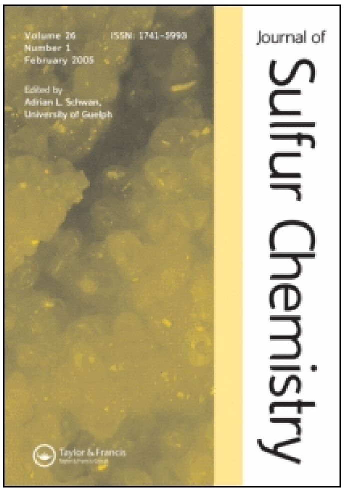

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Diorganyl Derivatives of Tellurium(IV) (σ-Telluranes of R_2TeX_2 Type)

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DIORGANYL DERIVATIVES OF TELLURIUM(IV) (σ-TELLURANES OF R_2TeX_2 TYPE)

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Literature data concerning the synthesis and reactions of diorganyl derivatives of tellurium(IV) (σ-telluranes of R_2TeX_2 type) are systematized and generalized in this review.

Keywords: Alkoxytelluration reaction; Aryltellurium trihalides; Detelluration reaction; Diorganyltellurium dihalides; Tellurium tetrahalides

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1. INTRODUCTION

Diorganyl derivatives of tellurium(IV) R_2TeX_2 (X=Hal, CN, SCN, OR, OCOR, $SC(S)NR_2$ and others) are, according to Musher classification [1], σ-telluranes in which valency electron pairs occupy localized σ-orbitals. A characteristic feature of these compounds in comparison to analogous derivatives of sulfur and selenium is their enhanced thermal stability. σ-Telluranes R_2TeX_2 serve as precursors in the preparation of other types of organotellurium compounds: diorganyltellurides, π-telluranes (telluronium ylides, tellurimides and diaryltelluroxides), tetraaryltelluranes and derivatives of hexacoordinated tellurium. As well as the other organotellurium derivatives [2,3], σ-telluranes R_2TeX_2 are applied in organic synthesis. They are used in preparation of halide derivatives of different types, biaryls, carboxylic acids and in the arylation of olefins.

Reviews on the synthesis and reactions of the σ-telluranes R_2TeX_2 have been published earlier [4–7] and some data on the structure of these compounds have been reported [8].

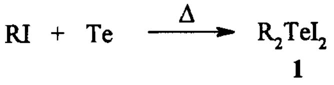
2. SYNTHESIS OF σ-TELLURANES R_2TeX_2

A classification of the preparative methods for the synthesis of diorganyl derivatives of tellurium(IV) according to the nature of the tellurium-containing substrate has been chosen among several possible ones.

2.1. From Elemental Tellurium

2.1.1. *From Organyl Halides*

Methyliodide reacts with powdered tellurium to give dimethyltellurium diiodide **1** (R = Me) in the yields higher than 50% [9–13]. This reaction has been applied for the synthesis of ^{125}Te and ^{129}Te isotopomers of **1** (R = Me) [14]. The reaction with other alkyl iodides results in lower yields of dialkyltellurium diiodides [11,15–17]. Thus, diamyltellurium diiodide was obtained in only 5% yield [11] (Scheme 1).

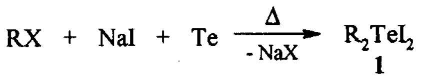


$$\mathrm{RI} + \mathrm{Te} \xrightarrow{\Delta} \underset{\mathbf{1}}{\mathrm{R_2TeI_2}}$$

R = CH_2I,[17] Me,[9-14] Et;[11,15,16] Pr, Bu, C_5H_{11};[11] $PhCH_2$[15]

SCHEME 1

Some of diorganyltellurium diiodides were prepared in 50–70% yields by heating mixtures of organyl chlorides [18,19] or bromides [20–22] with sodium iodide and powdered tellurium in DMF [18] or in the absence of the solvent [19–22].



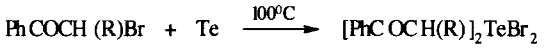
$$\mathrm{RX} + \mathrm{NaI} + \mathrm{Te} \xrightarrow[\text{- NaX}]{\Delta} \underset{\mathbf{1}}{\mathrm{R_2TeI_2}}$$

X = Cl; R = $PhCH_2$,[19] $C_{16}H_{33}$[18]

X = Br; R = *c*-C_6H_{11},[20] $PhCOCH_2$,[22] PhCOCH(Me)[21]

SCHEME 2

When an electron-accepting group is attached to the α-carbon of the organyl group the reaction of tellurium with such type organyl bromides proceeds rather smoothly [21,22] (the yields are 45–65%) (Scheme 3).

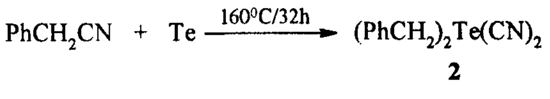


$$\mathrm{PhCOCH(R)Br} + \mathrm{Te} \xrightarrow{100^{\circ}\mathrm{C}} \mathrm{[PhCOCH(R)]_2TeBr_2}$$

R=H, Me

SCHEME 3

In a similar way, benzyl cyanide reacts with tellurium upon heating to give dibenzyltellurium dicyanide **2** in 60% yield [19] (Scheme 4).



$$\mathrm{PhCH_2CN} + \mathrm{Te} \xrightarrow{160^{\circ}\mathrm{C}/32\mathrm{h}} \underset{\mathbf{2}}{\mathrm{(PhCH_2)_2Te(CN)_2}}$$

SCHEME 4

Iodobenzene does not react with tellurium, but interaction of iodopolyfluoroarenes and Te at 230–260°C leads to *bis*(pentafluorophenyl)telluride **3a** (yield is 100%) [23] and *bis*(2-nonafluorobiphenyl)telluride **3b** (yield is 35%) [24] (Scheme 5).

$$R_FI + Te \xrightarrow{230^0\text{-}260^0C} (R_F)_2Te$$

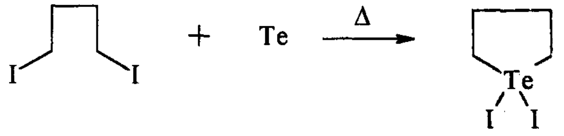
3

R_F=C_6F_5 (**a**), 2-$C_6F_5C_6F_4$ (**b**)

SCHEME 5

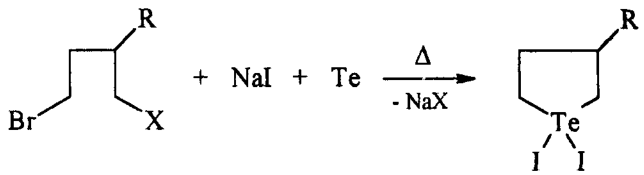
Probably the strong electronoacceptor properties of the polyfluoroaryl group weakening the Te–I bonds in intermediate σ-telluranes $(R_F)_2TeI_2$ as well as the high reaction temperature result in the decomposition of the σ-telluranes to diaryl tellurides **3** and iodine.

Organic dihalides react with powdered tellurium to give heterocyclic compounds. Thus, the heating of 1,4-diiodobutane with Te results in the formation of 1,1-diiodo-1-telluracyclopentane **4a** [17,25,26] (the yield is quantative) (Scheme 6). Tellurium diiodides **4a,b** were also prepared through heating of 1-chloro-4-bromobutane [27] or 1,4-dibromopentane [28] with NaI in 2-butoxyethanol (Scheme 7).



4a

SCHEME 6



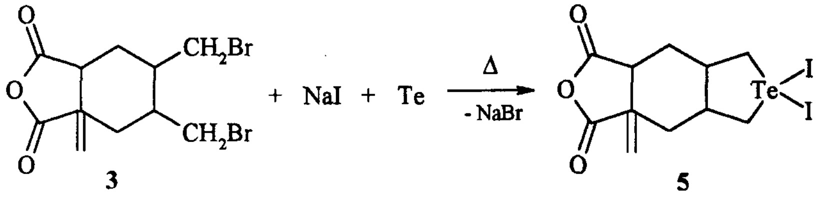
4 a,b

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

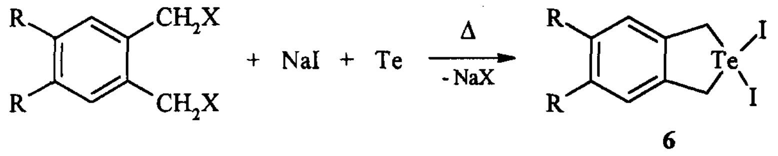
SCHEME 7

Substituted 2,5-dihydrotellurophene **5** [29] (the yields were not given) (Scheme 8), 1,1-diiodo-2,5-dihydrobenzo[c]tellurophenes **6** [30–33] (the yields were 80–85%) (Scheme 9) and 1,3-dihydro-2,2-diiodo-2λ^4-tellurolo[3,4-b]quinoxaline **7** [34,35] (the yields were 53–60%) (Scheme 10) were synthesized by heating of corresponding dibromides

[29,31,34–36] or dichlorides [30,32,33] with NaI and tellurium.

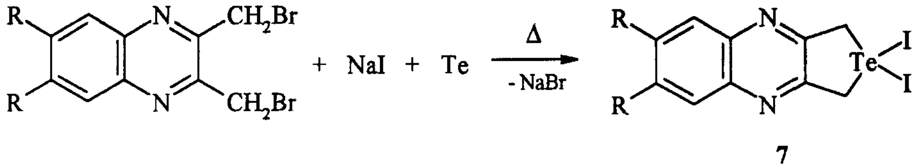


SCHEME 8



R=H: X=Cl,[30] Br; [31] R=Me: X=Cl [30, 32, 33]

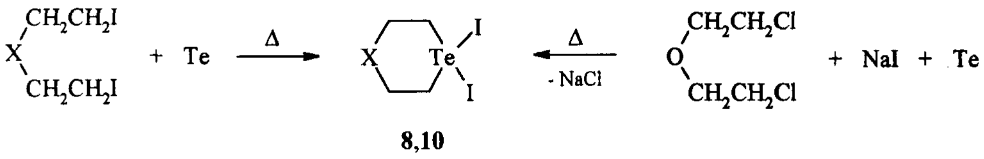
SCHEME 9



R=H,[34] Me[35]

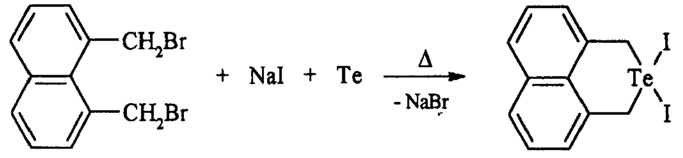
SCHEME 10

The six-membered heterocycles with 1,1-diiodo-1-telluracyclohexane **8** [17] (the yield was 63%) (Scheme 11) and 1,1-diiodo-3,5-naphto-1-telluracyclohexane **9** [36] (the yield was not given) (Scheme 12) and two heteroatoms (4,4-diiodo-1-oxa-4-telluracyclohexane **10** [17,37] (the yields were 10–13%) (Scheme 11)) were obtained in a similar way.



8 X=CH_2;[17] **10** X=O[17, 37]

SCHEME 11

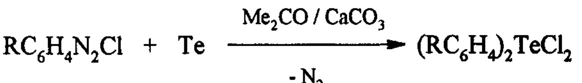


9

SCHEME 12

2.1.2. *From Diazocompounds and Iodonium Salts*

Symmetrical diaryltellurium dichlorides **11** were obtained in relatively low yields (4–44%) by coupling aryldiazonium chlorides with powdered tellurium in the presence of calcium carbonate [38,39] (Scheme 13).



$$RC_6H_4N_2Cl + Te \xrightarrow[-N_2]{Me_2CO\,/\,CaCO_3} (RC_6H_4)_2TeCl_2$$

11

R = H;[38] 2-Me, 3-Me, 4-Me, 2-MeO, 3-MeO, 4-MeO, 2-EtO, 3-EtO, 4-EtO, 2-Cl, 3-Cl, 4-Cl, 2-Br, 3-Br, 4-Br[39]

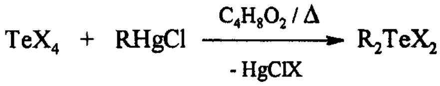
SCHEME 13

Diphenyltellurium dichloride can also be obtained by heating dry diphenyliodonium chloride with tellurium [40]. By carrying out this reaction in ether [40,41] in the presence of reductants (H_2S [40] or thioglycolic acid [41]) diphenyltelluride was formed.

2.2. From Tellurium Tetrahalides and Aryltellurium Trihalides

2.2.1. *Reactions with Organoelement Compounds*

The exchange reactions of tellurium tetrahalides and aryltellurium trihalides with organomercury compounds and main group 13 (IIIA) (In, Tl) and 14 (IVA) (Si, Sn, Pb) serve as important sources of diorganyltellurium dihalides R_2TeX_2. Symmetrical diorganyltellurium dihalides were prepared in 43–58% yields by coupling tellurium tetrahalides with organylmercury halides taken in the 1 : 2 ratio [42,43] (Scheme 14).



$$TeX_4 + RHgCl \xrightarrow[-HgClX]{C_4H_8O_2\,/\,\Delta} R_2TeX_2$$

X = Cl: R = $\underbrace{CH_2CHCH_2CPh_2C(O)O}$ [42]

X = Br: R = 2-NH_2-5-MeC_6H_3, 2-NH_2-5-BrC_6H_3, 2-NH_2-5-$NO_2C_6H_3$[43]

SCHEME 14

When the reaction of arylmercury halides and organyltellurium trihalides was performed with the equimolar amounts of the reactants both symmetrical and nonsymmetrical diorganyltellurium dichlorides were formed [44–52] (Scheme 15). This reaction represents a general approach to the synthesis of nonsymmetrical diaryltellurium dichlorides. It was also applied to the preparation of arylalkyl- and arylcycloalkyltellurium dichlorides. As for the reaction of $TeCl_4$ with arylmercury chlorides, dioxan serves as the most suitable solvent. The yields of diorganyltellurium dichlorides are 42–95%.

$$\mathrm{ArTeCl_3 + RHgCl \xrightarrow[-HgCl_2\cdot C_4H_8O_2]{C_4H_8O_2\,/\,\Delta} ArTeCl_2R}$$

$\mathrm{Ar = 4\text{-}FC_6H_4,\ 4\text{-}ClC_6H_4,\ 4\text{-}BrC_6H_4\text{: } R = 4\text{-}FC_6H_4}$[51]

$\mathrm{Ar = Ph\text{: } R = 4\text{-}FC_6H_4;}$[51] $\mathrm{1\text{-}C_{10}H_7,\ 2\text{-}C_{10}H_7;}$[44] $\mathrm{2\text{-}Me_2N\text{-}5\text{-}MeC_6H_3;}$[45]
$\mathrm{2\text{-}OH\text{-}5\text{-}MeC_6H_3}$[47]

$\mathrm{Ar = 4\text{-}MeC_6H_4\text{: } R = 4\text{-}FC_6H_4}$[51]

$\mathrm{Ar = 4\text{-}MeOC_6H_4\text{: } R = Et,\ PhCH_2;}$[49] $\mathrm{4\text{-}FC_6H_4;}$[51] $\mathrm{Ph,\ 1\text{-}C_{10}H_7,\ 2\text{-}C_{10}H_7;}$[44]
$\mathrm{4\text{-}Me_2CHC_6H_4;}$[50] $\mathrm{2\text{-}Me_2N\text{-}5\text{-}MeC_6H_3;}$[45, 46] $\mathrm{2\text{-}OH\text{-}5\text{-}MeC_6H_3}$[47]

$\mathrm{Ar = 4\text{-}EtOC_6H_4\text{: } R = 2\text{-}Me_2N\text{-}5\text{-}MeC_6H_3;}$[45, 46] $\mathrm{2\text{-}OH\text{-}5\text{-}MeC_6H_3;}$[47]
$\mathrm{2\text{-}PhN{=}NC_6H_4}$[52]

$\mathrm{Ar = 4\text{-}PhOC_6H_4\text{: } R = \underline{CH_2CHCH_2CPh_2C(O)O};}$[42] $\mathrm{Ph,\ 1\text{-}C_{10}H_7,\ 2\text{-}C_{10}H_7}$[44]

$\mathrm{Ar = 2\text{-}C_{10}H_7\text{: } R = c\text{-}C_6H_{11},\ PhCH_2;}$[49] $\mathrm{1\text{-}C_{10}H_7}$[44]

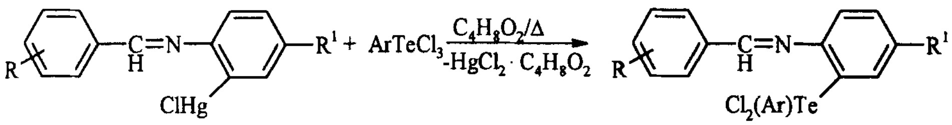
$\mathrm{Ar = 2\text{-}MeCONH\text{-}5\text{-}MeC_6H_3\text{: } R = 4\text{-}HOC_6H_4,\ 4\text{-}MeOC_6H_4,\ 4\text{-}EtOC_6H_4,}$
$\mathrm{2\text{-}MeCONH\text{-}5\text{-}BrC_6H_3,\ 2\text{-}MeCONH\text{-}5\text{-}NO_2C_6H_3}$[48]

$\mathrm{Ar = 2\text{-}MeCONH\text{-}5\text{-}BrC_6H_3\text{ : } R = 4\text{-}HOC_6H_4,\ 4\text{-}MeOC_6H_4,\ 4\text{-}EtOC_6H_4}$[48]

$\mathrm{Ar = R = 2\text{-}MeCONH\text{-}5\text{-}MeC_6H_3,\ 2\text{-}MeCONH\text{-}5\text{-}BrC_6H_3,}$
$\mathrm{2\text{-}MeCONH\text{-}5\text{-}NO_2C_6H_3}$[48]

SCHEME 15

By coupling benzalanilines *o*-mercurated at the *N*-phenyl ring with 4-ethoxyphenyl tellurium trichloride a series of tellurium-containing azomethines **12** has been prepared in 70–93% yields [53] (Scheme 16).



12

$\mathrm{Ar = EtOC_6H_4;\ R = H\text{: } R^1 = Me,\ MeO,\ Cl,\ Br;\ R^1 = Me\text{: } R = 4\text{-}MeO,\ 3\text{-}MeO,\ 2\text{-}MeO,}$
$\mathrm{4\text{-}Cl,\ 3\text{-}Cl,\ 2\text{-}Cl,\ 4\text{-}Br,\ 3\text{-}Br,\ 4\text{-}NO_2,\ 3\text{-}NO_2}$

SCHEME 16

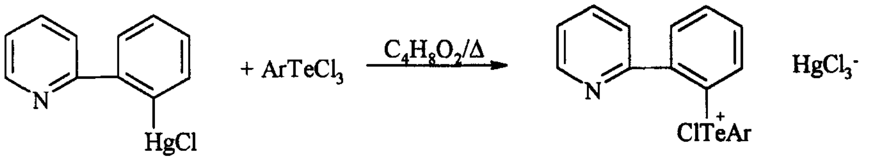
Aryl(4-dimethylaminophenyl)tellurium dichlorides **13** can be obtained in 17–41% yields when 4-dimethylaminophenylmercury acetate is employed in this reaction instead of the respective chloride [51,54] (Scheme 17).

$$RC_6H_4TeCl_3 + 4\text{-}Me_2NC_6H_4HgOAc \xrightarrow[\text{-Hg(OAc)Cl} \cdot C_4H_8O_2]{C_4H_8O_2/\Delta} \underset{\mathbf{13}}{RC_6H_4TeCl_2C_6H_4NMe_2\text{-}4}$$

R = H, 4-OMe, 4-OEt, 4-OPh, 4-Me, 4-Cl, 3-Cl, 4-Br, 3-Br, 3-NO_2;[54] 4-F[51]

SCHEME 17

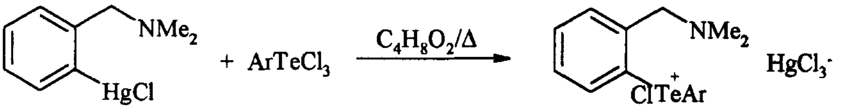
Intramolecularly N-Hg coordinated arylmercury chlorides react with aryltellurium trichlorides to give telluronium salts. 2-(2′-Pyridyl)phenylmercury chloride and 2-dimethylaminomethylphenylmercury chloride form in the reaction with 4-ethoxyphenyl tellurium trichloride the telluronium salts **14a** [55] (the yield is 67%) (Scheme 18) and **14b** [56] (the yield is 51%) (Scheme 19), respectively.



14a

Ar = 4-EtOC$_6$H$_4$

SCHEME 18



14b

Ar = 4-EtOC$_6$H$_4$

SCHEME 19

Diarylmercury reacts with TeCl$_4$ when refluxing their dioxane solution to give the compounds **11** in high yields (80–98%) [57,58] (Scheme 20).

$$(RC_6H_4)_2Hg + TeCl_4 \xrightarrow[\text{-HgCl}_2 \cdot C_4H_8O_2]{C_4H_8O_2/\Delta} \underset{\mathbf{11}}{(RC_6H_4)_2TeCl_2}$$

R = H;[57, 58] 4-Me, 4-OMe, 4-Br[57]

SCHEME 20

The use of aryltellurium trichlorides in this reaction instead of $TeCl_4$ yields nonsymmetric diaryl tellurium dichlorides in high yields (93–97%) [57] (Scheme 21).

$$(RC_6H_4)_2Hg + 4\text{-}MeOC_6H_4TeCl_3 \xrightarrow[-HgCl_2 \cdot C_4H_8O_2]{C_4H_8O_2/\Delta} RC_6H_4TeCl_2C_6H_4OMe\text{-}4$$

R = H, 4-Me

SCHEME 21

Diaryltellurium dichlorides were also obtained by using in the reaction with $TeCl_4$ main group 13 (IIIA) organoelement compounds, Ar_2MCl (M = In, Tl) [59]. The reaction proceeds smoothly when refluxing toluene solutions of the components to give **11** in 86–96% yields (Scheme 22).

$$Ar_2MCl + TeCl_4 \xrightarrow[-ArMCl_2]{PhMe/\Delta} \underset{\mathbf{11}}{Ar_2TeCl_2}$$

M = In: Ar = Ph; M = Tl: Ar = Ph, 4-MeC_6H_4

SCHEME 22

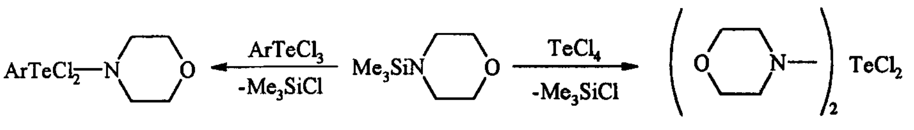
The reaction of aryltellurium trichlorides with aryltrimethylsilanes occurs at rather rigid conditions (large excess of silane, long-term refluxing of a dioxane solution) and leads to both symmetric and nonsymmetric diaryltellurium dichlorides in modest yields (32–58%) [60] (Scheme 23). The tellurium dichlorides thus obtained require additional purification.

$$RC_6H_4SiMe_3 + R_1C_6H_4TeCl_3 \xrightarrow[-Me_3SiCl]{C_4H_8O_2/\Delta} RC_6H_4TeCl_2C_6H_4R^1$$

$R = R^1$ = 4-Me, 3-Me; R = 4-Me, R^1 = 4-OMe

SCHEME 23

A useful modification of this reaction has been developed by Barton [61]. By coupling *N*-trimethylsilylmorpholine with 4-methoxyphenyltellurium trichloride or $TeCl_4$ then 4-methoxyphenyl(*N*-morpholinyl)tellurium dichloride and *bis*(morpholinyl)tellurium dichloride were obtained (the yields were not given) (Scheme 24). These compounds were employed as a mild oxidant of hydroquinones and thiols.



Ar = 4-$MeOC_6H_4$

SCHEME 24

Tellurium dichlorides, with Te–N bonds, were also prepared by interaction of tellurium tetrachloride and aryltellurium trichlorides with trimethylsilyl derivatives containing N–Si bonds [62–65] (Scheme 25–28).

$$TeCl_4 + RE{=}NSiMe_3 \xrightarrow[-Me_3SiCl]{} (RE{=}N)_2TeCl_2$$

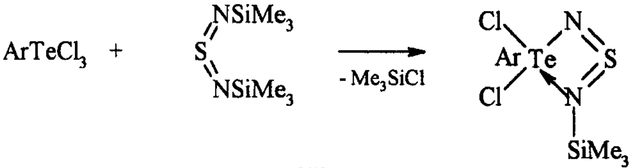
RE = Ph_3P(56%),[62, 63] Ph_2S(62%),[64] Ph_2C(24%)[64]

SCHEME 25

$$4\text{-}MeOC_6H_4TeCl_3 + RE{=}NSiMe_3 \xrightarrow[-Me_3SiCl]{} RE{=}NTeCl_2C_6H_4OMe\text{-}4$$

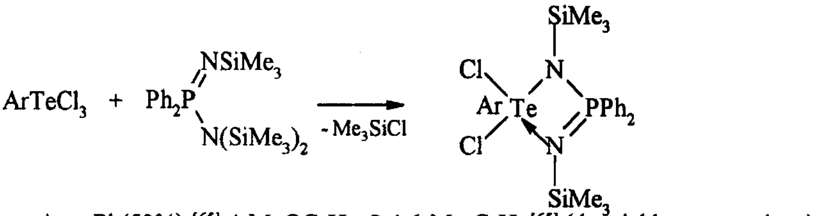
RE = Ph_3P(68%),[62, 63] $Me_2S(O)$(63%),[62] Ph_2S(60%),[64] Ph_2C(60%)[64]

SCHEME 26



Ar = 4-$MeOC_6H_4$(63%)[62]

SCHEME 27



Ar = Ph(53%);[65] 4-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$[65] (the yields are not given)

SCHEME 28

The Csp^3–Si bond does not split under the action of tellurium tetrachloride. Thus on 12 h refluxing of benzyltrimethylsilane with $TeCl_4$ in toluene a mixture of 4-$Me_3SiCH_2C_6H_4TeCl_3$ and (4-$Me_3SiCH_2C_6H_4)_2TeCl_2$ was formed [66].

Organotin and organolead compounds are more reactive than their silicon analogues. Refluxing toluene solutions of tellurium tetrahalides with tetraorganylstannanes [59,67–69] or triorganyltin chlorides [48,68] affords symmetric and nonsymmetric diorganyltellurium dichlorides and dibromides in high yields (75–92%) (Scheme 29, 30).

$$R_4Sn + TeX_4 \xrightarrow[-R_2SnX_2]{PhMe/\Delta} R_2TeX_2$$

$X = Cl$: $R = Me$;[69] Et;[67, 69] Pr;[69] Ph;[68, 69] $4\text{-}MeC_6H_4$[59]

$X = Br$: $R = Me$;[69] Et;[67, 69] Pr;[69] Ph[67, 69]

$X = I$: $R = Ph$[67]

SCHEME 29

$$R_3SnCl + ArTeCl_3 \xrightarrow[-R_2SnCl_2]{PhMe/\Delta} ArTeCl_2R$$

$R = Ph$: $Ar = Ph$, $4\text{-}MeOC_6H_4$;[68] $2\text{-}MeCONH\text{-}5\text{-}BrC_6H_3$[68]

SCHEME 30

The electrophilicity of tellurium tetrahalides decreases in the order of $TeCl_4 > TeBr_4 > TeI_4$. By this reason the synthesis of tellurium dibromides and tellurium diiodides from tetraarylstannanes requires more rigid conditions than those used in the synthesis of tellurium dichlorides. Refluxing Ph_4Sn with $TeBr_4$ for 12 h affords diphenyltellurium dibromide in 92%. However, diphenyltellurium diiodide was obtained in only 20% yield even after 48 h refluxing of a mixture of TeI_4 and Ph_4Sn [67]. It is worth noting that the reaction of dialkyldiarylstannanes with $TeCl_4$ is accompanied by scission of the C_{Ar}–Sn bonds. Diphenyltellurium dichloride was prepared through interaction of Ph_2SnBu_2 with $TeCl_4$ in 84% yield [59].

Organolead compounds readily react with $TeCl_4$ and aryltellurium trihalides in toluene solution even at room temperature to give diorganyltellurium dichlorides in 73–94% yields [70,71]. As in the case of organotin compounds, diaryldialkylplumbanes split their C_{Ar}–Pb bonds in the reaction with $TeCl_4$ [70] (Schemes 31–34).

$$R_4Pb + TeCl_4 \xrightarrow[-R_2PbCl_2]{PhMe/r.t.} R_2TeCl_2$$

$R = Me$;[71] Ph, $4\text{-}MeC_6H_4$[70]

SCHEME 31

$$Ph_3PbCl + RC_6H_4TeCl_3 \xrightarrow[-R_2PbCl_2]{PhMe/r.t.} PhTeCl_2C_6H_4R$$

R= H, 4-OEt[70]

SCHEME 32

$$R_6Pb_2 + TeCl_4 \xrightarrow{PhMe/r.t.} R_2TeCl_2$$

R = Me, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$[71]

SCHEME 33

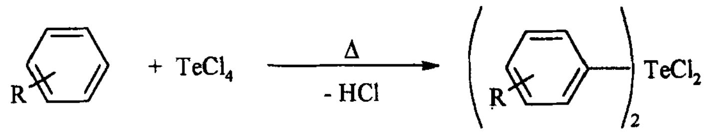
$$Ph_6Pb_2 + RC_6H_4TeCl_3 \xrightarrow{PhMe/r.t.} PhTeCl_2C_6H_4R$$

R = 4-EtO, 3-Me-4-OMe, 3,4-$(OMe)_2$[71]

SCHEME 34

2.2.2. *Electrophilic Substitution Reactions*

2.2.2.1. *Reactions with Arenes* It is known that the reaction of arenes containing electron-releasing substituents with $TeCl_4$ results in aryltellurium trichlorides [72]. When boiling the reagents in an excess of the arene, symmetrical diaryltellurium dichlorides can be obtained in 52–95% yields [73–77] (Scheme 35).



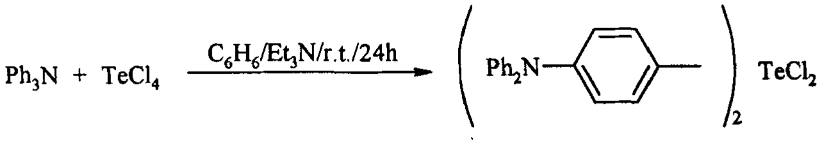
11

R = 4-OMe,[73] 4-EtO,[74] 2,4-$(OH)_2$,[75] 2,4-$(OMe)_2$,[74,76] 3,4-$(OMe)_2$,[76] 3-Me-4-OMe,[76] 3-Me-4-OH, 2-Me-4-OH, 2-OH-5-Me[77]

SCHEME 35

No such reaction occurs with alkoxynaphthalenes, monoalkylated resorcinol, hydroquinone and *p*-nitroanisole [73]. Also unsuccessful were attempts of the synthesis of *bis*(*p*-dimethylaminophenyl)tellurium dichloride by direct coupling of dimethylaminobenzene with $TeCl_4$. The reaction stopped at the formation of the complex $(Me_2NC_6H_5)_2 \cdot TeCl_4$ which was formed in quantitative yield [78]. However, under treatment with boiling water, the complex yielded to the desirable dichloride (20–30%). The mechanism of this transformation remains unclear, although the structure of the product was proven [78,79].

Triphenylamine, less basic than dimethylaminobenzene, readily reacts with $TeCl_4$ to give *bis*(4-diphenylaminophenyl)tellurium dichloride [80] (the yield was not given) (Scheme 36).



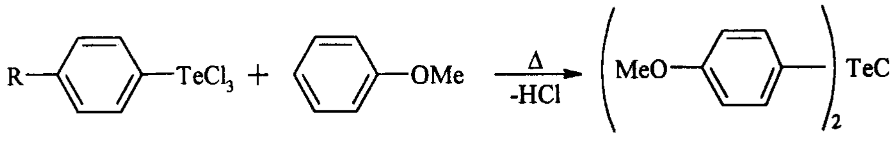
SCHEME 36

Formation of diaryltellurium dichlorides **11** by coupling arenes with $TeCl_4$ is a two-step reaction (Scheme 37).

$$TeCl_4 + C_6H_5R \xrightarrow[\text{-HCl}]{\Delta} 4\text{-}RC_6H_4TeCl_3 \xrightarrow[\text{-HCl}]{C_6H_5R/\Delta} \underset{\mathbf{11}}{(4\text{-}RC_6H_4)_2TeCl_2}$$

SCHEME 37

It was found indeed that by coupling 4-methoxyphenyltellurium trichloride with anisole [76] and 4-phenoxyphenyltellurium trichloride with diphenyl oxide [81] correspondingly symmetrical diaryltellurium dichlorides can be obtained. As Morgan reported [82], reaction of 4-ethoxyphenyl tellurium trichloride with anisole gave rise to 4-ethoxyphenyl(4′-methoxyphenyl)tellurium dichloride. However, in a more recent study [76] it was found that at prolonged heating of aryl tellurium trichlorides with aromatic compounds, the aryl exchange reaction took place (Scheme 38). The yields of final compounds are about 80%.



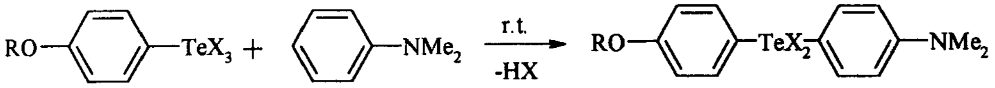
11

R = EtO, Me, Br

SCHEME 38

Although the *p*-isomer represented the main product of this reaction, small amounts of other isomers are formed. In the reaction of anisole with $TeCl_4$ at 160°C about 1% of 4-methoxyphenyl(2′-methoxyphenyl)tellurium dichloride was isolated along with di(4-methoxyphenyl)tellurium dichloride [83].

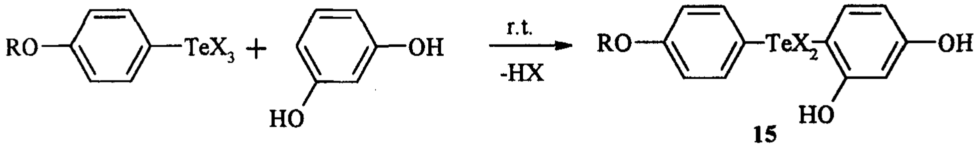
Aryltellurium trichlorides react with arenes bearing strong electron-releasing groups in the aryl ring at milder conditions allowing avoidance of the aryl exchange. A series of aryl(4-dimethylaminophenyl)tellurium dihalides **13** (the yields are 51–75%) (Scheme 39) and aryl(2,4-dihydroxyphenyl)tellurium dihalides **15** (the yields are 61–70%) (Scheme 40) were obtained by coupling aryltellurium trichlorides with dimethylaniline and resorcinol at room temperature [84].



13

R = Me, Et, Ph; X = Cl, Br

SCHEME 39



15

R = Me, Et, Ph; X = Cl, Br

SCHEME 40

The electrophilicity of aryltellurium trichlorides is significantly enhanced in the presence of catalytic amounts of $AlCl_3$. This is due to formation of complex $[ArTeCl_2]^+[AlCl_4]^-$ whose ionic structure was assigned by analogy with the adduct of $TeCl_4$ and $AlCl_3$ [85]. In the presence of $AlCl_3$ symmetrical diaryltellurium dichlorides can be obtained by reaction of $TeCl_4$ with such aromatic compounds as benzene, toluene, chlorobenzene and bromobenzene [76]. Diaryltellurium dichlorides thus obtained are usually admixed with aryltellurium trichlorides. In the case of the reaction of $TeCl_4$ with benzene, a procedure has been elaborated [86] that involves interruption of the process when two moles of HCl per mole of $TeCl_4$ are eliminated.

The use of $TeOCl_2$ (obtained by a treatment of "telluroxynitrate" with concentrated hydrochloric acid) is exemplified by the reaction with three isomeric cresols in ether solution. Subsequent evaporation of the solvent and heating the residue at 110–130°C gives rise to di(2-hydroxy-5-methylphenyl)-, di(2-methyl-4-hydroxyphenyl)- and di(3-methyl-4-hydroxyphenyl) tellurium dichlorides [87].

2.2.2.2. *Reactions with Compounds Containing Active Methylene Groups* Tellurium tetrachloride and aryltellurium trichlorides enter into electrophilic substitution reaction at the sp^3-carbon of activated methyl or methylene groups. Thus the reaction of Te Cl_4 and acetic acid anhydride at mole ratio 1:2 of the reagents affords carboxymethyltellurium trichloride and methylene*bis*(tellurium trichloride) **16** [88]. When six-fold molar excess of acetic anhydride was used, **16** and *bis*(carboxymethyl)tellurium dichloride **17** were formed as the products of this reaction [88] (Scheme 41).

$$(CH_3CO)_2O + TeCl_4 \xrightarrow{CHCl_3/\Delta} \underset{\mathbf{16}}{CH_2(TeCl_3)_2} + \underset{\mathbf{17}}{(HOOCCH_2)_2TeCl_2}$$

SCHEME 41

Reaction of $TeCl_4$ with other acid anhydrides does not lead to compounds of type **17** [88]. The reaction of methylketones in chloroform or tetrachloromethane solution with $TeCl_4$ forms diorganyl tellurium dichlorides **18** [75,89–98]. In some cases formation of the dichlorides **18** is accompanied by organyltellurium trichlorides **19** (Scheme 42). *Bis*(benzoylmethyl)tellurium dichloride was also obtained in 75% yield by a treatment of acetophenone with solution of TeO_2 in a mixture of hydrochloric and sulfuric acids [95].

$$RCOCH_3 + TeCl_4 \xrightarrow[\text{-HCl}]{\Delta} \underset{\mathbf{18}}{(RCOCH_2)_2TeCl_2} + \underset{\mathbf{19}}{RCOCH_2TeCl_3}$$

R = Me,[90, 96] Pr,[90, 96] Pr^{i},[90, 96] Bu,[90] Bu^{i},[90] Bu^{t},[90, 94, 96] 2-thienyl,[93,94] 3-thienyl,[91] Ph,[75, 89, 90, 93, 94] 4-BrC$_6$H$_4$,[93] 4-ClC$_6$H$_4$,[93] 4-MeC$_6$H$_3$,[75, 93, 94] 4-MeOC$_6$H$_4$,[75, 93, 94] 3-MeOC$_6$H$_4$,[97] 2-MeOC$_6$H$_4$,[98] 4-EtOC$_6$H$_4$,[89] 2,4-Me$_2$C$_6$H$_3$,[89] 2,4,5-Me$_3$C$_6$H$_2$,[89] 4-Pr^{i}C$_6$H$_4$,[89] 1-C$_{10}$H$_7$,[89, 93] 2-C$_{10}$H$_7$,[93] 9-anthryl,[93] 2-benzo[*b*]furanyl[93]

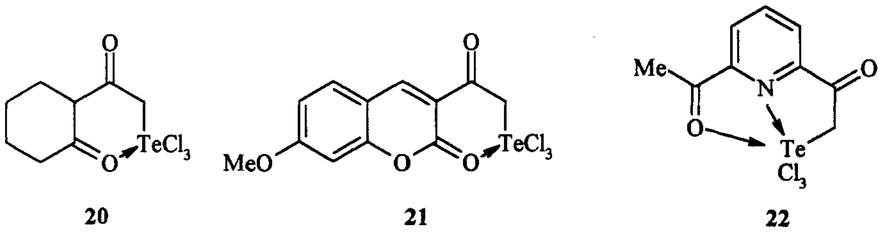
SCHEME 42

It is obvious that the formation of tellurium dichlorides **18** is a two-stage process (Scheme 43).

$$RCOCH_3 + TeCl_4 \xrightarrow[\text{-HCl}]{\Delta} \underset{\mathbf{19}}{RCOCH_2TeCl_3} \xrightarrow[\text{-HCl}]{RCOCH_3} \underset{\mathbf{18}}{(RCOCH_2)_2TeCl_2}$$

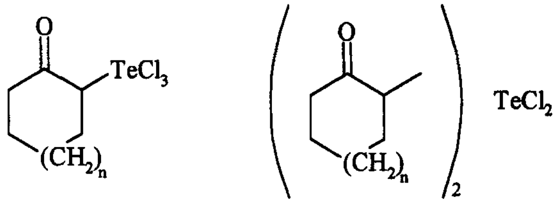
SCHEME 43

In some cases, depending upon the structure of the initial ketone and to a lesser degree on the reaction conditions, a mixture of tellurium dichlorides **18** and tellurium trichlorides **19** or exclusively compounds **19** may be obtained. Thus, the mixture of PrCOCH$_2$TeCl$_3$ (47%) and (PrCOCH$_2$)$_2$TeCl$_2$ (61%) is formed when 2-pentanone is reacted with TeCl$_4$ [96]. Trichloride of the type **19** is obtained by refluxing a solution of 3-methoxyacetophenone and TeCl$_4$ (molar ratio 1 : 1) in CCl$_4$ for 7 h, whereas 76 h refluxing of these substrates (molar ratio 2 : 1) in CHCl$_3$ leads to the corresponding tellurium dichlorides of type **18** [97]. The tellurium trichlorides **19** are the only products of reactions TeCl$_4$ and some polyfunctional ketones [91]. Thus, 2-acetylcyclohexanone, 3-acetyl-7-methoxycoumarin and 2,6-diacetylpyridine are tellurated with formation of tellurium trichlorides **20–22** even when a twofold molar excess of ketone is used (Fig. 1).



20 **21** **22**

FIGURE 1



23 **24**

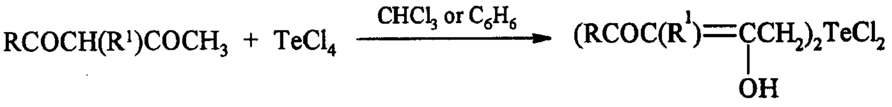
n = 1,2 n = 3

FIGURE 2

It is obvious that the electrophilicity of the $TeCl_3$ groups in compound **20–22** is reduced as a result of intramolecular coordination between O and Te and the reaction stops at this stage.

The structure of the products of reaction of cycloalkanones with $TeCl_4$ is determined by the size of the cycle [93]. Whereas the tellurium trichlorides **23** are formed in the case of cyclohexanone ($n = 1$) and cycloheptanone ($n = 2$), the tellurium dichloride **24** is the product of the reaction with cyclooctanone ($n = 3$) (Fig. 2).

Some diketones react with $TeCl_4$ to form, along with 1,1-dichloro-1-telluracyclohexane-3,5-diones, diorganyltellurium dichlorides **25** [99,100] (the yields were not given) (Scheme 44).



$$RCOCH(R^1)COCH_3 + TeCl_4 \xrightarrow{CHCl_3 \text{ or } C_6H_6} (RCOC(R^1){=}\underset{\displaystyle OH}{C}CH_2)_2TeCl_2$$

25

$R^1 = H$: $R = Bu^t$, Ph;[99] Bu^i;[100] $R^1 = Cl$, $R = Me$[99]

SCHEME 44

α-Telluroketones **26** were obtained in 57–97% yields in the reactions of aryltellurium trichlorides [84,93,101] and tribromides [84] occurring at rather mild conditions (r.t. in the absence of solvent [84]; Δ, CCl_4 [94]; Δ, C_6H_6 [101]) (Scheme 45).

$$4\text{-}RC_6H_4TeX_3 + R^1COCH_3 \xrightarrow[-HX]{} 4\text{-}RC_6H_4TeX_2CH_2COR^1$$

26

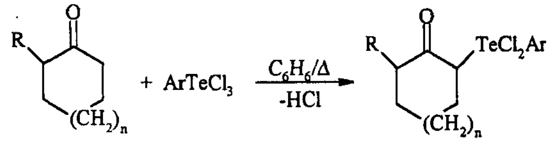
$X = Br$: $R = OMe, OEt, OPh$; $R^1 = Me$, Ph[84]

$X = Cl$: $R = OMe$: $R^1 = Me$,[84, 101] Bu^t,[101] Ph;[84, 93, 101] $R = OEt, OPh$: $R^1 = Me$, Ph;[84]

$R = 3,4\text{-}C_4H_4$, $R^1 = Ph$[93]

SCHEME 45

With cycloalkanones aryltellurium trichlorides form the dichlorides **27** in 82–100% yields [101] (Scheme 46).

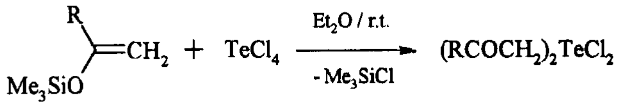


27

$Ar = 4\text{-}MeOC_6H_4$: R = H: n = 0,1,2; R = Me, n = 1

SCHEME 46

Another approach to the synthesis of the ketones **18** (R = Ph) is the coupling of the silyl enol ether of ketone **28** (R = Ph) with $TeCl_4$ [102] (Scheme 47). The yield of **28** was 63%.

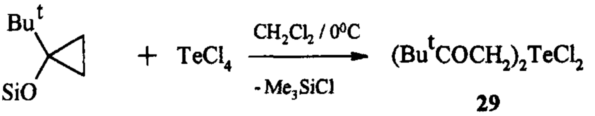


28 **18**

R=Ph

SCHEME 47

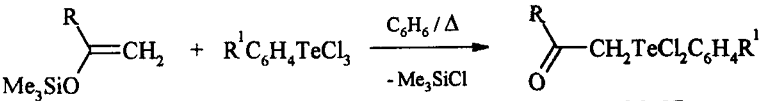
The reactions of trimethylsilyloxycyclopropane with $TeCl_4$ results in the tellurium dichloride **29** in 95% yield [103] (Scheme 48).



29

SCHEME 48

α-Telluroketones **26** and **27** were also obtained by reaction of aryltellurium trichlorides with silyl ethers of ketones when refluxing a benzene solution of the components [101,102] (Scheme 49). First examples of this reaction were described in 1978 [102]. In this case, the reactions are faster and the yields of telluroketones (70–100%) are higher than in the reactions of ketones and $TeCl_4$.



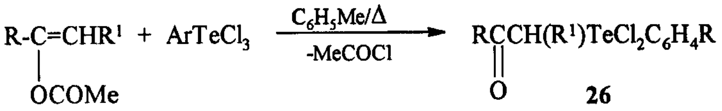
26, 27

$R^1 = 4\text{-}MeO$: R = Me, Bu^t, $(CH_2)_4$, $(CH_2)_5$;[101] Ph[101, 102]

$R = Ph$: $R^1 = 4\text{-}EtO$, $3,4\text{-}(MeO)_2$[102]

SCHEME 49

The ketones **26** were also prepared in 60–90% yields by coupling the enolacetates of ketones with aryltellurium trichlorides [104] (Scheme 50).

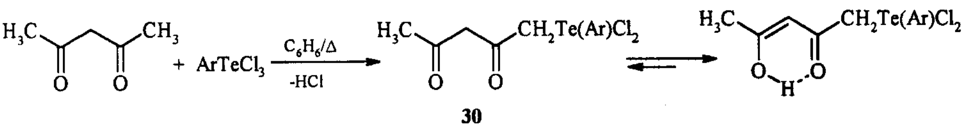


$$\underset{\displaystyle OCOMe}{R\text{-}C}{=}CHR^1 + ArTeCl_3 \xrightarrow[-MeCOCl]{C_6H_5Me/\Delta} R\underset{\displaystyle O}{\overset{}{C}}CH(R^1)TeCl_2C_6H_4R \quad \mathbf{26}$$

Ar = 3,4-$(MeO)_2C_6H_3$: R = R^1 = Me; R + R^1 = $(CH_2)_4$

SCHEME 50

As with $TeCl_4$, reaction of acetylacetone with aryltellurium trichlorides occurs at a methyl group of the diketone to give the compounds **30** in 30–90% yields [105] (Scheme 51). In a deuterochloroform solution of **30** (R = Ph) the keto–enol equilibrium is shifted to the enol form (95%). Electron donor substituents in the aryl ring of **30** favor the keto form.



Ar = Ph, 4-HOC_6H_4, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$, 3-Me-4-HOC_6H_3, 2,4-$(OH)_2C_6H_3$

SCHEME 51

2.2.3. *Electrophilic Addition Reactions*

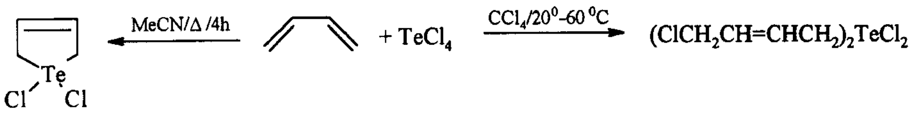
2.2.3.1. *Reactions with Alkenes* Tellurium tetrachloride adds to a double bond of alkenes and cycloalkenes to give *bis*[chloroalkyl(β-cycloalkyl)]tellurium dichlorides **31** in 20–100% yields [106–113] (Scheme 52). The reactions are usually carried out in tetrachloromethane or acetonitrile solutions at 5–60°C with a molar ratio of alkene : $TeCl_4$ = 2 : 1. Solvents with high dielectric constant provide for higher yields of **31** [109].

$$TeCl_4 + R^1CH{=}CHR^2 \longrightarrow \underset{\mathbf{31}}{(R^1CHClCHR^2)_2TeCl_2}$$

$R^1 = R^2 = H;^{[107,110,112]}\ R^2 = H{:}\ R^1 = Me,^{[109,111,112]}\ Et;^{[108]}\ R^1 + R^2 = (CH_2)_4{}^{[106\text{-}108,113]}$

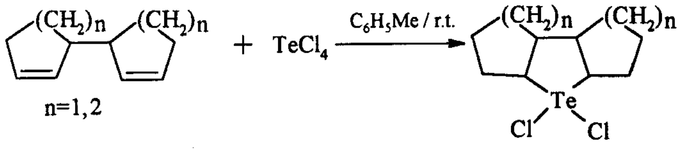
SCHEME 52

Some alkenes (e.g. stilbene) and dienes are inert with respect to $TeCl_4$ [42] and others (styrene, diisobutylene, 1,4-diphenylbutadiene-1,3) act as reductants reducing $TeCl_4$ to elemental tellurium [42]. In certain cases, the direction of the reaction can be modified by the reaction conditions (solvent, temperature). Thus, by carrying out the reaction of 1,3-butadiene with $TeCl_4$ in acetonitrile solution, 1,1-dichloro-2,5-dihydrotellurophene is formed [114,115], in 62% yield, whereas by passing 1,3-butadiene through a suspension of $TeCl_4$ in tetrachlomethane results in *bis*(4-chloro-2-butenyl)tellurium dichloride [112] in 20–30% yield (Scheme 53).



SCHEME 53

Cyclohexene reacts with $TeCl_4$ in tetrachloromethane solution at room or lower temperature to afford the dichloride **31** ($R^1 + R^2 = (CH_2)_4$). By refluxing the components, benzene was formed as the main product of this reaction [116,117]. Under similar conditions, aromatization of methyl- and halogenocyclohexenes occurs [117]. The conjugated dienes, e.g. 1,1′-bicyclohexene, are chlorinated by $TeCl_4$, whereas the dienes with separated double bonds (2,2′-bicyclopentene [116,117] and 2,2′-bicyclohexene [117] react with $TeCl_4$ to give derivatives of tetrahydrotellurophene (Scheme 54).



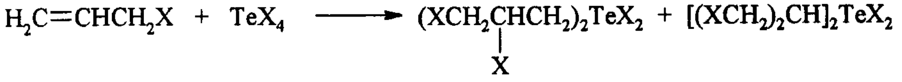
SCHEME 54

Reports on the reaction of 1,1-diarylethylenes with $TeCl_4$ are controversial. The first statement [118] on the π-complex structure of the product from the reaction was later discarded [119] and the compound was assigned to a σ-tellurane type of **32** (Scheme 55).

$$Ph_2C{=}CH_2 + TeCl_4 \xrightarrow[-HCl]{} \underset{\mathbf{32}}{(Ph_2C{=}CH)_2TeCl_2}$$

SCHEME 55

While terminal alkenes add $TeCl_4$ to their double bonds in accordance with the Markovnikov rule, reaction of functionalized alkenes with tellurium tetrahalides give rise to mixtures of the Markovnikov and anti-Markovnikov products **33** and **34** [120] (Scheme 56) (the yields of compounds of types **33** and **34** are 48% and 12% for X=Cl; 13% and 51% for X=Br).



$$H_2C{=}CHCH_2X + TeX_4 \longrightarrow (XCH_2\underset{X}{C}HCH_2)_2TeX_2 + [(XCH_2)_2CH]_2TeX_2$$

33 **34**

X = Cl, Br

SCHEME 56

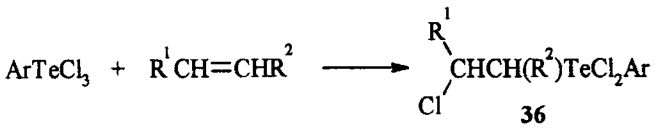
The data on the addition of $TeBr_4$ to alkenes are absent. It reacts, however, with triphenylphosphonium carboxymethylide to give the dibromide **35** [121] (Scheme 57) (the yield was not given).

$$Ph_3P{=}CHCO_2Et + TeBr_4 \longrightarrow [Ph_3PCH(CO_2Et)\text{-}TeBr_2\text{-}CH(CO_2Et)PPh_3]^{2+}2Br^-$$

35

SCHEME 57

Aryltellurium trichlorides readily add to the alkene double bonds to form aryl-2-chloroalkyl(cycloalkyl)tellurium dichlorides **36** in yields of 42–98% [42,122–126]. The reactions are usually performed by refluxing the components (small excess of an alkene) in chloroform or tetrachloromethane solution (Scheme 58).



$$ArTeCl_3 + R^1CH{=}CHR^2 \longrightarrow R^1(Cl)CHCH(R^2)TeCl_2Ar$$

36

$R^2 = H$: $R^1 = Me$, $Ar = 2\text{-}C_{10}H_7$;[125] $R^1 = C_8H_{17}$, $Ar = 2\text{-}C_{10}H_7$;[126] $R^2 = D$: $R^1 = C_8H_{17}$, $Ar = 2\text{-}C_{10}H_7$;[126] $R^1 = R^2 = Me$: $Ar = 2\text{-}C_{10}H_7$[125, 126]

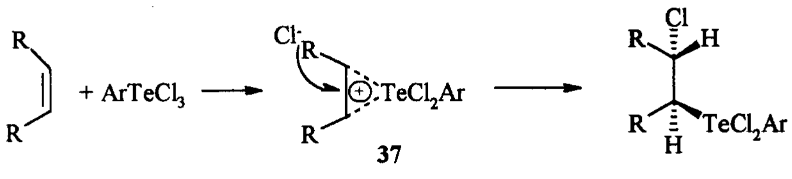
$R^1 + R^2 = (CH_2)_3$: $Ar = 2\text{-}C_{10}H_7$[126]

$R^1 + R^2 = (CH_2)_4$: $Ar = Ph$;[42] $4\text{-}EtOC_6H_4$;[42, 122] $4\text{-}PhOC_6H_4$, $1\text{-}C_{10}H_7$;[42] $2\text{-}C_{10}H_7$,[42, 126] $4\text{-}MeC_6H_4$[123]

$R^1 + R^2 = CH(Me)(CH_2)_3$: $Ar = 4\text{-}MeOC_6H_4$, $4\text{-}EtOC_6H_4$, $2,4\text{-}(MeO)_2C_6H_3$, $3,4\text{-}(MeO)_2C_6H_3$, $3,5\text{-}Me_2\text{-}4\text{-}HOC_6H_2$[124]

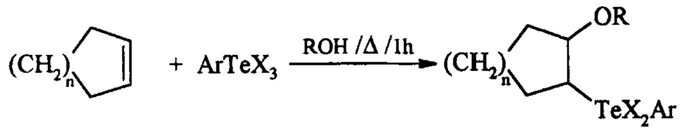
SCHEME 58

The compounds **36** are obtained via a stereospecific anti-addition to the alkenes [126]. Thus, the threo isomer is obtained from (*Z*)-2-butene, and only the erythro isomer is obtained from (*E*)-2-butene. These results are in accord with the mechanism that involves intermediacy of the cyclic telluronium ion **37** (Scheme 59).



SCHEME 59

σ-Telluranes R_2TeX_2 **38–40** were prepared by the use of reactions of electrophilic addition of phenyltellurium tribromide to the double bond of various alkenes [127–129]. The reactions were performed through short-term heating of a mixture of reactants in hydroxyl-containing solvents. By this method the products of the reaction contain alkoxy (the solvents are alcohols) or hydroxyl (the solvents are aqueous THF or Bu^{t}OH [129]) groups at the *β*-carbon. The alkoxytelluration reaction can also be performed with the use of aryltellurium trichlorides or the PhTeCN/$CuCl_2$ reagent [127–129]. All types of alkenes are susceptible to the alkoxytelluration reaction (Scheme 60–62) (the yields of compounds **38–40** are 28–100%).



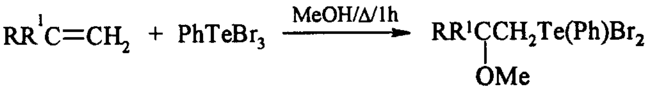
38

n = 1: Ar = Ph: X = Br: R = Me;[127, 129] n = 2: Ar = Ph: X = Br: R = Me;[127–129] Et, Pr^i;[127, 129] H[129]

n = 2: X = Cl: R = Me: Ar = Ph;[127, 129] 4-MeC_6H_4, 4-$MeOC_6H_4$;[129]

n = 3,4: Ar = Ph: X = Br: R = Me[128, 129]

SCHEME 60



$$RR^1C{=}CH_2 + PhTeBr_3 \xrightarrow{MeOH/\Delta/1h} RR^1\underset{OMe}{\underset{|}{C}}CH_2Te(Ph)Br_2$$

39

R^1 = H: R = Bu,[127, 129] C_6H_{13},[129] C_8H_{17},[127, 129] Ph;[127–129] R^1 = Me: R = Me, Pr, Ph[129]

SCHEME 61

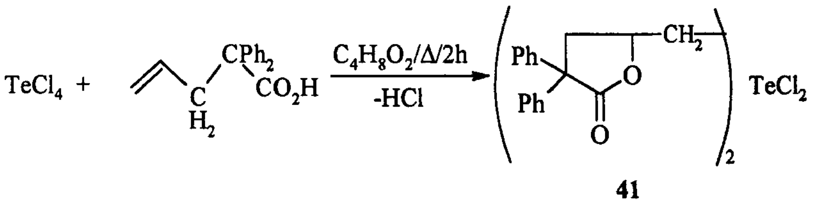
$$RCH{=}CHR + PhTeBr_3 \xrightarrow{MeOH/\Delta/1h} RH\underset{OMe}{\underset{|}{C}}CHRTe(Ph)Br_2$$

40

R = Me,[127, 129] Pr[128, 129]

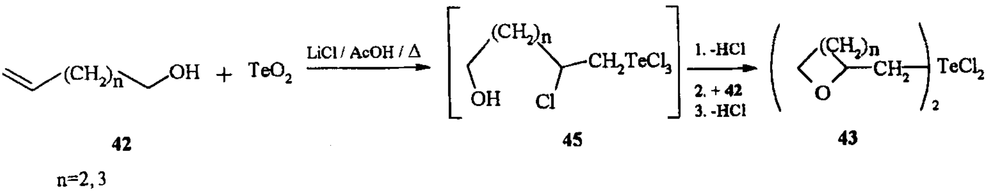
SCHEME 62

The addition of $TeCl_4$ and aryltellurium trihalides to double bonds of *γ*-carboxy, *γ*- and *δ*-hydroxyalkenes is accompained by elimination of HX from the initially formed adducts to give tellurium-containing lactones or cyclic ethers. By coupling $TeCl_4$ with 2,2-diphenyl-4-pentenonic acid, the dichloride **41** was prepared in almost quantitative yield [42] (Scheme 63).

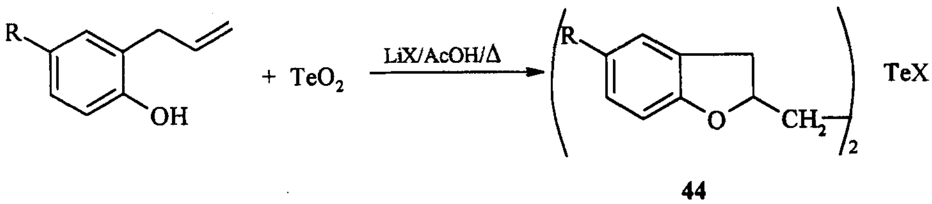


SCHEME 63

Instead of $TeCl_4$, TeO_2 was employed for the cyclization of γ- and δ-hydroxyalkenes **42**. The reaction was carried out in a solution of acetic acid containing LiCl [130] or LiBr [131] and resulted in dialkyltellurium dihalides **43, 44** with a possible inclusion of **45** as the intermediate [130] (Schemes 64, 65).



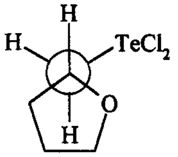
SCHEME 64



X = Cl: R = H, Me, Cl ;[130] X = Br: R = H[131]

SCHEME 65

The compound **43** ($n = 2$) and **44** exist in the conformation **46** whose stability is ensured by the intramolecular coordination between O and Te [130]. (Fig. 3)



46

FIGURE 3

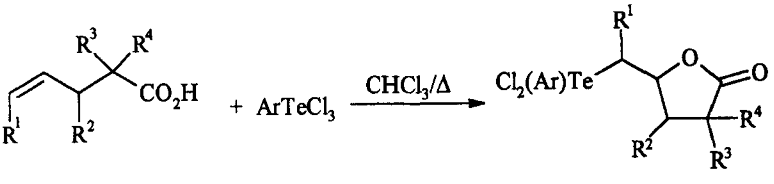
Attempts of cyclization of α- and β-hydroxyalkenes were unsuccessful giving rise to products of their oxidation. Thus, a treatment of 3-buten-1-ol with TeO_2 in acetic acid solution containing LiCl led to the triacetate **47** in 43% yield and elemental tellurium [130] (Scheme 66). Allylic alcohol reacts with TeO_2 analogously [130].

47

SCHEME 66

It should be mentioned that oxidation of 1,3-butadiene and its analogues in AcOH/LiBr solution affords mixtures of 1,2- and 1,4-diacetoxyalkenes [131].

These cyclization reactions, involving participance of aryltellurium trichlorides, were first studied with 2,2-diphenyl-4-pentenonic acid [132]. At a later time, the reaction was extended to various other aryltellurium trichlorides and γ-carboxyalkenes [42,133,134]. Refluxing the components in chloroform solution affords aryltellurium dichlorolacetones **48** in above 80% yields (Scheme 67).

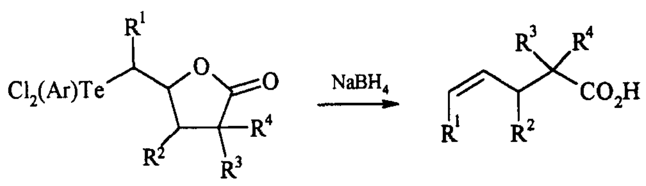


48

Ar = 4-$MeOC_6H_4$: $R^1 = R^2 = R^3 = R^4 = H$; $R^1 = R^2 = R^3 = H$, $R^4 = Me$; $R^1 = R^2 = H$, $R^3 = R^4 = Me$; $R^1 = R^2 = H$, $R^3 = R^4 = Ph$; $R^1 + R^2 = (CH_2)_2$, $R^3 = R^4 = H$; $R^1 + R^2 = (CH_2)_3$: $R^3 = R^4 = H$, Me; $R^3 = H$, $R^4 = Me$;[133] $R^1 = R^2 = H$, $R^3 = R^4 = Ph$: Ar = Ph, 4-$PhOC_6H_4$, 1-$C_{10}H_7$[42]; 2-$C_{10}H_7$[132]

SCHEME 67

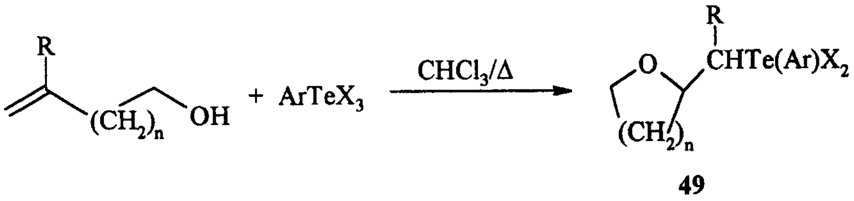
Reduction of tellurium dichlorides **48** with $NaBH_4$ (Scheme 68) restores the initial γ-carboxyalkenes which allows consideration of the process of aryltellurolactonization as a method for protection of unsaturated acids [134].



48

SCHEME 68

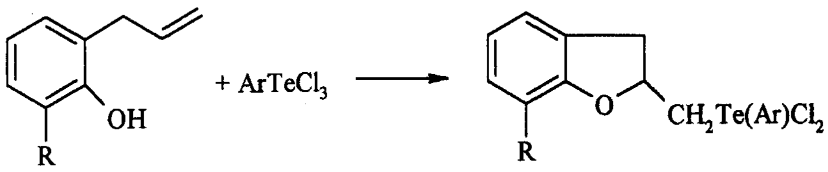
The σ-telluranes **49–52** were obtained in high yields by coupling aryltellurium trihalides with γ- or δ-hydroxyalkenes [134,135] under conditions similar to those used for preparation of the lactones **48** (Scheme 69, 70, Fig. 4).



49

R = H: n = 2: X = Cl: Ar = 4-MeC_6H_4, 4-$PhOC_6H_4$, 4-$MeOC_6H_4$; X = Br:
Ar = 4-$MeOC_6H_4$;
R = Me: n = 2: X = Cl: Ar = 4-$MeOC_6H_4$; R = H: n = 3: X = Cl: Ar = 4-$MeOC_6H_4$

SCHEME 69

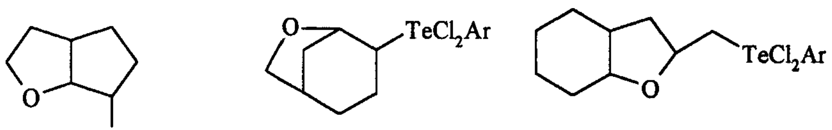


50

50 R = H, Me: Ar = 4-$MeOC_6H_4$: X = Cl

SCHEME 70

When β-hydroxyalkenes were entered into the reaction with aryltellurium trihalides instead of their γ- and δ-isomers only the products of addition at a double bond **53**



51 **52a** **52b**

51 Ar = 4-$MeOC_6H_4$: X = Cl, Br
52 Ar = 4-$PhOC_6H_4$ (**a**); Ar = 4-$MeOC_6H_4$ (**b**)

FIGURE 4

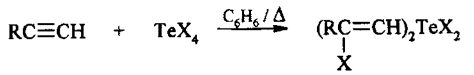
were formed in 85–91% yields [135] (Scheme 71) (Fig. 4).

53

Ar = 4-$MeOC_6H_4$, 4-$PhOC_6H_4$

SCHEME 71

2.2.3.2. *Reactions with Alkynes* The addition of tellurium tetrachloride to alkynes under neat conditions gives *Z*-β-chlorovinylaryltellurium trichlorides [136,137]. However, in severe conditions (refluxing in benzene solution) tellurium tetrachloride reacts with terminal alkynes giving di(β-chlorovinylaryl)tellurium dichlorides **54** in 57–70% yields [138,139] (Scheme 72). In the case of the tellurium tetrabromide reaction a mixture of *Z*- and *E*-isomers is obtained (*Z* : *E* ratio is 4.5 : 1 for R=Ph and 3.4 : 1 for R=C_5H_{11} [139].)



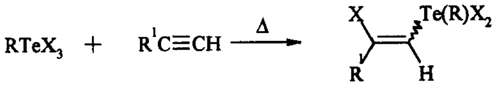
$$RC{\equiv}CH + TeX_4 \xrightarrow{C_6H_6/\Delta} (R\underset{X}{C}{=}CH)_2TeX_2$$

54

R=Ph : X=Cl,[138] Br;[139] R=C_5H_{11} : X=Br[139]

SCHEME 72

Long-term refluxing chloroform solutions of aryltellurium trichlorides and alkynes leaves the reactant intact, which leads to the conclusion about the inertness of alkynes in this reaction [136]. In more recent studies [138–142] it was found that refluxing solutions of terminal alkynes with organyltellurium trihalides resulted in regioselective addition of the latter to the triple bond of the alkynes with formation of the alkenes **55** in 60–85% yields [138–142] (Scheme 73).



55

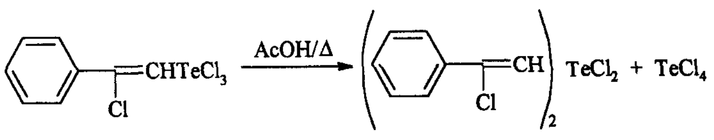
X=Cl : R=4-$MeOC_6H_4$: R^1=Bu,[138] $HOCH_2$,[138,140] C_6H_{11},[140] HO-c-C_6H_{10},[140] Ph;[138,140] 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$, 4-ClC_6H_4;[140] 4-BrC_6H_4[138,140]
X=Br : R=Ph, Bu : R^1=$HOCH_2$, C_5H_{11}, Ph[139]

SCHEME 73

In the case of the aryltellurium trichlorides reactions, the addition is stereoselective resulting in *Z*-isomers exclusively [140]. The addition of aryltellurium tribromides to alkynes in benzene solution results in mixtures of *Z*- and *E*-isomers (*Z* : *E* ratio is 5 : 1 for R=R^1=Ph and 1 : 1 for R=Bu, R^1=$HOCH_2$).

2.2.4. Reaction of Symmetrization of Organyltellurium Trichlorides

Organyltellurium trichlorides can be converted to diorganyltellurium dichlorides with the use of the symmetrization reaction. 2-Chloro-2-phenylvinyltellurium trichloride eliminates $TeCl_4$ when heating its acetic acid or ethanol solutions [136] (Scheme 74).



SCHEME 74

Other organyltellurium trichlorides are not susceptible to such types of spontaneous symmetrization reaction. Aryltellurium trichlorides afford symmetric diaryltellurium dichlorides only in the presence of a catalyst, powdered copper. The reaction occurs on refluxing of a benzene solution of an aryltellurium trichloride with the yields of diaryltellurium dichlorides in the range of 60–70% [143] (Scheme 75).

$$4\text{-}RC_6H_4TeCl_3 + Cu \xrightarrow[\text{-}TeCl_4]{C_6H_6/\Delta} (4\text{-}RC_6H_4)_2TeCl_2$$

R = OMe, OEt

SCHEME 75

When carrying out the reaction at higher temperature (refluxing a toluene solution) with an excess of copper, diaryltellurides were obtained as the result of reduction of their dichlorides. Transformation of aryltellurium trichlorides into diaryltellurium dichlorides can also be achieved with the use of organosilicon hydrides [144]. Stirring a 3 : 4 mixture of the latter with aryltellurium trichlorides for 6–8 h results in formation of diarylditellurides, whereas refluxing a 1 : 2 mixture of the reactants for 6–10 h affords diaryltellurium dichlorides in 75–95% yields (Scheme 76).

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

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

SCHEME 76

2.3. From Organic Derivatives of Di- and Tricoordinate Tellurium

Preparatively important for the synthesis of the σ-telluranes, R_2TeX_2, are the methods based on the use of diorganyltellurides and ditellurides and π-telluranes as starting materials.

2.3.1. From Diorganylditellurides

Reactions of diorganylditellurides resulting in σ-telluranes, R_2TeX_2, proceed in the majority of cases with elimination of the tellurium atom. This takes place upon interaction between diarylditellurides and tellurium tetrahalides [145] and also upon interaction between diarylditellurides and tellurium trihalides [145] (the yields of diaryltellurium dihalides are 78–95%) (Schemes 77, 78).

$$Ar_2Te_2 + TeX_4 \xrightarrow{PhMe/\Delta} Ar_2TeX_2 + Te$$

Ar = 4-$MeOC_6H_4$, 4-$EtOC_6H_4$; X = Cl, Br, I

SCHEME 77

$$Ar_2Te_2 + ArTeX_3 \xrightarrow{PhMe/\Delta} Ar_2TeX_2 + Te$$

Ar = 4-$MeOC_6H_4$, 4-$EtOC_6H_4$; X = Cl

SCHEME 78

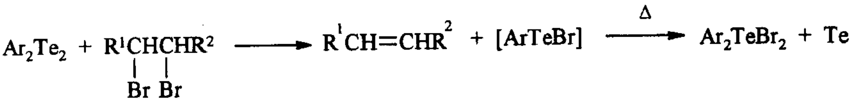
Elimination of the tellurium atom and formation of diorganyltellurium difluorides is also observed upon oxidation of diarylditellurides with SF_4 [146]. The yields of the difluorides exceed 70% (Scheme 79).

$$Ar_2Te_2 + SF_4 \xrightarrow{C_6H_6/\Delta} Ar_2TeF_2$$

Ar = Ph, 4-$MeOC_6H_4$

SCHEME 79

The high halogenophilicity of diarylditellurides allows their employment for the dehalogenation of vicinal dibromides [145]. Refluxing of an equimolar mixture of diarylditellurides and organic dihalides in toluene or acetic acid leads to the (*E*)-isomers of the corresponding alkenes in 68–90% yields and diaryltellurium dibromides in 75–95% yields. The reaction probably proceeds *via* an arenetellurenyl bromide intermediate with subsequent disproportionation to a diaryltellurium dibromide and elemental tellurium (Scheme 80).



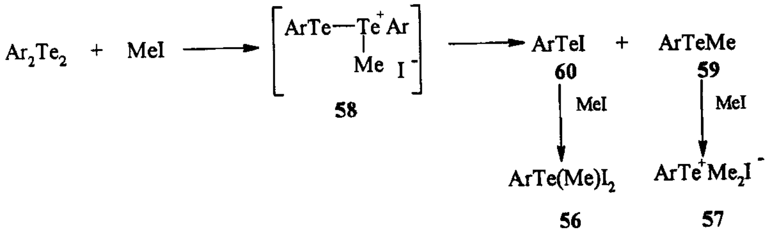
$$Ar_2Te_2 + R^1\underset{Br}{CH}\underset{Br}{CH}R^2 \longrightarrow R^1CH{=}CHR^2 + [ArTeBr] \xrightarrow{\Delta} Ar_2TeBr_2 + Te$$

Ar = 4-$MeOC_6H_4$, 4-$EtOC_6H_4$; $R^1 = R^2$ = H, Ph, CO_2H; R^1 = Ph, $R^2 = CO_2H$

SCHEME 80

Treatment of diorganylditellurides with excess methyliodide leads to an equimolar mixture of arylmethyltellurium diiodide **56** and aryldimethyltelluronium iodide

57 [74,147,148]. The first stage of the reaction is probably methylation of the ditelluride leading to the intermediate aryltelluromethylaryltelluronium iodide **58** which decomposes subsequently to an arylmethyl telluride and an arenetellurenyl iodide **60**. Subsequent reaction of the compounds formed and the excess of methyliodide gives rise to **56** and **57** as shown in the Scheme 81 (the yields of compounds were not given).



$Ar = 4\text{-}MeC_6H_4$,[148] $4\text{-}MeOC_6H_4$,[74, 147, 148] $4\text{-}EtOC_6H_4$[148]

SCHEME 81

The reaction of dibenzylditelluride with bromine in CCl_4 leads to cleavage of both C–Te bonds with formation of benzylbromide and tellurium tetrabromide. When an equivalent amount of bromine is used, elimination of one tellurium atom occurs and dibenzyltellurium dibromide is formed in 72% yield [149] (Scheme 82).

$$C_6H_5CH_2Br + TeBr_4 \xleftarrow{2Br_2} (C_6H_5CH_2)_2Te_2 \xrightarrow{Br_2} (C_6H_5CH_2)_2TeBr_2 + Te$$

SCHEME 82

The reaction of Ar_2Te_2 with aryldiazonium salts is probably a quite promising approach to the synthesis of unsymmetric σ-telluranes $ArAr^1TeX_2$ **61** [150,151]. Interaction of diphenylditelluride with *p*-bromophenyldiazonium bromide in aqueous acetone gave a high yield of an equimolar mixture of phenyl *p*-bromophenyltelluride and the corresponding Te-dibromide **61** (X=Br) [151] (Scheme 83).

$$Ph_2Te_2 + 2\,(4\text{-}BrC_6H_4N_2^+Br^-) \xrightarrow[-N_2]{} PhTeC_6H_4Br\text{-}4 + \underset{\textbf{61}}{PhTeBr_2C_6H_4Br\text{-}4}$$

SCHEME 83

This suggests that Ar_2Te_2 are effective one-electron reduction agents for aryldiazonium cations and the following mechanism of the above reaction has been postulated [151] (Scheme 84).

$$\begin{aligned} Ar_2Te_2 + Ar^1N_2^+X^- &\longrightarrow Ar^{1\bullet} + ArTe^{\bullet} + ArTeX + N_2 \\ Ar^{1\bullet} + ArTe^{\bullet} &\longrightarrow ArTeAr^1 \\ ArTeX + Ar^1N_2^+X^- &\longrightarrow ArTeX_2Ar^1 + N_2 \end{aligned}$$

SCHEME 84

However, this reaction leads to a mixture of two compounds which require separation or the chemical transformation into one certain derivative (by reduction of the dihalide or the oxidation of the telluride) and thus this is inconvenient as a preparative method. As long as the copper(II) salts readily oxidize the tellurides to the corresponding dihalides, the interaction between Ar_2Te_2 and a diazonium salt in the presence of two moles of copper(II) halide produces the corresponding diaryltellurium dihalide as a sole product in good (60–90%) yields [151] (Scheme 85). The availability of the starting materials and the possibility to vary the substituents in both reaction components, as well as the ease with which the dihalides can be transformed to the corresponding tellurides, make this method one of the most suitable for the preparation of unsymmetric diaryltellurides.

$$(R^1C_6H_4)_2Te_2 + R^2C_6H_4N_2X + Cu \xrightarrow[\substack{-N_2 \\ -CuX}]{} \underset{\mathbf{61}}{R^1C_6H_4TeX_2C_6H_4R^2}$$

X=Cl: R^1=H: R^2=H, 4-OMe, 3-OMe, 4-Me, 3-Me, 2-Me, 4-F, 3-F, 4-Cl, 4-Br;
$R^1 = R^2$ = 4-OMe
X = Br: R^1 = H: R^2 = H, 4-Cl, 4-Br, 3,4-C_4H_4

SCHEME 85

This reaction has been employed in the synthesis of arylvinyltellurium dichlorides [151] (Scheme 86).

$$(RC_6H_4)_2Te_2 + [PhC(Cl){=}CH]_2Te_2 + CuCl_2 \xrightarrow[\substack{-N_2 \\ -CuCl}]{} RC_6H_4TeCl_2CH{=}C(Cl)Ph$$

R = H (65%), 4-Me (39%)

SCHEME 86

The use of diazonium tetrafluoroborates, instead of chlorides, in the synthesis of non-symmetric diaryltellurium dihalides allows one to work with lesser volumes of the solutions and to minimize the competing Sandmeyer reaction [151]. The yields of diaryltellurium dihalides are 58–95% (Scheme 87).

$$(R^1C_6H_4)_2Te_2 + R^2C_6H_4N_2BF_4 + CuX_2 \xrightarrow[\substack{-N_2 \\ -CuBF_4}]{} \underset{\mathbf{61}}{R^1C_6H_4TeX_2C_6H_4R^2}$$

X = Cl: R^1 = 4-F: R^2 = 4-Me, 4-OMe, 4-Br
X = Br: R^1 = H: R^2 = 2-Br

SCHEME 87

2.3.2. *From Diorganyltellurides*

A good number of diorganyltellurium dihalides has been obtained from the oxidation addition reactions of diorganyltellurides with halogens or their synthetic equivalents

[18,39,40,44,49,52,56,79,82,84,136,149,152–217] (Scheme 88). This method is of special importance for the preparation of tellurium dibromides and diiodides that are less accessible from other methods. The reactions are usually performed in benzene, methylene chloride, chloroform or tetrachloromethane solutions. The formed diorganyltellurium dihalides precipitate from these solutions in a sufficiently pure state. Due to the exothermic character of these reactions external cooling is required when dealing with large amounts of the reactants. With fluorine the reactions are performed with mixing under an excess of an inert gas at – 70 to – 80°C [194].

$$R^1R^2Te + X_2 \longrightarrow R^{1R2}TeX_2$$

X = F: $R^1 = R^2 =$ Me,[194, 197] Ph,[194] 2,6-$Me_2C_6H_3$;[208] R^1 = Me, R^2 = Ph[194]

X = Cl: $R^1 = R^2 = CF_3$,[196] C_2F_5,[195] $C_{16}H_{33}$,[18] 2-C_4H_3S,[169] C_6F_5,[216] 4-FC_6H_4,[79] 4-ClC_6H_4,[79, 214] 4-BrC_6H_4,[79] Ph,[154, 168, 173, 177-179, 183, 189, 216] 4-MeC_6H_4,[177, 216] 3-MeC_6H_4,[79, 158, 177] 2-MeC_6H_4,[177, 216] $PhCH_2$,[216] 4-$MeOC_6H_4$,[159,216] 3-$MeOC_6H_4$,[165] 2-$MeOC_6H_4$,[166] 2-$HOCH_2C_6H_4$ [184] 4-$EtOC_6H_4$,[82,164] 2-$EtOC_6H_4$,[162] 2,4-$Me_2C_6H_3$,[156] 2,5-$Me_2C_6H_3$,[156] 2,6-$Me_2C_6H_3$,[208] 2,4,6-$Me_3C_6H_2$,[157] 1-$C_{10}H_7$,[154, 163, 173] 2-$C_6H_4CH{=}NPh$[191, 193]

R^1 = Ph: R^2 = Et,[199] c-C_6H_{11},[181] CH_2CH_2OMe, CH_2CH_2OEt;[199] 4-ClC_6H_4,[183] 4-MeC_6H_4, [160, 183] 2-MeC_6H_4,[167] 4-$MeOC_6H_4$,[44] 4-$Me_2NC_6H_4$,[185] 4-$PhOC_6H_4$,[44,175] 1-$C_{10}H_7$,[44] 2-$C_{10}H_7$;[44, 174] $C_{11}H_{23}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $Ph(CH_2)_2$, $Ph(CH_2)_3$, $C_{12}H_{25}CHMe$[215]

R^1 = 3-FC_6H_4, 4-FC_6H_4: R^2 = Me[186]

R^1 = 4-ClC_6H_4: R^2 = 4-$Me_2NC_6H_4$[185]

R^1 = 4-BrC_6H_4: R^2 = Me,[180] 4-$Me_2NC_6H_4$[185]

R^1 = 3-BrC_6H_4: R^2 = 4-$Me_2NC_6H_4$[185]

R^1 = 3-$O_2NC_6H_4$: R^2 = 4-$Me_2NC_6H_4$[185, 187]

R^1 = 4-MeC_6H_4: R^2 = Me,[180] CH_2CH_2OMe, CH_2-CH_2OEt;[199] c-C_6H_{11},[181] 4-$Me_2NC_6H_4$[185, 187]

R^1 = 3-MeC_6H_4: R^2 = 4-$Me_2NC_6H_4$[187]

R^1 = 2-MeC_6H_4: R^2 = Me[211]

R^1 = 4-$MeOC_6H_4$: R^2 = Et, $PhCH_2$;[49] 4-$Me_2NC_6H_4$;[185] 1-$C_{10}H_7$, 2-$C_{10}H_7$[44]

R^1 = 2-$HOCC_6H_4$: R^2 = Bu, Me[211]

R^1 = 2-$HOCH_2C_6H_4$: R^2 = Bu[203]

R^1 = 2-MeCOPh : R^2=Me[212]

R^1 = 2-$EtO_2CC_6H_4$: R=Bu[211]

R^1 = 4-$EtOC_6H_4$: R^2 = c-C_6H_{11},[181] 4-$Me_2NC_6H_4$,[185] 1-$C_{10}H_7$,[175] 2-$PhN{=}NC_6H_4$[52]

R^1 = 2-$Me_2NCH_2C_6H_4$: R^2 = Me, Et, Bu[56]

R^1 = 4-$PhOC_6H_4$: R^2 = 4-$Me_2NC_6H_4$;[185] 1-$C_{10}H_7$, 2-$C_{10}H_7$[44]

R^1 = 2-$C_{10}H_7$: R^2 = Et,[174] c-C_6H_{11},[49, 174] 1-$C_{10}H_7$[44]

R^1 = 2-formylcyclohexene-1-yl-1: R^2 = Me[209]

X = Br: R^1 = R^2 = CF$_3$,[196] CH$_2$=CH,[188] CH$_2$CH$_2$CN,[176] 2-C$_4$H$_3$S,[169] C$_6$F$_5$,[216] 4-BrC$_6$H$_4$, [39, 79, 161] 3-BrC$_6$H$_4$,[79] 4-ClC$_6$H$_4$,[79, 161, 214] 3-ClC$_6$H$_4$,[79] 4-FC$_6$H$_4$,[79] Ph,[40, 79, 152, 167, 168, 190, 207, 216] 4-MeC$_6$H$_4$,[79,152,153,155,216] 3-MeC$_6$H$_4$,[79, 158] 2-MeC$_6$H$_4$,[153, 155, 167, 216] PhCH$_2$,[149, 216] 4-MeOC$_6$H$_4$, [39, 73, 79, 159, 216] 3-MeOC$_6$H$_4$,[165, 190] 2-MeOC$_6$H$_4$,[166] 4-EtOC$_6$H$_4$,[79, 82, 164] 2-EtOC$_6$H$_4$,[162] 2,4-Me$_2$C$_6$H$_3$,[156] 2,5-Me$_2$C$_6$H$_3$,[156] 2,6-Me$_2$C$_6$H$_3$,[208] 4-Me$_2$NC$_6$H$_4$,[79,185,187] 2,4,6-Me$_3$C$_6$H$_2$,[157] 4-Me$_2$CHC$_6$H$_4$,[192] 1-C$_{10}$H$_7$[154, 163]

R^1=Bu : R^2=PhC$\equiv$C, C$_5$H$_{11}$C$\equiv$C[201]

R^1 = 4-BrC$_6$H$_4$: R^2 = 4-Me$_2$NC$_6$H$_4$[79, 185]

R^1 = 4-ClC$_6$H$_4$: R^2 = 4-Me$_2$NC$_6$H$_4$[185]

R^1 = 3-BrC$_6$H$_4$: R^2 = 4-Me$_2$NC$_6$H$_4$[185]

R^1 = 3-FC$_6$H$_4$, 4-FC$_6$H$_4$: R^2 = Me[186]

R^1 = Ph: R^2 = Me,[190] Bu,[180, 182] CH$_2$CH$_2$CO$_2$H,[198] 4-MeC$_6$H$_4$,[160, 181] 2-MeC$_6$H$_4$,[167] 4-MeOC$_6$H$_4$,[44] 4-EtOC$_6$H$_4$,[181] 4-Me$_2$NC$_6$H$_4$;[79, 185] 4-PhOC$_6$H$_4$, 1-C$_{10}$H$_7$, 2-C$_{10}$H$_7$;[44] C$_{11}$H$_{23}$, C$_{12}$H$_{25}$, C$_{14}$H$_{29}$, C$_{16}$H$_{33}$, Ph(CH$_2$)$_2$, Ph(CH$_2$)$_3$, C$_{12}$H$_{25}$CHMe[215]

R^1 = 4-MeC$_6$H$_4$: R^2 = CH$_2$CH$_2$CO$_2$H,[198] 4-Me$_2$NC$_6$H$_4$[187]

R^1 = 4-MeOC$_6$H$_4$: R^2 = Et,[49] 4-Me$_2$NC$_6$H$_4$;[79, 185] 1-C$_{10}$H$_7$, 2-C$_{10}$H$_7$[44]

R^1 = 2-OHCC$_6$H$_4$: R^2 = Bu[202, 210]

R^1 = 2-OHCH$_2$C$_6$H$_4$: R^2 = Bu[202, 203]

R^1 = 2,6-Me$_2$C$_6$H$_3$: R^2 = 2,4,6-Me$_3$C$_6$H$_2$[208]

R^1 = 4-EtOC$_6$H$_4$: R^2 = CH$_2$CH$_2$CO$_2$H,[198] 4-Me$_2$NC$_6$H$_4$,[185] 2-PhN=NC$_6$H$_4$[52]

R^1 = 2-C$_4$H$_3$S-3-(2-pyridyl): R^2 = Me[200]

R^1 = 2-Me$_2$NCH(Me)C$_6$H$_4$: R^2 = Me[205]

R^1 = 4-PhOC$_6$H$_4$: R^2 = 4-Me$_2$NC$_6$H$_4$;[185] 1-C$_{10}$H$_7$, 2-C$_{10}$H$_7$[44]

R^1 = 2-C$_{10}$H$_7$: R^2 = Et,[174] c-C$_6$H$_{11}$,[49] 1-C$_{10}$H$_7$[44]

R^1 = 2-(4-PhC$_6$H$_4$CONH)C$_6$H$_4$: R^2 = Bu[204]

R^1=2-R^{3}C$_6$H$_4$NHN=CHC$_6$H$_4$ (R^3=H, 2,4-(NO)$_2$) : R^2=Bu[217]

R^1 = 4-BrC$_6$H$_4$CH=CHCHO: R^2 = Me[213]

R^1 = 2-formylcyclohexen-1-yl-1: R^2 = Me[209, 213]

X = I: R^1 = R^2 = Me,[172] Bu,[170] C$_5$H$_{11}$,[171] 2-C$_4$H$_3$S,[169] C$_{16}$H$_{33}$,[206] 4-BrC$_6$H$_4$,[39, 79] 4-ClC$_6$H$_4$,[79, 214] 4-MeC$_6$H$_4$,[79, 214, 216] 3-MeC$_6$H$_4$,[158] 2-MeC$_6$H$_4$,[216] 4-MeOC$_6$H$_4$,[79, 159, 187, 206, 214] 3-MeOC$_6$H$_4$,[165] 2-MeOC$_6$H$_4$,[166] 2,4-Me$_2$C$_6$H$_3$,[156] 2,5-Me$_2$C$_6$H$_3$,[156] PhC(Cl)=CH,[136] 4-EtOC$_6$H$_4$, [79, 82, 164] 2-EtOC$_6$H$_4$,[162] 4-Me$_2$NC$_6$H$_4$,[79] 2,4,6-Me$_3$C$_6$H$_2$,[157] 1-C$_{10}$H$_7$[163]

R^1 = 4-BrC$_6$H$_4$: R^2 = 4-Me$_2$NC$_6$H$_4$[79, 185]

$R^1 = 3\text{-}BrC_6H_4$: $R^2 = 4\text{-}Me_2NC_6H_4$[185]

$R^1 = 4\text{-}ClC_6H_4$: $R^2 = 4\text{-}Me_2NC_6H_4$[185]

$R^1 = 3\text{-}FC_6H_4$, $4\text{-}FC_6H_4$: $R^2 = Me$[186]

$R^1 = 2\text{-}H_2NC_6H_4$: $R^2 = Bu$[204]

$R^1 = Ph$: $R^2 = Me$;[182] Et, Pr, Pr^i, Bu, $C_{14}H_{29}$;[182] $4\text{-}MeC_6H_4$,[160] $2\text{-}MeC_6H_4$,[167] $4\text{-}MeOC_6H_4$,[44] $4\text{-}Me_2NC_6H_4$,[79, 185] $4\text{-}PhOC_6H_4$;[44] $1\text{-}C_{10}H_7$, $2\text{-}C_{10}H_7$;[44] $C_{11}H_{23}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $Ph(CH_2)_2$, $Ph(CH_2)_3$, $C_{12}H_{25}CHMe$[215]

$R^1 = 4\text{-}MeC_6H_4$: $R^2 = 4\text{-}Me_2NC_6H_4$[185]

$R^1 = 4\text{-}MeOC_6H_4$: $R^2 = Et$,[49] $4\text{-}Me_2NC_6H_4$;[79, 84, 185] $1\text{-}C_{10}H_7$, $2\text{-}C_{10}H_7$[44]

$R^1 = 2\text{-}OHCH_2C_6H_4$: $R^2 = Bu$[203]

$R^1 = 4\text{-}EtOC_6H_4$: $R^2 = 4\text{-}Me_2NC_6H_4$[84, 185]

$R^1 = 4\text{-}Me_2NC_6H_4$: $R^2 = 4\text{-}PhOC_6H_4$[84, 185]

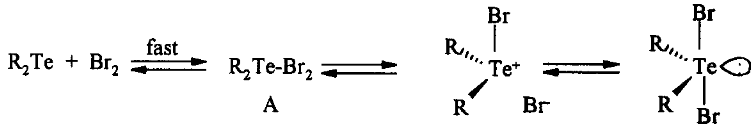
$R^1 = 1\text{-}C_{10}H_7$: $R^2 = 2\text{-}C_{10}H_7$, $4\text{-}PhOC_6H_4$[44]

$R^1 = 2\text{-}C_{10}H_7$: $R^2 = Et$,[174] $c\text{-}C_6H_{11}$,[49] $4\text{-}PhOC_6H_4$[44]

R^1=2-formylcyclohexen-1-yl-1 : R^2=Me[209]

SCHEME 88

The kinetics of the oxidation–addition reactions of bromine [207] and iodine [206] with diorganyl tellurides was studied and the mechanism of the reactions was found to be represented by a three-step process. The rapidly formed charge–transfer complex A converts to the products through elimination–addition of a bromide anion [207] (Scheme 89).



SCHEME 89

With iodine, the reaction mechanism is more complicated [206]. The η^1-type complexes $R_2Te\text{-}I_2$ and $R_2Te\text{-}I_4$ formed at the first stage of the reaction dissociate to give telluronium intermediates which then add an iodide anion and convert to diorganyltellurium diiodides. Both reactions are accelerated with an increase in the solvent polarity, consistent with partial charge separation in both processes [206] (Scheme 90).

$$R_2Te + I_2 \rightleftharpoons R_2Te...I\text{-}I$$

$$R_2Te...I\text{-}I + I_2 \rightleftharpoons R_2Te\text{-}I...I\text{-}I\text{-}I$$

$$R_2Te\text{-}I...I\text{-}I\text{-}I \rightleftharpoons \text{products}$$

SCHEME 90

Diorganyltellurides with two tellurium atoms undergo oxidation–addition reactions with halogens in which both telluriums participate to give the σ-telluranes **62** in 72–98% yields [218–220] (Scheme 91).

$$\mathrm{RTe{-}A{-}TeR} + \mathrm{X_2} \longrightarrow \underset{\mathbf{62}}{\mathrm{X_2(R)Te{-}A{-}Te(R)X_2}}$$

A = CH_2: R = Me, Ph: X = Cl, Br, I[218]

A = p-C_6H_4-p: R = Me: X = Br; R = Et: X = Cl[219]

A = o-C_6H_4-o: X = Cl: R = Me, Et, Bu[220]

SCHEME 91

Instead of gaseous chlorine, sulfuryl chloride [44,49,56,79,173,174,181,185,186,189, 191,193,201,216] and, more rarely, thionyl chloride [18,44] have been employed for the preparation of tellurium dichlorides. For the synthesis of tellurium dibromides [84] and tellurium difluorides [195], one can use sulfuryl bromide and XeF_2, respectively. ClF is less preferable as a fluorinating agent. The interaction of this compound with di(perfluoroethyl)telluride does not lead to pure $(C_2F_5)_2TeF_2$ as it was mistakenly noted [221], but to a mixture of the latter compound with $(C_2F_5)TeClF$ and $(C_2F_5)TeCl_2$ [195]. In some cases the oxidation–addition reactions are accompanied by fission of a Te–C bond. This is the case, for instance, in the reaction of arylbenzyltellurides with halogens and SO_2Cl_2 in which one benzyl group is expended with the formation of benzylhalide [49] (Scheme 92) (the yields of reaction products are not given). At the same time the reaction of dibenzyltelluride with bromine in tetrachloromethane solution affords dibenzyltellurium dibromide [149,216].

$$\mathrm{ArTeCH_2Ph} + \mathrm{X_2(SO_2Cl_2)} \longrightarrow \mathrm{ArTeX_3} + \mathrm{PhCH_2X}$$

Ar = 4-$MeOC_6H_4$, 2-$C_{10}H_7$; X=Cl, Br, I

SCHEME 92

Other examples of reactions of arylalkyltellurides accompanied by scission of Te–C bonds under the action of halogens or SO_2Cl_2 resulting in aryltellurenyl halides pertain to the compounds with intramolecular coordination N(O)→Te bonds. This chemistry has been reviewed recently [222].

Reactions of diorganyltellurides with metal halides lead, depending on the nature of metal and reaction conditions, to either adducts of the components or diorganyltellurium dihalides. These reactions have been reviewed previously [223]. Thus, on heating in a sealed ampule an acetic acid solution of di(4-methylphenyl)telluride containing Fe(III), Cu(II) or Hg(II) chlorides, di(4-methylphenyl)tellurium dichloride was formed in high yields [224]. When hydrates of these salts, e.g. $FeCl_3 \cdot 6H_2O$, were used in these reactions *bis*(diarylchlorotellurium) oxide [$(Ar_2TeCl_2)_2O$] was formed as the result of hydrolysis of the tellurium dichloride [224]. Heating water–acetone solutions of diaryltellurides with Cu(II) halides affords diaryltellurium dihalides in almost quantitative yields [151] (Scheme 93).

$$Ar_2Te + CuX_2 \xrightarrow[-CuX]{H_2O/Me_2CO/\Delta} Ar_2TeX_2$$

$X = Cl, Br$: $Ar = 4\text{-}MeC_6H_4$

SCHEME 93

On oxidation of diethyltelluride with $CuCl_2$ a 1 : 1 complex formed by the telluride and CuCl was isolated along with diethyltellurium dichloride [225] (the yields were not given) (Scheme 94).

$$Et_2Te + CuCl_2 \xrightarrow{EtOH/\Delta} Et_2TeCl_2 + Et_2Te{\cdot}CuCl$$

SCHEME 94

Diaryltellurium difluorides were obtained by oxidation–addition reactions of fluorine with diaryltellurides and by exchange reactions between diaryltellurides and *tris*(4-methylphenyl)bismuth difluoride [226–228] (Scheme 95) (the yields were not given).

$$Ar_2Te + (4\text{-}MeC_6H_4)_3BiF_2 \xrightarrow[-(4\text{-}MeC_6H_4)_3Bi]{} Ar_2TeF_2$$

$Ar = 4\text{-}MeC_6H_4$,[226] $4\text{-}MeOC_6H_4$,[227] $1\text{-}C_{10}H_7$[228]

SCHEME 95

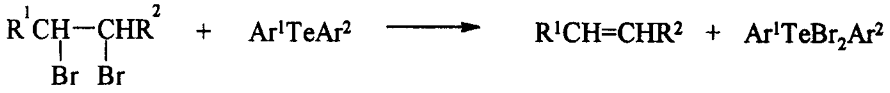
The reaction with the triarylbismuth difluoride has no preparative significance. The most convenient method for preparation of diaryltellurium difluorides consists of passing gaseous sulfur tetrafluoride through boiling benzene solutions of diaryltellurides (the yields are 87–92%) [146] (Scheme 96).

$$Ar_2Te + SF_4 \xrightarrow{C_6H_6/\Delta} Ar_2TeF_2$$

$Ar = Ph, 4\text{-}MeOC_6H_4$

SCHEME 96

The considerable ability of tellurides to add halogens with formation σ-telluranes of the type R_2TeX_2 allows their use as dehalogenation agents in the synthesis of alkenes from the appropriate organic dihalides. Vicinal [229–231] and geminal [232] dibromides have been converted to the corresponding alkenes in quite high yields by treatment with diaryltellurides [229,231] (Scheme 97) or with their cyclic analog phenoxatellurine [230,232].



$$R^1CH(Br)-CH(Br)R^2 + Ar^1TeAr^2 \longrightarrow R^1CH{=}CHR^2 + Ar^1TeBr_2Ar^2$$

R^1=R^2=Ph[229, 231]

R^1=R^2=cholesterol[229]

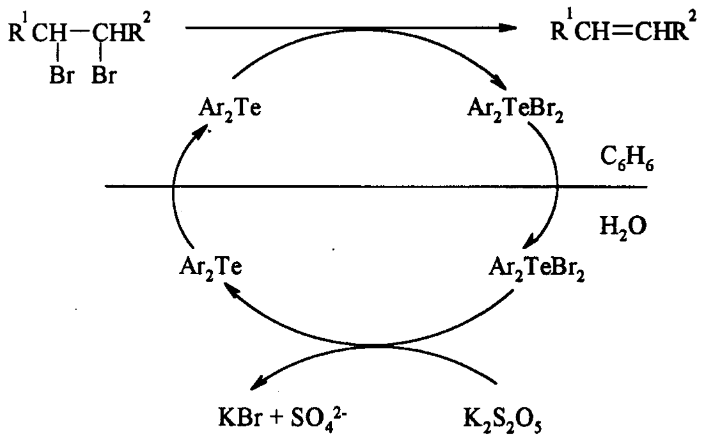
R^1=Ph : R^2=CO$_2$H,[229] CO$_2$Et,[231] COPh,[231] 4-pyridyl[231]

Ar^1=Ar^2=Ph,[229] 4-MeOC$_6$H$_4$[231]

Ar^1=4-MeOC$_6$H$_4$, Ar^2=1-C$_{10}$H$_7$, 2-C$_{10}$H$_7$[229]

SCHEME 97

The possibility to use catalytic amounts of diaryltellurides [231] (5 mol% of quantity of halogenated substrate in the case of *bis*(4-methoxyphenyl)telluride) is of special interest in preparative respects. Such processes have been carried out in two-phase systems (benzene–water) and the tellurium dibromide formed was regenerated to telluride with potassium metabisulfite which itself was unable to reduce vicinal dibromides. Scheme 98 illustrates this procedure.

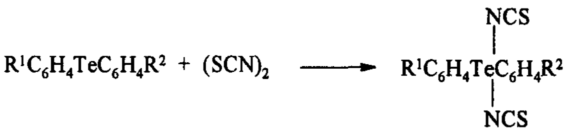


SCHEME 98

The rate of the debromination reactions of vicinal dibromides is a function of the electronic demands of diaryltellurides. Thus the debromination reactions of 1,2-dibromo-1,2-diphenylethane with (4-RC$_6$H$_4$)$_2$Te (R=Cl, H, OMe, NMe$_2$) in refluxing chloroform have half-lives of 120, 15, 9 and 2 h, respectively [214]. In this way the more electron-rich diaryltellurides result in faster debromination.

Oxidation–addition reactions can be also applied for the synthesis of σ-telluranes of the type R$_2$TeX$_2$ in which X$\neq$halogen. Thus diaryltellurium diisothiocyanates were obtained in 70–100% yields by oxidative addition of rhodane to diaryltellurides

[233–237] (Scheme 99).



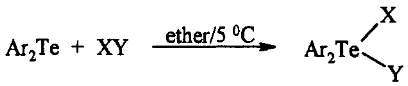
$$R^1C_6H_4TeC_6H_4R^2 + (SCN)_2 \longrightarrow R^1C_6H_4\underset{NCS}{\overset{NCS}{Te}}C_6H_4R^2$$

$R^1 = R^2 = H$,[233,235-237] 4-Me,[233] 4-OMe,[233,235-237] 4-OEt,[235,236] 4-Br[233]

$R^1 = H$; R^2 = 3-F, 4-F[234]

SCHEME 99

Diaryltellurium mixed halides and halide/pseudohalides **63** were obtained in 80–100% yields by oxidative addition reactions of diaryltellurides with iodine monohalides and cyanogen halides, correspondingly [237] (Scheme 100).



63

Ar = Ph, 4-MeOC$_6$H$_4$; X = I: Y = Cl, Br, CN; X = Br, Y = CN

SCHEME 100

The oxidation of diorganyltellurides with lead tetraacetate at room temperature leads to diorganyl tellurium diacetates **64** in 90–98% yields [18,238,239] (Scheme 101).

$$R^1R^2Te + Pb(OAc)_4 \xrightarrow[-Pb(OAc)_2]{} \underset{\mathbf{64}}{R^1R^2Te(OAc)_2}$$

$R^1=R^2=Ph$;[238,239] C_6F_5, 4-MeC$_6$H$_4$;[238] 4-MeOC$_6$H$_4$, 4-EtOC$_6$H$_4$;[238,239] $C_{16}H_{33}$;[18]

$R^1=Ph$, R^2=4-EtOC$_6$H$_4$[239]

SCHEME 101

Interaction between diaryltellurides, carboxylic acid and hydrogen peroxide in chloroform provides a convenient synthetic route to diaryltellurium dicarboxylates of the type **64** containing various acyloxy groups in 82–92% yields [240] (Scheme 102). The reaction proceeds via formation of a diaryltelluroxide intermediate. It is known [18,187,241–244] that interaction between telluroxides and carboxylic acids gives rise to σ-telluranes $Ar_2Te(OCOR)_2$.

$$Ar_2Te + H_2O_2 \xrightarrow[-H_2O]{} [Ar_2Te{=}O] \xrightarrow[-H_2O]{RCOOH} \underset{\mathbf{64}}{Ar_2Te(OCOR)_2}$$

Ar=Ph : R=Me, CH$_2$Cl, Ph; Ar=4-MeC$_6$H$_4$: R=Me, Ph; Ar=4-MeOC$_6$H$_4$: R=CH$_2$Cl

SCHEME 102

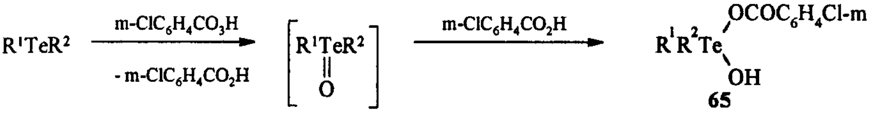
Undoubtedly telluroxides are also intermediates in the reaction of tellurides with benzoyl peroxide leading to diorganyltellurium dibenzoates [170,171] (Scheme 103). The preparation of diaryl tellurium dicarboxylates **64** starting from diaryltelluroxides and carboxylic acid anhydrides [18,208,241,242,245] confirms this assumption.

$$R^1TeR^2 + (PhCOO)_2 \xrightarrow[-(PhCO)_2O]{} [R^1(R^2)Te{=}O] \xrightarrow{(PhCO)_2O} \underset{\mathbf{64}}{R^1(R^2)Te(OCOPh)_2}$$

R^1=Bu : R^2=CH_2CO_2-1-menthyl;[170] R^1=C_5H_{11} : R^2=CH_2CO_2Et[171]

SCHEME 103

However, the reaction of tellurides with an equivalent amount of *m*-chloroperoxybenzoic acid gave σ-tellurane **65** [246] (Scheme 104). In this case the initially formed telluroxide reacts with one equivalent of carboxylic acid, formed in the oxidation of the telluride, to give the σ-tellurane **65** (the yield was not given).



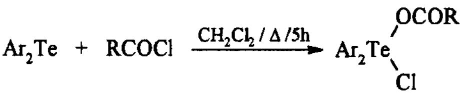
$$R^1TeR^2 \xrightarrow[-\,m\text{-}ClC_6H_4CO_2H]{m\text{-}ClC_6H_4CO_3H} \left[\begin{array}{c} R^1TeR^2 \\ \| \\ O \end{array}\right] \xrightarrow{m\text{-}ClC_6H_4CO_2H} R^1R^2Te\begin{array}{l} \diagup OCOC_6H_4Cl\text{-}m \\ \diagdown OH \end{array}$$

65

R^1=Ph, R^2=c-C_6H_{13}

SCHEME 104

The representative of another type of mixed σ-telluranes, namely, di(4-methoxyphenyl)(3,5-dinitrobenzoyloxy)tellurium chloride **66** was obtained by the oxidation–addition reaction of 3,5-dinitrobenzoyl chloride to di(4-methoxyphenyl)telluride (the yield was not given) [247] (Scheme 105). Benzoyl chloride does not enter this type of reaction.



$$Ar_2Te + RCOCl \xrightarrow{CH_2Cl_2/\Delta/5h} Ar_2Te\begin{array}{l} \diagup OCOR \\ \diagdown Cl \end{array}$$

66

Ar=4-$MeOC_6H_4$, R=3,5-$(NO_2)_2C_6H_3$

SCHEME 105

A "telluroxide" intermediate can also explain the results of the reactions between tellurides and dilute nitric acid that lead to diorganyltellurium dinitrates [248] (also referred to as diorganyl tellurium hydroxynitrates $R_2Te(OH)(ONO_2)$ [170]) (Scheme 106).

$$R_2Te + HONO_2 \longrightarrow R_2Te(ONO_2)_2$$

R=Ph, 4-MeC_6H_4

SCHEME 106

The oxidation–addition reactions can also be applied to the synthesis of diorganyltellurium dithiocarbamates **67**. Thus, dimethyltellurium dithiocarbamates were obtained in yields 85–93% by coupling of dimethyltelluride and thiuram disulfides [249] (Scheme 107).

$$\mathrm{Me_2Te} + [\mathrm{R_2NC(S)S}]_2 \underset{\Delta}{\overset{\mathrm{CHCl_3\,/\,0\text{-}23^{\circ}C}}{\rightleftharpoons}} \underset{\mathbf{67}}{\mathrm{Me_2Te[SC(S)NR_2]_2}}$$

R=Me, Et, $\mathrm{Pr^i}$, Ph

SCHEME 107

2.3.3. *From π-Telluranes*

σ-Telluranes of the type R_2TeX_2 where X=Hal or OCOR may be obtained starting from π-telluranes (telluronium ylides, imides and oxides).

The reaction of diorganyltelluroxides with protonic acids containing sufficiently nucleophilic anions (HHal, RCOOH) is an important method for preparation of diorganyltellurium dicarboxylates (the yields are 56–98% [18,187,241–244]) (Scheme 108).

$$\mathrm{Ar_2TeO} + \mathrm{RCOOH} \xrightarrow[-\mathrm{H_2O}]{} \underset{\mathbf{64}}{\mathrm{Ar_2Te(OCOR)_2}}$$

Ar=Ph : R=H,[242-244] CCl_3;[187, 244] Me, $\mathrm{Pr^i}$, $\mathrm{Bu^t}$, CH_2Ph;[242] Ph;[187, 242] 4-BrC_6H_4[187]

Ar=4-MeC_6H_4 : R=H;[243, 244] CCl_3[244]

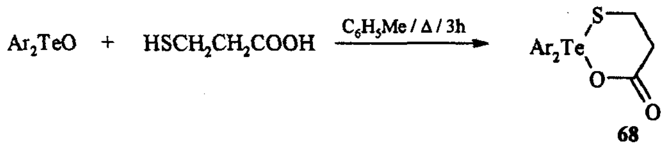
Ar=4-$MeOC_6H_4$: R=H;[243, 244] CCl_3;[241, 244] Me;[241] 2,4-$(HO)_2C_6H_3$[187]

Ar=4-$EtOC_6H_4$: R=Me[187]

Ar=4-$Me_2NC_6H_4$: R=H;[243, 244] CCl_3[244]

SCHEME 108

The interaction of diaryltelluroxides with β-mercaptopropionic acid leads to cyclic compounds **68** [18] (Scheme 109) (the yields were not given) although simple mercaptans RSH (R=4-MeC_6H_4, 4-$MeC_6H_4CH_2$) are oxidized into disulfides under the action of diaryltelluroxides [250].

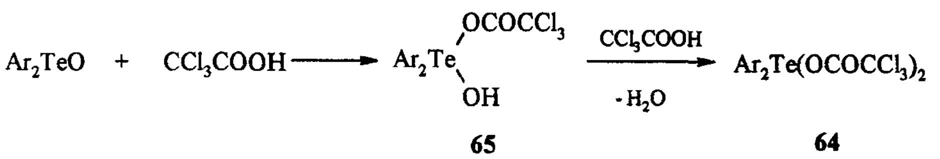


68

Ar=Ph, 4-$EtOC_6H_4$

SCHEME 109

Reaction of diaryltelluroxides with carboxylic acids in 1 : 1 molar ratio gives σ-telluranes of the type **65** [241] (see also Section 2.3.2). A two-stage mechanism for the formation of diaryltellurium dicarboxylates **64** via the diaryltellurium oxides **65** is proposed (Scheme 110).



$$Ar_2TeO + CCl_3COOH \longrightarrow \underset{\textbf{65}}{Ar_2Te(OCOCCl_3)(OH)} \xrightarrow[-H_2O]{CCl_3COOH} \underset{\textbf{64}}{Ar_2Te(OCOCCl_3)_2}$$

Ar=Ph, 4-MeOC$_6$H$_4$

SCHEME 110

Diorganyltelluronium ylides [187,251,252] and diorganyltellurimides [253,254] react with protonic acids (molar ratio 1 : 2) with cleavage of Te=C and Te=N bonds, respectively, forming σ-telluranes R$_2$TeX$_2$ in nearly quantitative yields (Scheme 111).

$$Ar(R)\overset{+}{Te}—\overset{-}{X}R^1 + 2HY \xrightarrow[-R^1XH_2]{} Ar(R)TeY_2$$

XR^1=CC(O)CH$_2$CMe$_2$CH$_2$CO : Y=F : Ar=R=Ph [252]; 4-MeC$_6$H$_4$ [187]; 4-ClC$_6$H$_4$, 4-BrC$_6$H$_4$;
R=Me, Ar=3-FC$_6$H$_4$, 4-FC$_6$H$_4$;[252] Y=Cl : Ar=R=Ph, 4-MeC$_6$H$_4$,[251] 4-MeOC$_6$H$_4$;[251, 252]
R=4-MeOC$_6$H$_4$, Ar=4-Pr^{i}C$_6$H$_4$, PhCH$_2$;[251] R=Me, Ar=4-MeC$_6$H$_4$,[252] Y=Br : Ar=R, Ph,
4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$; R=Me, Ar=4-MeC$_6$H$_4$;[252] Y=I, R=Ar=4-MeOC$_6$H$_4$[252]
XR^1=NSO$_2$C$_6$H$_4$Me-4, NC(O)CF$_3$: Y=Cl, O$_2$CMe : Ar=R=Ph, 4-MeOC$_6$H$_4$[253, 254]

SCHEME 111

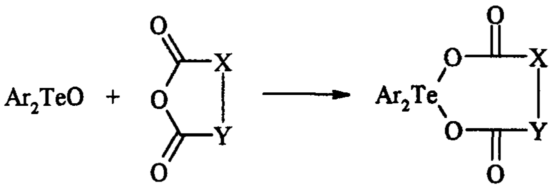
π-Telluranes of all types react easily with carboxylic acid anhydrides to give diorganyl tellurium dicarboxylates **64**. In the case of diorganyltelluroxides the reaction occurs very rapidly even in nonpolar solvents (benzene, chloroform, CCl$_4$) and the yields are nearly quantitative [208,241,242,245] (Scheme 112).

$$Ar^1Ar^2TeO + (RCO)_2O \longrightarrow \underset{\textbf{64}}{Ar^1Ar^2Te(OCOR)_2}$$

Ar^1=Ar^2=Ph : R=Me,[241, 242] Pr^i,[242] CH$_2$Cl,[241] Ph[242]
Ar^1=Ar^2=4-MeC$_6$H$_4$: R=Me, Pr, CH$_2$Cl, Ph[241]
Ar^1=Ar^2=4-MeOC$_6$H$_4$: R=Me, Pr, Ph;[241, 245] CH$_2$Cl, CF$_3$[241]
Ar^1=Ar^2=4-Me$_2$NC$_6$H$_4$: R=Me, Pr, CH$_2$Cl, Ph[241]
Ar^1=Ar^2=2,6-Me$_2$C$_6$H$_3$: R=Me, CF$_3$[208]
Ar^1=2,6-Me$_2$C$_6$H$_3$, Ar^2=2,4,6-Me$_3$C$_6$H$_2$: R=Me, CF$_3$, Et, Bu^t[208]

SCHEME 112

The cyclic σ-telluranes **69** are the products of the reaction diaryltelluroxides and dicarboxylic acid anhydrides [18,242] (the yields according to [242] are 93–98%) (Scheme 113).



69

Ar=Ph : X-Y= CH=CH;[18] o(CH$_2$)$_2$-C$_6$H$_4$;[242] Ar=4-EtOC$_6$H$_4$: X-Y = CH=CH[18]

SCHEME 113

Diphenyltelluroxide also reacts with sulfonic acid anhydrides to give di(*p*-toluenesulfonate) **70** in 71% yield [242] (Scheme 114).

$$Ph_2TeO + (4\text{-}MeC_6H_4SO_2)_2O \longrightarrow \underset{\mathbf{70}}{Ph_2Te(OSO_2C_6H_4Me\text{-}4)_2}$$

SCHEME 114

Diaryltellurimides react with acetic anhydride to give diaryltellurium dicarboxylates **64** (the yields are 50–60%) and *N*,*N*-diacyl amides which during the work-up of the reaction mixtures are hydrolyzed to monoacetyl derivatives [253] (Scheme 115).

$$Ar_2\overset{+}{Te}-\overset{-}{N}R + 2Me(CO)_2O \longrightarrow \underset{\mathbf{64}}{Ar_2Te(OCOMe)_2} + RN(COMe)_2$$

Ar=4-MeOC$_6$H$_4$: R=4-MeC$_6$H$_4$SO$_2$, CF$_3$C(O)

SCHEME 115

Interaction between tellurimides and acyl chlorides also proceeds via cleavage of the Te–N bond resulting in the formation of diaryltellurium dichlorides (the yields are 70–85%) [253] (Scheme 116).

$$Ar_2\overset{+}{Te}-\overset{-}{N}R + 2MeCOCl \longrightarrow Ar_2TeCl_2 + RN(COMe)_2$$

Ar=4-MeOC$_6$H$_4$: R=4-MeC$_6$H$_4$SO$_2$, CF$_3$C(O)

SCHEME 116

Halogens cleave Te–C bonds in telluronium dimedone ylides [251,252] and Te–N bonds in tellurimides [253,254] under very mild conditions. σ-Telluranes (the yields are 60–70%) and dihalide derivatives of dimedone or amides are the products of these reactions (Scheme 117).

$$\mathrm{Ar(R)\overset{+}{Te}{-}\overset{-}{X}R^1} + 2\mathrm{Y_2} \xrightarrow[\mathrm{-R^1XY_2}]{} \mathrm{Ar(R)TeY_2}$$

$\mathrm{XR^1{=}\underline{CC(O)CH_2CMe_2CH_2CO}}$: Ar=R=4-MeOC$_6H_4$, 4-Me$_2NC_6H_4$; Y=Cl, Br, I;

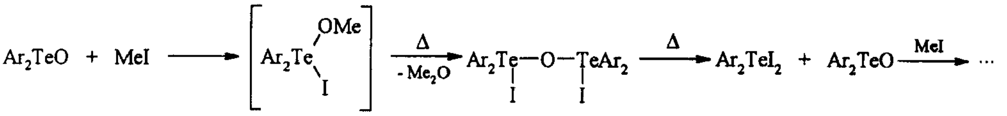
Ar=R=4-MeC$_6$H$_4$, Y=Cl; Ar=R=Ph, Y=Cl, Br; Ar=4-MeC$_6$H$_4$, R=Me, Y=Cl, Br;[251, 252]

XR^1=NSO$_2$C$_6$H$_4$Me-4, NC(O)CF$_3$: Ar=R=Ph, Y=Cl[253, 254]

SCHEME 117

In contrast, doubly stabilized sulfonium ylides react with halogens to give dihalide derivatives of the carbanionic moieties of the molecules and sulfides [255].

Diaryltellurium dihalides as well as σ-telluranes of the types **71** and **72** may be prepared using diaryltelluroxides as starting materials. Thus, heating of the latter with a large excess of methyliodide in a sealed tube results in diaryltellurium diiodides in 80–90% yields, probably via the intermediates **73** [192, 256]. Diaryltellurides were isolated as the minor products of these reactions. A possible mechanism for the formation of diaryltellurium diiodides is represented in Scheme 118.

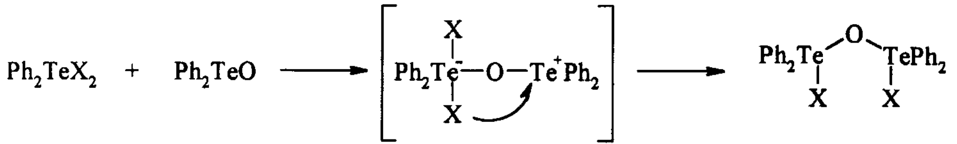


73 **71**

Ar=Ph, 4-MeC$_6$H$_4$, 4MeOC$_6$H$_4$

SCHEME 118

A specific method for the preparation of *bis*(diarylhalotellurium) oxides **71**, which has no analogy in the chemistry of diarylsulfoxides and diarylselenoxides, is based on the reaction of diaryl telluroxides with diaryltellurium dihalides or carboxylates. The reaction may involve the intermediate pertellurane **74**; the yields of **71** are near to quantitative [257] (Scheme 119).

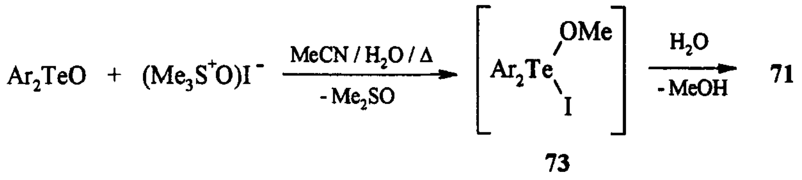


74 **71**

X=F, Cl, Br, OCOMe

SCHEME 119

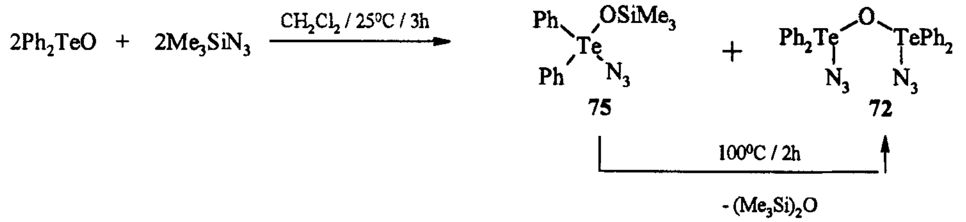
Compounds of the type **71** were also obtained in high yields by the reaction of diaryl telluroxides with trimethylsulfoxonium iodide [192,258] (Scheme 120).



Ar=Ph, 4-MeC$_6$H$_4$

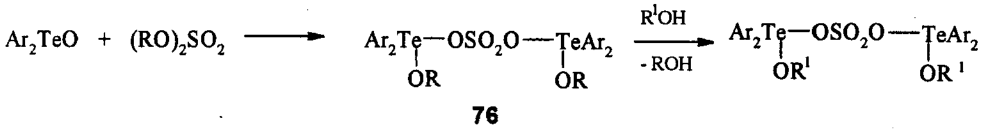
SCHEME 120

Structurally similar to **71**, the σ-tellurane **72** was obtained in a mixture with **75** from the reaction of diphenyltelluroxide with trimethylsilyl azide. Under heating at 100°C *in vacuo* **75** rearranged to **72** (in 92% yield) (Scheme 121) which exhibits surprising thermal stability (no decomposition up to 200°C) [259]. As stems from an X-ray study of **72** a possible reason for such enhanced thermal stability is the occurrence of secondary Te···N bonds in the crystals of **72** which provide for pseudo-octahedral coordination of the tellurium [259].



SCHEME 121

Another type of σ-telluranes, *bis*(diarylalkoxytellurium)sulfates **76**, have been obtained in 90–95% yields by coupling diaryltelluroxides with diakyl sulfates in the appropriate alcohols [192,260]. As is the case of alkoxysulfonium salts [261], the exchange of alkoxy groups takes place during interaction of σ-telluranes **76** with larger molecular weight alcohols [192] (Scheme 122).



R=Me, Ar=4-DC$_6$H$_4$[192] Pr^{i}C$_6$H$_4$;[192, 260]

R=Et: Ar=Ph, 4-DC$_6$H$_4$,[192, 260] Pr^{i}C$_6$H$_4$;[192]

R=Et: Ar=Ph: R^1=Pr^i, Bu^i, PhCH$_2$[192]

SCHEME 122

Diphenyltellurium dichloride is also obtained in 75–80% yields when diphenyltelluroxide reacts with $SnCl_4$, $TiCl_4$ or $SbCl_5$ in chloroform [262] and $AlCl_3$, $SiCl_4$ or PCl_5 in ethanol [263] (Scheme 123).

$$Ph_2TeO + MCL_n \longrightarrow Ph_2TeCl_2 + MOCl_{n-2}$$

M=Al, n=3; M=Si, Sn, Ti, n=4; M=P, Sb, n=5

SCHEME 123

2.4. Exchange Reactions of the Anionoid Groups

Strong polarization of the Te–X bonds in σ-telluranes R_2TeX_2 facilitates occurrence of the exchange reactions shown in Scheme 124.

$$R_2TeX_2 + 2MY \longrightarrow R_2TeY_2 + 2MX$$

SCHEME 124

Higher nucleophilicity of Y^- as compared with X^- and addition of the cations M^+ forming poorly soluble salts MX are the factors favoring the exchange reaction. Substitution of the chlorine groups in diorganyltellurium dichlorides by bromine or iodine proceeds smoothly under action of methanol, acetone or dioxan solution of potassium (sodium) bromide or iodide [49,77,78,84,119,136,185] (Scheme 125).

$$R^1R^2TeCl_2 + MX \xrightarrow[-MCl]{} R^1R^2TeX_2$$

M=Na, K

X=Br, I : $R^1 = R^2 = Ph_2C{=}CH$,[119] $4\text{-}Me_2NC_6H_4$;[78,185] $3\text{-}Me\text{-}4\text{-}OHC_6H_3$, $4\text{-}Me\text{-}2\text{-}OHC_6H_3$[77]

$R^1{=}4\text{-}MeOC_6H_4$: $R^2{=}Et$, $PhCH_2$;[49] $R^1{=}2\text{-}C_{10}H_7$: $R^2{=}c\text{-}C_6H_{11}$, $PhCH_2$[49]

$R^1{=}2,4\text{-}(HO)_2C_6H_3$ * : $R^2{=}4\text{-}MeOC_6H_4$, $4\text{-}EtOC_6H_4$, $4\text{-}PhOC_6H_4$[84]

X=Br : $R^1{=}4\text{-}Me_2NC_6H_4$* : $R^2{=}4\text{-}MeOC_6H_4$, $4\text{-}EtOC_6H_4$, $4\text{-}PhOC_6H_4$[84]

X=I : $R^1{=}R^2{=}PhC(Cl){=}CH$[136]

*** Dibromides were obtained from corresponding dichlorides and HBr**

SCHEME 125

By using differences in solubility of silver salts transformation of tellurium diiodides to tellurium dicyanides can be achieved [19,20,22] (Scheme 126). A similar approach was employed for the exchange of iodine by chloride or bromine by chlorine with the use of mercury halides [264] (Scheme 127).

$$R_2TeI_2 + AgCN \xrightarrow[-AgI]{} R_2Te(CN)_2$$

R=$PhCH_2$,[19] c-C_6H_{11},[20] $PhCOCH_2$[22]

SCHEME 126

$$R_2TeX_2 + HgY_2 \xrightarrow{EtOH/\Delta} R_2TeY_2$$

R = Me; X = I; Y = Cl, Br; R = Ph; X = Br; Y = Cl

SCHEME 127

Substitution of chlorines in dimethyltellurium dichloride by bromine occurs in the reaction with BBr_3 [265]. With an excess of BBr_3 the adduct **77** is formed in almost quantitative yield (Scheme 128).

$$Me_2TeCl_2 + BBr_3 \longrightarrow Me_2TeBr_2 \xrightarrow{BBr_3} \underset{\textbf{77}}{[Me_2TeBr_2]_2BBr_3}$$

SCHEME 128

Of preparative importance is the synthesis of diorganyltellurium difluorides by the reaction of diorganyltellurium dihalides with silver [148,203,266], sodium [267] or potassium [208] fluorides (Scheme 129).

$$R^1R^2TeX_2 + MF \xrightarrow[-MX]{} R^1R^2TeF_2$$

$R^1 = R^2 = CF_3$;[267] Me, Ph;[266] 4-$MeOC_6H_4$, 4-$EtOC_6H_4$;[148] 2,6-$Me_2C_6H_3$;[208]

R^1 = 2-$HOCH_2C_6H_4$, R^2 = Bu[203]*

* The compound cyclizes spontaneously to give 1-butyl-1-fluorobenzoxatellurole-2,1 [203]

SCHEME 129

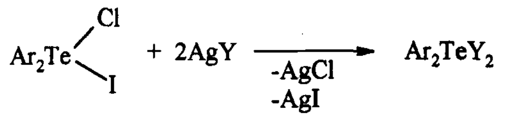
Exchange reactions of diorganyltellurium dihalides with NH_4SCN [235,236] or AgSCN [19–22] give rise to diorganyltellurium diisothiocyanates **78** (Scheme 130).

$$R_2TeX_2 + MSCN \xrightarrow[-MX]{} \underset{\textbf{78}}{R_2Te(NCS)_2}$$

R= Ph, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$;[235, 236] c-C_6H_{11},[20] $PhCH_2$,[19] $PhCOCH_2$,[21] PhCOCHMe [22]

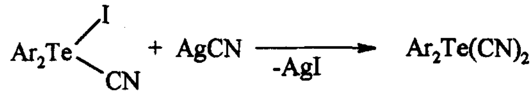
SCHEME 130

By the use of silver pseudohalides diaryltellurium dipseudohalides and dicyanides were obtained [237] (Schemes 131, 132).



Ar = Ph: Y = NCO, NCS, NCSe; Ar = 4-$MeOC_6H_4$: Y = NCS, NC

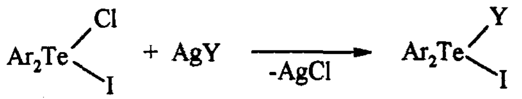
SCHEME 131



Ar = Ph, 4-$MeOC_6H_4$

SCHEME 132

Interestingly, treatment of diaryltellurium iodochlorides with silver pseudohalides resulted in not expected exchange by pseudohalide of iodine but chlorine [237] (the yields of final products were 80–100%) (Scheme 133).



Ar = Ph: Y = CN, NCO, NCS; Ar = 4-$MeOC_6H_4$: Y = CN, NCO, NCS

SCHEME 133

Reactions of diorganyltelluroxides with carbonic acids and carbonic acid anhydrides represents the most preparatively important method for the synthesis of diaryltellurium dicarboxylates (see Section 2.3.3). These compounds were also obtained by exchange reactions of diorganyltellurium dihalides (commonly dichlorides) with silver salts of carbonic acids [10,18,224,239,268,268,269]. (Corresponding tellurium dibromide was used for preparation of $Me(CH_2)_7Te(OAc)_2(CH_2)_7COOH$ [27].) (Scheme 134.)

$$R_2TeCl_2 + AgOCOR^1 \longrightarrow R_2Te(OCOR^1)_2$$

R = Me, R^1 = Ph;[10] R = Ph: R^1 = Me, Ph,[239,269] CH=$CHCO_2Bu$;[18] R = 4-MeC_6H_4:
R^1 = Me;[239] Pr, Ph, C_7H_{15}, $C_{11}H_{23}$;[224] R = 4-$MeOC_6H_4$: R^1 = Me;[268]
R = 4-$EtOC_6H_4$: R^1 = Me[239, 269]

SCHEME 134

By coupling silver maleate with dicetyltellurium dichloride, dicetyltellurium maleate [18] was prepared. A convenient modification of the general method for preparation of diaryltellurium dicarboxylates is refluxing a benzene solution of diorganyltellurium dichlorides or diiodides with silver oxide and carboxylic acids taken in a 1 : 1 : 2 ratio [271]. Such an approach allows avoidance of the labour-consuming procedure of the preparation of silver carboxylates. A series of diaryltellurium [271] and dimethyltellurium [272] dicarboxylates has been prepared using this method (Schemes 135, 136).

$$Ar_2TeCl_2 + Ag_2O + 2RCOOH \xrightarrow[-AgCl \atop -H_2O]{C_6H_6/\Delta} Ar_2Te(OCOR)_2$$

Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$: R = Me, Et, Pr^i, Bu^t, Ph, CH_2Ph, $CHPh_2$, CH=CHPh

SCHEME 135

$$Me_2TeI_2 + Ag_2O + RCOOH \xrightarrow[-AgI \atop -H_2O]{CHCl_3/r.t.} Me_2Te(OCOR)_2$$

R = CH_2Cl, $CHCl_2$, CCl_3, 4-$H_2NC_6H_4$, 4-MeC_6H_4, 3,5-$(O_2N)_2C_6H_3$, PhCH=CH

SCHEME 136

Another useful procedure for the synthesis of diaryltellurium dicarboxylates consists of treatment of diorganyltellurium dichlorides with a basic anionic resin in which the OH^- was previously exchanged with carboxylate anion [271].

For the $Cl^-/RCOO^-$ exchange sodium salts of carbonic acids can also be employed. By coupling freshly prepared sodium *o*-phthalate and tetrabromo-*o*-phthalate with diaryltellurium dichlorides in chloroform solution dimeric 14-membered cyclic carboxylates $(4\text{-}RC_6H_4)_2Te(C_8X_4O_2)$ (R=H, OMe, OEt; X=H; R=H, OMe : X=Br) were obtained [273]. Di(trifluoromethyl)tellurium di(trifluoroacetate) was obtained in high yield by coupling di(trifluoromethyl)tellurium dihalides with trifluoroacetic acid anhydride [267] (Scheme 137).

$$(CF_3)_2TeX_2 + (CF_3CO)_2O \longrightarrow (CF_3)_3Te(OCOCF_3)_2 + CF_3COX$$

X = Cl, Br

SCHEME 137

By treating diaryltellurium diacetates with an excess of another acid various diaryltellurium dicarboxylates were obtained [242] (Scheme 138).

$$Ph_2Te(OCOMe)_2 + RCOOH \xrightarrow[-MeCO_2H]{} Ph_2Te(OCOR)_2$$

R = H, Pr^i, Bu^t, Ph, $PhCH_2$

SCHEME 138

In the same way the use of strong chlorosulfonic acid leads to replacement of iodine in dialkyltellurium diiodides [274] and acetate residues in diaryltellurium diacetates

[275] by chlorosulfate groups with formation of diorganyltellurium di(chlorosulfates) **79** (Scheme 139).

$$\underset{\mathbf{79}}{R^1R^2Te(SO_3Cl)_2} \xleftarrow[-HI]{HSO_3Cl} R^1R_2TeX_2 \xrightarrow[-MeCO_2H]{HSO_3Cl} \underset{\mathbf{79}}{R^1R^2Te(SO_3Cl)_2}$$

$R^1 = R^2 =$ Me, Et

$R^1 = R^2 =$ Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$
$R^1 =$ Ph, $R^2 =$ 4-$EtOC_6H_4$

SCHEME 139

The coupling of dialkyltellurium diiodides with NaI and KI (Scheme 140) or $SnCl_2$ (Scheme 141) and an excess of chlorosulfonic acids results in derivatives of hexacoordinated tellurium, namely, dialkyltetrakis(chlorosulfate)tellurates **80** [276]. The observed molar conductance values of compounds **80** in DMSO confirm that they are 1 : 1 and 1 : 2 electrolytes.

$$MI + R_2TeI_2 + HSO_3Cl\ \text{excess} \xrightarrow{\text{r.t.}} \underset{\mathbf{80}}{M_2[R_2Te(SO_3Cl)_4]}$$

M=Na, K; R=Me, Et, Pr, Bu

SCHEME 140

$$SnCl_2 + R_2TeI_2 + HSO_3Cl\ \text{excess} \xrightarrow{\text{r.t.}} \underset{\mathbf{80}}{Sn_2[R_2Te(SO_3Cl)_4]}$$

M=Na, K; R=Me, Et, Pr, Bu

SCHEME 141

Transformation of diaryltellurium dicarboxylates into the diiodides can be realized through a treatment of the former compounds with an acetone solution of KI [239]. Diaryltellurium dichlorides were isolated in high yields in the reaction of diaryltellurium diacetates with trimethylsilyl chloride [239] (Scheme 142) and diaryltellurium dicarboxylates with acyl chlorides [241,277] (Scheme 143). The latter reaction represents a convenient method for the preparation of carboxylic acid anhydrides obtained in more than 80% yields.

$$Ph_2Te(OCOMe)_2 + Me_3SiCl \xrightarrow[-MeCO_2SiMe_3]{} Ph_2TeCl_2$$

SCHEME 142

$$(4\text{-}RC_6H_4)_2Te(OCOR^1)_2 + R^1COCl \xrightarrow{CHCl_3/\Delta/5h} Ph_2TeCl_2 + (R^1CO)_2O$$

$R = H$: $R^1 = Me$; $R = OMe$: $R^1 = Et, Ph$

SCHEME 143

Less common is application of the exchange reactions for preparation of diorgany tellurium dinitrates [10,12,278] (Scheme 144).

$$R_2TeX_2 + AgNO_3 \xrightarrow[-AgX]{} R_2Te(ONO_2)_2$$

$R = Me, X = I$;[10,12] $R = Ph, X = Cl$[278]

SCHEME 144

Di(trifluoromethyl)tellurium dinitrate was obtained by the reaction of di(trifluoromethyl)tellurium difluoride with N_2O_5 [267] (Scheme 145).

$$(CF_3)_2TeF_2 + N_2O_5 \longrightarrow (CF_3)_2Te(ONO_2)_2 + NO_2F$$

SCHEME 145

Exchange reactions represent the basic method for preparation of the σ-telluranes R_2TeX_2 with the sulfur-containing groups X: $SC(S)NR_2$, [19–22,249] $SP(S)(OR)_2$, [279–282] $SC(S)OR$ [283] and $SP(S)R_2$ [284].

Diorganyltellurium dithiocarbamates were prepared by the use of exchange reactions of diorganyltellurium dihalides with sodium [249] or ammonium [19–22] dithiocarbamates (Scheme 146).

$$R_2TeX_2 + MSC(S)NR^1R^2 \xrightarrow[-MX]{} \underset{\mathbf{67}}{R_2Te[SC(S)NR^1R^2]_2}$$

$X = Cl, I$; $M = Na, NH_4$

$R = Me, Ph$: $R^1 = R^2 = Me, Et, Pr^i, Ph$;[249] $R = Ph$: $R^1 = R^2 = s\text{-}C_6H_{13}$[249]

$R^1 = H$, $R^2 = Ph$; $R^1 + R^2 = (CH_2)_5$: $R = c\text{-}C_6H_{11}$,[20] $PhCH_2$,[19] $PhCOCH_2$,[22] $PhCOCHMe$[21]

SCHEME 146

With sodium ethylene *bis*(*N*,*N*-dimethyldithiocarbamates) polymeric dithiocarbamates **81** were obtained [249] (Scheme 147).

$$R_2TeX_2 + [NaSC(S)NMeCH_2]_2 \xrightarrow[-NaX]{} \underset{\mathbf{81}}{\{[R_2Te[SC(S)NMeCH_2]_2\}_n}$$

$R = Me, Ph$

SCHEME 147

Cyclic diorganyltellurium alkylene dithiophosphates **82** [279,280] obtained by the exchange reaction of diorganyltellurium dichlorides with dithiophosphoric acid salts are less prone to the reduction–elimination transformation into Te(II) derivatives than their alkyl counterparts. Compounds of the type **82** were also obtained in more than 80% yield by the reaction of diorganyl tellurium dialkoxides $R_2Te(OR^1)_2$ (R^1=Me, Et) with dithiophosphoric acids [279] (Scheme 148).

$$R_2TeCl_2 + MSP(S)OGO \xrightarrow[\text{-MCl}]{C_6H_5Me/30\,^{\circ}C/2h} R_2Te[SP(S)OGO]_2 \xleftarrow[\text{-HCl}]{C_6H_5Me/30\,^{\circ}C/2h} R_2Te(OR^1)_2 + HSP(S)OGO$$

82

M = Na, NH_4; R = Me: G = $-CMe_2CMe_2-$, -CHMeCHMe-, $-CH_2CMe_2CH_2-$,

$CH_2-CEt_2CEt_2-$[280]

R = Ph, $4-MeOC_6H_4$: -CHMeCHMe-, Me_2C-CMe_2, $-CH_2CMe_2CH_2-$, $-CHMeCH_2CMe_2-$,

$-CH_2-CEt_2CH_2-$[279]

SCHEME 148

A similar approach has also been applied to the synthesis of diorganyl *bis*(diorganyldithiophosphato)tellurium(IV) containing non-cyclic $-SP(S)(OR)_2$ fragments **82a** [280,282] (Scheme 149) and dimethyltellurium *bis*(alkylxanthates) **83** [283] (Scheme 150).

$$R_2TeCl_2 + MSP(S)(OR^1)_2 \xrightarrow[\text{-MCl}]{} \underset{\mathbf{82a}}{R_2Te[SP(S)(OR^1)_2]_2}$$

N = NH_4,[280] Na;[282] R = Me, R^1 = Ph;[280] R = Ph, $4-MeOC_6H_4$: R^1 = Me, Et, Pr^i[282]

SCHEME 149

$$Me_2TeI_2 + NaSC(S)OR \xrightarrow[\text{- NaX}]{ROH} \underset{\mathbf{83}}{Me_2Te[SC(S)OR]_2}$$

R = Me, Et, Pr^i

SCHEME 150

Dimethyltellurium *bis*(alkylxanthates) were also obtained in yields 49–56% by reaction of dimethyltellurium *bis*(alkoxides) with CS_2 in benzene [283] (Scheme 151).

$$Me_2Te(OR)_2 + CS_2 \xrightarrow{C_6H_6} \underset{\mathbf{83}}{Me_2Te[SC(S)OR]_2}$$

R = Me, Et

SCHEME 151

The reduction–elimination reactions of compounds with Te–S bonds are also characteristic of diphenyltellurium *bis*(diorganyl)phosphinodithioates **84** [284]. Of the compounds **84**, only the phenyl derivative **84c** was isolated in the pure crystal form, whereas its alkyl analogues decompose according to Scheme 152.

$$Ph_2TeCl_2 + MSP(S)R_2 \xrightarrow[-MCl]{CHCl_3} \underset{\mathbf{84}}{Ph_2Te[SP(S)R_2]_2} \longrightarrow Ph_2Te + [R_2P(S)S]_2$$

$M = Na, NH_4$; $R = Me$ (**a**), Et (**b**), Ph (**c**) $R = Me, Et$

SCHEME 152

In their reactions with sodium alkoxides, in the corresponding alcohol solution, diorganyl tellurium dihalides afford diorganyltellurium dialkoxides **85** [199,285] (Scheme 153).

$$R^1R^2TeX_2 + NaOR \xrightarrow[-NaX]{} \underset{\mathbf{85}}{R^1R^2Te(OR)_2}$$

$X = Cl, I$; $R^1 = R^2 = R = Me$; $R^1 = R^2 = Me$, $R = Et$; $R^1 = R^2 = Ph$: $R = Me$, Et[285]

$R = CF_3CH_2$: $R^1 = Ph$: $R^2 = Et$, $MeOCH_2CH_2$, $EtOCH_2CH_2$; $R^1 = 4\text{-}MeC_6H_4$:

$R^2 = MeOCH_2CH_2$, $EtOCH_2CH_2$[199]

SCHEME 153

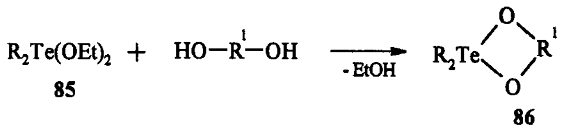
The compounds **85** were also obtained using ligand exchange reactions of diaryltellurium diethoxides with *p*-methylphenol [285] (Scheme 154).

$$R_2Te(OEt)_2 + R^1OH \xrightarrow[-EtOH]{} \underset{\mathbf{85}}{R_2Te(OR^1)_2}$$

$R = Me, Ph$: $R^1 = 4\text{-}MeC_6H_4$

SCHEME 154

With diols and dihydroxyarenes, diorganyltellurium diethoxides form heterocyclic compounds of the type **86** containing O-TeR$_2$-O moieties [285] (Scheme 155).



R=Me : R^1=$(CH_2)_2$, 1,2-C_6H_4, 2,3-naphto, 1,2-$C_6H_4CH_2$, 2,2′-biphenyl

R=Ph : R^1=$(CH_2)_2$, $(CH_2)_3$, 1,2-C_6H_4, 2,3-naphto, 1,2-$C_6H_4CH_2$, 2,2′-biphenyl

SCHEME 155

A broad series of σ-telluranes with Te–O or Te–S bonds were synthesized by the reactions of diaryltellurium dimethoxides or diethoxides with 8-hydroxyquinolines [286], benzylidene-*o*-amionophenols [287,288], salicylic aldehydes [289], acetylacetone and its derivatives [290], carboxylic acids [291], and *O*,*O*-alkylenedithiophosphoric acid [279]. Some of these compounds were also prepared by exchange reactions between diorganyltellurium dihalides and sodium salts of oxyazomethines [292] and 8-oxyquinolines [293]. No exchange of the alkoxy groups in diorganyl tellurium dialkoxides [285] or dihalides [294] occurs under their treatment with dithiols. These reactions lead to the formation of disulfides and diorganyltellurides.

On the basis of measurements of the electric conductivity the product of the reaction of dimethyltellurium diiodide with $AgClO_4$ [10,15,295] was assigned the structure of the telluronium salt $[Me_2Te(OClO_3)]^+ClO_4^-$ [295]. Attempts on the isolation of diphenyltellurium diperchlorate from the reaction of diphenyltellurium dichloride and $AgClO_4$ in methylene dichloride were unsuccessful [296]. However, this compound was isolated in the form of its stable complex with DMSO as shown in structure **87** [296] (Scheme 156). Analysis of the IR spectrum in **87** indicated that both perchlorate groups are covalently linked to the tellurium.

$$Ph_2TeCl_2 \xrightarrow[\text{2.DMSO}]{\text{1.}AgClO_4/CH_2Cl_2} \underset{\mathbf{87}}{Ph_2Te(DMSO)(OClO_3)_2}$$

SCHEME 156

Reactions of diorganyltellurium dihalides with halogens are scarcely studied. By passing gaseous chlorine through a chloroform solution of dimethyltellurium diiodide the dimethyltellurium dichloride was obtained in high yield [50]. Halogen exchange occurs on treatment of solutions of *bis*(trifluoromethyl)tellurium dihalides with chlorine or bromine. The parallel reaction of fission of the Te–C bonds leads to formation of CF_3TeCl_3 and CF_3TeBr_3 along with products of the halogen exchange reaction [267] (Scheme 157).

$$(CF_3)_2TeX_2 + Y_2 \longrightarrow (CF_3)_2TeY_2 + CF_3Y$$

$X = F$: $Y = Cl, Br$; $X = Cl$: $Y = Br$; $X = Br$: $Y = Cl$

SCHEME 157

Only the products of detelluration of $(CF_3)_2TeX_2$ ($X = F,Cl,Br$), CF_3I and TeI_4, were isolated in the reactions of these tellurium dihalides with iodine [267].

2.5. Other Methods

Other reactions leading to diorganyltellurium dihalides are few.

Diaryltellurium dichlorides **11** were prepared in 27–40% yields by oxidation of arylhydrazines with TeO_2 in the presence of LiCl [297] (Scheme 158).

$$RC_6H_4NHNH_2 + LiCl + TeO_2 \xrightarrow[\text{- Te, -LiOH}]{\text{- }N_2\text{, - }H_2O\text{,}} \underset{\mathbf{11}}{(RC_6H_4)_2TeCl_2}$$

R=H, 4-Br, 3-F, 4-NO_2, 4-Me

SCHEME 158

Compounds **11** were also prepared starting from the adducts of aryldiazonium chlorides with tellurium tetrachloride whose formula is $(ArN_2)_2TeCl_6$ [298–300]. The reductions of the latter with activated copper in acetone leads to diaryltellurium dichlorides with 20–50% yields [301] (Scheme 159).

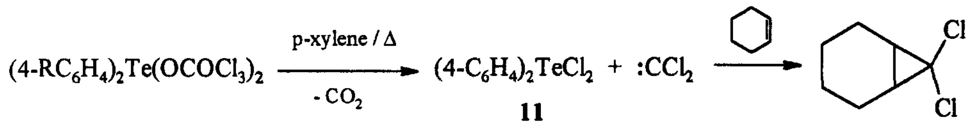
$$(ArN_2)_2TeCl_6 + Cu \xrightarrow[-N_2,\ CuCl]{Me_2CO/-15\,^0C\ to\ -10\,^0C} \underset{\mathbf{11}}{Ar_2TeCl_2}$$

Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-ClC_6H_4

SCHEME 159

Another modification of this reaction consists of treatment of aryldiazonium tetrafluoroborates $RC_6H_4N_2BF_4$ (R=H, 4-Me) with powdered zinc in acetone in the presence of $TeCl_4$ [152]. Initially formed diaryltellurium dichlorides are reduced by an excess of zinc to diaryl tellurides. The yields of the latter (usually isolated as their dibromides) are very low ($\sim$ 6%) due to a competitive reduction of $TeCl_4$ by zinc to elemental tellurium.

Diaryltellurium dichlorides are formed by thermal decomposition of diaryltellurium di(trichloroacetates) [244]. By carrying out the latter reaction in refluxing *p*-xylene solution in the presence of cyclohexene then 7,7-dichlorobicyclo[4.1.0] heptane (in 20–30% yields) was obtained along with diaryltellurium dichlorides (55–70% yields) (Scheme 160).



R=H, Me, OMe, Me_2N

SCHEME 160

Exchange reactions of diaryltellurides with diaryltellurium dihalides leads to novel diaryl tellurides and tellurium dihalides [302–304] (Scheme 161).

$$(4\text{-}RC_6H_4)_2Te + (4\text{-}R'C_6H_4)_2TeX_2 \rightleftharpoons (4\text{-}RC_6H_4)_2TeX_2 + (4\text{-}R'C_6H_4)_2Te$$

SCHEME 161

The rates of this process depend on the solvent as well as on the substituents in the aryl groups and at the tellurium atom; it decreases in the order PhCN > $PhNO_2$ > *o*-$Cl_2C_6H_4$ > PhMe [304]; Br $\gg$ Cl > F [303,304]. The exchange reaction is also sensitive to catalytic agents and to the method of purification of the solvent. Since this reaction results in an equilibrium it is of limited preparative significance.

3. REACTIONS OF σ-TELLURANES R_2TeX_2

Reactions of σ-telluranes R_2TeX_2 belong to one of the following types. (1) Reactions occurring with decrease of tellurium coordination number (reduction–elimination reactions resulting in diorganyltellurides and conversion into derivatives of tricoordinated tellurium). (2) Reaction in which the coordination number of tellurium does not change. Exchange reactions of anionoid substituents described in Section 2.4 and also transformation of functional groups in R_2TeX_2 as well as preparation σ-telluranes of other types (*bis*(diorganylhalotellurium)oxides, aryltellurium trichlorides and tetraaryltelluranes) are the reactions of this type. (3) Reactions occurring with increase of tellurium coordination number (preparation of derivatives of hexacoordinated tellurium and complexation reactions). (4) Reactions accompanied by scission of Te–C bonds. These types of reactions of R_2TeX_2 are the most important for preparative application of the σ-telluranes.

3.1. Reactions Occurring with Decrease of Tellurium Coordination Number

3.1.1. Reduction–Elimination Reaction

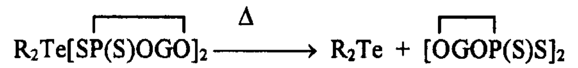
The reduction of σ-telluranes R_2TeX_2 is one the most general methods for preparation of symmetrical and unsymmetrical diorganyltellurides, R^1R^2Te. These reductions proceed in high yields, and in many cases are close to quantitative [223].

Some of the thermolysis reactions are reduction–elimination processes resulting in formation of diorganyltellurides. Reduction–elimination of σ-telluranes containing Te–S bonds **67** [249], **82** [279] and **83** [283] proceeds particularly smoothly. Thus, compounds **82** completely decompose in CH_2Cl_2, CCl_4 or $CHCl_3$ solution over 24 h at room temperature and during 10–12 h at reflux temperature [279] (Schemes 162–164).

$$\underset{\textbf{67}}{R_2Te[SC(S)NR^1_2]_2} \longrightarrow R_2Te + [R^1_2NC(S)S]_2$$

R = Me, Ph: R^1 = Me, Et, Pr^i, Ph

SCHEME 162



$$R_2Te[SP(S)OGO]_2 \xrightarrow{\Delta} R_2Te + [OGOP(S)S]_2$$

82

G = -CHMeCHMe-, $-CMe_2CMe_2-$, $-Me_2CCH_2CHMe-$, $-CH_2CEt_2CH_2-$, $-CH_2CMe_2CH_2-$,

R = Ph, $4\text{-}MeOC_6H_4$

SCHEME 163

$$Me_2Te[SC(S)OR]_2 \xrightarrow{\Delta} Me_2Te + (ROC(S)S)_2$$

R = Me, Et, Pr^i

SCHEME 164

The compounds **84**, with the exception of the phenyl derivative (R=Ph), completely decompose under their preparation by exchange reactions (see Section 2.4).

The thermolysis of diaryltellurium diformates **64** (R=H) gives diaryltellurides in high yields (95–100%) under more severe conditions (refluxing in *o*-xylene) [243,244] (Scheme 165).

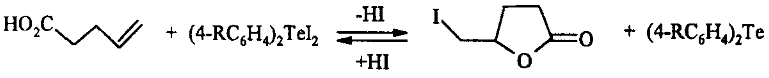
$$(4\text{-}RC_6H_4)_2Te(OCHO)_2 \xrightarrow{\Delta} (4\text{-}RC_6H_4)_2Te + CO_2 + HCOOH$$

64

R=H, Me, OMe, Me_2N

SCHEME 165

The ability of diaryltellurium dihalides to convert easily into diaryltellurides permitted these compounds to be used as mild halogenating agents [214]. Thus, the iodolactone **88** was prepared in 65% yield by coupling 4-pentenoic acid with di(4-chlorophenyl)tellurium diiodide (the yields of iodolactone in the case of other tellurium diodides are not given) (Scheme 166). The reaction is accelerated by electron-releasing and is retarded by electron-withdrawing substituents in the aryl rings.

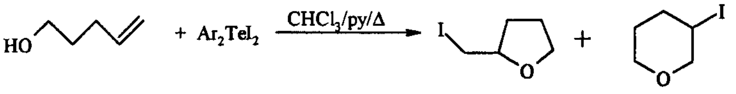


88

R = OMe, Me, H, Cl

SCHEME 166

Di-(4-chlorophenyl)tellurium diiodide reacts with 4-pentene-1-ol to give an 85 : 15 mixture of 2-(iodomethyl)tetrahydrofuran and 2-iodotetrahydropyrane [214] (Scheme 167) (only 2-(iodomethyl)tetrahydrofuran was isolated from reaction mixture in 57% yield).



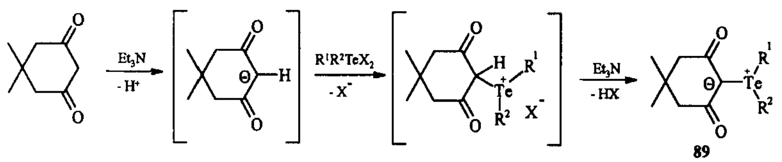
Ar = 4-ClC_6H_4

SCHEME 167

In contrast to di(4-chlorophenyl)tellurium diiodide, the corresponding dibromide is inert with respect to 4-pentenoic acid which is in accord with the increase in strength of Te–X bonds in the order of Te–I < Te–Br < Te–Cl < Te–F [214]. Diarylselenium dibromides, with the Se–Br bond being weaker than the Te–Br bond in the corresponding tellurium analogs, are more efficient brominating agents than the latter. The chlorination reaction can be promoted by Lewis acids. In the presence of $AgNO_3$ diphenyltellurium dichloride and di(4-methoxyphenyl)tellurium dichloride react with anthracene to give 9-chloroanthracene and the corresponding tellurides [305].

3.1.2. *Reactions Resulting in Formation of Derivatives of Tricoordinated Tellurium*

3.1.2.1. Synthesis of Telluronium Ylides By the treatment of diorganyltellurium dibromides or dichlorides with dimedone in solution of benzene or chloroform in the presence of two equivalents of triethylamine a variety of ylides **89** was synthesized [50,306] (Scheme 168).



89
(75-100%)

X=Cl, Br

R^1=R^2=Me, Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$, 4-$Me_2NC_6H_4$, 4-FC_6H_4, 4-BrC_6H_4;

R^1=Me : R^2= Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$

R^1= 4-$MeOC_6H_4$: R^2=$PhCH_2$, 4-$Pr^iC_6H_4$

SCHEME 168

The principal factor favoring this reaction is this high CH-acidity of dimedone which facilitates formation of the intermediate carbanions. Other compounds with active methylene groups (acetylacetone, malonodinitrile, acetoacetic and malonic ester) possessing lower CH-acidity do not form ylides under similar conditions [50]. In these cases triethylamine ($pK_a = 11$) cannot generate the corresponding carbanions in sufficiently high concentrations for these reactions to be successful.

3.1.2.2. Preparation of Diaryl Telluroxides The most general method for the synthesis of various diaryltelluroxides **90** is the hydrolysis of diaryltellurium dihalides by the use of an aqueous solution of ammonia or dilute alkali solution [82,156–160,162–168,187,190,192,208,307–310] (Scheme 169).

$$Ar^1Ar^2TeX_2 \xrightarrow[-2X^-]{2OH^-} Ar^1Ar^2TeO$$

90

Ar^1=Ar^2=4-BrC_6H_4,[310] 3-BrC_6H_4,[310] 4-ClC_6H_4,[187, 310] 3-ClC_6H_4,[310] 4-FC_6H_4,[187] Ph,[168,187,190,307–310] 4-MeC_6H_4,[160, 187, 309, 310] 3-MeC_6H_4,[158, 310] 2-MeC_6H_4,[307] 4-$MeOC_6H_4$,[159, 187, 309, 310] 3-$MeOC_6H_4$,[165, 190] 2-$MeOC_6H_4$;[166] 2,4-$Me_2C_6H_3$, 2,5-$Me_2C_6H_3$;[156] 2,6-$Me_2C_6H_3$,[208] 4-$EtOC_6H_4$,[82, 164] 2-$EtOC_6H_4$,[162] 4-$Me_2NC_6H_4$,[190, 309, 310] 2,4,6-$Me_3C_6H_2$,[157, 190] 4-$Pr^iC_6H_4$,[192] 1-$C_{10}H_7$;[163]

Ar^1=Ph : Ar^2=2-$MeOC_6H_4$;[167] 2,5-$(MeO)_2C_6H_3$, 3,4-$(MeO)_2C_6H_3$[309]

Ar^1=4-$MeOC_6H_4$, Ar^2=4-$Me_2NC_6H_4$[190]

Ar^1=2,6-$Me_2C_6H_3$, Ar^2=2,4,6-$Me_3C_6H_2$[208]

SCHEME 169

The use of dichlorides and dibromides yields the best results. Diiodides are not readily hydrolyzed. The application of difluorides is not expedient due to their limited accessibility. The hydrolysis of other types of σ-telluranes (diaryltellurium dicarboxylates, dinitrates, oxyhalides or their anhydrides) is of no practical use.

3.1.2.3. Synthesis of Triorganyltelluronium Salts Symmetrical and unsymmetrical triaryltelluronium salts $Ar_2Ar^1Te^+Y^-$ were obtained by treatment of solutions of diaryltellurium dihalides Ar_2TeX_2 (X=Cl, Br) with an excess of ArMgBr [160,169,177,311] or ArLi [312] followed by hydrolysis with dilute HCl. Treatment of thus obtained solutions with KI or KBr leads to the corresponding telluronium iodides or bromides (Scheme 170).

$$Ar_2TeX_2 + Ar^1MgBr(Ar^1Li)_{excess} \xrightarrow{H^+/H_2O/Y^-} Ar_2Ar^1Te^+Y^-$$

Y=Cl : Ar=Ar^1=Ph, 4-MeC_6H_4;[177] Ar=4-$CF_3C_6H_4$, Ar^1=2-$Me_2NCH_2C_6H_4$; Ar=2-$Me_2NCH_2C_6H_4$, Ar^1=4-$CF_3C_6H_4$;[312] Y=Br : Ar=Ar^1=2-thienyl;[169] Y=I Ar=Ar^1=Ph;[311] Ar=Ph : Ar^1=2-MeC_6H_4, 3-MeC_6H_4, 4-MeC_6H_4, 2,4-$Me_2C_6H_3$, 2,5-$Me_2C_6H_3$, 3,4-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$, 4-$MeOC_6H_4$, 3-$MeOC_6H_4$, 2-$MeOC_6H_4$, 4-$EtOC_6H_4$, 2-$EtOC_6H_4$, 1-$C_{10}H_7$;[311] Ar=4-MeC_6H_4, Ar^1=Ph[180]

SCHEME 170

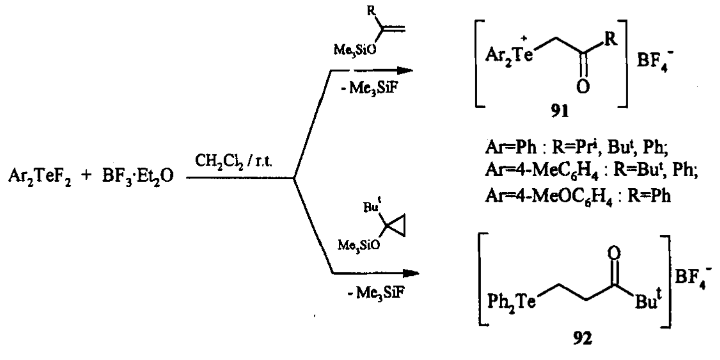
The reaction of diorganyltellurium dichlorides with sodium tetraphenylborate in methanol or aqueous solution affords triorganyltelluronium tetraphenylborates [313] (Scheme 171).

$$R_2TeCl_2 \xrightarrow{NaBPh_4\ /\ MeOH\ or\ H_2O} R_2PhTe^+BPh_4^-$$

R=Me (65%), Ph (50%)

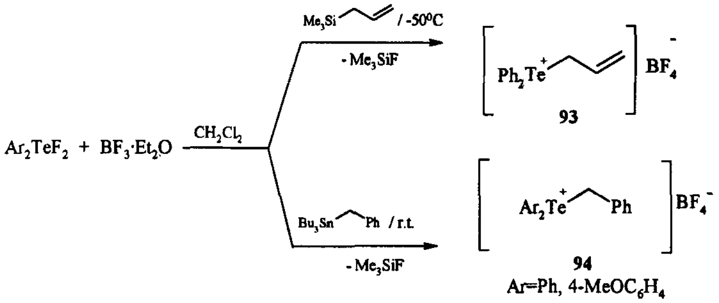
SCHEME 171

Recently [314] electrophilic organotellurium reagents obtained from the reaction of Ar_2TeF_2 and $BF_3 \cdot Et_2O$ were used for the synthesis of various telluronium salts. As well as the corresponding iodonium derivative [315,316], this reagent readily reacts with organic substrates possessing such nucleofugal groups as trimethylsilyl or tributylstannyl [314]. By this reaction (2-oxoalkyl)diaryltelluronium tetrafluoroborates **91** were obtained from enol silyl ethers and (3-oxoalkyl)diphenyltelluronium tetrafluoroborate **92** from geminal trimethylsilyloxy(*tert*-butyl)cyclopropane (Scheme 172).



SCHEME 172

With trimethylallylsilane and tributylbenzylstannane then diphenylallyltelluronium, **93**, and diarylbenzyltelluronium **94**, were correspondingly obtained as their tetrafluoroborates (Scheme 173).



SCHEME 173

The employment of tributylstannyl derivatives allowed the synthesis of telluronium salts with Te–Csp^2 (**95** and **96**) and Te–Csp (**97**) bonds (Scheme 174). Such compounds are less accessible by the usual methods. The advantage of these reactions is that the only by-products are volatile R_3MF compounds (M=Si, R=Me or M=Sn, R=Bu), thus allowing analytically pure compounds **91–97** to be obtained in 87–100% yields by simple evaporation of the solvent from the reaction mixture.

$$Ar_2TeF_2 + BF_3\cdot Et_2O + Bu_3SnR \xrightarrow[-Bu_3SnF]{CH_2Cl_2\,/\,r.t.} [Ar_2\overset{+}{Te}R]BF_4^- \quad \mathbf{95\text{-}97}$$

95 : R= $-CH=CMe_2$, Ar=Ph; **96** : R=4-$MeOC_6H_4$, Ar=Ph; **97** : R= PhC≡C–, Ar=Ph, 4-$MeOC_6H_4$

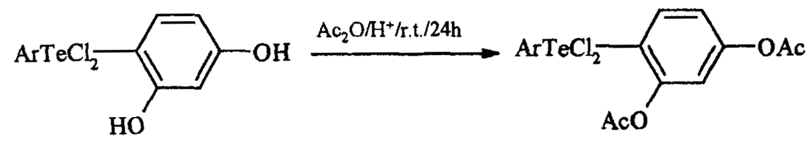
SCHEME 174

3.2. Reactions Occurring Without Change of Tellurium Coordination Number

The tellurium coordination number and also the number of organogroups bound with tellurium does not change in exchange reactions of anionoid substituents (Sections 2.4), transformations of functional groups and conversions of R_2TeX_2 to *bis*(diarylhalogeno tellurium)oxides. The transformation of R_2TeX_2 into σ-telluranes $RTeX_3$ and tetraaryltelluranes is accompanied by a change in the number organogroups bound to the tellurium atom.

3.2.1. Transformation of Functional Groups

Reactions of this type are rarely used for modification of organyl groups in R_2TeX_2. An example is acylation of the hydroxy groups of aryl(2,4-dihydroxyphenyl)tellurium dichloride [84]. Aryl(2,4-diacetoxyphenyl)tellurium dichlorides were obtained in 88–100% yields (Scheme 175).

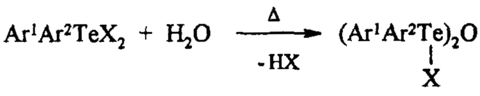


Ar = 4-$MeOC_6H_4$, 4-$EtOC_6H_4$, 4-$PhOC_6H_4$

SCHEME 175

3.2.2. *Preparation of bis(diarylhalogenotellurium)oxides*

Refluxing of water solutions of diaryltellurium dichlorides and diaryltellurium dibromides leads to *bis*(diarylhalogenotellurium)oxides **71** [39,82,156,158–160,307,317] (see also Section 2.3.3) (Scheme 176). The diiodides are inert towards water.



$$Ar^1Ar^2TeX_2 + H_2O \xrightarrow[-HX]{\Delta} (Ar^1Ar^2\underset{X}{Te})_2O$$

71

X=Cl : $Ar^1=Ar^2=Ph$,[39,307] 4-MeC_6H_4,[39,307,317] 3-MeC_6H_4,[158] 2-MeC_6H_4,[307] 4-$MeOC_6H_4$, [159] 2,4-$Me_2C_6H_3$, 2,5-$Me_2C_6H_3$;[156] 4-$EtOC_6H_4$;[82];X=Br : Ar=Ph, 2-MeC_6H_4[307]

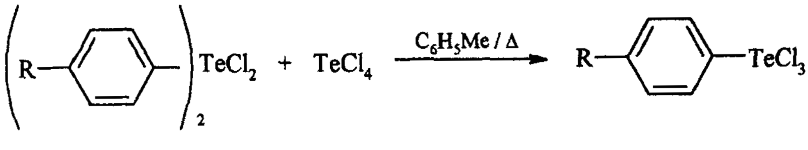
X=Cl, Br : Ar^1=Ph, Ar^2=4-MeC_6H_4[160]

SCHEME 176

Diorganyltellurium dihalides 4-$ROC_6H_4TeX_2CH_2COR$ **26** are unstable toward water. The Te–CH_2COR bond in acetonyl derivatives (R=Me) is cleaved under the action of cold water while boiling water cleaves this bond in the phenacyl derivatives (R=Ph) [84].

3.2.3. *Synthesis of aryltellurium trichlorides*

The refluxing of a toluene solution of diaryltellurium dichlorides and $TeCl_4$ taken in equimolar amounts results in aryltellurium trichlorides in high yields [143] (Scheme 177).



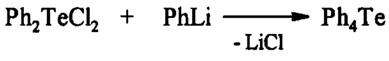
R=OEt, OMe, H, Br

SCHEME 177

Electron donor substituents in the aryl rings favour occurrence of the reaction. 4-Methoxyphenyl- and 4-ethoxyphenyltellurium trichlorides were obtained in, respectively, 93% and 81% yields by refluxing toluene solutions of equimolar amounts of diaryltellurium dichlorides and $TeCl_4$ for 5 h. For diphenyltellurium and di(4-bromophenyl)tellurium dichlorides more rigorous conditions (longer reaction time and two-fold excess of $TeCl_4$) are required.

3.2.4. Transformation in Tetraaryltelluranes

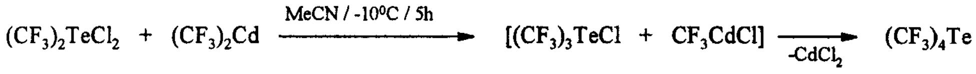
Tetraphenyltellurane may be prepared from the reaction of diphenyltellurium dichloride with phenyllithium [318,319] (Scheme 178).



$$Ph_2TeCl_2 + PhLi \xrightarrow[-LiCl]{} Ph_4Te$$

SCHEME 178

The reaction between *bis*(trifluoromethyl)tellurium dichloride and $(CF_3)_2Cd$ in glyme leads to tetrakis(trifluoromethyl)tellurane in 70% yield [320]. *Tris*(trifluoromethyl)telluronium chloride is an intermediate of this reaction (Scheme 179).



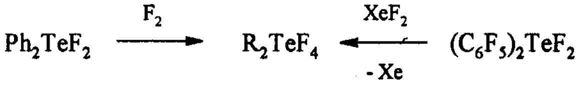
$$(CF_3)_2TeCl_2 + (CF_3)_2Cd \xrightarrow{MeCN\,/\,-10^oC\,/\,5h} [(CF_3)_3TeCl + CF_3CdCl] \xrightarrow[-CdCl_2]{} (CF_3)_4Te$$

SCHEME 179

3.3. Reactions Occurring with Increase of Tellurium Coordination Number

3.3.1. Conversion to Derivatives of Hexacoordinated Tellurium

Diaryltellurium difluorides were converted into their corresponding derivatives of hexacoordinated tellurium under the action of such strong oxidants as fluorine [321] and xenon difluoride [322] (Scheme 180).



$$Ph_2TeF_2 \xrightarrow{F_2} R_2TeF_4 \xleftarrow[-Xe]{XeF_2} (C_6F_5)_2TeF_2$$

SCHEME 180

3.3.2. Complexation Reactions

σ-Telluranes R_2TeX_2 display properties of both Lewis acids and bases. With N,P,O,S,As-centered Lewis bases (trialkylamines, ethylene- and propylene diamines, 1-naphthylamine, pyridines, triphenylphosphine, pyridine-*N*-oxides, triphenylphosphine oxide and triphenylarsine oxide, DMSO, and thiourea) diphenyltellurium dichloride [323], dinitrate [278] and diperchlorate [296] form 1 : 1 adducts. The complexes of the former two σ-telluranes are monomeric, their acetonitrile and nitrobenzene solutions do not conduct an electric current [278,323]. By contrast, the complexes formed by diaryltellurium diperchlorate in acetonitrile and acetone solutions have molar conductivity of 120–160 $ohm^{-1} mol^{-1} cm^{-2}$ characteristic of the type 1 : 1 electrolytes.

The adducts of dicyclohexyltellurium dihalides [20], *bis*(α-methylphenacyl)tellurium dihalides [21] and *bis*(phenacyl)tellurium dihalides [22] with amines ($EtNH_2$, $4\text{-}BrC_6H_4NH_2$, pyrrolidine, piperidine, morpholine) have the 1 : 2 composition. The heat of formation of the 1 : 1 adduct of diphenyltellurium dichloride with di(hexyl)sulfoxide is about $1\,\text{kcal mol}^{-1}$ [324]. This value is much lower than that measured for the adducts of this sulfoxide with $TeCl_4$ ($10.7\,\text{kcal mol}^{-1}$) and phenyltellurium trichloride ($6.3\,\text{kcal mol}^{-1}$). These data indicate the following order of decrease in acceptor ability of $TeCl_4$ and its organic derivatives: $TeCl_4 > PhTeCl_3 > Ph_2TeCl_2$ [324].

Dialkyltellurium diiodides react with iodine in ethyl acetate or chloroform to form the adducts **98** in quantitative yields [11,15,16,325,326] (Scheme 181).

$$R_2TeI_2 + I_2 \longrightarrow \underset{\mathbf{98}}{R_2TeI{\cdot}I_2}$$

R = Me, Et, Pr, Bu

SCHEME 181

The molecular and crystal structure of the complex $Me_2TeI_2 \cdot I_2$ was determined using X-ray crystallography [327]. Separated molecules of Me_2TeI_2 and I_2 are bound in the crystal by secondary –I···I–I bonds. With mixed halogens dialkyltellurium diiodides form similar types of adducts $R_2TeI_2 \cdot IX$ (X = Cl, Br) [328].

With strong Lewis acids diorganyltellurium dihalides act as donors of their lone electron pairs centered at the tellurium. By coupling $SbCl_5$ with dialkyl- and diaryltellurium dihalides $R^1R^2TeX_2$ ($X = Cl$, Br; $R^1 = R^2 = Ar$, Me, $R^1 = Ar^1$, $R^2 = Ar^2$) the complexes of two types, $R^1R^2TeX_2 \cdot SbCl_5$ and $R^1R^2TeX_2 \cdot 3SbCl_5$, are formed [329,330]. The complexes have large values of dipole moments (6–8 D for the former and 10–13 D for the latter). Very high values of dipole moments of $R^1R^2TeX_2 \cdot 3SbCl_5$ indicate their ionic character [329] (Scheme 182).

$$Ph_2TeCl_2 + SbCl_5 \rightleftharpoons [Ph_2TeCl{\cdot}SbCl_5]^+SbCl_6^-$$

$$[Ph_2TeCl \bullet SbCl_5]^+SbCl_6^- + SbCl_5 \rightleftharpoons [Ph_2TeCl{\cdot}SbCl_5]^{2+}(SbCl_6)_2^-$$

SCHEME 182

The donor properties of tellurium in Ph_nTeCl_{4-n} compounds are evident by the formation of their stable 1 : 1 complexes with $AlBr_3$. Heats of formation of these complexes increase in the order of ($n = 0$) $39.9\,\text{kcal mol}^{-1} <$ ($n = 1$) $41\,\text{kcal mol}^{-1} <$ ($n = 2$) $43.8\,\text{kcal mol}^{-1}$ [324] which is the reverse to the acceptor abilities of these compounds as measured by the heats of formation of their complexes with di(hexyl)sulfoxide.

3.4. Reactions Resulting in C–Te Bond Rupture

The reactions resulting in C–Te bond rupture may be performed under the action of heat, UV-irradiation and various reagents. The course of pyrolysis depends on the nature of the organogroups and anionoid substituents on the tellurium atom. Thus, σ-telluranes R_2TeX_2, where $X = SC(S)NR_2$, $SP(S)(OR)_2$, $SP(S)R_2$, $SC(S)OR$ and

OCHO are decomposed under heating with formation of diorganyltellurides (see Section 3.1.1). Dialkyl- and arylalkyltellurium dihalides may be decomposed under heating with rupture of one Te–C bond, although the structure of the tellurium-containing residue has not always been determined. Thus, dimethyltellurium diiodide is decomposed in acetone solution resulting in Te–O-containing polymers, methyliodide, I_2 and others [331]. It is supposed that the intermediate of this reaction is methyltellurenyl iodide (MeTeI).

Pyrolysis of phenylalkyltellurium dihalides was used as a preparative method for obtaining some alkyl halides. Heating DMF solutions of phenylalkyltellurium dihalides containing alkaline metal or ammonium halides affords alkyl halides in 70–90% yields (Scheme 183). A modification of the method consists of treatment of DMF solutions of phenylalkyltellurides with methyliodide and NaI (yields 80–90%) [215]. A series of alkyl halides and alkyl(cycloalkyl)bromides was obtained in 70–95% yields by heating the corresponding tellurium dihalides in a Kugelrohr distillation apparatus under 3 Torr [332].

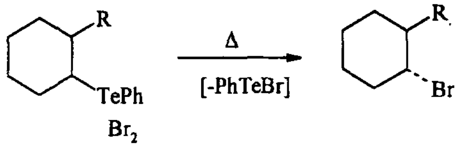
$$\mathrm{PhTeX_2R} \xrightarrow{\Delta} \mathrm{RX}$$

X = Cl, I: R = $C_{11}H_{23}$, $C_{12}H_{25}$, $C_{12}H_{25}CHMe$, $C_{14}H_{19}$, $C_{16}H_{33}$, $Ph(CH_2)_2$, $Ph(CH_2)_3$[215]

X = Br: R = $C_6H_{13}CHMe$,[332] $C_{11}H_{23}$,[215] $C_{12}H_{25}$,[215, 332] $C_{14}H_{29}$,[215] $C_{12}H_{25}CHMe$,[215, 332] $C_{16}H_{33}$,[215] $Ph(CH_2)_2$, $Ph(CH_2)_3$[215]

SCHEME 183

Pyrolysis of phenyl(cyclohexyl)tellurium dibromides gives rise to cyclohexylbromides in 60–70% yields [332] (Scheme 184).



R = H, OMe

SCHEME 184

It was assumed [332] that the pyrolytic elimination of the above alkyl halides occurred through a 1,2-tellurium halogen shift, although it is not clear whether the reaction involves a radical or an ionic intermediate.

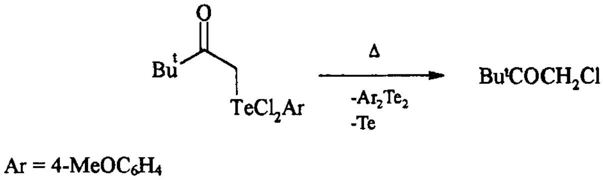
Pyrolysis of 1,1-*bis*(phenyldibromotelluro)alkanes in the presence of sodium bromide is a convenient method for the preparation of 1,1-dibromoalkanes (76–86% yields). Pyrolysis of 1,1-*bis*(phenyldiiodotelluro)alkanes in the presence of sodium iodide leads to aldehydes in 77–93% yields [215] (Scheme 185).

$$\mathrm{RCHO} \xleftarrow[\text{-[PhTeI]}]{\text{NaI}/\Delta} \mathrm{RCH(TeX_2Ph)_2} \xrightarrow[\text{-[PhTeBr]}]{\text{NaBr}/\Delta} \mathrm{RCHBr_2}$$

R = $C_{11}H_{23}$, $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $Ph(CH_2)_3$

SCHEME 185

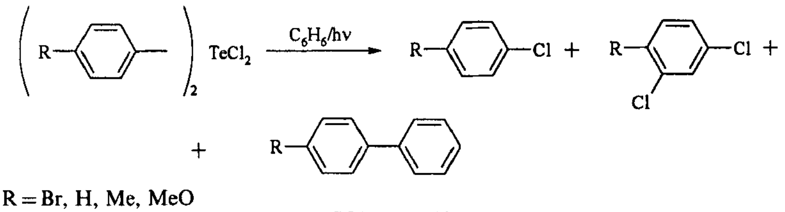
α-Chloroketones were obtained by pyrolysis of α-(aryldichlorotelluro)ketones. By heating pinacoyl(4-methoxyphenyl)tellurium dichloride at 210°C under a water pump vacuum then α-chloropinacolone was obtained in 85% yield [101] (Scheme 186).



SCHEME 186

Pyrolysis of *bis*(2-chlorocyclohexyl)tellurium dichloride (150°C, 1 mm) leads to a mixture of products of decomposition (cyclohexene, chlorocyclohexane, benzene, Te and HCl) [108,109]. In a similar way, pyrolysis of 2-chloroalkyltellurium dichlorides leads to a mixture of alkenes, chloroalkenes, chloroalkanes, 1,2-dichloroalkanes, HCl, Te and $TeCl_4$ [108,109]. Elemental tellurium and 1-chloro-4-methoxybenzene are the main products of the pyrolytic decomposition (250°C) of di(4-methoxyphenyl)-tellurium dichloride [83]. Photolysis of diorganyltellurium dichlorides proceeds with rupture of two C–Te bonds.

Diaryltellurium dichlorides are susceptible to photolytic elimination of aryl chlorides resulting in 4-chloroarenes (4–37%), 2,4-dichloroarenes (1–15%) and biaryls (9–13%), the latter being formed by coupling of the organic moiety of σ-tellurane with the benzene used as the solvent [332,333] (Scheme 187). Yields of aryl halides decrease as the electron donor properties of the substituents in the aryl rings of σ-telluranes diminishes.



SCHEME 187

When *bis*(4-methoxyphenyl)tellurium diacetate was similarly irradiated in acetic acid, *p*-acetoxyanisole was formed only in 6% yield [332].

Photolysis of di(benzoylmethyl)tellurium dichloride involves homolytic fission of the Te–C bonds accompanied by formation of phenacyl radicals [334] (Scheme 188).

$$(PhCOCH_2)_2TeCl_2 \xrightarrow{h\nu} PhCOCH_2^{\bullet} + PhCOCH_2TeCl_2^{\bullet}$$

$$PhCOCH_2TeCl_2^{\bullet} \longrightarrow PhCOCH_2^{\bullet} + TeCl_2^{\bullet}$$

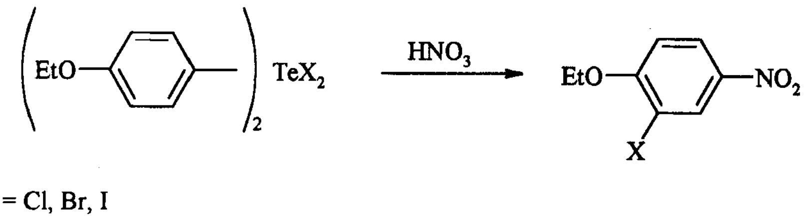
$$TeCl_2^{\bullet} \longrightarrow TeCl_4$$

SCHEME 188

Reacting with proton donor solvents these radicals form acetophenone, while in inert solvents, along with the formation of acetophenone or chloroacetophenone, recombination of the radicals resulted in the formation of 1,2-dibenzoylethane [334].

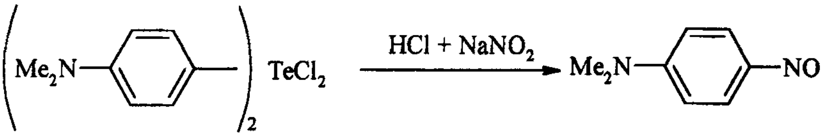
Detelluration reactions of R_2TeX_2 σ-telluranes may occur under the action of various reagents.

When treated with concentrated nitric acid diaryltellurium dihalides convert to 2-halogeno-4-nitroarenes (the yields were not given) [82] (Scheme 189).



SCHEME 189

An addition to a suspension of di(4-dimethylaminophenyl)tellurium dichloride in diluted hydrochloric acid of aqueous solution of $NaNO_2$ affords 4-nitrosodimethylaniline in 80% yield [78] (Scheme 190).



SCHEME 190

Dibenzyltellurium dibromide reacts with an excess of bromine to give benzylbromide and $TeBr_4$ [149] (Scheme 191).

$$(PhCH_2)_2TeBr_2 + Br_2 \longrightarrow PhCH_2Br + TeBr_4$$

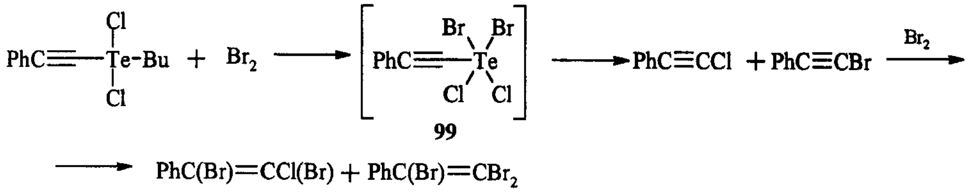
SCHEME 191

Both Te–C bonds of di(2,2-diphenylvinyl)tellurium dichloride are ruptured in its reaction with chlorine [119] (Scheme 192).

$$(Ph_2C{=}CH)_2TeCl_2 + Cl_2 \longrightarrow Ph_2C{=}CHCl + TeCl_4$$

SCHEME 192

The reaction of phenylethynyl(butyl)tellurium dichloride with bromine results into a mixture of 1,1,2-tribromo-2-phenylethene and 1,2-dibromo-1-chloro-2-phenylethene in a 3 : 1 ratio [201]. Probably this reaction occurs through the hexacoordinate tellurium intermediate **99** (Scheme 193).

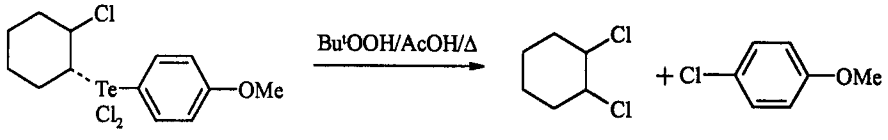


$$PhC\equiv C-TeCl_2-Bu + Br_2 \longrightarrow \left[PhC\equiv C-TeBr_2Cl_2\right] \longrightarrow PhC\equiv CCl + PhC\equiv CBr \xrightarrow{Br_2} PhC(Br)=CCl(Br) + PhC(Br)=CBr_2$$

99

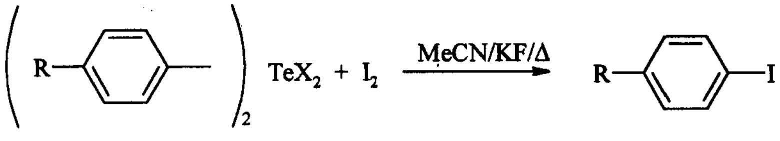
SCHEME 193

Like aryltellurium trihalides [332,335] diorganyltellurium dihalides readily undergo oxidative α-elimination of organyl halides [332] (Scheme 194) and halodetelluration reactions [335]. The former reactions occur under treatment of solutions of tellurium dihalides with Bu^tOOH in acetic acid solution. Under these conditions 4-methoxyphenyl(2-chlorocyclohexyl)tellurium dichloride affords 1,2-dichlorocyclohexane and 1-chloro-4-methoxybenzene in 55% and 22% yields, respectively. Diaryltellurium dihalides do not enter into this reaction [332].



SCHEME 194

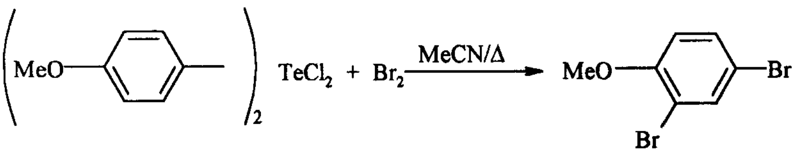
The iododetelluration reactions of diaryltellurium dihalides (Scheme 195), performed by refluxing their acetonitrile solutions containing KF, gave aryl iodides in lower yields than those attained in the similar transformations of aryltellurium trihalides [335]. The yields are not substantially affected by the type of the anionoid substituent, but are higher when donor substituents are introduced into the aryl rings [335].



R = MeO: X = Cl (23%), OAc (24%); R = H: X = Cl (4%), OAc (2%), $OCOCF_3$ (1%)

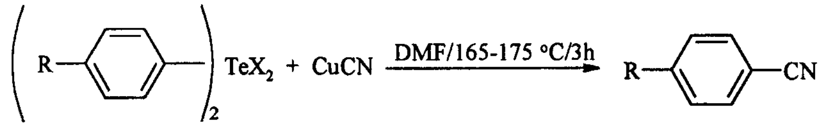
SCHEME 195

Under the action of bromine in acetonitrile solution di(4-methoxyphenyl)tellurium dichloride undergoes a bromodetelluration reaction resulting in 1-methoxy-2,4-dibromobenzene in 78% yield [335] (Scheme 196). The dibromo derivative is the product of bromination of the initially formed 1-methoxy-4-bromobenzene. The bromination is catalyzed by the tellurium dichloride. Diphenyltellurium dichloride and di(trifluoroacetate) are inert to such types of reactions [335].



SCHEME 196

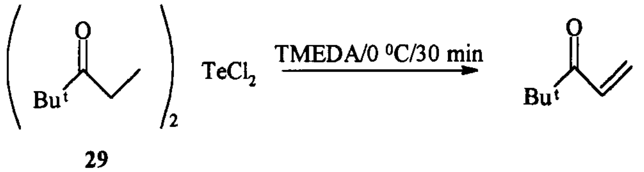
Cyanodetelluration of σ-telluranes R_2TeX_2 under the action of CuCN proceeds with very low yields (2–8%) of the nitriles [335] (Scheme 197).



R = Br, H, OMe; X = Cl, OAc, $OCOCF_3$

SCHEME 197

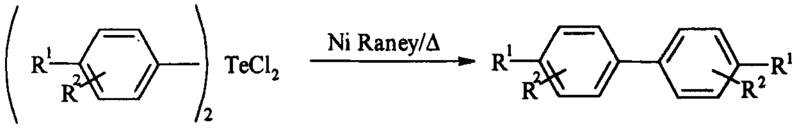
Examples of reactions of tellurium dihalides with nucleophilic reagents that have resulted in fission of both Te–C bonds are rare. When treated with two equivalents of TMEDA, ketone **29** affords an α-methyleneketone [103] (Scheme 198).



29

SCHEME 198

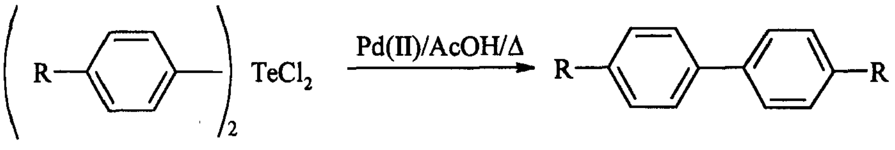
Detelluration of diaryltellurium dichlorides and congeners is also effected by Raney nickel [76,83,125], Pd(II) salts [336], nickel tetracarbonyl [237] and tributyltin hydride [134]. On heating of diaryltellurium dichlorides in 2-methoxyethyl ether in the presence of Raney Ni, symmetric biaryls (58–91%) are produced [76,83] (Scheme 199).



R^2 = H: R^1 = OMe,[76, 83] OEt, H, Me, Br, NMe_2;[76] R^1 = OMe : R^2 = 3-Me, 3-OMe, 2-OMe; $R^1 + R^2$ = 3,4-C_4H_4[76]

SCHEME 199

2-Naphthyl(2-chloro-1-methylpropyl)tellurium dichloride upon treatment with Raney Ni afforded 2,2′-binaphthyl (in 88% yield), but not the expected 2-(2-chloro-1-methylpropyl)naphthalene [125]. Biaryls are formed in 10–51% yields from the reaction of diaryltellurium dichlorides with $Pd(OAc)_2$ in acetic acid solution [336] (Scheme 200).



R = MeO, Me, H, Br

SCHEME 200

Reaction of diaryltellurium dichlorides with alkenes taken in 5–10-fold excess carried out in the presence of Pd(II) salts gives arylated alkenes in modest to almost quantitative yields [336] (Scheme 201). Biaryls and adducts arising from addition of acetic acid to the double bond of the alkene are the by-products of this reaction.

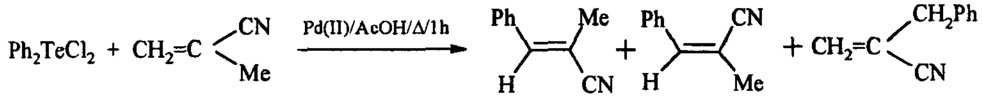
$$Ar_2TeCl_2 + CH_2{=}CHR \xrightarrow{Pd(II)/AcOH/\Delta/1h} ArCH{=}CHR$$

Ar = Ph: R = Ph, CO_2Me, CO_2Et, CN, CHO, COMe, CH_2OH, CH_2OAc, CH_2Br

Ar = 4-$MeOC_6H_4$, 4-MeC_6H_4, 4-BrC_6H_4: R = Ph

SCHEME 201

The reaction with acrylonitrile and methacrylonitrile affords a mixture of *trans*- and *cis*-cinnamonitriles. Metacrylonitrile affords the 1 : 1 : 1.5 mixture of the isomers **100–102** [336] (Scheme 202). Other arylalkenes are usually obtained as *trans*-isomers.

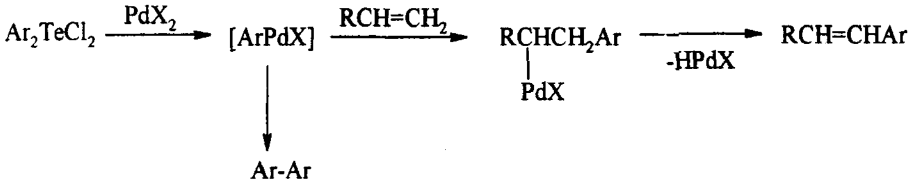


100 **101** **102**

SCHEME 202

β-Phenylpropionaldehyde is the product of the reaction of diphenyltellurium dichloride with allylic alcohol and allylbenzene was obtained on treating tellurium dichloride with allyl bromide [336].

The most efficient catalytic system for these reactions of diaryltellurium dihalides is $PdCl_2/NaOAc$. Other catalysts (Pd, $RuCl_3$, $RhCl_3$) provide for lower yields of arylated alkenes. The mechanism of the arylation reaction involves Te(IV)–Pd(II) exchange [336] (Scheme 203).



SCHEME 203

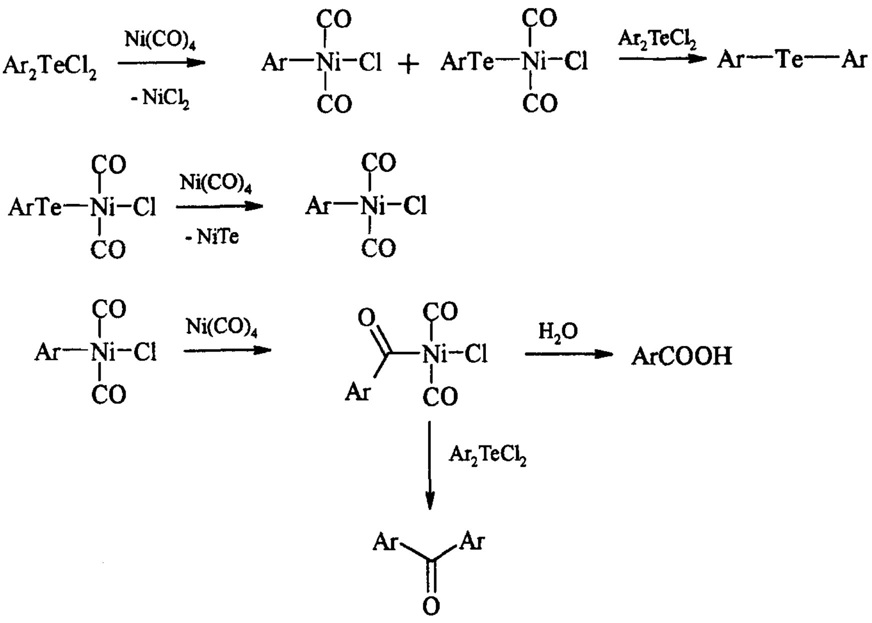
Reaction of diaryltellurium dichlorides with $Ni(CO)_4$ and DMF at 70°C followed by hydrolysis of the reaction mixture results in carboxylic acids (in 58–71% yields) [337] (Scheme 204). Diarylketones (up to 10%) and diaryl tellurides (15%) were isolated as the by-products. Dialkyl tellurium dichlorides, in particular *bis*(2-chloropropyl)-tellurium dichloride, do not enter into this reaction.

$$Ar_2TeCl_2 \xrightarrow[2.H_2O]{1.Ni(CO)_4/DMF/70^{\circ}C/24h} ArCOOH + NiTe + CO + HCl$$

$Ar = Ph, 4\text{-}MeOC_6H_4$

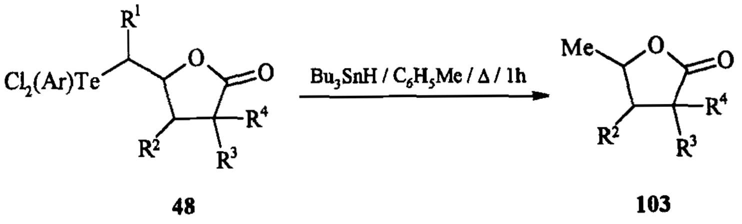
SCHEME 204

The following mechanism for the carbonylation of diaryltellurium dichlorides was suggested (Scheme 205).



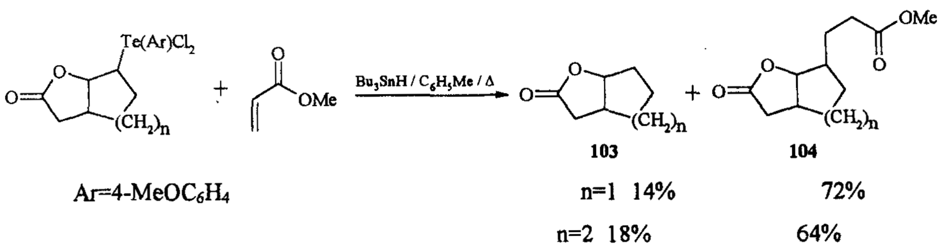
SCHEME 205

Lactones **48** obtained by reaction of aryltellurium trichlorides with γ,δ-unsaturated carboxylic acids [134] (see Section 2.2.3.1) are detellurated under a treatment with tributyltin hydride resulting in lactones **103** [134] (Scheme 206).



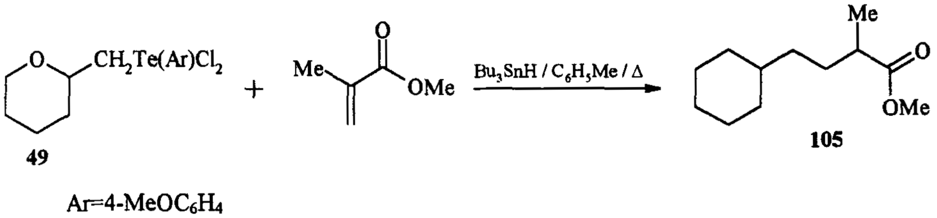
SCHEME 206

The reaction occurs as a radical process and when carried out in the presence of methylacrylate affords the lactones **103** and the **104** as the main products [134] (Scheme 207).



SCHEME 207

Similarly, trapping the intermediate free radical, formed from the reaction of the tellurium dichlorides **49** [135] with Bu_3SnH, the compound **105** was isolated [134] (Scheme 208).



SCHEME 208

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