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Synthesis and reactions of organic compounds containing bonds of Te to Group 14 elements

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Abstract. The data on the synthesis and reactions of organic compounds containing bonds of Te to Group 14 elements are generalised and systematised. The use of these compounds in the synthesis of organoelement compounds, complexes with organotellurium ligands, tellurium-containing clusters and metal tellurides is reviewed. The bibliography includes 99 references.

I. Introduction

The existence of four types of true, *i.e.*, containing at least one Te – C bond, organotellurium compounds with Group 14 elements, *viz.*, $(R^1Te)_4E$, $(R^1Te)_3ER^2$, $(R^1Te)_2ER^2_2$ and R^1TeER2_3 (R^1 = Alk, Ar; R^2 = H, Alk, Ar; E = Si, Ge, Sn, Pb), is possible in principle. Tellurides $R^1TeER^2_3$ are the most well studied among them. Compounds $(TeR)_4E$ have not been described so far, while the other two types are represented by only a few examples. The derivatives $(R_3E)_2Te$, the methods of synthesis and reactions of which are similar to those of tellurides $R^1TeER^2_3$ are also considered.

The interest in compounds $R^1TeER^2_3$ and $(R_3E)_2Te$ is determined by the fact that these are currently acquiring an ever increasing importance in the synthesis of organic and inorganic tellurium derivatives. Perfluoroalkyl trimethylstannyl tellurides ($R_FTeSnMe_3$) are used for the preparation of telluroketones and previously unknown telluracycles.[1–3] Compounds $R^1TeER^2_3$ are used as synthetic equivalents of organyl tellurolate anions RTe^- which are easily oxidised in air and are used exclusively *in situ*.[4–9] These types of compounds have been used in the synthesis of aryl methyl tellurides,[8] aryl tellurobenzoates[9] and aryl telluroformates[6,7] in high yields. Triphenylgermyl derivatives and their stannyl analogues, *viz.*, $ArTeEPh_3$ (E = Ge, Sn), are convenient starting compounds for the synthesis of metal tellurolates $(ArTe)_nM$ (M is metal),[4] whereas $BuTeSiMe_3$ is used for the synthesis of tellurium-containing clusters.[5] The reaction of bis(trialkylsilyl) tellurides with some organoelement compounds, which enables low-temperature synthesis of practically important metal tellurides M_xTe_y, attracts special attention.[10,11]

The use of other compounds with Te – E bonds for the synthesis of organic tellurium derivatives and some organic and organoelement compounds are described in more detail in the sections devoted to reactions of tellurides $R^1TeER^2_3$.

Earlier data on the synthesis and reactions of compounds $R^1TeER^2_3$ and $(R_3E)_2Te$ are described in the monographs.[12–14]

Spatially hindered (organoelement)tellurols of the type R_3ETeH (R = Me_3Si, E = Si, Ge; R = Ph, E = Si) as well as tin and lead tellurolates $[(Me_3Si)_3SiTe]_2E$ (E = Sn, Pb), which also contain Te – E bonds, are used as the starting compounds in low-temperature synthesis of tellurides of these metals and are considered in the reviews.[15,16]

II. Synthesis and reactions of compounds $R^1TeER^2_3$ (E = Si, Ge, Sn, Pb)

1. Synthesis of compounds $R^1TeER^2_3$

The most common approach to the synthesis of compounds $R^1TeER^2_3$ (**1**) with any element E is based on the reaction of alkali-metal tellurolates R^1TeM with chlorides R^2_3ECl.[4,5,17–19] Lithium tellurolates are usually prepared by insertion of tellurium into the C – Li bonds of alkyl(aryl)lithium,[5,17–19] whereas sodium tellurolates can be obtained by reducing diaryl ditellurides with either sodium borohydride in PhH – EtOH[4,19] or metallic sodium in THF.[18] The yields of compounds **1** usually vary from 60% to 80% with the exception of *p*-methoxyphenyl (triphenylgermyl) telluride (**1g**) obtained in 23% yield.[4] Bis(trimethylsilyl) telluride and dialkyl ditellurides are side products in the synthesis of alkyl trimethylsilyl tellurides **1a,b.**[5,17] $Ph_3SiTePh$ could not be obtained by this method.[4]

$$R^1TeM + R^2_3ECl \xrightarrow[-MCl]{} \underset{\mathbf{1a-o}}{R^1TeER^2_3}$$

M = Li, Na.

Compound **1**	E	R^1	R^2	Ref.
a	Si	Me	Me	17
b	Si	Bu	Me	5
c	Si	Ph	Me	17 – 19
d	Ge	Ph	Me	19
e	Ge	Ph	Ph	4, 19
f	Ge	Ph	4-MeC_6H_4	4
g	Ge	4-$MeOC_6H_4$	Ph	4
h	Sn	Ph	Me	19

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Compound **1**	E	R^1	R^2	Ref.
i	Sn	Ph	Ph	4, 19
j	Sn	Ph	4-MeC_6H_4	4
k	Sn	Ph	4-$MeOC_6H_4$	4
l	Pb	Ph	Ph	4, 19
m	Pb	Ph	4-BrC_6H_4	4
n	Pb	Ph	4-MeC_6H_4	4
o	Pb	Ph	4-$MeOC_6H_4$	4

The silyl derivatives **1a–c** represent pale yellow fluids with an unpleasant odour; their analogues containing heavier Group 14 elements are colourless or pale yellow solids readily soluble in ordinary organic solvents.

The reaction of lithium ethanetellurolate with chlorosilanes was used in the synthesis of the silyl derivatives **2a,b** containing alkyl groups and a hydrogen atom at the silicon atom.[20]

$$EtTeLi + R_2ClSiH \xrightarrow[-LiCl]{} \underset{\mathbf{2a,b}}{EtTeSi(H)R_2}$$

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

Aryl trimethylsilyl tellurides **3a,b** are obtained in 30%–40% yields by treatment of aryl telluromagnesium bromides with chlorotrimethylsilane in THF.[21,22]

$$ArTeMgBr + ClSiMe_3 \xrightarrow[-MgBrCl]{THF} \underset{\mathbf{3a,b}}{ArTeSiMe_3}$$

Ar = Ph (**a**), 4-MeC_6H_4 (**b**).

$(Me_2Si)_2Te$ and $Me_3SiO(CH_2)_4TePh$ were isolated along with compound **3a** in 10% and 45% yields, respectively.[21] The latter seems to result from the tetrahydrofuran ring opening under the action of chlorotrimethylsilane and the reaction of $Me_3SiO(CH_2)_4Cl$ formed with PhTeMgBr.

Yet another approach to the synthesis of compounds **1**, *viz.*, the reaction of the lithium derivatives R_3ETeLi with alkyl halides, is represented by a single example. Thus butyl (triethylsilyl) telluride **1p** was synthesised[23] in 79% yield by treatment of tetrameric lithium triethylsilanetellurolate (**4**) with butyl chloride. Compound **4** is prepared from ethyllithium and the corresponding tellurol.[23]

$$Et_3SiTeH + EtLi \xrightarrow[-C_2H_6]{} \underset{\mathbf{4}}{(Et_3SiTeLi)_4} \xrightarrow[-LiCl]{BuCl} \underset{\mathbf{1p}}{BuTeSiEt_3}.$$

Reactions of diorganyl ditellurides[1–3,24] and diorganyl tellurides[6,7,25–27] with organoelement hydrides afford tellurides **1** containing Si, Ge and Sn atoms. The synthetic potential of this method is inferior to that based on the reaction of alkali-metal tellurolates with chlorides R^2_3ECl and is mainly employed for the synthesis of organyl (triorganylstannyl) tellurides **1** (E = Sn). The reaction of diaryl ditellurides with triphenylstannane proceeds under mild conditions (heating of the reactants at 60–70 °C without a solvent) and results in aryl (triphenylstannyl) tellurides **1i, 5a–c** in 50%–70% yields.[24]

$$Ar_2Te_2 + Ph_3SnH \xrightarrow[-H_2]{} \underset{\mathbf{1i,\ 5a-c}}{ArTeSnPh_3}$$

Ar = Ph (**1i**), 4-$MeOC_6H_4$ (**5a**), 4-$EtOC_6H_4$ (**5b**), 4-$PhOC_6H_4$ (**5c**).

If tributylstannane is used instead of triphenylstannane, no individual compounds similar to compounds **5** could be isolated. However, the mass spectra of oily reaction products contain peaks of molecular ions corresponding to aryl (tributylstannyl) tellurides $ArTeSnBu_3$.[24]

The reaction of bis(perfluoroalkyl) ditellurides with trimethylstannane is employed in the synthesis of perfluoroalkyl trimethylstannyl tellurides **6a–e**.[1–3] Thus trifluoromethyl trimethylstannyl telluride **6a** was obtained in ~90% yield on warming of a 1 : 3 $(CF_3)_2Te_2$–Me_3SnH mixture in diethyl ether from −196 to 0 °C (see Ref. 1).

Compounds **6b–e** were synthesised under nearly identical conditions.[2,3] The reaction of the corresponding ditellurides with Me_3SnH (molar ratio 1 : 1) affords perfluorohydrocarbons and Te together with perfluoroalkyl trimethylstannyl tellurides.

$$(R_F)_2Te_2 + Me_3SnH \xrightarrow[-R_FH,\ -Te]{} \underset{\mathbf{6a-e}}{R_FTeSnMe_3}$$

R_F = CF_3 (**a**), C_2F_5 (**b**), $(CF_3)_2CF$ (**c**), C_3F_7 (**d**), C_4F_9 (**e**).

It is noteworthy that the yields of compounds **6** with a ditelluride : Me_3SnH molar ratio of 1 : 2 are much lower due to their reaction with Me_3SnH.[2]

$$R_FTeSnMe_3 + Me_3SnH \xrightarrow[-R_FH]{} Me_3SnTeSnMe_3.$$

Reactions of diorganyl tellurides with organoelement hydrides proceed with the cleavage of one or two C–Te bonds resulting in compounds **1** or bis[triorganylsilyl (germyl, stannyl)] tellurides $(R_3E)_2Te$ **7**. Sometimes, mixtures of both types of compounds are formed. The nature of the reactants is the main factor which determines the direction of these reactions. Thus in the case of dialkyl tellurides, a crucial role is played by the nature of the hydrides R_3EH the reactivities of which increase in the following order: Si < Ge < Sn. The reaction of triethylsilane with diethyl telluride (200 °C, 7 h) affords a mixture of compounds **1q** and **7a** (yields 12% and 55%, respectively). The reaction of triethylgermane with the same telluride (140 °C, 7 h) gives a mixture of compounds **1r** and **7b** in comparable yields (39% and 59%, respectively), whereas a similar reaction of triethylsilane yields only telluride **7c** even at 20 °C.[25,26]

$$R^1_3EH + R^2_2Te \xrightarrow[-RH]{} \underset{\mathbf{1q,r}}{R^2TeER^1_3} + \underset{\mathbf{7a-c}}{(R^1_3E)_2Te}$$

$R^1 = R^2$ = Et: E = Si (**1q**, **7a**), Ge (**1r**, **7b**), Sn (**7c**).

In contrast to dialkyl tellurides, the reaction of bis(perfluoroalkyl) tellurides with trimethylstannane (molar ratio 1 : 1) gives exclusively perfluoroalkyl trimethylstannyl tellurides **6b,d,e** in 50%–65% yields.[2,3]

$$(R_F)_2Te + Me_3SnH \xrightarrow[-R_FH]{Et_2O,\ -196\ ^\circ C\ to\ 0\ ^\circ C} \underset{\mathbf{6b,d,e}}{R_FTeSnMe_3}$$

R_F = C_2F_5 (**b**), C_3F_7 (**d**), C_4F_9 (**e**).

Irrespective of the nature of the hydrides R_3EH, their reaction with aryl cyclohexyl tellurides leads to the cleavage of only the C_{sp^3}–Te bond. Thus tellurides **8a–f** were prepared by heating an equimolar mixture of the reactants in benzene in the presence of catalytic amounts of azoisobutyronitrile (AIBN).[6,7,27,28] Compounds **8** were not isolated due to their low stabilities and were used in subsequent conversions (see Section II.2) *in situ*.

$$\text{cyclo-}C_6H_{11}TeAr + R_3EH \xrightarrow[80\ ^\circ C]{PhH,\ AIBN} \underset{\mathbf{8a-f}}{ArTeER_3} + \text{cyclo-}C_6H_{12}$$

Compound **8**	Ar	E	R	Ref.
a	Ph	Si	Me_3Si	6, 7, 28
b	4-FC_6H_4	Si	Me_3Si	6, 7, 28
c	Ph	Ge	Bu	28
d	4-FC_6H_4	Ge	Bu	28
e	Ph	Sn	Bu	27
f	4-FC_6H_4	Sn	Bu	28

In contrast to tris(trimethylsilyl)silane, triphenylsilane does not split the C–Te bonds in aryl cyclohexyl tellurides.[28]

It is of note that reaction of alkyl (or cycloalkyl) phenyl tellurides with triphenylstannane was proposed[29] as an efficient preparative procedure for the synthesis of alkanes (or cycloalkanes) in high yields long before the publication of the works.[6,7,27,28]

$$PhTeR + Ph_3SnH \xrightarrow[-PhTeSnPh_3]{PhH,\ 25\ ^\circ C} RH.$$

In all probability, this reaction follows a radical mechanism.[29]

$$Ph_3SnH \longrightarrow Ph_3Sn^{\bullet},$$

$$Ph_3Sn^{\bullet} + PhTeR \longrightarrow R^{\bullet} + PhTeSnPh_3,$$

$$R^{\bullet} + Ph_3SnH \longrightarrow RH + Ph_3Sn^{\bullet}.$$

Germyl (**9**) and stannyl (**1h**) derivatives were prepared in nearly quantitative yields by exchange reactions of organyl trimethylsilyl tellurides with the corresponding fluorogermane or chlorostannane.[17]

$$MeTeSiMe_3 + H_3GeF \xrightarrow[-Me_3SiF]{} \underset{\mathbf{9}}{MeTeGeH_3},$$

$$PhTeSiMe_3 + Me_3SnCl \xrightarrow[-Me_3SiCl]{} \underset{\mathbf{1h}}{PhTeSnMe_3}.$$

A similar reaction was used in the synthesis of organyl silyl tellurides **10a**,**b**.[17]

$$RTeSiMe_3 + H_3SiX \xrightarrow[-Me_3SiX]{} \underset{\mathbf{10a,b}}{RTeSiH_3}$$

R = Me (**a**), Ph (**b**); X = Br, I.

The attempts to synthesise compounds of the type **10** by the reaction of lithium methane(benzene)tellurolate with $BrSiH_3$ were unsuccessful, bis(silyl) telluride $(H_3Si)_2Te$ being the only reaction product.[17]

Other reactions resulting in compounds **1** are represented by single examples. Thus ethyl (triethylgermyl) telluride (**1r**) was synthesised by reaction of diethyl ditelluride with triethylgermyllithium (yield 89%)[20] or from the same ditelluride and bis(triethylgermyl)mercury (yield 73%).[30]

$$\left.\begin{array}{l} Et_2Te_2 + Et_3GeLi \xrightarrow{-EtTeLi} \\ Et_2Te_2 + (Et_3Ge)_2Hg \xrightarrow[-Hg]{} \end{array}\right\rightarrow \underset{\mathbf{1r}}{EtTeGeEt_3}.$$

Methyl tris(trimethylsilyl)silyl telluride (**1s**) was synthesised by treatment of lithium tris(trimethylsilyl)silanetellurolate with trimethyltelluronium iodide.[31] Photolysis of a hexabutyldistannane–dimethyl telluride mixture yields methyl tributylstannyl telluride (**1t**).[32]

$$(Me_3Si)_3SiTeLi + Me_3Te^+I^- \xrightarrow[-Me_2Te,\ -LiI]{} \underset{\mathbf{1s}}{(Me_3Si)_3SiTeMe},$$

$$Bu_3SnSnBu_3 \xrightarrow{h\nu} Bu_3Sn^{\bullet} \xrightarrow[-Me^{\bullet}]{Me_2Te} \underset{\mathbf{1t}}{MeTeSnBu_3}.$$

2. Reactions of compounds $R^1TeER^2_3$

In most cases, reactions of compounds **1** were studied using silyl and stannyl derivatives as examples. Some of these reactions represent valuable procedures for preparative synthesis of various organotellurium compounds including those used in synthetic organic chemistry.

The Te–Si bond in organyl triorganylsilyl tellurides is easily cleaved under the action of hydrohalic acids, alcohols and water to give organyl tellurols and halogenosilanes, alkoxysilanes or siloxanes, respectively.[17]

$$R^1TeSiMe_3 + HX \longrightarrow R^1TeH + Me_3SiX$$

R^1 = Me, Ph; X = Br, I, OAlk, OH.

Benzenetellurol *in situ* manifests strong reducing properties.[33–35] Several methods for the synthesis of this compound are known, they include methanolysis of phenyl trimethylsilyl telluride[33–35] and reduction of diphenyl ditelluride with hypophosphorous acid or sodium borohydride.[33] The former approach is especially convenient. Phenyltellurol thus generated reduces nitro compounds into amines (in benzene or chloroform),[33,34] alkenes and alkynes into alkanes,[34] aldehydes and ketones into alcohols[34] and reduction of carbonyl compounds in alcohols in the presence of catalytic amounts of ZnI_2 affords ethers.[35] These reactions proceed under mild conditions and in high yields.

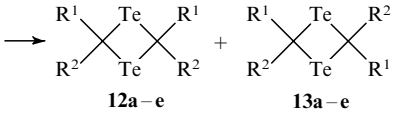
Compounds **1** readily undergo disproportionation. Thus methyl germyl telluride disproportionates into di(germyl) telluride (**7d**) and dimethyl telluride, whereas disproportionation of methyl silyl telluride yields bis(methyltelluro)silane and silane.[17]

$$MeTeEH_3 \begin{cases} \xrightarrow{E = Ge} \underset{\mathbf{7d}}{(H_3Ge)_2Te} + Me_2Te \\ \xrightarrow{E = Si} SiH_4 + H_2Si(TeMe)_2 \end{cases}$$

The disproportionation of methyl trimethylstannyl telluride upon long-term storage or irradiation at 488 nm follows the same scheme as in the case of methyl germyl telluride, bis(trimethylstannyl) telluride and dimethyl telluride being formed.[17]

Pyrolysis of perfluoroalkyl trimethylstannyl tellurides **6** proceeds in quite a different manner.[1–3] This results in trimethylfluorostannane and telluroketones **11**, which easily dimerise into the 1,3-ditelluretane derivatives **12** and **13**.[1–3]

$$\underset{\mathbf{6a-e}}{Me_3SnTeCF(R^1)R^2} \xrightarrow[-Me_3SnF]{\Delta} \underset{\mathbf{11a-e}}{R^1(R^2)C{=}Te} \longrightarrow$$

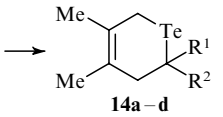


12a–e **13a–e**

R^1 = F; R^2 = F (**a**), CF_3 (**b**), C_2F_5 (**d**), C_3F_7 (**e**);
$R^1 = R^2 = CF_3$ (**c**).

Heating of tellurides **6a–d** in chloroform with a large excess of 2,3-dimethylbutadiene yields initially the telluroketones **11a–d**, which then enter into a [4 + 2]-cycloaddition reaction[1–3] to give 5,6-dihydro-3,4-dimethyl-2*H*-tellurine derivatives **14a–d** in 70%–90% yields.

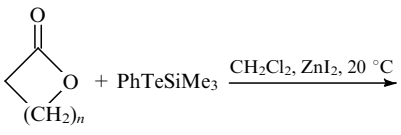
$$\underset{\mathbf{6a-d}}{Me_3SnTeCF(R^1)R^2} \xrightarrow[-Me_3SnF]{CHCl_3,\ \Delta} \underset{\mathbf{11a-d}}{R^1(R^2)C{=}Te} \xrightarrow{\text{Me, Me}}$$



14a–d

$R^1 = R^2 = F$ (**a**); R^1 = F, $R^2 = CF_3$ (**b**); $R^1 = R^2 = CF_3$ (**c**);
R^1 = F, $R^2 = C_2F_5$ (**d**).

Phenyl trimethylsilyl telluride cleaves lactones and ethers under mild conditions (dichloromethane, 20 °C) in the presence of catalytic amounts of ZnI_2 to give C-tellurination and O-silylation products.[18] Thus acids **16** are prepared from lactones **15** and $PhTeSiMe_3$ in > 80% yields. Intermediate *O*-trimethylsilyl esters **17** are hydrolysed upon work-up of reaction mixtures.



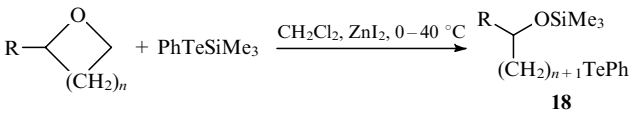
$$\longrightarrow \underset{\mathbf{17}}{PhTe(CH_2)_{n+1}CO_2SiMe_3} \xrightarrow{H_2O} \underset{\mathbf{16}}{PhTe(CH_2)_{n+1}CO_2H}$$

n = 2–4.

Phenyl trimethylsilyl telluride markedly exceeds related sulfur- and selenium-containing compounds in reactivity. The lac-

tone ring opening under the action of telluride occurs at 20 °C ($PhSSiMe_3$ reacts at 70 °C,[36] whereas $PhSeSiMe_3$, at 80–100 °C).[37]

Oxirane and other cyclic ethers are cleaved with the same efficiency under the action of phenyl trimethylsilyl telluride to give trimethylsilyloxy-substituted tellurides **18**.[18] Other examples of such reactions have also been described.[18]



18

R = Me, Et, n = 0; R = H, n = 1–4; R = Me, n = 2.

Organyl trimethylsilyl tellurides $RTeSiMe_3$ are synthetic equivalents of organyl tellurolate anions RTe^- (see Refs 4–9). In some cases, the use of tellurides gives better results in comparison with alkali-metal tellurolates. Thus the reaction of $MeTeSiMe_3$, generated *in situ* from MeTeLi and Me_3SiCl, with arylazo sulfones in MeCN containing catalytic amounts of 18-crown-6 afforded aryl methyl tellurides in 36%–62% yields.[8]

$$MeTeSiMe_3 + RC_6H_4N_2SO_2C_6H_4Me\text{-}4 \xrightarrow{MeCN,\ 20\ ^\circ C,\ 18\text{-}C\text{-}6} RC_6H_4TeMe$$

R = H, 4-Br, 4-COMe, 2-CO_2Me.

The use of MeTeLi prepared from MeLi and Te in THF does not lead to aryl methyl tellurides in this reaction. Deazosulfonation in THF does not take place, but substitution of MeCN for THF yields a mixture of dimethyl telluride and dimethyl ditelluride which are inert with respect to arylazosulfones.[8]

Under mild conditions (THF, 20 °C), phenyl trimethylsilyl telluride reacts with aroyl chlorides to give phenyl tellurobenzoates **19a–i** (yield 62%–91%).[9] The advantages of this procedure in comparison with the classical methods based on the use of sodium arenetellurolates lie in higher yields of the esters formed and the simplicity of their isolation from reaction mixtures.[38]

$$PhTeSiMe_3 + ArCOCl \xrightarrow[-Me_3SiCl]{THF,\ 20\ ^\circ C} \underset{\mathbf{19a-h}}{ArCOTePh}$$

Ar = 4-ClC_6H_4 (**a**), 3-ClC_6H_4 (**b**), 4-BrC_6H_4 (**c**), 4-$NO_2C_6H_4$ (**d**), 4-NCC_6H_4 (**e**), Ph (**f**), 4-MeC_6H_4 (**g**), 4-$MeOC_6H_4$ (**h**).

$$PhTeSiMe_3 + 1\text{-}ClOCC_6H_4COCl\text{-}4 \xrightarrow[-Me_3SiCl]{THF,\ 20\ ^\circ C} \underset{\mathbf{19i}}{PhTeOCC_6H_4COTePh}.$$

Aryl tris(trimethylsilyl)silyl tellurides **8a**,**b** used *in situ* react with chloroformates exclusively in the presence of catalytic amounts of tetrakis(triphenylphosphine)palladium(0) to give aryl tellurocarbonates **20a–j** [6,7] (for the use of compounds **20a–j** as precursors of oxyacyl and alkyl radicals see Refs 39, 40). Aryl tellurocarbonates **20e**,**j** with a phenyl radical at the ester oxygen atom can be prepared [6,7] only from compounds **8a**,**b**. They could not be obtained in the reaction of chloroformates with sodium arenetellurolate.[6,7]

$$\underset{\mathbf{8a,b}}{ArTeSi(SiMe_3)_3} + ROC(O)Cl \xrightarrow[-(Me_3Si)_3SiCl]{PhH,\ (Ph_3P)_4Pd,\ 20\ ^\circ C} \underset{\mathbf{20a-j}}{ROC(O)TeAr}.$$

Compound **20**	Ar	R	Compound **20**	Ar	R
a	Ph	Me	**f**	4-FC_6H_4	Me
b	Ph	Pr^i	**g**	4-FC_6H_4	Pr^i
c	Ph	cyclo-C_6H_{11}	**h**	4-FC_6H_4	cyclo-C_6H_{11}
d	Ph	C_8H_{17}	**i**	4-FC_6H_4	C_8H_{17}
e	Ph	Ph	**j**	4-FC_6H_4	Ph

Compounds **1** react with some metal halides to give the corresponding metal tellurolates. Thus the reaction of phenyl triphenylgermyl(stannyl) tellurides **1e**,**i** with the palladium(II) chloride–benzonitrile complex results in elimination of Ph_3ECl followed by the formation of red-brown palladium tellurolates **21** which seem to possess polymeric structures.[4]

$$\underset{\mathbf{1e,i}}{PhTeEPh_3} + Pd(PhCN)_2Cl_2 \xrightarrow[-Ph_3ECl,\ -PhCN]{CHCl_3,\ 20\ ^\circ C} \underset{\mathbf{21}}{[(PhTe)_2Pd]_n}$$

E = Ge (**1e**), Sn (**1i**).

The reaction of compounds **1** with CuCl in chloroform [4] or acetonitrile [41] gives polymeric copper(I) tellurolates **22**.

$$\underset{\mathbf{1}}{ArTeEPh_3} + CuCl \xrightarrow[-Ph_3ECl]{} \underset{\mathbf{22}}{(ArTeCu)_n}$$

Ar = Ph, 4-$EtOC_6H_4$; E = Ge, Sn, Pb.

Metal tellurolates are also formed in those cases where phenyl trimethylsilyl telluride is used as a source of the ligand PhTe. Thus reaction of this compound with dimethylcadmium in CH_2Cl_2 gave cadmium(II) benzenetellurolate (**23**).[10]

$$PhTeSiMe_3 + CdMe_2 \xrightarrow[-Me_4Si]{20\ ^\circ C} \underset{\mathbf{23}}{(PhTe)_2Cd}.$$

Reaction of organyl trimethylsilyl tellurides, particularly, $BuTeSiMe_3$, with copper(I) salts results in tellurium-containing clusters which were characterised by the X-ray diffraction method.[5]

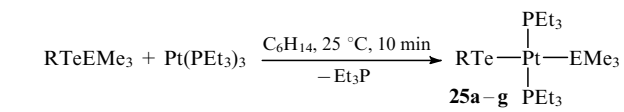
$$BuTeSiMe_3 + CuX \xrightarrow{a} [Cu_{11}(\mu_3\text{-}TeBu)_7(\mu_4\text{-}TeBu)_2(\mu_7\text{-}Te)(PPh_3)_5]$$
$$\xrightarrow{b} [Cu_{18}(\mu_3\text{-}Te)_6Te_6(PPr_3)_8]$$
$$\xrightarrow{c} [Cu_{23}Te_{13}(PEt_3)_{12}]$$
$$\xrightarrow{d} [Cu_{58}Te_{32}(PPh_3)_{16}]$$

X = Cl, OAc; (*a*) PPh_3, THF; (*b*) PPr_3, diglyme; (*c*) PEt_3, THF; (*d*) PPh_3, diglyme.

The cluster **24** is the only reaction product of phenyl trimethylsilyl telluride with a complex cobalt(II) salt.[5]

$$PhTeSiMe_3 + [CoCl_2(PPh_2Pr)_2] \xrightarrow{THF,\ 20\ ^\circ C} \underset{\mathbf{24}}{[Co_6(\mu\text{-}Te)_8(PPh_2Pr)_6]}.$$

It has been shown recently [42] that compounds $RTeEMe_3$, similar to $(Me_3E)_2Te$ (E = Si, Sn), enter into oxidative addition with triethylphosphine platinum complexes $Pt(PEt_3)_n$ (n = 3, 4) to give complexes **25a–g** in 76%–100% yields.



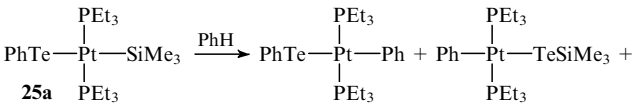
25a–g

E = Si: R = Ph (**a**), 4-PhC_6H_4 (**b**), Bu (**c**), Me_3Si (**d**);
E = Ge, R = Ph (**e**); E = Sn: R = Ph (**f**), Me_3Sn (**g**).

The structures of compounds **25** were confirmed by NMR spectroscopy and the X-ray diffraction analysis using complex **25b** [42] as an example. They represent solid red-coloured substances stable under an argon atmosphere but extremely sensitive to oxygen and moisture.[42]

The reactivities of phenyl trimethylsilyl chalcogenides $PhM(SiMe_3)_3$ (M = S, Se, Te) in this reaction increase in the following order: S < Se < Te. Thus phenyl trimethylsilyl sulfide does not react with $Pt(PEt_3)_3$ even after 5-h heating at 50 °C, whereas phenyl trimethylsilyl selenide reacts with the Pt(0) complex at 25 °C, albeit at a much slower rate than its tellurium analogue.[42]

Complexes **25** are gradually decomposed in benzene even at 25 °C. The following decomposition products of compound **25a** have been identified:[42]



+ $PhSiMe_3$ + $(Me_3Si)_2Te$.

The decomposition reaction is reversible, *i.e.*, the addition of even 1 equiv. of PEt_3 inhibits this process.[42]

III. Methods of synthesis and reactions of compounds $(R_3E)_2Te$ (E = Si, Ge, Sn, Pb)

Compounds containing two bonds of Te to Group 14 elements include both symmetrical $(R_3E)_2Te$ (E is a Group 14 element) (**7**) and non-symmetrical derivatives of the type $R^1_3ETeER^2_3$ (**26**). The methods of their syntheses and reactions of both types of compounds are very similar and will therefore be considered in the same section.

1. Methods of synthesis

Two reactions affording tellurides **7** are described in Section II. The first of them is the reaction of hydrides R_3EH with diorganyl tellurides. Depending on the nature of substrates, this reaction gives compounds **1** and **7** or their mixtures.[25,26] The second reaction is disproportionation of tellurides **1**.[17]

The addition of Me_3SiCl to an ethereal solution of PhTeMgBr leads to the formation of bis(trimethylsilyl) telluride,[43] apparently also as a result of disproportionation of $PhTeSiMe_3$ under the reaction conditions. It should be noted that the same reactants in THF (see Section II.1) give $PhTeSiMe_3$.

The general method for the synthesis of both symmetrical (**7**) and non-symmetrical (**26**) tellurides is based on the reaction of organolithium derivatives $R^1_3E^1TeLi$ with chlorides $R^2_3E^2Cl$.[44–48] However, this method is only seldom employed, *e.g.*, in the synthesis of phenyl derivatives containing various combinations of Ge, Sn and Pb atoms. This reaction was also used in the synthesis of bis(triphenylsilyl) telluride.[49]

$$Ph_3E^1TeLi + Ph_3E^2Cl \xrightarrow[-LiCl]{} Ph_3E^1{-}Te{-}E^2Ph_3 .$$

7e–g, **26a–c**

Compound	E^1	E^2	Ref.
7e	Ge	Ge	46
7f	Sn	Sn	44, 45
7g	Pb	Pb	47
26a	Sn	Ge	46
26b	Sn	Pb	45
26c	Pb	Ge	46

Non-symmetrical derivatives **26d–f** are also obtained by reactions of triethyltin or -germanium hydrides with tellurides **1q**,**r** (yields 60%–90%)[26] or **7a**,**b**.[50]

$$EtTeE^1Et_3 + Et_3E^2H \xrightarrow[-C_2H_6]{\Delta} Et_3E^1TeE^2Et_3$$

1q,**r** **26d**,**e**

$$(Et_3E^1)_2Te + Et_3E^2H \xrightarrow[-Et_3E^1H]{\Delta} Et_3E^1TeE^2Et_3$$

7a,**b** **26e**,**f**

E^1 = Si (**1q**, **7a**), Ge (**1r**, **7b**); E^1 = Si, E^2 = Sn (**26d**); E^1 = Ge, E^2 = Sn (**26e**); E^1 = Si, E^2 = Ge (**26f**).

In these reactions, the reactivities of the hydrides decrease in the following order: Sn > Ge > Si. Thus the reaction of Et_3GeH with $(Et_3Si)_2Te$ yields $(Et_3Ge)_2Te$ (yield 79%) and Et_3SiH (yield 50%) at 235 °C for 6 h, while the reaction of Et_3SnH with $(Et_3Ge)_2Te$ results in $(Et_3Sn)_2Te$ (yield 76%) and Et_3GeH (yield 57%) at 70 °C for 1 h.[50]

Reactions of the mercury derivatives $(Et_3E^1)_2Hg$ with the hydrides R_3E^2TeH also yield non-symmetrical tellurides **26**,[51] however, this method has been studied relatively little. Reaction of bis(triethylgermyl)mercury with Et_3SiTeH (molar ratio 1 : 1) yields compound **27** with the Si–Te–Hg–Ge fragment, which can easily eliminate the mercury atom to yield the non-symmetrical telluride **26f** under mild conditions (−78 °C, 2–3 min).

$$Et_3SiTeH + (Et_3Ge)_2Hg \xrightarrow[-Et_3GeH]{} Et_3SiTeHgGeEt_3 \xrightarrow[-Hg]{20\ ^\circ C} Et_3SiTeGeEt_3 .$$

27 **26f**

It is of note that in contrast to compound **27**, bis(triethylsilyltelluro)mercury (**28**) formed with a tellurol : mercury molar ratio of 2 : 1 is thermally stable and is not decomposed even on heating to 130 °C for 7 h.[51]

$$Et_3SiTeH + (Et_3Ge)_2Hg \xrightarrow[-Et_3GeH]{} Et_3SiTeHgTeSiEt_3 .$$

28

The synthesis of symmetrical tellurides **7** has been studied in much more detail than that of the non-symmetrical analogues **26**. Reaction of sodium[52] or lithium[21,53–57] tellurides with the halides R_3EX is the most general approach to their synthesis. The yields of tellurides **7** vary from very low (5%)[57] to quantitative.[55]

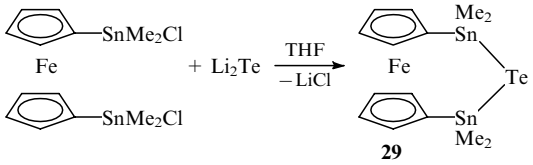
$$M_2Te + R_3EX \xrightarrow[-MX]{} (R_3E)_2Te$$

7h–n

M = Na, Li.

Compound **7**	E	R_3	Ref.
h	Si	H_3	53, 55
i	Si	Me_3	21, 52–54, 56
j	Si	Bu^tMe_2	56
k	Ge	$(CF_3)_3$	57
l	Ge	Me_3	52
m	Sn	Me_3	52
n	Pb	Me_3	52

Reaction of 1,1′-bis(chlorodimethylstannyl)ferrocene[58] with lithium telluride was used to obtain 1,3-distanna-2-tellura[3]ferrocenophane **29** (yield 28%).[59]



29

Sodium hydrotelluride was employed in the synthesis of bis(triphenylstannyl) telluride (**7f**).[19,60]

Some digermyl tellurides were prepared using hydrogen telluride as the tellurium-containing reagent.[61] Thus warming of a mixture of carbodiimides **30** with an excess of H_2Te from −196 °C to room temperature results in bis(germyl) tellurides **31** in 60%–90% yields.[61]

$$Me_nH_{3-n}Ge{-}N{=}C{=}N{-}GeMe_nH_{3-n} + H_2Te \xrightarrow[-H_2NCN]{} (Me_nH_{3-n}Ge)_2Te$$

30 **31**

n = 1–3.

Silicon analogues of carbodiimides **30** do not enter into such reactions.[61]

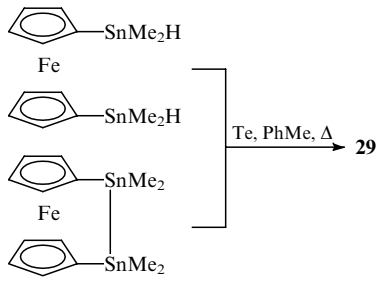
The symmetrical tellurides **7a–c** were obtained by heating hydrides R_3EH with tellurium powder.[26,50,62,63] As in the previous cases, the reactivities of the hydrides increase in the following order: Si < Ge < Sn. Whereas the reaction of tellurium with

Et_3SnH proceeds at 130 °C[26,62] and that with Et_3GeH, at 190–210 °C,[26,62] the reaction of Te with Et_3SiH resulting in bis(triethylsilyl) telluride **7a** in 71% yield can be realised only at 280 °C.[50,63]

$$Te + Et_3EH \xrightarrow[-H_2]{\Delta} \underset{\mathbf{7a-c}}{(Et_3E)_2Te}$$

E = Si (**a**), Ge (**b**), Sn (**c**).

The reaction of 1,1′-bis(dimethylstannyl)ferrocene[58] with tellurium powder was used for the synthesis of telluride **29** (yield 90%);[59] the same compound was obtained in 79% yield by reaction of 1,1,2,2-tetramethyl-1,2-distanna[2]ferrocenophane with tellurium.[59]



Depending on the nature of the hydride and the chalcogen, reactions of sulfur and selenium with hydrides R_3EH yield either organoelement hydrochalcogenides R_3EMH [E = Si,[50,63] Ge;[26] M = S,[63] Se (see Refs 26, 50 and 63)] or their mixtures with compounds $(R_3E)_2M$. The stabilities of hydrides R_3EMH increase in the following order: Te < Se < S. Thus heating of sulfur with triphenylsilane at 200 °C gives triphenylsilanethiol Ph_3SiSH as the only product (yield 70%),[63] whereas reaction of selenium with triethylsilane (260 °C) results in a mixture of Et_3SiSeH (yield 62%) and $(Et_3Si)_2Se$ (yield 32%).[50,63] The latter represents a symmetrisation product.[63]

$$Et_3SiSeH \longrightarrow (Et_3Si)_2Se + H_2Se.$$

Whereas triethylsilanetellurol Et_3SiTeH, which is the least stable of all chalcogenols, is symmetrised completely, the degree of conversion of more stable triethylsilaneselenol into bis(triethylsilyl) selenide and H_2Se is only 40%.[63]

It should be noted that reaction of selenium with germanes R_3GeH (R = Pr^i, cyclo-C_6H_{11}) yields predominantly germane selenols R_3GeSeH.

Tributylphosphine telluride $Bu_3P{=}Te$, a synthetic equivalent of metallic tellurium, was used instead of the latter in reactions with triorganylstannyl hydrides.[64] Its solubility in organic solvents makes it possible to synthesise bis(triorganylstannyl) tellurides, *e.g.*, bis(tributylstannyl) telluride **7o**, under mild conditions in the presence of catalytic amounts (2 mol.% – 10 mol.%) of Cp^*_2TiH ($Cp^* = Me_5C_5$). In the absence of a catalyst, the yield of the target product does not exceed 2%.[64]

$$Te{=}Bu_3P + Bu_3SnH \xrightarrow[-H_2,\ -Bu_3P]{C_6D_6,\ 25\ ^\circ C,\ Cp^*_2TiH} \underset{\mathbf{7o}}{(Bu_3Sn)_2Te}.$$

Tellurides **7** (E = Ge, Sn) were also synthesised by exchange reactions of compounds **7** containing more light weight Group 14 elements with the halides R_3EX. Thus bis[tris(pentafluorophenyl)stannyl] telluride **7p** was obtained (in 57% and 51% yields, respectively) by reaction of bis(triethylgermyl) (**7b**) or bis(triethylsilyl) tellurides (**7a**) with $(C_6F_5)_3SnBr$.[65] This reaction seems to involve stepwise exchange of Et_3E groups (E = Si, Ge) for $(C_6F_5)_3Sn$ groups and proceeds through four-membered transition states.

$$\underset{\mathbf{7a,b}}{(Et_3E)_2Te} + (C_6F_5)_3SnBr \xrightarrow[-Et_3EBr]{PhMe,\ \Delta} \underset{\mathbf{7p}}{[(C_6F_5)_3Sn]_2Te}$$

E = Si (**a**), Ge (**b**).

With an excess of germyl bromide, di(silyl) telluride (**7q**) is quantitatively converted into di(germyl) telluride (**7d**), apparently, by the same mechanism.[55]

$$\underset{\mathbf{7q}}{(H_3Si)_2Te} + H_3GeBr \xrightarrow[-H_3SiBr]{0\ ^\circ C,\ 18\ h} \underset{\mathbf{7d}}{(H_3Ge)_2Te}.$$

Other methods of synthesis of tellurides **7** were studied in separate reactions, although some of them can be used for the synthesis of a larger number of compounds. Thus bis(triisopropylgermyl) telluride (**7r**) was obtained in 78% yield by reaction of bis(triisopropylgermyl)mercury with tellurium powder.[30]

$$(Pr^i_3Ge)_2Hg + Te \xrightarrow[-Hg]{THF,\ 20\ ^\circ C,\ 30\ h} \underset{\mathbf{7r}}{(Pr^i_3Ge)_2Te}.$$

Bis(trifluorosilyl) telluride (**7s**) was prepared by reaction of trifluorosilyl radicals generated by decomposition of hexafluorodisilane with tellurium vapour in a low-temperature matrix.[66,67]

$$F_3Si^{\bullet} + Te \longrightarrow \underset{\mathbf{7s}\ (25\%)}{(F_3Si)_2Te}.$$

The synthesis of silyl derivatives of the type **7,** which contain sterically hindered silane residues, requires special strategies. Thus bis(triphenylsilyl) telluride (**7t**) was obtained by protonation of lithium triphenylsilanetellurolate (**32**) in THF or by oxidation of this salt with atmospheric oxygen.[49]

$$\underset{\mathbf{32}}{Ph_3SiTeLi\cdot 3\,THF} \xrightarrow{CF_3CO_2H,\ THF} \underset{\mathbf{7t}}{(Ph_3Si)_2Te}.$$

It should be noted that oxidation of tris(trimethylsilyl)silanetellurol $(Me_3Si)_3SiTeH$ or its lithium salt results in the ditelluride $[(Me_3Si)_3Si]_2Te_2$.[68,69]

The symmetrical telluride **33** is formed together with the corresponding metal tellurides by pyrolysis of tellurolates **34**.[16]

$$\underset{\mathbf{34}}{[(Me_3Si)_3SiTe]_2M} \xrightarrow{\Delta} \underset{\mathbf{33}}{[(Me_3Si)_3Si]_2Te} + MTe$$

M = Zn, Cd, Sn, Pb, Yb.

The symmetrical and non-symmetrical tellurides considered above containing two Te–E bonds have identical substituents on the Group 14 elements. Presumably, telluride **35**[69] synthesised from lithium tris(trimethylsilyl)silanetellurolate and trimethylchlorosilane is the only compound which has different substituents on these atoms.

$$\underset{\mathbf{35}}{(Me_3Si)_3SiTeSiMe_3}.$$

2. Reactions of compounds $(R_3E)_2Te$

It should be noted that the majority of reactions of tellurides **7** and **26** have been studied for a limited number of compounds only; therefore, it is sometimes difficult to judge the general type of one or another reaction.

Most reactions of tellurides **7** (reactions of the non-symmetrical derivatives **26** have been studied relatively little) occur with elimination of tellurium. The hydride derivatives $(H_3E)_2Te$ are photosensitive and are decomposed on rough glass surfaces even at room temperature,[53] while bis[tris(trifluoromethyl)germyl] telluride (**7k**) eliminates tellurium only at 115 °C.[57] Tellurides **7**

containing alkyl and trifluoromethyl radicals are rather easily hydrolysed.[57]

$$[(CF_3)_3Ge]_2Te \xrightarrow{115\ ^\circ C} (CF_3)_3GeGe(CF_3)_3 + Te$$
$$\mathbf{7k} \xrightarrow{H_2O} [(CF_3)_3Ge]_2O + CF_3GeH + Te$$

Symmetrical (**7e**–**g**) and non-symmetrical phenyl derivatives (**26a**–**c**) are thermally and hydrolytically stable compounds. Their stabilities with respect to moisture and oxygen increase in the following order: $(Ph_3Ge)_2Te < (Ph_3Pb)_2Te$ and $(Ph_3Ge)_2Te < Ph_3GeTeSnPh_3 < Ph_3GeTePbPh_3$.[47] The non-symmetrical aliphatic derivatives $R^1_3E^1TeE^2R^2_3$ easily disproportionate to give the symmetrical tellurides $(R^1_3E^1)_2Te$ and $(R^2_3E^2)_2Te$.[70]

The Te–E bonds in tellurides **7** are easily cleaved under the action of various oxidants. Thus the silyl derivatives **7h**,**i** react with oxygen to give elementary tellurium and the corresponding siloxane.[53]

$$(R_3Si)_2Te + O_2 \longrightarrow (R_3Si)_2O + Te$$
$$\mathbf{7h,i}$$

R = H (**h**), Me (**i**).

The oxidation of tellurides **7** by halogens proceeds under mild conditions and gives halides R_3EX (yields 50%–85%) and Te; some amount of R_2SnX_2 is formed in the case of stannyl derivatives.[56, 71]

$$(R_3E)_2Te + X_2 \xrightarrow{PhH,\ 0\ ^\circ C} R_3EX + Te$$
$$\mathbf{7a-c,i}$$

R = Et: E = Si (**a**), Ge (**b**), Sn (**c**); R = Me, E = Si (**i**); X = Cl, Br, I.

The reactions of the tellurides **7** with Ag(I)[43] and Hg(II)[51] salts also afford halides R_3EX and, in addition, metal tellurides. Noteworthy, the reactions of these salts with diorganyl tellurides R_2Te give complexes with the compositions 1 : 1 or 1 : 2.[72]

$$(Et_3E)_2Te + HgCl_2 \xrightarrow{THF,\ 20\ ^\circ C} Et_3ECl + HgTe$$
$$\mathbf{7a,b}$$

E = Si (**a**), Ge (**b**).

$$(Me_3Si)_2Te + AgI \xrightarrow{20\ ^\circ C} Me_3SiI + Ag_2Te.$$
$$\mathbf{7i}$$

It has been shown for the first time[63] that the cleavage of E–Te bonds in compounds **7** is effected not only by free halogens but also by organic dihalides containing rather active halogen atoms. Thus boiling of ethyl derivatives **7a**–**c** with 1,2-dibromoethane leads to the formation of Et_3EBr, Te and ethylene.[63] The reaction with bis(triethylstannyl) telluride (**7c**) proceeds most smoothly.

$$(Et_3E)_2Te + BrCH_2CH_2Br \xrightarrow[-Te]{130-150\ ^\circ C} Et_3EBr + CH_2{=}CH_2$$
$$\mathbf{7a-c}$$

E = Si (**a**), Ge (**b**), Sn (**c**).

It is this reaction in particular that underlies the synthesis of alkenes from vicinal dibromides using bis(triphenylstannyl) telluride (**7f**) and CsF as a dehalogenating reagent.[73]

$$(Ph_3Sn)_2Te + R^1CH(Br)CH(Br)R^2 \xrightarrow[-Ph_3SnBr,\ -Te]{CsF,\ MeCN,\ 20\ ^\circ C,\ 3-4\ h}$$
$$\mathbf{7f}$$
$$\longrightarrow R^1CH{=}CHR^2$$

R^1 = H: R^2 = Ph, n-C_8H_{17}, $PhSO_2CH_2$; $R^1 = R^2$ = Ph;
$R^1-R^2 = CH_2OCH_2OCH_2$.

This reaction proceeds under mild conditions; alkenes are most frequently formed in virtually quantitative yields. Thus the reaction of *meso*-1,2-dibromo-1,2-diphenylethane with $(Ph_3Sn)_2Te$ results in *trans*-stilbene in 94% yield.[73]

Upon substitution of $KF\cdot H_2O$ for CsF, telluride **7f** effects dehalogenation of α-chloro(bromo) ketones under mild conditions (MeCN, 20 °C).[73] With a molar reagent ratio **7f** : $KF\cdot 2\,H_2O$: α-halogeno ketone of 1 : 3 : 1, the ketones are formed in 60%–90% yields. The feasible mechanism of this reaction includes the intermediate formation of triphenylstannanetellurol.[74]

$$(Ph_3Sn)_2Te \xrightarrow{KF\cdot 2H_2O} [Ph_3SnTeH] \xrightarrow[-Ph_3SnX,\ -Te]{R^1R^2C(X)C(O)R^3}$$
$$\mathbf{7f}$$
$$\longrightarrow R^1R^2CHCOR^3$$

$R^1 = R^2$ = H: R^3 = Me, Et, Ph; R^1 = Me, R^3 = Ph: R^2 = H, Me;
$R^1-R^3 = (CH_2)_4$, R^2 = H.

Cleavage of the Te–E bonds in tellurides **7a**–**c** proceeds smoothly under the action of symmetrical and non-symmetrical acyl peroxides.[75] This reaction gives high yields of elementary tellurium and triorganylsilyl (germyl, stannyl) esters of the corresponding acids.

$$(Et_3E)_2Te + R^1CO_3COR^2 \xrightarrow[-Te]{} Et_3EOCOR^1 + Et_3EOCOR^2$$
$$\mathbf{7a-c}$$

E = Si (**a**), Ge (**b**), Sn (**c**); R^1 = Ph, R^2 = Ph, Me.

Reaction of bis(triethylgermyl) telluride (**7b**) with dicyclohexyl percarbonate yields CO_2 and cyclohexyloxytriethylgermane together with Te, apparently as a result of decomposition of the initially formed triethylgermyl cyclohexanecarboxylate.[75]

$$(Et_3Ge)_2Te + (\text{cyclo-}C_6H_{11}OCO_2)_2 \xrightarrow[-Te]{}$$
$$\mathbf{7b}$$
$$\longrightarrow [\text{cyclo-}C_6H_{11}OCO_2GeEt_3] \xrightarrow[-CO_2]{}$$
$$\longrightarrow \text{cyclo-}C_6H_{11}OGeEt_3\,.$$

Like diaryl tellurides Ar_2Te,[72] tellurides **7a**,**c** eliminate Te upon heating with sulfur or selenium to give sulfides and selenides, respectively.[50, 63] As in the reaction with diaryl tellurides,[72] sulfur surpasses selenium in activity. Thus reaction of $(Et_3Sn)_2Te$ with sulfur proceeds at 20 °C (90 h), whereas reaction of the same telluride with selenium requires heating at 150 °C for 30 h.[50, 63]

$$(Et_3E)_2Te + M \xrightarrow[-Te]{\Delta} (Et_3E)_2M$$
$$\mathbf{7a,c}$$

E = Si, M = S; E = Sn: M = S, Se.

Formally, reduction of diorganyl chalcogen oxides by bis(trialkylsilyl) tellurides is related to the same class of reactions.[56] This can be regarded as a preparative method for the synthesis of chalcogenides from chalcogen oxides because of their high yields (80%–100%) and easy separation from other products, *viz.*, hexaalkyldisiloxanes and elementary tellurium. It should be noted that bis(trimethylsilyl) sulfide and selenide are also rather efficient reagents.[56]

$$(R^1_3Si)_2Te + R^2_2MO \xrightarrow[-Te]{THF} R^2_2M + (R^1_3Si)_2O$$

R^1 = Me: R^2 = Ph, M = Te; R^2 = Me, M = S;
R^1_3 = Bu^tMe_2: R^2 = Ph, M = Se; R^2 = Me, M = S.

The use of bis(triphenylstannyl) telluride (**7f**) for monodesulfurisation of organic trisulfides[76] and synthesis of aryl triphenylstannyl sulfides[77] is based on easy elimination of the Te atom from compounds **7**. Various types of organic trisulfides (aryl-, benzyl-, alkyl-) are readily converted into the corresponding disulfides under the action of $(Ph_3Sn)_2Te$. The rate of the desulfurisation reaction increases with an increase in the solvent polarity.

$$R{-}S{-}S{-}S{-}R + \underset{\mathbf{7f}}{(Ph_3Sn)_2Te} \xrightarrow[-Te]{MeCN,\ 20\ ^\circ C} R{-}S{-}S{-}R + (Ph_3Sn)_2S$$

R = FC_6H_4, MeC_6H_4, Bn, PhCHMe, $Me(CH_2)_2$.

Other bis(triphenylstannyl) chalcogenides $(Ph_3Sn)_2M$ (M = S, Se) can monosulfurise organic trisulfides; the reactivities of chalcogenides $(Ph_3Sn)_2M$ decrease in the following order: Te > Se > S. Bis(triphenylstannyl) selenide causes desulfurisation of only diaryl and dibenzyl trisulfides, whereas desulfurisation by bis(triphenylstannyl) sulfide proceeds with very low yields and only upon long-term boiling of the reaction mixture.[76]

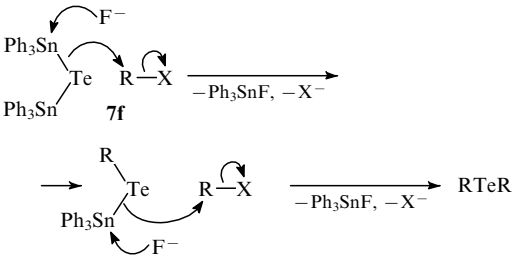
Reaction of telluride **7f** with diaryl disulfides under mild conditions (MeCN, 20 °C) results in aryl triphenylstannyl sulfides **36** in high, sometimes quantitative, yields.[77] Dialkyl and dibenzyl disulfides do not enter into such reactions. Compounds **36** can be synthesised from diaryl disulfides and bis(triphenylstannyl) selenide.[77] However, the latter is much less efficient than tellurides. 4-Methylphenyl triphenylstannyl sulfide is formed in a quantitative yield upon treatment of the corresponding disulfide with telluride **7f** and in only 28% yield when a selenium derivative is used, other conditions (solvent, temperature, reaction time) being the same.[77]

$$Ar_2S_2 + \underset{\mathbf{7f}}{(Ph_3Sn)_2Te} \xrightarrow[-Te]{MeCN,\ 20\ ^\circ C,\ 3\ h} \underset{\mathbf{36}}{ArSSnPh_3}$$

Ar = 4-ClC_6H_4, 4-FC_6H_4, Ph, 4-MeC_6H_4, 2-$C_{10}H_7$.

If organyl trimethylsilyl tellurides $RTeSiMe_3$ represent synthetic equivalents of organyltellurolate anions RTe^- (see Section II.2), compounds **7** and particularly bis(triphenylstannyl) telluride **7f** act as synthetic equivalents of the telluride anion Te^{2-} (see Refs 73, 78).

Bis(triphenylstannyl) telluride **7f** used in combination with CsF (4 equiv.) is a mild tellurinating reagent.[73,78] Reactions of this reagent with organic bromides and iodides in MeCN at 20 °C afford symmetrical diorganyl tellurides in high yields.[73,78] Aryl iodides and alkyl chlorides are inert with respect to compound **7f**, which makes it possible to synthesise diorganyl tellurides containing chlorine atoms. It is believed [73] that the synthesis of diorganyl tellurides proceeds in two steps and includes an attack of the fluoride ion on the tin atom.



X = Br, I; R = Pr^i, Bn, $Cl(CH_2)_6$, $Me(CH_2)_9$, $PhCOCH_2$, CH_2CO_2Et, CH_2CO_2Me, $CH_2CO_2Pr^n$, $CH_2CO_2Bu^t$, $(CH_2)_3CO_2Et$.

Reactions of bis(trialkylsilyl) tellurides with certain organoelement compounds occur with the cleavage of both Te–Si bonds and lead to the formation of tellurides of the corresponding metals rather than elementary Te; these reactions are of special interest. Thus reactions of bis(trimethylsilyl) telluride (**7i**) with tris(dimethylamino)antimony or -bismuth occur under very mild conditions (hexane, −30 °C) and yield polycrystalline antimony and bismuth tellurides [11] which manifest semiconducting properties.

$$\underset{\mathbf{7i}}{(Me_3Si)_2Te} + M(NMe_2)_3 \xrightarrow[-Me_3SiNMe_2]{} M_2Te_3$$

M = Sb, Bi.

Metal dialkyls can be used instead of dimethylamino derivatives. This method was used in the synthesis of Cd(II) telluride.[10]

$$(Pr^iMe_2Si)_2Te + Me_2Cd \xrightarrow[-Pr^iMe_3Si]{} CdTe.$$

Reaction of bis(trimethylsilyl) telluride (**7i**) with copper(I) chloride in the presence of phosphines results in the formation of cluster copper complexes [79] which differ from those obtained using butyl trimethylsilyl telluride (see Section II.2).

$$\underset{\mathbf{7i}}{(Me_3Si)_2Te} + CuCl \longrightarrow$$

a → $[Cu_{16}Te_9(PEt_3)_8]$

b → $[Cu_{16}Te_9(PPhEt_2)_8] + [Cu_{28}Te_{17}(PPhEt_2)_{12}]$

c → $[Cu_4Te_4(PPr^i_3)_4] + [Cu_{23}Te_{13}(PPr^i_3)_{10}] + [Cu_{29}Te_{16}(PPr^i_3)_{12}]$

d → $[Cu_{26}Te_{16}(PBu^t_3)_{10}]$

(*a*) PEt_3, Et_2O; (*b*) $PPhEt_2$, Et_2O; (*c*) PPr^i_3, Et_2O; (*d*) PBu^t_3, THF.

Reactions of tellurides **7** with other than Sb, Bi and Cd organoelement derivatives occur with the cleavage of two (less frequently, one) Te–E bonds; in this case, tellurium becomes a constituent of one of the reaction products.

Bis(tributylstannyl) telluride undergoes transmetallation with trimethylaluminium.[80,81] Bis(dimethylaluminium) telluride $(Me_2Al)_2Te$ used *in situ* is an efficient tellurinating reagent. Treatment of aldehydes, ketones [80] and *N*-methylformanilide [81] with this reagent results in telluroaldehydes (ketones) [80] and *N*-methyltelluroformanilide,[81] respectively.

$$(Bu_3Sn)_2Te + Me_3Al \xrightarrow[-Bu_3SnMe]{PhMe,\ 80\ ^\circ C} (Me_2Al)_2Te \xrightarrow[-(Me_2Al)_2O]{R^1R^2CO} R^1CR^2 \,\|\, Te$$

R^1 = H: R^2 = Pr^n, Bu^t, Ph, N(Me)Ph; R^1R^2CO — adamantanone, bicyclo[3.3.1]nonan-7-one.

Tellurides $(H_3E)_2Te$ react with PF_2Br with the cleavage of one and two Te–E bonds to give a mixture of compounds **37** and **38**.[82] These compounds were not isolated; their formation was deduced from the ^1H and ^{19}F NMR spectra.

$$(H_3E)_2Te + PF_2Br \xrightarrow[-H_3EBr]{} \underset{\mathbf{37}}{H_3ETePF_2} + \underset{\mathbf{38}}{(F_2P)_2Te}$$

E = Si, Ge.

At the same time, reaction of bis(trimethylsilyl) telluride **7i** with Bu^tPCl_2 occurs with the cleavage of both Te–Si bonds resulting in a mixture of cyclic compounds **39** and **40**.[83]

$$\underset{\mathbf{7i}}{(Me_3Si)_2Te} + Bu^tPCl_2 \xrightarrow[-Me_3SiCl]{} \underset{\mathbf{39}}{Bu^tP(Te)PBu^t} + \underset{\mathbf{40}}{Bu^tP(Te)PBu^t}$$

Reactions of bis(trialkylsilyl) tellurides with acyl chlorides and bisacyl tellurides have been considered in the recently published review.[84]

The Te–E bond in tellurides **7** is easily cleaved by protic acids (HCl, anhydrous CF_3CO_2H).[63] Thus the first silanetellurol, *viz.*, triethylsilanetellurol, was obtained by treating bis(triethylsilyl) telluride (**7a**) with trifluoroacetic acid (molar ratio 1 : 1) at 20 °C. In the presence of an excess of the acid, the Te–Si bond of tellurol is cleaved to give triethylsilyl trifluoroacetate and elementary Te, presumably as a result of oxidation of the intermediate H_2Te.[63]

$$(Et_3Si)_2Te + CF_3CO_2H \xrightarrow[-CF_3CO_2SiEt_3]{} Et_3SiTeH \xrightarrow[-CF_3CO_2SiEt_3]{CF_3CO_2H}$$
7a
$$\longrightarrow H_2Te \xrightarrow[-H_2O]{O_2} Te.$$

Reaction of germyl tellurides **31** with gaseous HI at 20 °C results in the cleavage of both Te–Ge bonds [55, 61] to give germyl iodides and H_2Te.

$$(Me_nH_{3-n}Ge)_2Te + HI \longrightarrow Me_nH_{3-n}GeI + H_2Te$$
31

$n = 0-3$.

Silane- and germane-tellurols **41** are formed by an exchange reaction between the corresponding tellurides and H_2Te.[85] The equilibrium constants are equal to 0.90 (E = Si) and 0.95 (E = Ge).

$$(H_3E)_2Te + H_2Te \rightleftharpoons 2\,H_3ETeH$$
41

E = Si, Ge.

The signals for the Te–H protons in the ^1H NMR spectra of tellurols **41** are observed at very high fields. Thus δ_{TeH} of silanetellurol is equal to −7.46 ppm, while that of germanetellurol is −7.44 ppm.[85]

The Te–E bonds are not affected upon complexation of tellurides **7** with some Lewis acids. The stable complexes **42a–c** (1 : 1) were prepared from bis[tris(pentafluorophenyl)germyl]cadmium (**43**) and tellurides **7a–c**.[86] A complex with the composition 1 : 2 was also isolated in the case of the stannyl derivative.

$$[(C_6F_5)_3Ge]_2Cd + (Et_3E)_2Te \longrightarrow [(C_6F_5)_3Ge]_2Cd\cdot Te(EEt_3)_2$$
43 **7a–c** **42a–c**

E = Si (**a**), Ge (**b**), Sn (**c**).

The complexes **42a–c** are rapidly oxidised in air. It is noteworthy that tellurides **7a–c** form predominantly 1 : 1 complexes, while diorganyl sulfides R_2S react with compound **43** to give 1 : 2 complexes. This is attributed to the decrease in the donor activity of the Te atoms of tellurides **7a–c** as a result of $d_\pi-p_\pi$ coupling of Te with the E atoms and steric hindrances.[86]

Tellurides **7** react with chromium, molybdenum and tungsten carbonyls $(CO_5)M\cdot THF$ (M = Cr, Mo, W) resulting in the displacement of the tetrahydrofuran molecule and the formation of complexes **44** which are sensitive to oxygen and atmospheric moisture.[52, 87] The yields of the latter are relatively low (17%–45%). The attempts to obtain complexes **44** by irradiation of solutions containing metal hexacarbonyls and tellurides failed due to decomposition of tellurides upon illumination.

$$(Me_3E)_2Te + M(CO)_5\cdot THF \xrightarrow[-THF]{THF} (Me_3E)_2Te\cdot M(CO)_5$$
44

E = Ge, Sn, Pb; M = Cr, Mo, W.

Unlike bis(trimethylstannyl) selenide, which forms binuclear complexes **45** in high yields upon reaction with manganese and rhenium halogen carbonyls, bis(trimethylstannyl) tellurides (**7m**) react with these carbonyls to give complexes **45a**,**b** in very low yields (*e.g.*, the yield of compound **45a** is 11%, whereas the formation of complex **45b** followed only from spectroscopic data).[88] Treatment of complex **45a** with HCl in ether yields tellurol **46** (δ_{TeH} −12.80 ppm).

$$(Me_3Sn)_2Te + (CO)_5MX \xrightarrow[-Me_3SnX,\ -CO]{} (CO)_4M\langle Te_2 M(CO)_4$$
7m

45a,**b** (Te bridges, SnMe$_3$ on each Te)

$$\mathbf{45a} \xrightarrow[-Me_3SnCl]{HCl} (CO)_4MnTeH$$
46

M = Mn (**45a**), Re (**45b**); X = Br, Cl.

IV. Other types of non-cyclic compounds containing Te – E bonds

Apart from $R^1TeER^2_3$ and $(R_3E)_2Te$ derivatives, several non-cyclic compounds containing Te–E bonds, *e.g.*, di(organyltelluro)silanes (germanes, stannanes) $(R^1Te)_2ER^2_2$ **47** (see Refs 17, 19, 20) and tris(ethyltelluro)silane (**48**), have been described.[20] Synthesis of both types of compounds was performed by reactions of the corresponding chloro derivatives of Group 14 elements with lithium tellurolates in THF [19] or ether.[20]

$$R^2_2ECl_2 + R^1TeLi \xrightarrow[-LiCl]{} (R^1Te)_2ER^2_2$$
47a–c

47a: E = Sn, R^1 = Ph, R^2 = Me;
47b: E = Sn, R^1 = Ph, R^2 = Bu^t;
47c: E = Si, R^1 = Et: R^2_2 = Et, H.

$$HSiCl_3 + EtTeLi \xrightarrow[-LiCl]{Et_2O} HSi(TeEt)_3.$$
48

Dimethylbis(methyltelluro)germane (**47d**) was prepared by reaction of dimethylchlorogermane with methyl trimethylsilyl telluride.[17]

$$Me_2GeCl_2 + MeTeSiMe_3 \xrightarrow[-Me_3SiCl]{} Me_2Ge(TeMe)_2.$$
47d

Reactions of compounds **47a–d** and **48** have not been studied yet.

V. Cyclic compounds containing Te – E bonds

A series of three-, four-, five- and six-membered cyclic compounds with rings built exclusively of Group 14 elements (Si, Ge, Sn) and tellurium have been described. The methods for the synthesis of rings containing 4 to 6 atoms are similar to those for non-cyclic tellurides $(R_3E)_2Te$, whereas reactions resulting in three-membered cycles have no analogues.

The reaction of compounds $R_2E=ER_2$ **50a–d** with tellurium powder is a common procedure for the synthesis of three-membered cyclic compounds **49a–d** containing two Group 14 elements and one tellurium atom. Synthesis of telluradisilirane (**49a**) [89] and telluradigermirane (**49b**) [90] is performed in benzene at 20 and 80 °C, respectively; telluradistannirane (**49c**) [91] is prepared by boiling the reactants in toluene for 2 h. The yields are 66%, 80% and 71%, respectively.

$$R_2E{=}ER_2 + Te \longrightarrow R_2E\langle Te_2 ER_2$$
50a–d **49a–d**

E = Si, R = 2,4,6-$Me_3C_6H_2$ (**a**); E = Ge, R = 2,6-$Et_2C_6H_3$ (**b**);
E = Sn, R = 2,4,6-$Pr^i_3C_6H_2$ (**c**); E = Ge, R = 2,4,6-$Me_3C_6H_2$ (**d**).

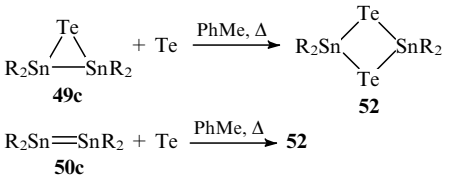
The synthesis of the Te,Ge-cycle **49d** was also carried out by boiling hexamesitylcyclotrigermane (**51**) with tellurium powder in toluene.[90] Presumably, this reaction proceeds *via* the intermediate digermene **50** (E = Ge, R = 2,4,6-$Me_3C_6H_2$).

$$[(2,4,6\text{-}Me_3C_6H_2)_2Ge]_3 + Te \longrightarrow \mathbf{49d}.$$
51

Compounds **49a–d** represent high-melting crystalline substances which are resistant against oxygen and atmospheric moisture. The germyl derivatives **49b**,**d** manifest thermochromic

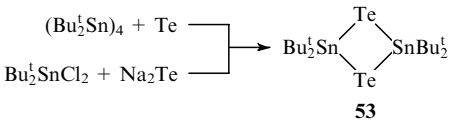
properties: they are colourless at −196 °C but become pale yellow (20 °C) and orange (140 °C) colour.[90] The structures of the cyclic compounds **49a**–**c** were studied by the X-ray diffraction method.

Reaction of compound **49c** with an excess of tellurium powder in toluene affords cyclo-1,3-ditellura-2,4-distannane **52** in a quantitative yield.[91] The same cycle is obtained in 73% yield by boiling a mixture of the corresponding distannene **50c** with tellurium powder in toluene (molar ratio 1 : 3).[91]

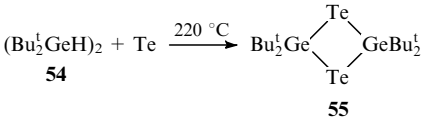


R = 2,4,6-$Pr^i_3C_6H_2$.

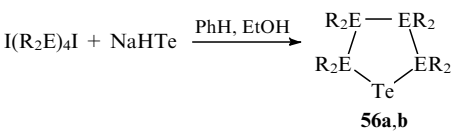
The *tert*-butyl analogue of compound **52**, *viz*., cyclo-1,3-ditellura-2,4-distannane **53**, was synthesised by reaction of tetrameric di(*tert*-butyl)tin with tellurium as well as by reaction of $Bu^t_2SnCl_2$ with sodium telluride.[92]



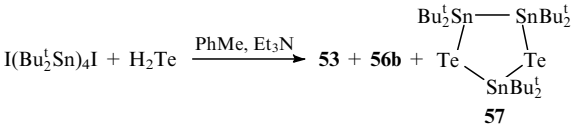
The reaction similar to that used in the synthesis of tellurides $(R_3E)_2Te$ (see Section III.1) was used to prepare cyclo-1,3-ditellura-2,4-digermane **55**. Heating of the hydride **54** with tellurium powder gives a cyclic compound **55** in a nearly quantitative yield.[93] It is noteworthy that reaction of the hydride **54** with selenium yields a mixture of four- and five-membered cyclic products.[93]



The synthesis of the five-membered derivatives R_8E_4Te (**56a**,**b**, E = Ge, Sn) was carried out using structurally similar derivatives of Group 14 elements. Octaphenyltelluratetragermacyclopentane (**56a**) was obtained by reaction of 1,4-diiodooctaphenyltetragermane with sodium hydrotelluride in a benzene–ethanol mixture.[94] Reaction of 1,4-diiodocta(*tert*-butyl)tetrastannane with H_2Te in the presence of triethylamine leads to octa(*tert*-butyl)telluratetrastannacyclopentane (**56b**).[95] Since the reaction of triethylamine with H_2Te yields triethylammonium hydrotelluride $Er_3NH^+HTe^-$, it may be assumed that the HTe^- anion is a tellurium-containing substrate of this reaction. Sodium telluride is not suitable for the synthesis of the heterocycle **56b**, since it cleaves the Sn–Sn bonds in the starting compound. Compound **53** and the five-membered *tert*-butyl derivative of 1,3-ditellura-2,4,5-tristannacyclopentane **57** are by-products in the synthesis of telluratetrastannacyclopentane **56b**.[95]



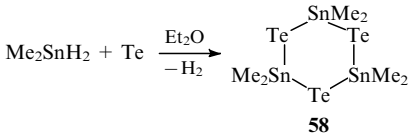
E = Ge, R = Ph (**a**); E = Sn, R = Bu^t (**b**).



Compound **56b** is rather stable upon storage, whereas its germanium analogue **56a** is rapidly oxidised in air to give Ph_2Ge-Ph_2Ge-O-$GePh_2$-$GePh_2$.[94] According to X-ray diffraction analysis data,[95] the ring in compound **56b** is practically planar.

2,4,5-Hexamethyl-1,3-ditellura-2,4,5-tristannacyclopentane, a representative of yet another type of five-membered cyclic compound containing Te and Sn atoms, was prepared by reaction of tellurium powder with dimethylstannane which in turn was synthesised by reduction of dichlorodimethylstannane with lithium aluminium hydride in an Et_2O–DMF mixture (30 : 1, by volume).[96] It was characterised by mass spectrometry as well as by ^1H (see Ref. 96) and ^{119}Sn NMR spectroscopy (see Ref. 97).

Reduction of dichlorodimethylstannane or Me_2SnO with lithium aluminium hydride in Et_2O and subsequent reaction of dimethylstannane with tellurium powder results in 2,2,4,4,6,6-hexamethyl-1,3,5-tritellura-2,4,6-tristannacyclohexane (**58**) in 58% yield.[98]



Compound **59** was also synthesised in 62% yield by reaction of dimethyldichlorostannane with sodium hydrotelluride synthesised from Te and $NaBH_4$ in water [99] and was characterised by the X-ray diffraction method [99] and mass spectrometry.[98]

VI. Conclusion

The data presented suggest that compounds containing bonds of Te with Group 14 elements belong to a synthetically promising class of organoelement compounds. They can be used for the synthesis of organotellurium derivatives of various types, *e.g*., organoelement tellurols, alkyl aryl tellurides, aryl tellurobenzoates and aryl telluroformates, various telluroketones and heterocycles. A promising, although still insufficiently studied area of application of these compounds is the synthesis of various metal tellurolates and tellurium-containing clusters and low-temperature synthesis of metal tellurides. These are only a very few examples which illustrate possible applications of compounds containing Te–E bonds in organic synthesis, particularly, in the synthesis of organic sulfur derivatives and some other organoelement compounds.

The expansion of the range of well-studied reactions, primarily those resulting in tellurolates and metal tellurides, a search for novel procedures for the synthesis and characterisation of various compounds, *e.g*., $R^1_3ETeR^2$ and $(R_3E)_2Te$, elaboration of synthetic procedures for and studies of reactions of other types of compounds containing bonds of Te with Group 14 elements, *e.g*., $(RTe)_4E$ and $(R^1Te)_nER^2_{4-n}$ (n = 2, 3), present indisputable interest for both organotellurium chemistry and organic chemistry in general.

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