionoid substituents can be synthesised with the use of organyltellurium trichlorides in which the chlorine atoms are readily replaced by more nucleophilic anions X^-. Exchange reactions were used for the synthesis of a series of organyltellurium tribromides [61, 73, 74, 82] and organyltellurium triiodides.[13, 61, 73, 74, 82–95] Generally, exchange reactions are performed in aqueous-methanolic (ethanolic) solutions under the action of potassium halides.

$$RTeCl_3 + KX \longrightarrow RTeX_3$$

X	R	Ref.	X	R	Ref.
Br, I	4-$Me_2NC_6H_4$	61	Br, I	4-$ClC_6H_4COCH_2$	82
Br, I	3-Me-4-HOC_6H_3	73	I	4-HOC_6H_4	13
Br, I	2-Cl-4-HOC_6H_3	74			
Br, I	3-Cl-4-HOC_6H_3	74	I		95
Br, I	2-$HOC_6H_4COCH_2$	82			
Br, I	3-$MeOC_6H_4COCH_2$	82			

The exchange reactions were also used for the synthesis of aryltellurium trifluorides **45c**,**d**.[51]

$$RTeCl_3 + AgF \longrightarrow \underset{\textbf{45c,d}}{RTeF_3}$$

R = 4-$MeOC_6H_4$ (**c**), 4-$EtOC_6H_4$ (**d**).

An analogous reaction was carried out with $MeTeI_3$, but attempts to isolate the resulting $MeTeF_3$ in the pure form failed.[144]

The exchange of chlorine atoms in organyltellurium trichlorides is used as the major procedure for the synthesis of σ-telluranes $RTeX_3$ containing such substituents as $SC(S)NR_2$ or $SP(S)(OR)_2$. Thus aryltris(thiocarbamoylthio)tellurium(IV) **47** was prepared by treatment of solutions of $RTeCl_3$ in CH_2Cl_2, acetone or methanol with *N*-substituted sodium dithiocarbamates.[116, 117, 140, 145, 146]

$$ArTeCl_3 + NaSC(S)NR_2 \longrightarrow \underset{\textbf{47}}{ArTe[SC(S)NR_2]_3}$$

Ar = Ph, 4-$MeOC_6H_4$, 2-$C_6H_4N{=}NPh$, 2-$Me_2NCH(Me)C_6H_4$, 2-$Me_2NCH_2C_6H_4$; R = Me, Et, Bn.

The σ-telluranes **47** were also prepared by exchange reactions of aryltellurium trichlorides with $Pb[SC(S)NEt_2]_2$ in dry benzene.[147]

$$ArTeCl_3 + Pb[SC(S)NEt_2]_2 \longrightarrow ArTe[SC(S)NEt_2]_3$$

Ar = Ph, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$, 3-Me-4-$MeOC_6H_3$.

It should be noted that (according to the data from ^{125}Te NMR and Mössbauer spectroscopy [146]) 2-(phenylazo)phenyltris(thiocarbamoylthio)tellurium(II) **47** (Ar = 2-$C_6H_4N{=}N{-}C_6H_4$-2) is very unstable and dissociates in solution to form 2-(phenylazo)phenylbis(thiocarbamoylthio)tellurium(II) and $[R_2NC(S)S]_2$.

The evidence for the possible existence of mixed organyltellurium trihalides of the $RTeX_2Y$ type is contradictory (see Section II.7). However, compounds of this type were prepared upon treatment of aryltellurium trichlorides with sodium dialkyldithiocarbamates. Thus bis(*N*,*N*-diethylthiocarbamoylthio)-(chloro)phenyltellurium(IV) (**49a**) was synthesised in high yield starting from $PhTeCl_3$ and $NaSC(S)NEt_2$.[148] Treatment of the compound **49a** with potassium *O*,*O*-diethyl dithiophosphate afforded the mixed σ-tellurane **49b** whose structure was established by X-ray diffraction analysis.[148]

Mixed σ-telluranes of this type formed in the reactions of $PhTeCl_3$ with salts containing the $[SC(S)NEt_2]^-$, $[S(P)S(OR)_2]^-$ or $[SC(S)OEt]^-$ anions were studied in solutions by ^{13}C, ^{31}P and ^{125}Te NMR spectroscopy.[148]

$$PhTeCl_3 + NaSC(S)NEt_2 \xrightarrow{CH_2Cl_2} \underset{\textbf{49a}}{PhTe(Cl)[SC(S)NEt_2]_2} \xrightarrow{KSP(S)(OEt)_2} \underset{\textbf{49b}}{PhTe[SC(S)NEt_2]_2[SP(S)(OEt)_2]}$$

Yet another approach to the synthesis of the mixed derivatives **49** is based on oxidative addition of alkyl iodides to bis(*N*,*N*-diethylthiocarbamoylthio)tellurium(II) (**50**).[148]

$$MeI + \underset{\textbf{50}}{Te[SC(S)NEt_2]_2} \xrightarrow{CH_2Cl_2} MeTe(I)[SC(S)NEt_2]_2$$

The mixed derivatives **49c**–**e** were also synthesised by the reactions of aryltris(*N*,*N*-dialkylthiocarbamoylthio)tellurium with halogens.[149–151]

$$ArTe[SC(S)NR_2]_3 + X_2 \longrightarrow \underset{\textbf{49c–e}}{ArTe(X)[SC(S)NR_2]_2} + [R_2NC(S)S]_2$$

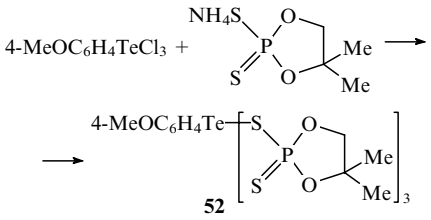
Compound **49**	Ar	R	X	Ref.
c	Ph	Et	I	149
d	4-$MeOC_6H_4$	Me	Br	150
e	4-$MeOC_6H_4$	Et	I	151

It is noteworthy that the reaction of the compound **49e** with bromine was accompanied by partial replacement of the iodine atoms. The structure of the reaction product **49f** was established by X-ray diffraction analysis.[151]

$$4\text{-}MeOC_6H_4Te(I)[SC(S)NEt_2]_2 + Br_2 \longrightarrow \underset{\textbf{49e}}{} \longrightarrow \underset{\textbf{49f}}{4\text{-}MeOC_6H_4Te(Br_{0.41})(I_{0.59})[SC(S)NEt_2]_2}$$

The exchange of the chlorine atoms in aryltellurium trichlorides was also used for the synthesis of aryltris(dialkoxythiophosphorylthio)tellurium (compounds **51** and **52**).[152]

$$PhTeCl_3 + NH_4SP(S)(OPr^i)_2 \longrightarrow \underset{\textbf{51}}{ArTe[SP(S)(OR)_2]_3}$$



52

Compounds of the type **51** were prepared by the reactions of $PhTe(OEt)_3$ (which has been prepared *in situ* from $PhTeCl_3$ and EtONa in EtOH) with *O*,*O*-dialkyl dithiophosphates, *e.g.*, $HSP(S)(OPr^i_2)_3$.[152]

As in the case of derivatives of dithiocarbamic acid, mixed derivatives can be synthesised.[153]

$$ArTeX_3 + NH_4[SP(S)(OR)_2] \xrightarrow{CS_2,\ 20\ ^\circ C} ArTeX_2[SP(S)(OR)_2]$$

Ar = Ph, 4-$MeOC_6H_4$; X = Br, Cl; R = Me, Et, Pr^i.

Attempts to prepare σ-telluranes $RTeX_3$ containing $SP(S)R_2$ ligands, unlike compounds containing $SC(S)NR_2$ or $SP(S)(OR)_2$ ligands, were unsuccessful. The reaction of $PhTeCl_3$ with $Na[SP(S)R_2]$ gave rise only to [diorganyl(thiophosphorylthio)]-phenyltellurium(II) **53** due apparently to decomposition of intermediate σ-telluranes of the type **54**.[154]

$$PhTeCl_3 + Na[SP(S)R_2]\cdot 2H_2O \longrightarrow \underset{\textbf{54}}{PhTe[SP(S)R_2]_3} \longrightarrow \underset{\textbf{53}}{PhTe[SP(S)R_2]} + [R_2P(S)S]_2$$

7. Symmetrisation and reverse conversions

Symmetrisation and reverse conversions are well known, have been studied in detail for organic derivatives of Groups II – IV elements and are of preparative importance in the chemistry of organic derivatives of these elements. It was demonstrated [115] that the symmetrisation reverse reaction also occurs in the case of diaryltellurium dichlorides.

$$(4\text{-}RC_6H_4)_2TeCl_2 + TeCl_4 \longrightarrow 4\text{-}RC_6H_4TeCl_3$$

R = OEt, OMe, H, Br.

Donor substituents favour these reactions. 4-Methoxy- and 4-ethoxyphenyltellurium trichlorides were prepared in 93% and 81% yields, respectively, upon refluxing (5 h) of equimolar mixtures of the reagents. Phenyl- and 4-bromophenyltellurium dichlorides were synthesised under more drastic conditions (a twofold excess of $TeCl_4$ and prolonged boiling).

8. Miscellaneous procedures

In this section, we consider syntheses of σ-telluranes $RTeX_3$, which are exemplified in a few compounds and are of no preparative importance.

Thus 4-hydroxy-3-methoxyphenyltellurium trichloride was prepared along with the corresponding dichloride by condensation of *o*-cresol with $TeOCl_2$.[155] It was the only aryltellurium trichloride synthesised according to this procedure.

Organyltellurium trihalides were prepared by the reactions of some organotellurium compounds, *viz*., organyltellurenyl halides, organyl tellurocyanates, diorganyl tellurides and organyltellurinic acids, with halides (see Section II).

Oxidation of diorganyl ditellurides to form organyltellurium trihalides proceeds through intermediate formation of organyltellurenyl halides RTeX **55**.[131, 156] Compounds of this type, which do not contain coordinating substituents, are unstable and readily undergo disproportionation to form R_2TeX_2 and Te.[157] Certain groups which can form strong intramolecular coordinate bonds with the Te atom through the N or O atoms stabilise the tellurenyl halides **55**. For example, the NO_2, CHO, COR, CH=N, N=N and CH_2NR_2 groups located at position 2 of the aryl or alkenyl substituent exert such a stabilising effect.[158, 159] Compounds **55** can be synthesised not only by oxidation of ditellurides but also according to other procedures.[160] Hence, oxidation of the organyltellurenyl halides **55** was used for the preparation of organyltellurium trihalides.[161 – 169]

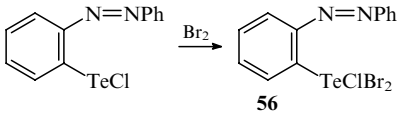
$$RTeX \xrightarrow{X_2} RTeX_3$$

55

X	R	Ref.
Cl	2-$PhCOC_6H_4$	164
Cl	2-$C_6H_4CH=NC_6H_4Me$-4	165 – 167
Cl	2-$C_6H_4CH=NPh$	166, 167
Cl	2-$C_6H_4CH=NC_6H_4OMe$-4	166, 167
Cl	$(2\text{-}C_6H_4CH=NCH_2)_2$	168
Cl	PhCOCH=CH	169
Cl	PhCOCH=CPh	169
Br	2-$NO_2C_6H_4$	161
Br	2-$HOCC_6H_4$	162
Br	2-$PhCOC_6H_4$	163
Br	2-$C_6H_4CH=NC_6H_4Me$-4	165 – 167
Br	2-$C_6H_4CH=NPh$	166, 167
Br	2-$C_6H_4CH=NC_6H_4OMe$-4	166, 167
Br	2-$C_6H_4CH=NC_6F_5$	166, 167
Br	$(2\text{-}C_6H_4CH=NCH_2)_2$	168
Br	PhCOCH=CH	169
Br	PhCOCH=CPh	169
I	2-$C_6H_4CH=NC_6H_4Me$-4	165 – 167
I	2-$C_6H_4CH=NPh$	166, 167
I	2-$C_6H_4CH=NC_6H_4OMe$-4	166, 167
I	2-$C_6H_4CH=NC_6F_5$	166, 167

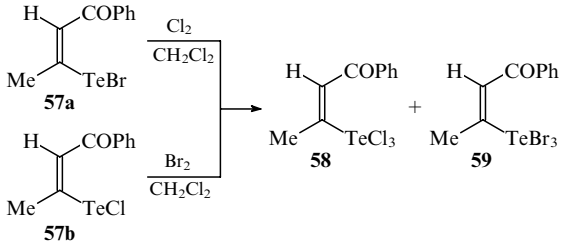
The oxidative addition is often performed with the use of SO_2Cl_2 instead of chlorine.[165 – 167] Some tellurenyl iodides, for example, PhCOCH=C(Ph)TeI, were not oxidised with iodine to form the corresponding triiodides.[169]

Aryltellurenyl chlorides can be used for the preparation of mixed aryltellurium trihalides $ArTeX_2Y$ **56**.[18]

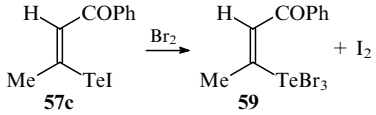


56

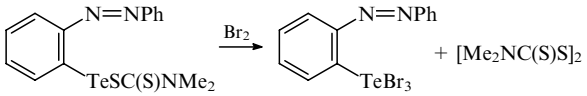
Attempts to synthesise compounds **56** starting from aryl 2-(halogenotellurenyl)vinyl ketones **57** were unsuccessful.[169] Thus the reaction of tellurenyl bromide **57a** with chlorine afforded a mixture of trichloride **58** and tribromide **59** in a ratio of 2 : 1. Treatment of tellurenyl chloride **57b** with bromine gave rise to a mixture of the same compounds, but the ratio was 1 : 2.[169]



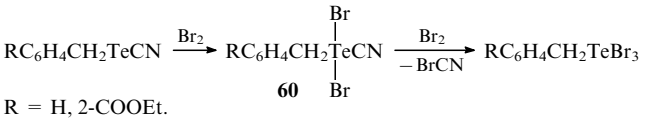
On the contrary, oxidative addition of bromine to tellurenyl iodide **57c** afforded vinyltellurium tribromide **59**.[169]



2-(*N*,*N*-Dimethylthiocarbamoyltellurenyl)azobenzene reacted analogously.[146]

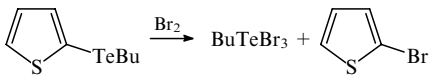


The reactions of benzyl tellurocyanates with two equivalents of bromine were accompanied by the cleavage of the Te – CN bond yielding the corresponding benzyltellurium tribromides.[170, 171] Apparently, σ-telluranes **60** were formed in these reactions as intermediates.[170]

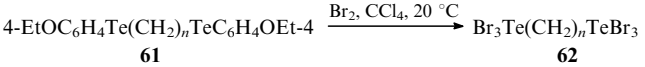


R = H, 2-COOEt.

It is known [3, 4, 6, 7] that diorganyl tellurides R_2Te react with halogens to form diorganyltellurium dihalides R_2TeX_2. However, the reactions of some diorganyl tellurides with halogens proceed with the cleavage of one of the C – Te bonds giving rise to the corresponding organyltellurium trihalides. Thus butyltellurium tribromide was obtained from butyl-2-thienyl telluride.[172]



Compounds **61** underwent scission under the action of bromine in CCl_4 to form α,ω-bis(tribromotellurio)alkanes **62**.[173]



61 **62**

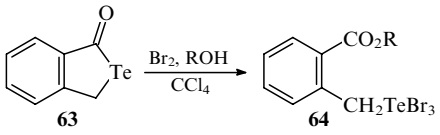
n = 6 (42%), 10 (40%).

Tellurium-substituted alkynes add bromine with simultaneous elimination of organyltellurium tribromide.[174]

$$R^1C{\equiv}CTeR^2 \xrightarrow[20\ ^\circ C,\ 20\ min]{Br_2,\ CH_2Cl_2} R^1C(Br){=}CBr_2 + R^2TeBr_3$$

R^1 = Ph, C_5H_{11}, 4-BrC_6H_4, R^2 = Bu; R^1 = Ph, R^2 = 4-$MeOC_6H_4$.

The C–Te bond was cleaved in the reaction of telluraphthalide **63** with bromine.[171] In the presence of alcohols, the reaction afforded 2-alkoxycarbonylbenzyltellurium tribromides **64**.[171]



63 **64**

R = Me, Et.

In the reactions with HI, tellurinic acids are converted into organyltellurium triiodides. Thus tellurinic acid as a component of the complexes $Bu_2TeO \cdot 3BuTe(O)OH$ and $2(Bu_2TeO) \cdot BuTe(O)OH$, which have been prepared by oxidation of dibutyl telluride, was converted into butyltellurium triiodide under the action of HI.[175]

$$BuTe(O)OH \xrightarrow{HI} BuTeI_3$$

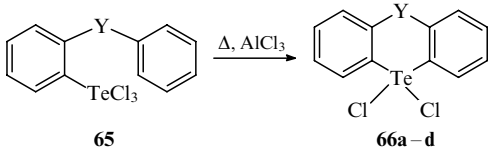
III. Reactions of σ-telluranes $RTeX_3$

The reactions of σ-telluranes $RTeX_3$ were studied primarily for organyltellurium trichlorides. Some of them proceed with retention of the coordination number of the tellurium atom. †

1. Transformations of σ-telluranes $RTeX_3$ into σ-telluranes R_2TeX_2

Transformations of σ-telluranes $RTeX_3$ into compounds R_2TeX_2 proceed with retention of the coordination number of the tellurium atom, but are accompanied by the formation of an additional C–Te bond. These reactions are of preparative importance in the synthesis of σ-telluranes $R^1R^2TeCl_2$ (for earlier data, see Refs 3, 4, 6 and 7). Since aryltellurium trichlorides exhibit electrophilic properties, they enter into reactions analogous to those of $TeCl_4$. Thus these compounds react with different heteroorganic compounds to form symmetrical and non-symmetrical organyltellurium dichlorides $R^1R^2TeCl_2$, are involved in electrophilic substitution with activated arenes to give diaryltellurium dichlorides $Ar^1Ar^2TeCl_2$, react with compounds containing the activated methylene group to form σ-telluranes ($ArTeCl_2CH_2COR$ in the case of ketones) and add to double and triple bonds yielding derivatives of the types $ArTeCl_2CH(R^1)CH(Cl)R^2$ and $ArTeCl_2C(R^1){=}C(Cl)R^2$, respectively. However, aryltellurium trichlorides are weaker electrophilic agents than $TeCl_4$, and hence, the above-mentioned reactions proceed under more drastic conditions.

Intramolecular cyclisation of aryl- and arylvinyltellurium trichlorides giving rise to different six- and five-membered tellurium-containing heterocycles is of particular interest.[176] Thus thermal or $AlCl_3$-catalysed cyclisation of aryltellurium trichlorides **65** afforded tetracoordinate tellurium derivatives, *viz*., phenoxatellurine **66a**,[56] thiophenoxatellurine **66b**,[13] phenotellurazine **66c** [20] and telluroxanthene **66d**.[26]

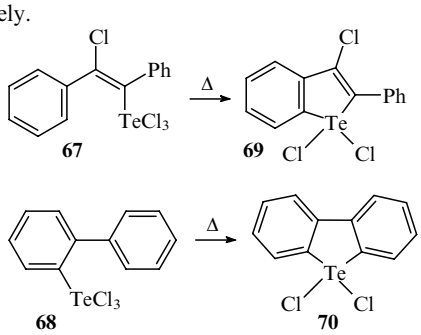


65 **66a–d**

Y = O (**a**), S (**b**), NH (**c**), CH_2 (**d**).

† Exchange reactions of anionoid substituents are considered in Section II.6.

Heating of organyltellurium trichlorides **67** and **68** at high temperature gave rise to 1,1,3-trichloro-2-phenylbenzo[*b*]tellurophene (**69**) [177] and 1,1-dichlorodibenzotellurophene (**70**),[8] respectively.



67 **69** **68** **70**

Aryltellurium trichlorides and vinyltellurium trichlorides can be converted into the corresponding dichlorides by symmetrisation. Thus heating of solutions of 2-chloro-2-phenylvinyltellurium chloride in EtOH or AcOH resulted in elimination of the $TeCl_4$ molecule.[110]

$$PhC(Cl){=}CHTeCl_3 \xrightarrow{\Delta} [PhC(Cl){=}CH]_2TeCl_2 + TeCl_4$$

Aryltellurium trichlorides do not undergo spontaneous symmetrisation. These compounds were converted into diaryltellurium dichlorides only upon boiling of their solutions in benzene in the presence of a copper powder (the yields were 60%–70%).[115]

$$4\text{-}RC_6H_4TeCl_3 + Cu \xrightarrow{PhH,\ \Delta} (4\text{-}RC_6H_4)_2TeCl_2$$

R = OMe, OEt.

Aryltellurium trichlorides were converted into diaryltellurium dichlorides also under the action of organylsilicon hydrides.[178] Aryltellurium trichlorides reacted with silicon hydrides (in a ratio of 3 : 4) with stirring at room temperature for 6–8 h to afford diaryl ditellurides. When refluxed for 6–10 h, the mixture of the reagents taken in a ratio of 1 : 2 gave rise to diaryltellurium dichlorides in 75%–95% yields.

$$ArTeCl_3 + R^1_nR^2_mSiH_{4-(n+m)} \xrightarrow{\Delta} Ar_2TeCl_2 + Te + R^1_nR^2_mSiCl_{4-(n+m)}$$

Ar = Ph, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$; R^1, R^2 = Ph, C_6H_{13}, Me;
n = 1, 2; m = 1, 2.

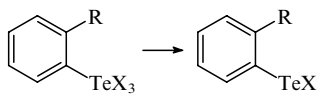
Certain reactions of σ-telluranes $RTeX_3$ are accompanied by a decrease in the coordination number of the Te atom to 2 (reduction) or 3 (hydrolysis).

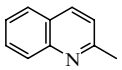
2. Reduction of aryltellurium trihalides to aryltellurenyl halides ‡

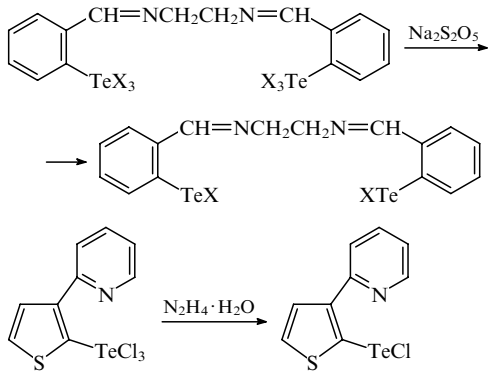
Reduction of aryltellurium trichlorides affords different products depending on the structure of the organic ligands. Aryltellurium trihalides containing coordinating substituents in the *ortho* position are reduced to aryltellurenyl halides, whereas organyltellurium trihalides in which such substituents are absent are reduced only to diorganyl ditellurides.

Aryltellurium trihalides containing CH=N,[23, 24, 120, 168] N=N,[18] NO_2,[161] CH_2NMe_2 (see Ref. 116) or $CH(Me)NMe_2$ (see Ref. 117) groups in the *ortho* position were reduced to aryltellurenyl halides. Hydrazine hydrate [23, 24, 116, 117, 120] $NaBH_4$,[18] $NaHSO_3$ (see Ref. 161) and $Na_2S_2O_5$ (see Ref. 168) were used as reducing agents.

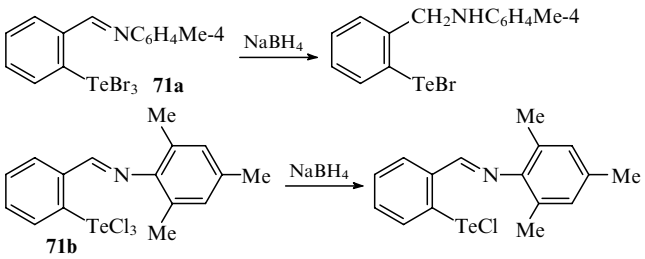
‡ Reduction of organyltellurium trihalides to ditellurides is not considered in the present review because these reactions have been surveyed in detail in a recent review.[179]



R	Reducing agent	Ref.
	$N_2H_4 \cdot H_2O$	23, 24
	$N_2H_4 \cdot H_2O$	24
N=NPh	$NaBH_4$	18
NO_2	$NaHSO_3$	161
CH_2NMe_2	$N_2H_4 \cdot H_2O$	116
$CH(Me)NMe_2$	$N_2H_4 \cdot H_2O$	117

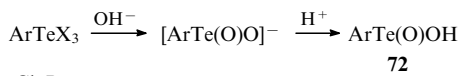


In the case of *N*-(2-tribromotelluriobenzylidene)-4-methylaniline (**71a**), both the $TeBr_3$ and azomethine groups were reduced under the action of sodium borohydride,[134] whereas the azomethine group in sterically hindered *N*-(2-trichlorotelluriobenzylidene)-2,4,6-trimethylaniline (**71b**) remained unchanged.

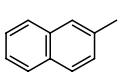


3. Hydrolysis of organyltellurium trihalides

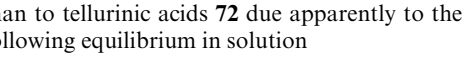
Alkaline hydrolysis of aryltellurium trihalides followed by acidification of the reaction mixture afforded aryltellurinic acids **72** in 70% – 100% yields.



X = Cl, Br.

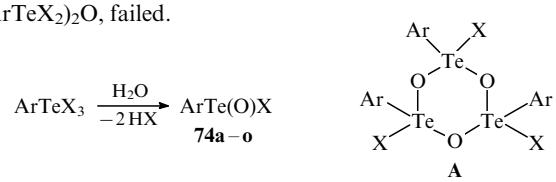
Ar	Ref.	Ar	Ref.
Ph	180	4-$BuOC_6H_4$	182
2-MeC_6H_4	113	4-$PhOC_6H_4$	180, 182
4-HOC_6H_4	46, 180	2-$HOCC_6H_4$	113
4-$EtOC_6H_4$	46, 180, 181		
4-$MeOC_6H_4$	46, 180, 182		129, 180, 182

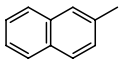
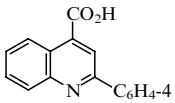
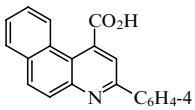
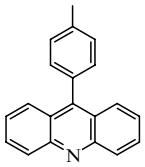
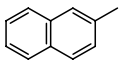
In some cases, acidification gives rise to anhydrides **73** rather than to tellurinic acids **72** due apparently to the existence of the following equilibrium in solution



Presumably, this equilibrium is shifted to the right only in a strongly acidic medium. In the presence of weak acids (for example, AcOH), the anhydrides **73** were formed as the final hydrolysis products of aryltellurium trihalides.[129, 180 – 182]

Aryltellurium trichlorides and tribromides undergo partial hydrolysis under the action of cold water to form aryltellurium oxohalides **74**.[46, 63, 180, 181, 183] Aryltellurium triiodides are inert to cold water. In most cases, hydrolysis at high temperature afforded unidentified compounds. Poor solubility of aryltellurium oxohalides in ordinary organic solvents was attributed [181] to the fact that they have a trimeric structure **A**. Attempts to isolate possible intermediate products of partial hydrolysis, *viz*., compounds $(ArTeX_2)_2O$, failed.



Compound **74**	X	R	Ref.
a	Cl	Ph	180
b	Cl	4-HOC_6H_4	46
c	Cl	4-$MeOC_6H_4$	46, 180, 183
d	Cl	4-$EtOC_6H_4$	46, 180, 181, 183
e	Cl	3,4-$(MeO)_2C_6H_3$	183
f	Cl	4-$PhOC_6H_4$	180
g	Cl		180
h	Cl		63
i	Cl		63
j	Cl		63
k	Br	Ph	180, 181
l	Br	4-$MeOC_6H_4$	180
m	Br	4-$EtOC_6H_4$	180, 181
n	Br	4-$PhOC_6H_4$	180
o	Br		180

Aryltellurium oxochlorides **74a**,**c**,**d** were also synthesised by treatment of the corresponding aryltellurium trichlorides with 2-phenyliodoniobenzoate monohydrate.[184]

Alkyltellurium oxohalides RTe(O)X (R = Me and X = Cl, Br or I; R = Et and X = I)[185] and anhydrides $[RTe(O)]_2O$ (R = C_8H_{17}, $C_{10}H_{21}$ or $C_{12}H_{25}$)[186] were prepared according to a procedure analogous to that used for the synthesis of the aryl analogues **74a** – **o**. Acidification of an aqueous solution of the salt $[Me_3Te]^+[MeTe(O)O]^-$ afforded a mixture of methyltellurinic acid and its anhydride.[187]

4. Synthesis of salts containing organyltetrahalogenotellurate anions

Reactions yielding salts containing organyltetrahalogenotellurate anions and complexation reactions are accompanied by an increase in the coordination number of the tellurium atom. The reactions of different organyltellurium trihalides with onium salts in organic solvents (MeOH or $CHCl_3$) give rise to salts containing organyltetrahalogenotellurate anions.[181, 187–192]

$$RTeX_3 + M^+Y^- \longrightarrow M^+(RTeX_3Y)^-$$

75

R	X	Y	M	Ref.
Me	I	Br	Me_3Te	187
Me	Br	Br	Me_3Te	187
Me	Br	I	Me_3Te	187
Me	Cl	Br	Et_4N	188
Ph	Cl	Cl	Et_4N	189
Ph	Cl	Cl	Ph_3PCH_2Ph	190
Ph	Cl	Cl	Ph_4P	190
Ph	Cl	Cl	Ph_4As	181, 189
Ph	Cl	Cl	Ph_3Se	189
Ph	Cl	Cl	Ph_2I	189
Ph	Cl	Cl	C_5H_5NH	181
Ph	Cl	Br	Ph_3PMe	190
Ph	Cl	Br	$Ph_3PCH_2CO_2Et$	190
Ph	Cl	Br	Ph_3Te	190
Ph	Cl	Br	cyclo-C_7H_7	190
Ph	Cl	I	Bu_4N	191
Ph	Br	Br	Me_4N	189
Ph	Br	Br	Et_4N	189
Ph	Br	Br	Ph_3PMe	190
Ph	Br	Br	Ph_4P	190
Ph	Br	Br	$Ph_3PCH_2CO_2Et$	190
Ph	Br	Br	Ph_3S	189
Ph	Br	Br	Ph_2I	189
Ph	Br	Br	cyclo-C_7H_7	190
Ph	I	I	Pr_4N	189
Ph	I	I	Me_3S	189
Ph	I	Cl	Ph_3PCH_2Ph	190
Ph	I	Br	cyclo-C_7H_7	190
4-$EtOC_6H_4$	Cl	Cl	Me_4N	189
4-$EtOC_6H_4$	Cl	Cl	C_5H_5NH	181
4-$EtOC_6H_4$	Cl	Cl	Ph_3PCH_2Ph	190
4-$EtOC_6H_4$	Cl	Cl	Ph_4P	190
4-$EtOC_6H_4$	Cl	Cl	Ph_4As	189
4-$EtOC_6H_4$	Cl	Cl	Ph_3Se	189
4-$EtOC_6H_4$	Cl	Cl	Ph_2I	189
4-$EtOC_6H_4$	Cl	Br	Ph_3P	190
4-$EtOC_6H_4$	Cl	Br	$Ph_3PCH_2CO_2Et$	190
4-$EtOC_6H_4$	Cl	Br	cyclo-C_7H_7	190
4-$EtOC_6H_4$	Br	Br	Et_4N	189
4-$EtOC_6H_4$	Br	Br	Ph_3PMe	189
4-$EtOC_6H_4$	Br	Br	$Ph_3PCH_2CO_2Et$	189
4-$EtOC_6H_4$	Br	Br	Ph_4P	189
4-$EtOC_6H_4$	Br	Br	Ph_3S	189
4-$EtOC_6H_4$	Br	Br	Ph_2I	189
4-$EtOC_6H_4$	Br	Br	cyclo-C_7H_7	190
4-$EtOC_6H_4$	Br	Cl	Ph_3PCH_2Ph	190
4-$EtOC_6H_4$	I	I	Pr_4N	189
4-$EtOC_6H_4$	I	I	Me_3S	189
4-$EtOC_6H_4$	I	Cl	Ph_3PCH_2Ph	190
4-$EtOC_6H_4$	I	Br	cyclo-C_7H_7	190
4-$PhOC_6H_4$	Cl	Cl	Et_2NH_2	192

Tropylium 4-ethoxyphenyltetrabromotellurate was prepared by the reaction of the corresponding aryltellurium trichloride with tropylium perchlorate followed by anion exchange.[190]

$$\text{cyclo-}C_7H_8 \xrightarrow{Ph_3C^+ClO_4^-} [\text{cyclo-}C_7H_7]^+ClO_4^- \xrightarrow{ArTeCl_3}$$

$$\longrightarrow [\text{cyclo-}C_7H_7]^+[ArTeCl_3(ClO_4)]^- \xrightarrow{Br^-} [\text{cyclo-}C_7H_7]^+[ArTeBr_4]^-$$

Ar = 4-$EtOC_6H_4$.

The reactions of aryltellurium trihalides with onium salts in aqueous solutions of hydrohalic acids also gave rise to salts **75** in high yields.[189, 190]

$$ArTeCl_3 + HX \longrightarrow H^+[ArTeX_4]^- \xrightarrow{M^+Y^-} \underset{\mathbf{75}}{M^+[ArTeY_4]^-}$$

Ar = Ph, 4-$EtOC_6H_4$; X = Cl, Br; M = cyclo-C_7H_7, Ph_3PMe, $Ph_3PCH_2CO_2Et$.

5. Complexation

σ-Telluranes $RTeX_3$ act as Lewis acids in complexation. In contrast to tellurium tetrahalides which typically form 2 : 1 adducts,[193] organyltellurium trihalides give rise mainly to 1 : 1 complexes.

Aryltellurium trichlorides $ArTeCl_3$ (Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$ or 4-$PhOC_6H_4$)[125–128] form 1 : 1 complexes with pyridine, picolines,[125–128] pyridine *N*-oxide and picoline *N*-oxide.[194–197] In solution in nitromethane, the complexes with pyridine and picolines act as electrolytes (1 : 1) and have, apparently, the structure $[ArTeCl_2 \cdot L]^+Cl^-$.[194] The complexes with *N*-oxides are weak electrolytes of the formula $ArTeCl_3 \cdot L$.[194]

In addition to the complexes with the above-mentioned ligands, complexes of aryltellurium trichlorides with a number of other nitrogen-, phosphorus- and oxygen-containing bases, *viz*., with trimethyl(ethyl)amine,[195–197] α-naphthylamine,[195] ethylenediamine,[195] benzimidazole,[195–197] benzothiazole,[195, 196] 2,2′-bipyridyl,[195, 197] 1,10-phenanthroline,[196, 197] triphenylphosphine,[195] triphenylphosphine oxide,[195–197] triphenylphosphine sulfide,[195] triphenylarsine oxide[195–197] and dimethyl sulfoxide,[195–197] were isolated in the individual state as 1 : 1 complexes. The composition and the enthalpy of formation of the complex of $PhTeCl_3$ with $(C_6H_{13})_2SO$ were determined by calorimetric titration.[198] Judging from the enthalpies of formation, the acceptor abilities of tetracoordinate tellurium derivatives decrease in the series $TeCl_4 > PhTeCl_3 > Ph_2TeCl_2$.[198]

It should be noted that Garad[199] assigned the 1 : 1 and 2 : 1 compositions to complexes of aryltellurium trichlorides with bidentate ligands (bipyridyl or phenanthroline) and monodentante ligands [pyridine, pyridine *N*-oxide or $(C_8H_{17})_3P=O$], respectively, contrary to the above-considered data.[194–197]

Organyltellurium trihalides exhibit acceptor properties also with respect to sulfur-containing donors. It was demonstrated[200] that organyltellurium trihalides 4-$EtOC_6H_4TeX_3$ (X = Cl, Br or I), like tellurium tetrahalides, react with tetramethylthiuram disulfide. These reactions are accompanied by extrusion of one sulfur atom to form 2 : 1 complexes of aryltellurium trihalides with tetramethylthiuram sulfide.

According to IR and ^1H NMR spectral data, the 1 : 1 complexes of $RTeCl_3$ and $RTeBr_3$ (R = Me, Et, 4-$MeOC_6H_4$ or 4-$EtOC_6H_4$) with tetramethylthiourea[130, 195, 201] have a square-pyramidal structure with the organic substituents in apical positions. Three halogen atoms and the *S*-coordinated ligand are located in the base of the pyramid.[130, 201] The reactions of phenyltellurium trihalides with thiourea in aqueous-methanolic solutions were accompanied by reduction of Te(IV) to form the complexes $PhTeX \cdot (NH_2)_2CS$.[202]

Tetramethyl-[124] and tetraethyldithiooxamides[123] belong to yet another type of sulfur-containing ligands giving the 1 : 1 complexes $ArTeX_3 \cdot C(S)(NR_2)C(S)(NR_2)$ (R = Me or Et) with aryltellurium trihalides 4-$RC_6H_4TeX_3$ (R = H, Me, MeO, EtO, PhO or PhS; X = Cl, Br or I). The long-wavelength IR spectra and Raman spectra provide evidence in favour of the octahedral

structure of the complexes containing bidentate ligands coordinated through the sulfur atoms of the thiocarbonyl groups.

Measurements of the dipole moments (in benzene) demonstrated that aryltellurium trichlorides form 1 : 1 complexes with donors of the $Ph_3P=X$ (X is a lone electron pair, O, S or Se) and $PhP(O)Me_2$ types.[203] The dipole moments are indicative of the donor-acceptor character of the bond between the components of the complexes. The coordination centres of the complexes adopt a pseudooctahedral configuration in which the donor is located in the *cis* position with respect to the lone electron pair of the tellurium atom and in the *trans* position with respect to the chlorine atom. It is noteworthy that the reactions of $4\text{-}RC_6H_4TeCl_3$ (R = H, OH or OMe) with thiosemicarbazones of benzaldehyde, acetophenone, salicylaldehyde and 2-hydroxyacetophenone afforded ionic tricoordinate Te(II) complexes $[ArTe(TSK)_2]^+Cl^-$ (TSK is the corresponding thiosemicarbazone) in which the Te atom is coordinated through the sulfur atom.[204]

In the reactions with strong Lewis acids, *e.g.*, with $SbCl_5$, organyltellurium trichlorides $RTeCl_3$ (R = Me, Et or $4\text{-}MeOC_6H_4$) act as donors to give 1 : 1 complexes.[119] Ionic structures were assigned to the complexes $[RTeCl_2]^+SbCl_6^-$ based on the facts that their IR spectra are similar to those of the ionic complexes $RSeCl_3 \cdot AlCl_3$ and have bands characteristic of the $SbCl_6^-$ ion.

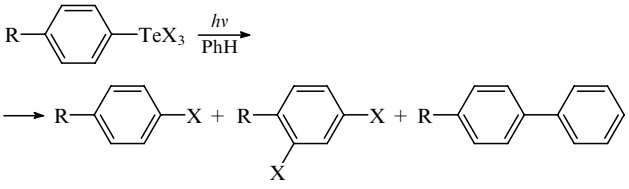
The enthalpies of formation of complexes of tetracoordinate tellurium derivatives with $AlBr_3$ (1 : 1 composition)[198] are indicative of an increase in the donating ability of the tellurium atom in the series $TeCl_4 < PhTeCl_3 < Ph_2TeCl_2$.

6. Detelluration

Elimination of tellurium (detelluration) is also characteristic of σ-telluranes $RTeX_3$. Some of these reactions are of particular preparative interest. Detelluration is performed by pyrolysis, photolysis or under the action of Raney nickel, Pd(II) salts, oxidants or some nucleophilic reagents.

Heating of 2-chloroethyl-[97] or 2-chloropropyltellurium trichlorides[96] afforded Te, HCl, saturated (isopropyl chloride) and unsaturated (vinyl chloride and allyl chloride) halogen-containing derivatives and 1,2-dichloroalkanes. Pyrolysis of 2-chlorocyclohexyltellurium trichloride gave rise to cyclohexyl chloride, hexene and benzene along with Te and HCl.[96]

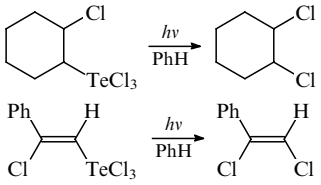
Photolysis of organyltellurium trihalides proceeds in a different way.[101,205] Irradiation of solutions of these compounds in benzene afforded organic halogen-containing derivatives, the halogen atoms occupying positions to which the tellurium-containing group was initially bound (*ipso* substitution).



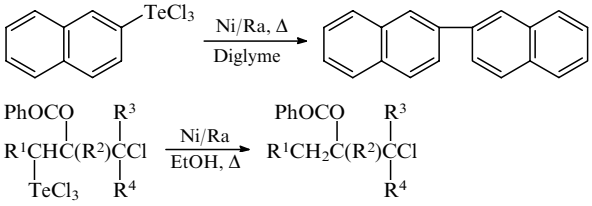
R = MeO, Me, H; X = Cl, Br, OAc.

Thus irradiation of a solution of 4-methoxyphenyltellurium trichloride in C_6H_6 using a high-pressure mercury lamp at 20–30 °C for 1 h afforded 4-chloroanisole in 70% yield and 2,4-dichloroanisole as a by-product (20%). Photolysis of 4-methoxyphenyltellurium tribromide gave rise to 4-bromoanisole in 30% yield. Irradiation of a solution of 4-methoxyphenyltellurium triacetate [prepared *in situ* from Ph_2Te_2 and $Pb(OAc)_4$ in AcOH] afforded 4-acetoxyanisole in 14% yield. In some cases, coupling products of organic radicals of σ-telluranes with benzene were also obtained in trace amounts.[101,205] The yields of aryl halides decrease as the donor properties of substituents in the aryl groups of σ-telluranes decrease.

The reactions of cycloalkyl- and vinyltellurium trichlorides proceed analogously.[101,205] In the latter case, the reaction proceeds with retention of the geometric configuration of the initial alkene.



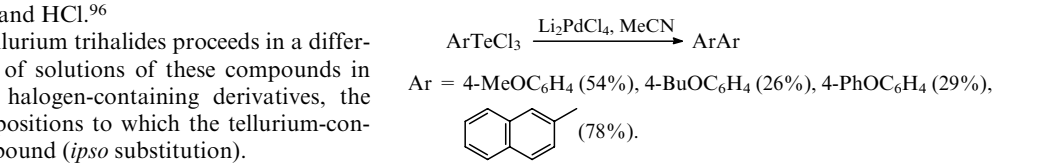
Aryltellurium trichlorides undergo detelluration upon heating with Raney nickel (Ni/Ra) in diglyme to form biaryls.[71] Apparently, this reaction proceeds through initial reduction of tellurium trichlorides to form ditellurides followed by elimination of tellurium.[107] Detelluration of (β-acyloxy-γ-chloroalkyl)tellurium trichlorides of the type **39** under the action of Raney nickel gave rise to chlorohydrin esters in 26% – 78% yields.[107]



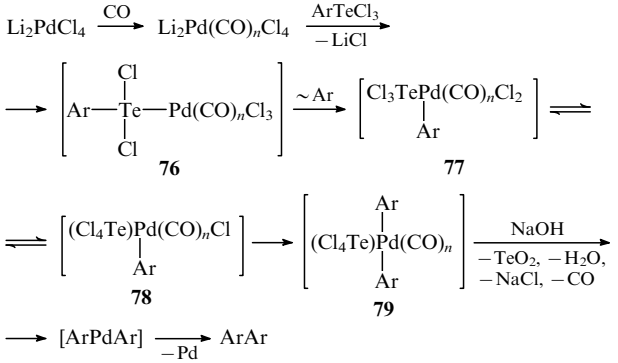
39

R^1	R^2	R^3	R^4
H	H	H	H
Me	H	H	H
H	Me	H	H
H	H	Me	H
H	H	Me	Me

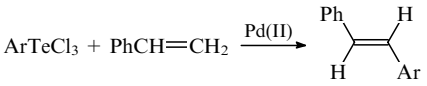
Biaryls were also formed upon treatment of aryltellurium trichlorides with $PdCl_2$ and NaOAc in AcOH[49] or with Li_2PdCl_4 in MeCN.[206] The latter reagent is more efficient than the former. The formation of biaryls is favoured by the presence of donor substituents in the aryl groups.



The reactions performed under a CO atmosphere afforded biaryls in approximately the same yields, but the reaction rates were substantially higher.[206] However, good yields of biaryls were achieved only after treatment of the reaction mixture with a solution of NaOH. In the latter case, carboxylic acids were obtained as by-products. The reactions were accelerated due to the formation of active intermediates **76**–**79** containing Pd–CO bonds.[206]

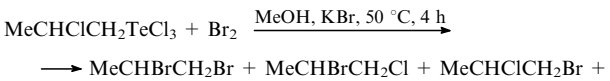


Treatment of a mixture of aryltellurium trichlorides, $PdCl_2$ and NaOAc in AcOH with a tenfold excess of styrene afforded *trans*-stilbenes in rather low yields (7%–38%) along with trace amounts of biaryls.[49] It should be noted that the yields of stilbenes in the reactions with aryltellurium trichlorides are lower than those obtained in the reactions with diaryltellurium dichlorides containing the same substituents.

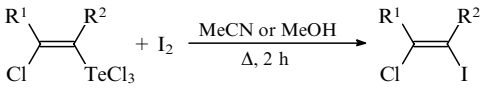


Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$.

Detelluration of different types of organyltellurium trihalides proceeds also under the action of halogens giving rise to the corresponding organyl halides (halodetelluration).[96, 111, 207] Apparently, halodetelluration was observed for the first time in the treatment of 2-chloropropyltellurium trichloride with bromine.[96]



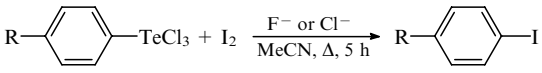
Iododetelluration of (*Z*)-2-chlorovinyltellurium trichlorides proceeded with retention of the configuration of the initial alkenes giving rise to (*Z*)-chloroiodoalkenes in 40%–94% yields.[111]



R^1 = Ph, R^2 = H, Me, Et, Ph; R^1 = CH_2OH, R^2 = H.

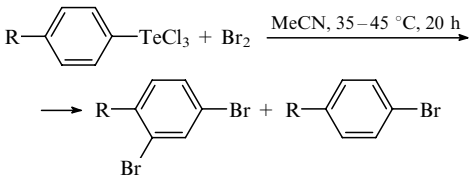
Bromodetelluration occurs only upon treatment of vinyltellurium trichlorides with *N*-bromosuccinimide in the presence of $AlCl_3$.[111]

Iododetelluration of aryltellurium trichlorides containing donor substituents under the action of iodine proceeded efficiently only in the presence of potassium fluoride, cesium fluoride, ammonium fluoride, mercury(II) chloride or $SbCl_5$ to form aryl iodides in yields higher than 80%.[207] However, the reactions of phenyl- and 4-bromophenyltellurium trichlorides with iodine under identical conditions gave rise to aryl iodides in very low yields. This fact is indicative of the electrophilic character of the reaction.[207] Apparently, the catalytic action of fluoride ions is associated with the formation of the intermediates $[ArTeCl_3F_2]^-$ due to which the electron density at the tellurium atom and at the C–Te bond increases, which favours the electrophilic attack of the halogen. The function of metal chlorides is to activate iodine by complexation or *in situ* formation of more reactive iodine monochloride.[207]



R = Me, OMe.

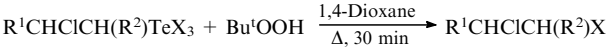
Bromodetelluration of aryltellurium trichlorides with bromine in MeCN, 1,4-dioxane or CCl_4 gave rise to 2,4-dibromoarenes in rather high yields, while 4-bromoarenes were obtained in trace amounts.[207] The selective formation of dibromides was attributed to bromination of the initial 4-bromoarenes catalysed by organic derivatives of tellurium(IV).[207]



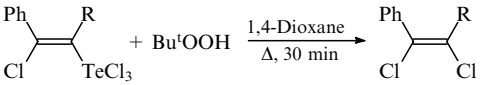
R = H, Me, OMe.

Chlorodetelluration of aryltellurium trichlorides under the action of different chlorinating agents (Cl_2, $SbCl_5$ or Bu^tOCl) proceeded with very low yields even in the case of highly reactive 4-methoxyphenyltellurium trichloride.[207] Cyanodetelluration of 4-methoxyphenyltellurium trichloride with CuCN in DMF also occurred in very low yield (5%).[207]

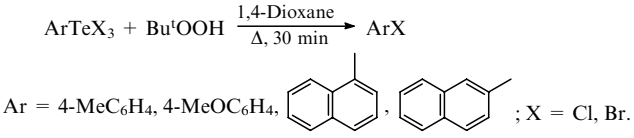
Halodetelluration of organyltellurium trichlorides proceeded rather readily under the action of *tert*-butyl hydroperoxide.[101, 208] Different types of organyltellurium trihalides, *viz*., with 2-chloroalkyl-, 2-chlorocyclohexyl-, alkenyl- and aryltellurium trihalides, enter into this reaction. In most of reactions with alkenyl derivatives, the initial configuration is retained.[101] The yields of alkenyl halides are lower than those of alkyl and aryl halides. It was thus assumed [101] that the reactivities of organyltellurium trihalides in oxidative detelluration change in the order: alkyl > aryl > alkenyl.



R^1 = C_8H_{17}, $PhCH_2$; R^2 = H; R^1–R^2 = $(CH_2)_4$; X = Cl, I.

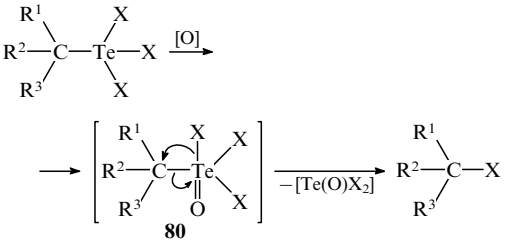


R = H, Ph.



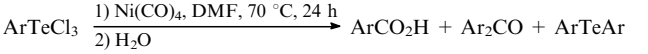
Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$, , ; X = Cl, Br.

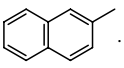
The possible reaction mechanism involving the formation of unstable organic derivatives of tellurium(VI) **80** is shown in the scheme.[101]



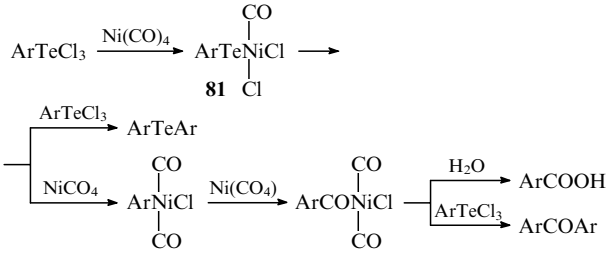
80

The reactions of aryltellurium trichlorides with $Ni(CO)_4$ in DMF resulted in detelluration. Subsequent treatment of the reaction mixtures with water afforded carboxylic acids in 35%–51% yields.[209] Symmetrical ketones and diaryl tellurides were obtained as by-products (sometimes in yields of up to 15%). The reaction of 4-methoxyphenyltellurium trichloride with $Fe_2(CO)_9$ yielded bis(4-methoxyphenyl) telluride as the only product.[209]

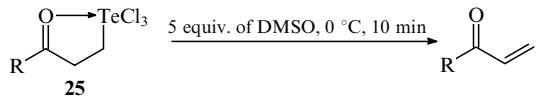


Ar = 4-$MeOC_6H_4$, .

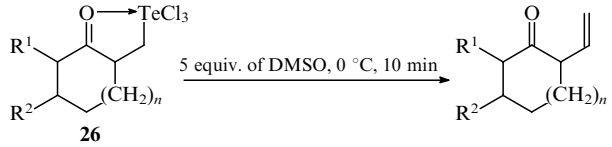
It is believed [209] that carbonylation of aryltellurium trichlorides proceeded according to a scheme involving intermediate aryltelluriocarbonylnickel dichloride **81**.



In some cases, the direction of detelluration of organyltellurium trichlorides under the action of nucleophiles is governed by the presence of intramolecular O → $TeCl_3$ coordinate bonds. Thus detelluration of β-trichlorotellurio ketones **25** and **26** proceeded smoothly under the action of basic agents, such as DMSO or amines.[85]

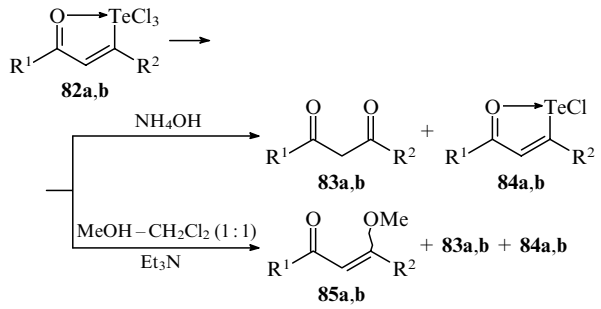


R = Bu^t, , Ph.



$R^1 = R^2 = H$, $n = 2, 5$; $R^1 - R^2 = (CH=CH)_2$, $n = 1$.

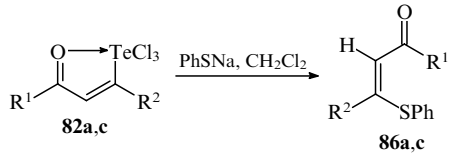
In the reactions with NH_4OH, σ-telluranes **82a**,**b** containing intramolecular O → Te coordinate bonds underwent detelluration with elimination of metallic tellurium to form a mixture of ketones **83a**,**b** (the yields were 56% – 63%) and tellurenyl halides **84a**,**b** (the yields were 13% – 36%).[169]



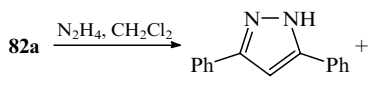
$R^1 = R^2 =$ Ph (**a**); $R^1 =$ Ph, $R^2 =$ Me (**b**).

The reactions of the organyltellurium trichlorides **82a**,**b** with Et_3N in a 1 : 1 CH_2Cl_2 – MeOH mixture afforded enol methyl ethers **85a**,**b** (a mixture of stereoisomers, the yields were 56% – 80%). The ketones **83a**,**b** and the tellurenyl halides **84a**,**b** (in trace amounts) were isolated as by-products.[169]

Detelluration of the ketones **82** proceeded under the action of other nucleophiles as well. Thus the reactions of the compounds **82a**,**c** with sodium benzenethiolate afforded exclusively *Z*-isomers of vinyl ketones **86a**,**c** in 74% – 82% yields, whereas the reaction of the ketone **82a** with hydrazine gave rise to 3,5-diphenylpyrazole and the tellurenyl halide **84a** in 44% and 22% yields, respectively.[169]



$R^1 = R^2 =$ Ph (**a**); $R^1 = 3\text{-}FC_6H_4$, $R^2 =$ Ph (**c**).



IV. Structures of σ-telluranes $RTeX_3$ in the crystalline state and in solution. Electronic effects of TeX_3 groups

1. Crystal structures of σ-telluranes $RTeX_3$

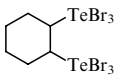
According to the polarity rule[210] extended to σ-telluranes,[211, 212] the axial positions in trigonal bipyramids in molecules of these compounds should be occupied by the most electronegative substituents. However, the real structures of a large number of σ-telluranes $RTeX_3$, being determined by the nature of both the electronegative substituents at the tellurium atom and the organic ligands, rarely correspond to trigonal bipyramids predicted theoretically. Three major groups of σ-telluranes $RTeX_3$, which differ in the degree of association in the crystalline state and in the coordinate bonding to the tellurium atom, can be distinguished. Organyltellurium trihalides $RTeHal_3$ whose organic ligands do not contain substituents capable of forming intramolecular coordinate bonds with tellurium atoms belong to the first group. The second group consists of organyltellurium trihalides containing a intramolecular O(N) → Te coordinate bond. The third group comprises σ-telluranes $RTeX_3$ containing bidentate (primarily, dithiocarbamate) ligands.

The data on the bond lengths, bond angles and types of associates in organyltellurium trihalides $RTeX_3$ whose organic ligands do not contain substituents capable of forming intramolecular coordinate bonds with tellurium atoms are given in Table 1.

Taking into account secondary interactions, the tellurium trihalides listed in Table 1 contain a pentacoordinate tellurium atom. The major structural unit in these compounds ($CTeX_4$) is characterised by a square-pyramidal configuration of the bonds about the tellurium atom, the organic radical being located in the apical position. The tellurium atom lies virtually in the base of the square pyramid formed by four halogen atoms (the deviation from the plane is insignificant). Two halogen atoms form shorter (terminal) bonds, whereas the two remaining halogen atoms are involved in longer (bridging) bonds through which the tellurium atoms are linked in polymeric or dimeric structures. The dimers are linked to each other through weak secondary bonds, which are substantially longer than the $Te-X_{bridge}$ bonds. σ-Telluranes containing two $TeHal_3$ groups bound to one carbon atom [for example, methylenebis(tellurium trichloride)[217]] or to the vicinal carbon atoms [for example, 1,2-bis(tribromotellurio)cyclohexane[219]] have monomeric structures. The bonds about each tellurium atom in these compounds adopt the square-pyramidal configuration, except that both bridging Te – X bonds are intramolecular.

2-Biphenylyltellurium trihalides containing the bulky 2-biphenylyl radical also have monomeric structures with a trigonal-bipyramidal arrangement of the ligands about the tellurium atom.[126, 132, 220] The axial positions are occupied by the halogen atoms. The angle between the axial bonds in 2-biphenylyltellurium tribromide is 178.5°. The corresponding angles in the α and β modifications of the triiodide are 176.5° and 176.0°, respectively. The axial Te – X bonds are substantially longer than the equatorial bonds in accordance with the polarity rule.[210] Short intramolecular Te···C contacts are observed in 2-biphenylyltellurium trihalides [2.945 Å in the tribromide and 3.32 and 3.18 Å in the α and β modifications of the triiodide, respectively; the sum of the van der Waals radii of the tellurium and carbon atoms is 3.90 Å (see Ref. 221)]. Due to these contacts, 2-biphenylyltellurium trihalides are readily converted into 5,5-dihalogenodibenzotellurophenes upon heating.[8] Two modifications of 2-biphenylyltellurium triiodide are structurally similar and differ only in intermolecular contacts involving the heavy atoms. In the β modification, the I···I contacts (3.337 Å) occur along with the secondary Te···I contacts,[220] whereas two I···I contacts (3.239 and 3.772 Å) are observed in the α modification.[132] The difference in the character of these intermolecular interactions is reflected in the colour of the compounds, *viz.*, the crystals of the α and β

Table 1. Average bond lengths (Å) and bond angles (deg) in σ-telluranes $RTeX_3$.

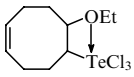
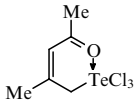
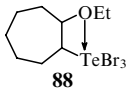
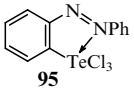
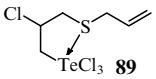
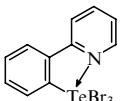
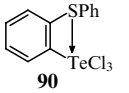
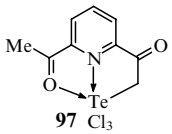
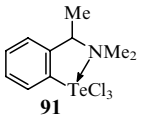
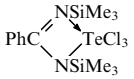
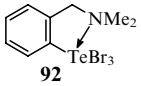
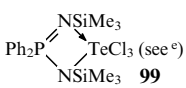
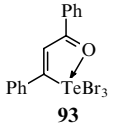
Compound	Bond length				Bond angle		Type of the associate	Ref.
	$Te-X_{term}$	$Te-X_{bridge}$	$Te\cdots X$	$Te-C$	$C-Te-X_{term}$	$C-Te-X_{bridge}$		
$C_2F_5TeF_3$	1.872	2.913	–	2.20	88.8	77.6	polymer	138
$ClCH_2CH_2TeCl_3$	2.386	2.717	–	2.164	92.7	82.5	"	98
$PhTeCl_3$ (see [a])	2.377	2.755	–	2.122	91.68	85.46	"	213, 214
4-$EtOC_6H_4TeCl_3$	2.396	2.749	–	2.12	91.0	88.2	"	121
4-$PhOC_6H_4TeCl_3$	2.374	2.768	3.702	2.111	91.3	87.2	dimer	216
$CH_2(TeCl_3)_2$	2.351	2.760	–	2.120	90.8	75.6	monomer	217
$PhTeBr_3$	2.526	2.829	–	2.140	92.2	85.4	polymer	218
4-$EtOC_6H_4TeBr_3$	2.531	2.932	4.143	2.10	93.6	88.4	dimer	121
2-$PhC_6H_4TeBr_3$	2.490,[b] 2.661[c]	–	3.713	2.136	–	–	monomer	126
	2.541	2.88	–	2.224	92.4	83.2	"	219
4-$MeOC_6H_4TeI_3$	2.788	3.153	3.827	2.15	94.6	89.7	dimer	121
2-$PhC_6H_4TeI_3$-α	2.769,[b] 2.966[c]	–	see [d]	2.15	–	–	monomer	132
2-$PhC_6H_4TeI_3$-β	2.748,[b] 2.928[c]	–	see [e]	2.153	–	–	"	220

[a] Phenyltellurium trihalide $PhTeCl_{1.7}Br_{1.3}$ prepared by the reaction of equimolar amounts of $TeCl_4$ and Ph_2BBr also has a polymeric structure;[215] [b] the $Te-X_{eq}$ bond length; [c] the average $Te-X_{ax}$ bond length; [d] the lengths of the I···I secondary bonds are 3.239 and 3.772 Å; [e] the lengths of the Te···I and I···I secondary bond are 3.703 and 3.337 Å, respectively.

modifications of 2-biphenylyltellurium triiodide are black and red, respectively.

The degree of association and, what is more important, the molecular geometry of organyltellurium trihalides are changed substantially if the molecules contain substituents with donor atoms (oxygen, nitrogen or sulfur) capable of being involved in intramolecular coordination with the tellurium atom. The results of X-ray diffraction studies of these compounds are given in Table 2.

Table 2. Average bond lengths (Å) and bond angles (deg) in σ-telluranes $RTeX_3$ containing intramolecular coordinate bonds.

Compound	Bond length			Bond angle		Ref.	Compound	Bond length			Bond angle		Ref.
	C–Te	Te–X	Y···Te[a]	CTeX	XTeX			C–Te	Te–X	Y···Te[a]	CTeX	XTeX	
 **87**	2.172	2.505, 2.481, 2.355	2.419	93.7	176.2	105	 **94**	2.135	2.516, 2.486, 2.364	2.438	92.4	172.8	224
 **88**	2.29	2.665, 2.653, 2.502	2.49	95.1	172.9	222	 **95**	2.114	2.491, 2.483, 2.406	2.417	92.9	171.7	57
 **89**	2.139	2.555, 2.453, 2.424	2.763	87.9	168.9	106	 **96**	2.110	2.673, 2.658, 2.589	2.244	92.5	172.4	24
 **90**	2.108	2.324, 2.477, 2.497	2.972	90.02	174.9	223	 **97**	2.129	2.500, 2.491, 2.438	2.402,[b] 2.878[c]	88.4	171.3	83
 **91**	2.078	2.538, 2.465, 2.447	2.406	92.6	175.4	117	 **98**	2.096, 2.192[d]	2.489, 2.479, 2.434	–	–	172.1	32
 **92**	2.12	2.758, 2.633, 2.632	2.42	92.4	178.7	116	 **99**	2.056, 2.185[d]	2.550, 2.496, 2.488	–	–	177.1	225
 **93**	2.175	2.661, 2.659, 2.513	2.362	95.0	–	169							

[a] Y = O, S or N; [b] the N → Te coordinate bond length; [c] the O → Te coordinate bond length; [d] the N–Te bond lengths are given; [e] in the complex with CH_2Cl_2.

8-Ethoxycyclooct-4-enyltellurium trichloride (**87**), like other organyltellurium trichlorides, adopts a square-pyramidal configuration. The carbon atom occupies the vertex of the pyramid. The base of the pyramid is formed by three chlorine atoms (the Cl—Te bond lengths have standard values; 2.335–2.505 Å) and the oxygen atom (in other σ-telluranes $RTeCl_3$, four chlorine atoms lie in the base of the pyramid, two of these atoms being bridging). The Te···O distance (2.419 Å) is substantially smaller than the sum of the van der Waals radii of the tellurium and oxygen atoms (3.60 Å). In the crystals, there are also very weak secondary Te···Cl bonds (3.558 Å) through which the molecules are linked in dimers. Apparently, 2-ethoxycycloheptyltellurium tribromide (**88**),[222] 2-chloro-3-(allylthio)propyltellurium trichloride (**89**)[106] and 2-(phenylthio)phenyltellurium trichloride (**90**)[223] have analogous structures.

In organyltellurium trihalides **91**–**96**, the bonds at the tellurium atoms adopt an octahedral configuration. Two halogen atoms are located in the apical positions. The equatorial positions are occupied by the third halogen atom, the bidentate organic ligand and the lone electron pair of the tellurium atom. Some compounds of this type have monomeric structures. In crystals of other compounds, the molecules are linked in dimers through intermolecular Te···X bonds. However, the lengths of these bonds (3.498 Å in the trichloride **91** and 3.596–3.896 Å in the tribromides **92**, **93** and **96**) are substantially larger than the lengths of the bridging Te—X bonds (see Table 1) and are close to the sums of the van der Waals radii of the corresponding elements. The N → TeX_3 coordinate bond lengths are in the range of 2.24–2.42 Å. The hybridisation state of the nitrogen atom affects only slightly the coordinate bond lengths.

The organic ligand in (6-acetyl-2-pyridyl)carbonylmethyltellurium trichloride (**97**) is polydentate, which results in a new structural type.[83] The coordination polyhedron about the tellurium atom can be described as a distorted pentagonal bipyramid with two axial Te—Cl bonds (2.492 and 2.500 Å). The equatorial positions are occupied by the Cl atom (Te—Cl_{eq} is 2.431 Å), three atoms of the tridentate organic radical, *viz*., the carbon (Te—C is 2.129 Å), nitrogen (Te···N is 2.402 Å) and oxygen atoms (Te···O is 2.878 Å), and the lone electron pair of the tellurium atom. The two last-mentioned bond lengths, though larger than the sums of the covalent radii of the corresponding elements (the sum of the Te and N radii is 2.07 Å and the sum of the Te and O radii is 2.03 Å), are substantially smaller than the sums of the van der Walls radii of these elements (the sum of the Te and N 3.70 Å and the sum of the Te and O radii is 3.60 Å[221]). The presence of the Te → N and Te → O coordinate bonds was also confirmed by IR spectroscopy.

Selected data for organyltellurium trichlorides containing N → $TeCl_3$ bonds (compounds **98** and **99**) are also given in Table 2. The N → Te bond lengths in these compounds have close values (the differences are only 0.1–0.12 Å). The four-membered PN_2Te ring in the compound **99** is virtually planar. The nitrogen atoms deviate from the plane of the ring by ~ 0.05 Å.[225]

σ-Telluranes containing *N*,*N*-diorganyldithiocarbamate ligands (**100a**–**g**) have analogous structures. Selected structural data for these compounds are listed in Table 3.

Compounds **100a**–**g** have pentagonal-bipyramidal structures. The equatorial positions of the bipyramid are occupied by five sulfur atoms (compounds **100a**,**b**) or four sulfur atoms and one halogen atom (compounds **100c**–**g**). In the tris(dithiocarbamate) derivative **100a**, the axial positions are occupied by the organic group and the sulfur atom of a dithiocarbamate ligand.[226,227] In the bis(dithiocarbamato)(dithiophosphate) derivative **100b**, the position of the second axial ligand is occupied by a sulfur atom of the $S_2P(OEt)_2$ group.[148] In the other compounds, the lone electron pair of the tellurium atom[148] or an atom of the adjacent molecule[149–151] serves as the second axial ligand. The compounds **100a**,**b**,**d** exist as monomers, whereas molecules **100c**,**e**–**g**[149–151] are linked as dimers through weak intermolecular Te···S or Te···Hal bonds.

The reason for the presence of secondary bonds of different nature in the compounds **100c**,**g** containing virtually identical substituents at the tellurium atom (one bromine atom in the compound **100c** or bromine and iodine atoms in a ratio of 41 : 59 in the compound **100g**) remains unclear. Thus the coordination polyhedron about the tellurium atom in the compound **100c** is completed by the weakly π-coordinated dithiocarbamate ligand of the adjacent molecule,[150] whereas the coordination polyhedron in the compound **100g** is completed by the bromine (iodine) atom.[151]

The structure of (4-methoxyphenyl)tellurium [(dimethyloxy)-thiophosphorylthio)] dibromide, (4-$MeOC_6H_4$)Te[$S_2P(OMe)_2$].Br_2, differs from that of bis-(and tris)(dithiocarbamate) derivatives **100a**–**g** due to the presence of one bidentate ligand in the former compound. The molecule of this compound has a distorted square-pyramidal structure with the bromine atoms (Te—Br bond lengths are 2.616 and 2.677 Å) in *cis* positions relative to each other.[153] The sulfur atoms of the thiophosphorylthio ligand (the Te—S bond lengths are 2.632 and 2.728 Å) lie in the base of the pyramid. The aryl group (the Te—Br bond length is 2.127 Å) occupies the apical position. In the crystal, weak secondary Te···Br bonds (3.810 Å) are also present.

The structures of σ-telluranes $RTeX_3$ were also studied by NQR[228] and Mössbauer spectroscopy.[146,229–232] The isomer chemical shifts for aryltellurium trichlorides, tribromides and triiodides in the region of 0.9–1.0 mm s^{-1} are substantially larger than those for the corresponding diaryltellurium dihalides and are

Table 3. Average bond lengths (Å) and bond angles (deg) in σ-telluranes containing *N*,*N*-diorganyldithiocarbamate ligands $R^1Te(S_2CNR^2)_2X$ (**100a**–**g**).

Compound **100**	R^1	R^2	X [a]	Bond length				Bond angle C—Te—X	Ref.
				Te—C	Te—S	Te—X	secondary bonds		
a	Ph	Et	S_2CNEt_2	2.124	2.606–2.816;[b] 3.228	—	—	144.6	226, 227
b	Ph	Et	$S_2P(OEt)_2$	2.14	2.674–2.700[c]	2.708, 3.436	—	148.0	148
c	4-$MeOC_6H_4$	Me	Br [d]	2.145	2.623–2.717[c]	2.890	3.751(Te···C)	107.20	150
d	Me	Et	I	2.115	2.618–2.723[c]	3.117	—	—	148
e	Ph	Et	I	2.153	2.625–2.716[c]	3.126[e]	3.823, 3.598 (Te···S)	166.1, 154.8	149
f	4-$MeOC_6H_4$	Et	I	2.211	2.626–2.733[c]	3.169	3.569 (Te···I)	176.7	151
g	4-$MeOC_6H_4$	Et	$I_{0.59}Br_{0.41}$ (see [f])	2.151	2.624–2.728[c]	3.164,[g] 2.904[h]	3.558 (Te···I), 3.476 (Te···Br)	174.9, 176.3	151

[a] X is the ligand occupying the second axial position; [b] the range of the five Te—S bonds in the equatorial plane is given; [c] the range of the four Te—S bonds in the equatorial plane is given; [d] solvated with 0.5 equiv. of CH_2Cl_2; [e] the average Te—I bond length for two crystallographically independent molecules is given; [f] the compound was prepared by the reaction of bis(*N*,*N*-diethyldithiocarbamato)(iodo)(4-methoxyphenyl)tellurium(IV) with bromine; [g] the Te—I bond length; [h] the Te—Br bond length.

similar to those for tellurium tetrahalides.[229] The quadrupole splitting (5.9 – 9.3 mm s^{-1}) decreases in the order: chlorides > bromides > iodides.

2. Structures of organyltellurium trihalides in solutions. ^{125}Te NMR spectra and dipole moments

The conductivities of solutions of organyltellurium trichlorides $RTeCl_3$ in MeCN, $PhNO_2$ and Me_2CO [73, 74, 194, 233] indicate that these compounds do not dissociate into ions. However, organyltellurium tribromides and triiodides in these solvents dissociate into ions ($RTeX_2^+$ and X^-),[73,74] although Chen and George [234] stated that $MeTeBr_3$ in nitrobenzene is not an electrolyte. On the contrary, aryltellurium trihalides containing amino(dimethylamino) groups in the aryl fragments are 1 : 1 electrolytes in the above-mentioned solvents regardless of the nature of the halogen atom.[61, 62] Apparently, this is due to the higher polarity of the Te – Hal bonds in the latter compounds owing to the presence of strong electron-donor groups.

The results of cryoscopic studies of organyltellurium trihalides agree on the whole with the data on conductivity. In solutions, aryltellurium trichlorides [except for amino(dimethylamino) derivatives] exist as monomers and tend to form weak associates as the concentration is increased,[74, 194, 233] whereas aryltellurium tribromides and triiodides partially dissociate.[61, 62, 73, 74] In the case of methyltellurium trihalides, the monomer – dimer equilibrium exists in benzene,[118, 234] the degree of association of methyltellurium tribromide being higher than that of the corresponding trichloride.

The above-considered data agree with the results of spectral studies of organyltellurium trihalides. The ^{125}Te NMR spectral data for σ-telluranes $RTeX_3$ are given in Table 4.

The chemical shifts of alkyltellurium and aryltellurium trihalides are in the ranges of 647 – 1204 and 892 – 1234 ppm, respectively. In the spectra of organyltellurium trichlorides with ligands containing carbonyl groups, the ^{125}Te resonance is substantially shifted downfield (1372 – 1632 ppm) compared to the spectra of alkyltellurium trichlorides. The highest deshielding of the ^{125}Te nuclei is observed in β-aroylvinyltellurium trichlorides whose chemical shifts are in the range of 2047 – 2104 ppm. The shielding of the ^{125}Te nuclei in PhTe increases on going from phenyltellurium trichloride to phenyltellurium triiodide. It should be noted that the chemical shifts of organyltellurium trihalides depend substantially on the nature of the solvent. Thus the chemical shifts for $PhTeCl_3$ and $PhTeBr_3$ increase by 312 and 301 ppm, respectively, on going from the PhH – PhMe system to the 2 : 1 CH_2Cl_2 – DMSO system. Apparently, this is associated with the above-mentioned effect of the solvent on the degree of aggregation of organyltellurium trihalides in solution.

The dipole moments of aryltellurium trihalides are given in Table 5. The dipole moments of aryltellurium tribromides are smaller that those of the corresponding trichlorides regardless of the substituents in the benzene ring,[211] which is indicative of a weaker electron-withdrawing effect of the $TeBr_3$ group compared to that of the $TeCl_3$ group.

Table 4. Chemical shifts in the ^{125}Te NMR spectra of σ-telluranes $RTeX_3$.

R	X	Solvent	δ [a] /ppm	Ref.	R	X	Solvent	δ [a] /ppm	Ref.
Me	Cl	PhH – PhMe	758	35	Ph	Br	CH_2Cl_2 – DMSO (2 : 1)	1193	236
Me	Br	PhH – PhMe	647	35	Ph	I	CH_2Cl_2 – DMSO (2 : 1)	1101	236
Cl_3TeCH_2	Cl	DMSO	1198	235 [b]	4-BrC_6H_4	Cl	CH_2Cl_2 – DMSO (2 : 1)	1208	236
Et	Cl	PhH – PhMe	900	35	4-ClC_6H_4	Cl	CH_2Cl_2 – DMSO (2 : 1)	1208	236
Et	Br	PhH – PhMe	849	35	4-MeC_6H_4	Cl	CH_2Cl_2 – DMSO (2 : 1)	1234	236
Pr	Cl	PhH – PhMe	920	35	4-$PhOC_6H_4$	Cl	CH_2Cl_2 – DMSO (2 : 1)	1226	236
Pr	Br	PhH – PhMe	1204	35	4-$MeOC_6H_4$	Cl	DMSO	1246	236
$MeCOCH_2$	Cl	$CHCl_3$	1372	79	4-$MeOC_6H_4$	Br	CH_2Cl_2 – DMSO (2 : 1)	1204	236
MeCOCHMe	Cl	$CHCl_3$	1483	79	4-$MeOC_6H_4$	I	CH_2Cl_2 – DMSO (2 : 1)	1078	236
MeCOCHEt	Cl	$CHCl_3$	1488	79	PhCOCH = CMe	Cl	CD_2Cl_2	2053 [e]	237
$MeCOCMe_2$	Cl	$CHCl_3$	1632	79	PhCOCH = CMe	Br	CD_2Cl_2	2074 [e]	237
$EtCOCH_2$	Cl	$CHCl_3$	1374	79	PhCOCH = CPh	Cl	CD_2Cl_2	2047 [e]	237
EtCOCHMe	Cl	$CHCl_3$	1485	79	4-MeC_6H_4COCH = CPh	Br	CD_2Cl_2	2086 [b]	237
EtCOCHEt	Cl	$CHCl_3$	1488	79	1-$C_{10}H_7$COCH = CPh	Cl	CD_2Cl_2	2053 [e]	237
$EtCOCMe_2$	Cl	$CHCl_3$	1621	79	1-$C_{10}H_7$COCH = CPh	Br	CD_2Cl_2	2104 [e]	237
$PrCOCH_2$	Cl	$CHCl_3$	1376	79	2-PhN = NC_6H_4	Cl	$CDCl_3$	1278	146
PrCOCHMe	Cl	$CHCl_3$	1484	79	Ph	S_2CNEt_2	THF	1455	148
PrCOCHEt	Cl	$CHCl_3$	1490	79	Ph	S_2CNEt_2	CH_2Cl_2	1472	148
$PrCOCMe_2$	Cl	$CHCl_3$	1625	79	Me	S_2CNEt_2	CH_2Cl_2	1673	148
Pr^iCOCH_2	Cl	$CHCl_3$	1373	79	2-PhN = NC_6H_4	S_2CNMe_2	$CDCl_3$	1225	146
$Pr^iCOCHMe$	Cl	$CHCl_3$	1482	79	2-PhN = NC_6H_4	$S_2CN(CH_2Ph)_2$	$CDCl_3$	1240	146
Bu^iCOCH_2	Cl	$CHCl_3$	1373	79	Ph	$(S_2CNEt_2)_2Cl$	THF	1622	148
$Bu^iCOCHMe$	Cl	$CHCl_3$	1489	79	Ph	$(S_2CNEt_2)_2Cl$	THF [c]	1660	148
Bu^tCOCH_2	Cl	$CHCl_3$	1364	79	Me	$(S_2CNEt_2)_2I$	CH_2Cl_2	1892	148
$Bu^tCOCHMe$	Cl	$CHCl_3$	1487	79	Ph	$(S_2CNEt_2)Cl_2$	THF [d, f]	1098	148
Ph	Cl	PhH – PhMe	917	35	Ph	$(S_2CNEt_2)_2Y$	CH_2Cl_2	1563	148
Ph	Cl	THF [c]	532	148	Ph	$(S_2CNEt_2)_2Y$	CH_2Cl_2 (see [d])	1612	148
Ph	Cl	DMF [d]	524	148	Me	$(S_2CNEt_2)_2Y$	CH_2Cl_2 (see [f])	1768	148
Ph	Cl	DMSO	503	148	Me	$(S_2CNEt_2)_2Y$	CH_2Cl_2 (see [c, f])	1796	148
Ph	Cl	CH_2Cl_2 – DMSO (2 : 1)	1229	236	Ph	$(S_2CNEt_2)_2Z$	CH_2Cl_2 (see [f])	1510	148
Ph	Br	PhH – PhMe	892	35	Me	$(S_2CNEt_2)_2Z$	CH_2Cl_2 (see [f])	1722	148

Note: Y = $S_2P(OEt)_2$; Z = S_2COEt; [a] the chemical shifts are given relative to Me_2Te; [b] for $(Cl_3TeCH_2CO)_2O$, $\delta_{^{125}Te}$ = 864 ppm;[235] [c] at −80 °C; [d] at −40 °C; [e] Ph_2Te was used as the standard ($\delta_{Me_2Te} = \delta_{Ph_2Te} + 688$); [f] the spectrum of a solution prepared by mixing of the corresponding substrates.

Table 5. Dipole moments of aryltellurium trihalides $RC_6H_4TeX_3$ (dioxane, 25 °C).[211]

R	X	μ_{exp}	μ_{calc}	R	X	μ_{exp}	μ_{calc}
H	Cl	3.66 [a]	–	4-MeO	Br	3.88	3.79
H	Br	3.35	–	4-NO_2	Cl	4.13	4.14
4-Me	Cl	3.94	3.84	3-NO_2	Cl	5.16	4.95
4-Me	Br	3.51	3.57	3-F	Cl	3.76	3.89
4-Cl	Cl	3.33	–	4-OH	Cl	4.20	3.97
4-Cl	Br	2.62	2.78	4-MeS	Cl	4.23	4.02
4-Br	Cl	3.20	3.32	3,4-$(MeO)_2$	Cl	4.36	4.33
4-Br	Br	2.78	–	3,4-Me_2	Cl	4.01	4.0
4-MeO	Cl	4.61	4.04				

[a] The dipole moment of $PhTeCl_3$ in C_6H_6 (40 °C) is 2.90 D.[238]

3. Electronic effects of the TeX_3 groups

The inductive and mesomeric constants of the TeX_3 groups were determined based on the chemical shifts in the ^{19}F NMR spectra of *m*- and *p*-fluorophenyltellurium trihalides.[114]

Substituent	δ^F_{meta} /ppm	δ^F_{para} /ppm	σ_I	σ_C	σ_P
$TeCl_3$	−3.28	−6.62	0.55	0.11	0.66
$TeBr_3$	−3.05	−6.43	0.51	0.11	0.62

The σ_I and σ_C values indicate that interactions between the TeX_3 groups and the π-electron system of the benzene ring are predominantly inductive in character because the σ_C constants comprise ~ 15% of the total electronic effect of the substituent. The σ_P constants of the TeX_3 groups, unlike those of the $Te(R)X_2$ groups (X = F, Cl, Br or I), decrease on going from chlorine to bromine.

The orbital populations were calculated and the nature of the highest bonding and lowest unoccupied orbitals of $PhTeCl_3$ was examined using the extended Hückel method.[211] According to the results of calculations, the π-electron system of the benzene ring is only slightly affected by the substituent and retains six electrons. A large positive charge on the tellurium atom exists due to the fact that its *p* orbitals and the combination of the p_x and p_z orbitals of the axial chlorine atoms with the appropriate symmetry are combined into the molecular orbital MO_π (E_{1a}).

Calculations demonstrated that the three highest occupied MOs are σ orbitals. The upper orbital is localised primarily at the tellurium atom, whereas the unoccupied orbital, which involves the d_π orbital of the tellurium atom, (MO_{34}) is far removed from the highest occupied π-MOs. These quantum-chemical data account for the absence of a noticeable effect of conjugation between the $TeCl_3$ group and the aryl groups.

V. Conclusion

The data surveyed in the present review suggest that σ-telluranes $RTeX_3$ are of preparative importance in the chemistry of organotellurium compounds. σ-Telluranes are used as the starting compounds in the synthesis of other classes of organic derivatives of tellurium, *viz*., of diorganyl ditellurides R_2Te_2, tellurinic acids RTe(O)OH, tellurium oxochlorides RTe(O)Cl, σ-telluranes of the R_2TeX_2 type and pentacoordinate tellurium derivatives $M^+[RTeX_4]^-$ (M is the onium group). Intramolecular electrophilic cyclisation of the corresponding organyltellurium trichlorides is used for the preparation of different five- and six-membered tellurium-containing heterocycles (benzotellurophenes, dibenzotellurophenes and telluroxanthenes) and six-membered heterocycles involving other heteroatoms along with the tellurium atom (phenoxatellurines, phenothiatellurines and phenotellurazines). These reactions are specific to the synthesis of tellurium-containing heterocycles and have virtually no analogues in the chemistry of the corresponding sulfur and selenium derivatives. Halodetelluration of organyltellurium trihalides, which in some cases proceeds with rather high yields, can be used for the preparation of biaryls, different types of mono- and dihalogeno derivatives, stilbenes, carboxylic acids and usaturated ketones.

The development of new procedures for the synthesis of organyltellurium trihalides, the synthesis of new tellurium-containing heterocycles starting from these compounds and examination of the possibilities of the use of these compounds in preparative organic chemistry are of obvious interest both in organotellurium chemistry and in organic chemistry as a whole.

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