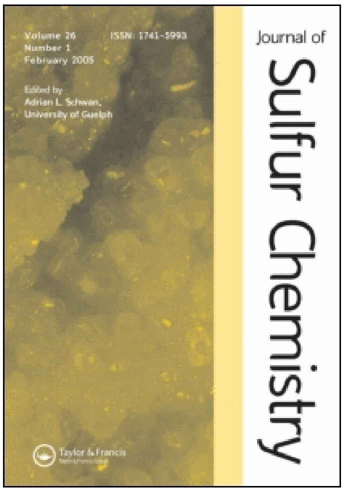

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Peculiarities in the Reactivity of Telluriumorganic Compounds in Comparison with their Sulfur and Selenium Analogs

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PECULIARITIES IN THE REACTIVITY OF TELLURIUMORGANIC COMPOUNDS IN COMPARISON WITH THEIR SULFUR AND SELENIUM ANALOGS

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The distinctive features of the telluriumorganic compounds' reactivity compared to their sulfur and selenium analogs are reviewed and generalized.

Key words: Ditellurides, telluranes, tellurenyl halides, tellurides, tellurocarbonyl compounds, telurocyanates, tellurols.

CONTENTS

1. INTRODUCTION

Although the starting point of telluriumorganic chemistry dates back to the preceding century (1840),[1] only during the two last decades considerable progress has been made in the development of efficient methods for the synthesis of a broad variety of telluriumorganic compounds and in the investigation of their structures and reactivity.[2-15] Telluriumorganic compounds are increasingly used in preparative syntheses of various organic compounds [16-18] which brings about a gradual development of distinctive organotellurium methodology. The available literature data on various aspects of the chemistry of telluriumorganic compounds point to essential differences in the reactivity and, accordingly, in the methods for obtaining these compounds as contrasted with their selenium and, particularly, sulfur analogs. This paper is concerned with the examination and generalization of the principal distinctive features of the reactivity of telluriumorganic compounds in comparison with their sulfur and selenium analogs. These have to be accounted for in preparation and synthetic applications of telluriumorganic compounds. The material is presented so as to cover all major types of telluriumorganic compounds known to date, classified according to the coordination number of the tellurium atom, i.e. the number of the ligands directly bonded to the tellurium atom.

Although the rapidly progressing chemistry of telluriumorganic compounds is still widely open to the impact of new theoretical advances and although some of its important areas (particularly heterocyclic tellurium-containing compounds and derivatives of penta- and hexacoordinate tellurium) have so far been studied insufficiently, nevertheless the following salient features of their chemical behavior responsible for the peculiar reactivity of telluriumorganic compounds compared with that of their sulfur and selenium analogs, seem to be firmly established.

1. The tellurolate anions RTe^- and the telluride anion Te^{2-} possess the highest nucleophilicity in the series of analogous chalcogen derivatives.

2. Diorganyl tellurides R_2Te, which are derivatives of dicoordinate tellurium, are more nucleophilic agents, capable to react with soft acids, than structurally related sulfides and selenides.

3. Compounds containing dicoordinate tellurium such as diorganyl tellurides R_2Te and diorganyl ditellurides R_2Te_2 readily undergo oxidative addition reactions to give derivatives of tetracoordinate tellurium, the σ-telluranes R_2TeX_2 and $RTeX_3$, which in turn are easily reduced to the corresponding derivatives of dicoordinate tellurium.

4. Because of the relatively low energies of C–Te bonds (as compared to those of the C–S and C–Se bonds), especially of the C_{sp^3}–Te bonds, they are prone to fission under mild reaction conditions thus rendering impossible transformations of telluriumorganic compounds which are quite feasible for the corresponding sulfur and selenium derivatives.

5. The strong polarization of the $Te{=}X \leftrightarrow Te^+{-}X^-$ bonds (X = C, N, O) accounts for the specific behavior of π-telluranes in reactions with electrophilic reagents which is different from that of other π-chalcogenuranes (ylides, imides, oxides).

6. σ-Telluranes R_2TeX_2 and $RTeX_3$ as well as tetraaryltelluranes Ar_4Te show an enhanced stability in comparison with the corresponsing σ-sulfuranes and σ-selenuranes. Equatorial and axial bonds in these compounds, even to identical substituents, are not equivalent. The axial bonds belong to the so-called hypervalent bonds[19,20] whose three-center orbitals are occupied by four electrons: two from the p-orbitals of the

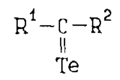
chalcogen atom, each axial ligand supplying one more. As a result of this the axial bonds are considerably lengthened compared to normal two-center covalent bonds. The axial positions are occupied by the most electronegative substituents capable of withdrawing electrons from the non-bonding ligand-chalcogen orbital. The enhanced stability of the σ-telluranes as contrasted with other σ-chalcogenuranes can be explained by an increase in the energy level of the orbitals of the tellurium p-electrons which enhances the bonding.[19,20]

2. DERIVATIVES OF MONOCOORDINATE TELLURIUM

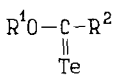
Phosphine tellurides $R_3P{=}Te$, tellurocarbonyl compounds $R_2C{=}Te$ and tellurolate anions RTe^- belong to this type. No comparative studies of phosphine tellurides and their selenium and sulfur analogs have been reported in the literature, but the very low stability of phosphine tellurides with respect to their decomposition resulting in tellurium elimination is known.[2,3]

2.1. Tellurocarbonyl compounds

Although their first representatives, dialkyl telluroketones **1** were already synthesized in 1931[21] by the standard method, i.e. by passing H_2Te through a solution of the respective ketone in concentrated aqueous HCl, they still remain a little studied class of telluriumorganic compounds*. These compounds, similarly to the telluroesters **2**, obtained via interaction of alkoxymethylenedimethylammonium chlorides with NaTeH,[22] are much less stable than their selenium and sulfur analogs. The same is true of the telluroamides **3** whose stabilization requires the presence of strong donor substituents attached to the carbon atom as well as the absence of steric hindrance blocking the conjugative interaction with the C=Te group.[23] Both these conditions are met in the stable 1,3-dimethyl-2-telluroxobenzimidazoline **4** which was synthesized by heating of 1,3-dimethylbenzimidazoline with powdered tellurium.[24]


$R^1{-}\underset{\displaystyle Te}{\underset{\|}{C}}{-}R^2$

1


$R^1O{-}\underset{\displaystyle Te}{\underset{\|}{C}}{-}R^2$

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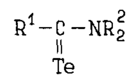
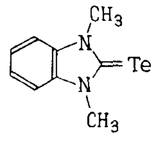

$R^1{-}\underset{\displaystyle Te}{\underset{\|}{C}}{-}NR^2_2$

3



4

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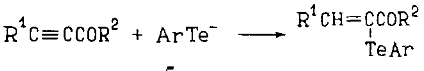
* There is no common agreement in the literature about the actual telluroketone structure of compounds prepared by interaction of carbonyl compounds with H_2Te. A referee pointed out that despite an early report by Lyons and Scudder[21] it is very unlikely that true telluroketones have ever been synthesized. Although thiones can be prepared by the reaction of ketones with hydrogen sulfide, attempted preparations of selones with hydrogen selenide fail. The originally reported selones were subsequently shown to be in fact diselenides, formed by reduction of the initially formed selone by hydrogen selenide and subsequent oxidation of the intermediate selenol (D. S. Margolis and R. W. Pittman, *J. Chem. Soc.*, **1957**, 799). By analogy, hydrogen telluride would be an even better reducing agent, more likely to reduce any intermediate telluroketone. This is also confirmed by the recent report (N. Kambe, T. Inagaki, N. Miyoshi, A. Ogawa, and N. Sonoda, *Chem. Lett.*, **1987**, 1171) that the reaction of aliphatic aldehydes with H_2Te under acidic conditions results in the formation of dialkyl ditellurides.

2.2. Tellurolate anions

Tellurolate anions **5** and **5a** are obtained by reaction of diorganyl ditellurides with borohydrides of alkali metals or via reaction of aryllithium derivatives with elemental tellurium.[2-4] The anions **5** possess the greatest nucleophilicity among analogous derivatives of the VIa group elements. Therefore, nucleophilic substitution and addition reactions with these anions proceed much faster than with similar organosulfur and organoselenium anions. Quantitative data concerning the relative reactivity of chalcogenolate anions are apparently available only for $S_{RN}1$ reactions.[25] When passing from sulfur to tellurium, the relative reactivity of the benzenechalcogenolate anions PhM^- (M = S, Se, Te) increases. In the case of interaction with 2-quinolyl radicals the following order of rate constants was found: PhS^- (1.0), $PhSe^-$ (5.8), $PhTe^-$ (28.0).

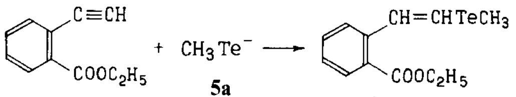
The high nucleophilicity of the tellurolate anions **5** and **5a** allows their easy addition to activated [26,27] and even non-activated triple bonds,[28-30], which makes it possible to obtain a series of organyl vinyl tellurides **6** and **6a** in high yield (60–90%).



$$R^1C{\equiv}CCOR^2 + ArTe^- \longrightarrow R^1CH{=}\underset{\displaystyle TeAr}{C}COR^2$$

5 **6**

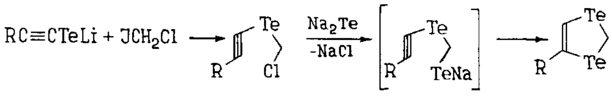
R^1 = Alk, Ar ; R^2 = H, Alk, Ar, OR



5a **6a**

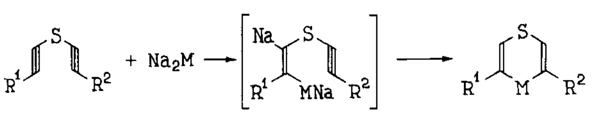
$$\underset{R\,=\,Alk,\,Ar}{RC{\equiv}CH} + \underset{\mathbf{5}}{C_6H_5Te^-} \longrightarrow \underset{\mathbf{6a}}{C_6H_5TeCH{=}CHR}$$

Furthermore, this property of tellurolate anions provides a convenient approach to the synthesis of various tellurium heterocycles not readily accessible by other means. Thus, 1,3-ditelluroles and 1-thia-4-chalcogenacyclohexanes can be obtained via intramolecular nucleophilic addition to triple bonds occurring in the intermediates **7**[31] and **8**,[32] respectively.



7

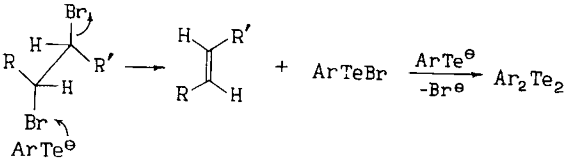
R=H (65%), CH_3 (4%), n-C_4H_9 (11%), C_6H_5 (49%)



M = S, Se, Te **8** 65–82%

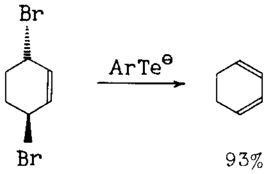
In the latter case sodium telluride reacts much faster than sodium selenide and, particularly, sodium sulfide.[32]

The tellurolate anions, especially the 2-thiophenetellurolate anion, possess, in contrast to other chalcogenolate anions, not only enhanced carbophilic character, but also enhanced halophilicity.[33] For this reason sodium 2-thiophenetellurolate is utilized to debrominate vicinal dibromides to olefins in very high yields (75–100%). This reaction serves as a useful preparative alkene synthesis because it can be run under catalytic conditions, i.e. employing small amounts of ditellurides (1 mmol per 10 mmol of halogen-containing substrate) and $NaBH_4$ which reduces the ditellurides which are formed in the course of the reaction back to tellurolate anions.[34]

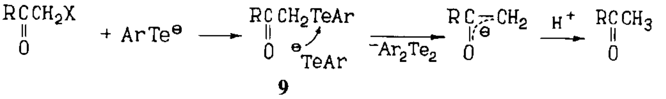


A similar debromination of substituted 1,2-dibromocyclohexanes takes also place when sodium thiophenolates are used.[35,36] However, in the case of 1,2-dihaloethanes only nucleophilic substitution of the halogen atoms by phenylthio group takes place.[37]

While the above-described debromination of vicinal dibromides is an example of a *β*-halophilic elimination, the synthesis of 1,3-dienes from 1,4-dibromo-2-alkenes with catalytic amounts of bis(2-thienyl) ditelluride and $NaBH_4$ provides a rare example of *δ*-halophilic elimination.[38] No examples of such eliminations initiated by sulfur or selenium nucleophiles are known.[33]



Another possible route of X-philic reactions, the reduction of C–Hal bonds, is followed in the reaction of sodium or lithium 2-thiophenetellurolate with *α*-halo ketones and carboxylic acids. With stoichiometric ratios of the reagents the final products are in this case not the products of nucleophilic substitution **9**, but the corresponding ketones (carboxylic acids) and diaryl ditellurides.[39] This outcome of the reaction is conceived to be the result of an attack of the arenetellurolate anion upon the tellurium atom in the initially forming products of the nucleophilic substitution **9**.[39] The tellurophilic reaction



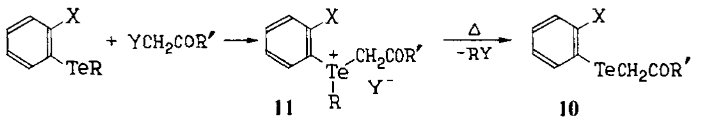
9

path manifests itself in the intermediate formation of tellurides **9** which in some cases ($R = CH_2CONHPh$) can be isolated.

Similar results were earlier obtained also for thiolate[40,41] and selenolate anions.[41]

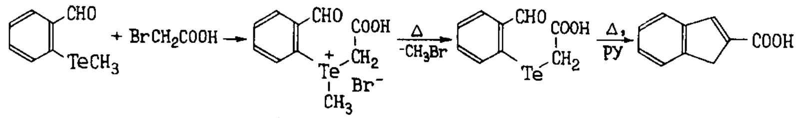
However, in their reactions with α-halocarbonyl compounds the preferable route of the reaction (nucleophilic substitution or reduction) is primarily determined by the nature of the halogen. In the case of α-chloro and α-bromo ketones the main products of the reaction are those of nucleophilic substitution,[40,41] while in the case of α-iodo ketones the reduction of the ketones, with formation of the corresponding disulfides (diselenides) occurs more readily.[41] Tellurolate anions react with α-halo ketones, regardless of the nature of the halogen, giving rise only to products of the reduction of the carbon-halogen bond in these compounds. This indirectly points to an appreciable halophilicity of tellurolate anions. Although in the literature there are so far no comparative data on the halophilicity of structurally related chalcogenolate anions, this assumption is corroborated by the greater halophilicity of the methaneselenolate anion compared to the methanethiolate anion, in reactions with benzyl halides[42] as well as by the fact that the 2-thiophenetellurolate anion reduces phenacyl phenyl sulfide to acetophenone.[39]

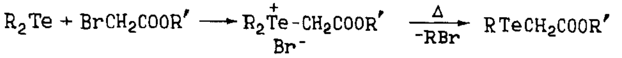
In this connection there arises the problem of the synthesis of type **10** compounds possessing reactive functional groups (CHO, COR, COOR) in the *o*-position to the CH_2COR moieties (R = Alk, OAlk) thus representing appropriate starting materials for a variety of tellurium-containing heterocycles. The best approach to the preparation of compounds **10** involves conversion of *o*-substituted aryl alkyl tellurides containing the required functional groups into telluronium salts **11** in high yields by treating the former with appropriate α-bromo (iodo) carbonyl compounds with subsequent elimination of alkyl halides upon heating.



X = CHO, COR, COOR ; R = CH_3, C_2H_5, C_4H_9 ; R′ = Alk, Ph, OR, H ;
Y = Br, I

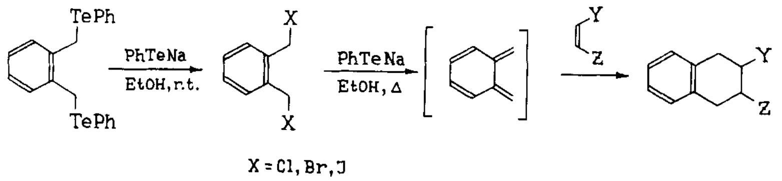
This method has so far been hardly utilized. It can be exemplified by the synthesis of 2-benzo[*b*]tellurophenecarboxylic acid[43] and carbalkoxymethyl alkyl tellurides.[44-46]



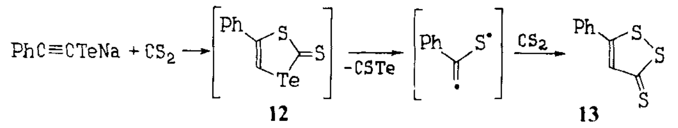


$$R_2Te + BrCH_2COOR' \longrightarrow \underset{Br^-}{R_2\overset{+}{Te}{-}CH_2COOR'} \xrightarrow[-RBr]{\Delta} RTeCH_2COOR'$$

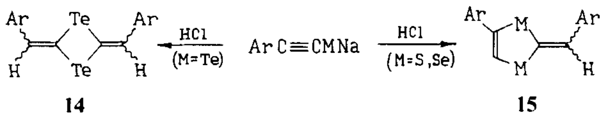
Sharply different are the results of the reactions of α,α′-dihalo-*o*-xylenes with tellurolate and selenolate anions. The use of the former reagent in boiling ethanol solution gives rise to *o*-quinodimethane derivatives isolated as Diels-Alder adducts (20–53%). The necessary by-product of this reaction is *o*-phthalic aldehyde (30%) which is formed upon oxidation of α,α′-bis(phenyltelluro)-*o*-xylene, formed by nucleophilic substitution of the halogens. The selenolate anion reacts affording α,α′-bis(phenylseleno)-*o*-xylene,[47] the product of nucleophilic substitution the C_{sp^3} center. An analogous product is formed if the reaction with the tellurolate anion proceeds in ethanol solution at ambient or lowered temperature.



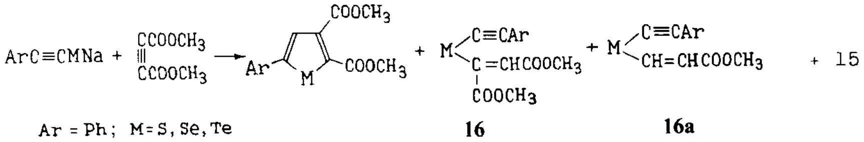
The origin of the chalcogen atom substantially affects the course of reactions of ethynechalcogenolate anions with different compounds. A likely approach to the synthesis of 1,3-thiatellurole-2-thiones **12**, including treatment of the ethynetellurolate anion with carbon disulfide, similar to the synthesis of the corresponding derivatives of selenium[48,49] failed. This reaction turned out to produce the 1,2-dithiole-2-thione **13** in extremely low yield by a possible mechanism[50] indicative of the C–Te bond fission processes.



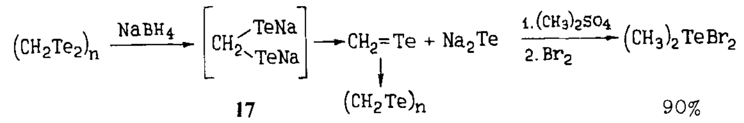
Another example is the protonation of the phenylethynetellurolate anion in DMSO solution upon addition of ethereal HCl. The only products of this reaction are the 1,3-ditelluretanes **14**.[50-53] For the compound with Ar = Ph the yield is 15–18%. In the case of analogous thiolate and selenolate anions the reaction leads to the 1,3-dichalcogenoles **15**.



A significant decrease of 1,3-dichalcogenole **15** yields as well as of thio(seleno, telluro)phenes with simultaneous increase in enyne (**16**, **16a**) yields has been observed.[53,54]

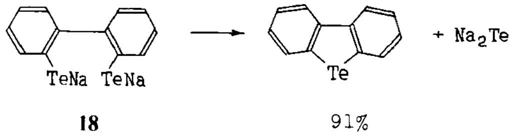


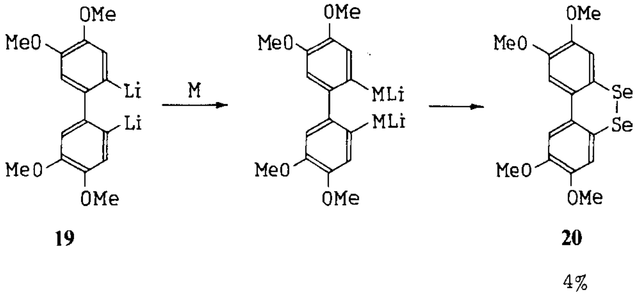
Geminal ditellurolate anions **17** behave differently from their sulfur and selenium analogs. Whereas the sulfur and selenium derivatives are sufficiently stable to heating and can undergo various chemical transformations,[55] the corresponding tellurium derivative formed upon reduction of poly(methylene ditelluride) with sodium borohydride in ethanol is easily decomposed into sodium telluride and telluroformaldehyde, the latter further polymerizing to give poly(methylene telluride).[56]



This makes dubious the suggested formation of poly(methylene telluride) as a result of primary interaction of **17** with dihalomethanes.[57] Poly(methylene telluride) was probably formed not by alkylation, but rather by disproportionation of **17**.

Analogous disproportionation with sodium telluride elimination occurs upon heating of the sodium salt of 2,2′-bis(tellurolo)biphenyl **18** with formation of dibenzotellurophene.[58] This reaction accounts apparently for the ready formation of a dibenzotellurophene upon treatment of 2,2-dilithio-4,4,5,5′-tetramethoxybiphenyl **19** with tellurium, whereas the corresponding reaction with selenium leads to the rather stable heterocyclic diselenide **20**, although in low yield.





3. DICOORDINATE TELLURIUM COMPOUNDS

The following compounds belong to this type: tellurenyl halides, RTeX, tellurocyanates, RTeCN, diorganyl tellurides, R_2Te, and diorganyl ditellurides, R_2Te_2.

3.1. *Tellurenyl halides*

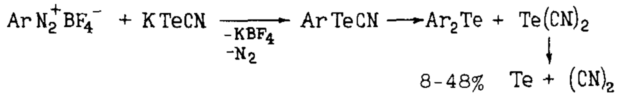
Tellurenyl halides, represented mainly by aromatic derivatives, are, in contrast to their sulfur and selenium analogs, rather unstable. These compounds, usually obtained by interaction of diaryl ditellurides with bromine or iodine in nonpolar solvents,[60-62] undergo rapid decomposition. The tellurenyl bromides completely decompose at ambient temperature in 24 hours, while the iodine derivatives can be kept for several days.[60,61] This does not, however, preclude the use of these compounds obtained *in situ* for the synthesis of unsymmetrical tellurides via reaction with magnesiumorganic derivatives.[63]

The stability of tellurenyl halides is substantially enhanced when functionalities such as CHO,[64-67] COR,[64,68-72] $CONR_2$,[73] NO_2,[74] N=N,[75] or CH=N[76,77] are present in the *o*-position with respect to the TeX group. Their stabilizing effect is a consequence of the coordination of the tellurium atom with these groups. The stabilizing influence of the nitro group is so strong that 2-nitrobenzenetellurenyl bromide can be synthesized not only by brominolysis of di(2-nitrophenyl) ditelluride, but also via controlled reduction of 2-nitrophenyltellurium tribromide[74] which is not possible in the case of other aryltellurium tribromides. It is possible that this stabilizing effect is also due to steric factors, which would explain the enhanced stability of 2-phenylbenzene-[61] and particularly 2-naphtalenetellurenyl iodide[78] in comparison with other tellurenyl iodides. The latter compound was the first tellurenyl iodide to be isolated in pure form.

3.2. *Tellurocyanates*

Organyl tellurocyanates have been studied much less extensively than thio- and selenocyanates. It is noteworthy that the first salts containing a $TeCN^-$ ion, viz. the solvate of tetraethylammonium tellurocyanate with DMF and tetramethylammonium and tetraphenylarsonium tellurocyanate, were synthesized only in 1968 and 1971, respectively.[2,3]

Organyl tellurocyanates can be synthesized by reactions which are also employed to obtain the corresponding derivatives of sulfur and selenium, namely from benzyl halides and KTeCN,[3] by exchange of halogen in stable tellurenyl halides[64,71] or arenetellurenyl chlorides obtained *in situ*[79] with cyanide anion or by interaction between tellurolate anions and BrCN.[80] It should be noted that the most general method for the synthesis of aryl thiocyanates and aryl selenocyanates, which consists in the treatment of diazonium salts with KSCN or KSeCN, fails to produce aryl tellurocyanates. Upon reaction of aryldiazonium borofluorides with KTeCN in dry DMF no aryl tellurocyanates, but diaryl tellurides have been obtained.[81] The latter compounds are formed via disproportionation of intermediate aryl tellurocyanates.[81] Decomposition of this type

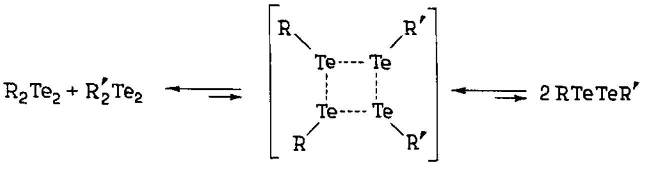


$$ArN_2^+BF_4^- + KTeCN \xrightarrow[-N_2]{-KBF_4} ArTeCN \longrightarrow \underset{8\text{-}48\%}{Ar_2Te} + Te(CN)_2 \longrightarrow Te + (CN)_2$$

does not occur with aryl selenocyanates. This mechanism does not, however, explain why aryl tellurocyanates synthesized by independent methods are not subject to such decomposition. Moreover, when substituents capable of intramolecular coordination to tellurium (such as a nitro group) are present in the *o*-position relative to the TeCN group or when steric hindrance (methyl groups in 2,6-positions) is introduced then, in addition to diaryl tellurides, aryl tellurocyanates are obtained in this reaction in 11% and 40% yield, respectively.

3.3. *Diorganyl ditellurides*

In the case of diorganyl disulfides and diorganyl diselenides, asymmetric compounds RMMR′ (M = S, Se) are isolable compounds. By contrast, all attempts to prepare asymmetric diorganyl ditellurides RTeTeR′ via reduction of mixtures of two different organyltellurium trichlorides or by irradiation of benzene solutions of mixtures of diaryl ditellurides failed.[82-84] The first asymmetric ditelluride to be mentioned in the literature was pentafluoroethyl nonafluorobutyl ditelluride. However, its presence among the reaction products was proven only by mass spectrometry.[85,86] The ^{1}H[84,87] and ^{125}Te NMR data suggest that the asymmetric ditellurides are formed in solution via redistribution of hydrocarbon radicals.[84] For example the ^{125}Te NMR spectrum of a mixture of equivalent amounts of Me_2Te_2 ($\delta^{125}Te$ 69 ppm) and i-Pr_2Te_2 ($\delta^{125}Te$ 313 ppm) in $CDCl_3$ solution shows, apart from the signals of the symmetric ditellurides, two additional peaks at −74 ppm and 455 ppm belonging to Me*Te*TePr-*i* and MeTe*Te*Pr-*i*,[84] the equilibrium being shifted towards the symmetric compounds. The reactions does not occur by a dissociative radical mechanism, but rather involves the intermediate formation of a bimolecular complex according to the following scheme: Assymmetric diaryl ditellurides can be stabilized by complexation with various Lewis acids.[88] Thus, through interaction of copper(I) and mercury(II) halides with equimolar mixtures of diphenyl ditelluride (R_2Te_2) and bis(4-ethoxyphenyl) ditelluride (R'_2Te_2) there are formed RTeTeR′·2 MX_n (M = Cu, X = Cl, Br; n = 1; M = Hg, X = Cl, n = 2).[88]

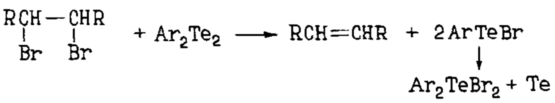


Diorganyl ditellurides are prone to oxidative addition reactions under mild conditions. When treated with halogens, sulfuryl chloride or thionyl chloride they readily form derivatives of tetracoordinated tellurium, i.e. σ-telluranes of the $RTeX_3$ type.[2-4] The example of the formation of aryltellurium triiodides shows that these reactions run stepwise. During the first step there occurs a very rapid formation of a tellurenyl iodide **21** which transforms to the adduct **22** and, finally, to the triiodide **23**.[89]

$$R_2Te_2 + I_2 \longrightarrow \underset{\mathbf{21}}{RTeI} \rightleftharpoons \underset{\mathbf{22}}{RTeI \cdot I_2} \longrightarrow \underset{\mathbf{23}}{RTeI_3}$$

$$R = 4\text{-}C_2H_5OC_6H_4$$

Due to their reductive properties ditellurdies may be used in preparative organic chemistry for obtaining olefins from vicinal dihalides.[90] The products of this reaction are mixtures of diaryltellurium dihalides and elemental tellurium probably formed through disproportionation of transient arenetellurenyl bromides[62]



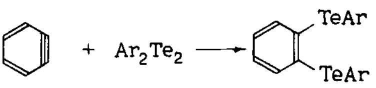
$$\underset{Br}{RCH}-\underset{Br}{CHR} + Ar_2Te_2 \longrightarrow RCH{=}CHR + 2ArTeBr \;\;\; 2ArTeBr \downarrow Ar_2TeBr_2 + Te$$

As powerful one-electron reductive agents diaryl ditellurides promote some of the electron transfer reactions that do not proceed with the analogous sulfur compounds. Thus, in the interaction of diaryl ditellurides with aryldiazonium halides diaryl tellurides and diaryltellurium dihalides in a 1:1 ratio are formed by, probably, the following scheme:[91,92]

$$\mathrm{Ar_2Te_2 + Ar'N_2X \xrightarrow[-N_2]{} ArTe^{\bullet} + Ar'^{\bullet} + ArTeX}$$
$$\mathrm{ArTe^{\bullet} + Ar'^{\bullet} \longrightarrow ArTeAr'}$$
$$\mathrm{ArTeX + Ar'N_2X \xrightarrow[-N_2]{} ArTeX_2Ar'}$$

In contrast, diaryl disulfides can be arylated with aryldiazonium halides only in the presence of copper(II) halides which facilitate the formation of aryl radicals.[93]

Diaryl ditellurides with donor substituents readily add to dehydrobenzene generated via thermal decomposition of 2-(phenyliodonio)benzoate[94,95] to give the bis(aryltelluro)benzenes **24** while diaryl disulfides do not undergo such a reaction.



24

Ar=4-$CH_3OC_6H_4$ (53%), 4-$C_2H_5OC_6H_4$ (64%), 4-$CH_3C_6H_4$ (50%)

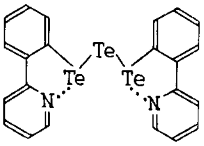
Different is also the behavior of diaryl disulfides and diaryl ditellurides in reactions with powdered copper. The former, when heated with copper in *N*,*N*-dimethylacetamide solution, are transformed into copper(I) arenethiolates[96] whereas the latter upon boiling in dioxane decompose with formation of diaryl tellurides and CuTe.[97] The latter reaction is employed as a preparative method for obtaining diaryl tellurides as well as for their purification from traces of diaryl ditellurides.

$$\underset{M\,=\,Te}{\mathrm{Ar_2M + CuM}} \xleftarrow{\mathrm{Cu}} \mathrm{Ar_2M_2} \xrightarrow{\mathrm{Cu}} \underset{M\,=\,S}{\mathrm{ArMCu}}$$

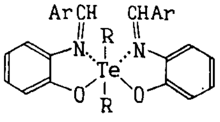
The above-presented results are largely determined by differences in the energies of C–M and M–M bonds where M = S, Se, Te. Data on the relative energies of homolytic rupture of these bonds obtained by studying the photolysis of diorganyl dichalcogenides R_2M_2 in the presence of phosphines can be found in.[98] The ease with which the chalcogen-carbon bond cleavage occurs, is enhanced in the following order: S, Se, Te, parallel to that of the respective bond energies. Though no definite data on the relative stabilities of chalcogen-chalcogen bonds are yet available it is safe to assume that an analogous decrease in these bonds energies from S to Te takes place. This may, apparently, account for the fact that, unlike polysulfides, polytellurides were unknown for a long time. The first representatives of these compounds, bis[tris(trimethylsilyl)-methyl] tritelluride **25**[99] and bis[2-(2-pyridyl)phenyl] tritelluride **26**,[100] were obtained quite recently. While the stability of the first compound is due to the presence of bulky substituents at the tellurium centers, in the latter compound strong intramolecular coordination bonds Te ← N (2.554 Å[100]) serve as a powerful structural stabilizing factor.

$[(Me_3Si)_3C]_2Te_3$

25



26



27

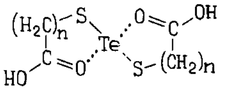
The propensity of tellurium for forming strong intramolecular coordination bonds of hypervalent nature with sp^2-hybridized oxygen[64-73] and nitrogen[75-77,100] atoms allows the synthesis of novel types of stabilized telluriumorganic compounds such as **26**. These bonds are also responsible for some unusual reactions of the respective telluriumorganic compounds. Thus, diorganyl dialkoxytelluranes $R_2Te(OR)_2$ [101] are rapidly hydrolyzed even by air moisture, while the diaryloxytelluranes **27** with the coordination bonds Te ← N are stable even after prolonged contact with water.[102,103]

The influence of intramolecular coordination on the thermal stability of organotellurium compounds is illustrated by the properties of the compounds **28**, **29**, and **29a**.[104] While bis(arylthio) tellurides **28** readily decompose with tellurium extrusion both in the crystalline state and in solution, the compounds **29** and **29a** in which intramolecular coordination Te ← O bonds exist, are quite stable.

$(ArS)_2Te$

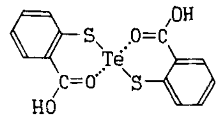
28

$Ar = C_6H_5, 1\text{-}C_{10}H_7$



29

n = 1,2

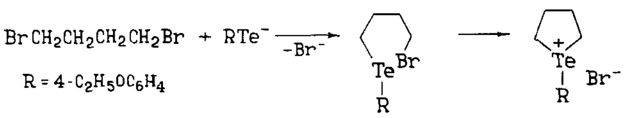


29a

3.4. *Diorganyl tellurides*

Diorganyl tellurides R_2Te are one of best studied types of tellurium organic compounds. There is a number of specific features in their reactivity in comparison with the corresponding selenium and sulfur organic derivatives.

Very typical of both diorganyl tellurides and ditellurides are the reactions resulting in the increase of the coordination number of the tellurium atom to 3 and 4. Dialkyl and aryl alkyl tellurides readily form telluronium salts through interaction both with α-carbonyl substituted and unsubstituted alkyl halides.[2,3] The high nucleophilicity of the tellurium atom of tellurides makes it possible to obtain by this reaction telluronium salts whose sulfur analogs can not be synthesized in a similar way. 1. Dimethyl telluride affords in good yield telluronium salts when treated not only with alkyl halides, but also with iodobenzene.[105] Phenyldimethyltelluronium iodide was obtained under these conditions in over 50% yield. 2. Not only dialkyl and aryl alkyl tellurides, but also diaryl tellurides[2-4] react with alkyl halides to produce telluronium salts. The alkylation of diphenyl sulfide[106] and diphenyl selenide[107] on the other hand can take place only in the presence of an equimolar amount of $AgBF_4$. Cyclic derivatives of tellurium and sulfur behave in the same manner. Whereas benzo[*b*]tellurophene is readily alkylated by methyl bromide[43] giving rise to the corresponding telluronium salt, benzo[*b*]thiophenium and dibenzo[*b*]thiophenium salts can be obtained only in the presence of $AgClO_4$ or $AgBF_4$.[108] In the reaction of 1,4-dibromobutane with sodium 4-ethoxyphenyltellurolate not the expected 1,4-bis(4-ethoxyphenyltelluro)butane is formed, but telluronium salt **30** via intramolecular alkylation of the intermediate 1-(4-ethoxyphenyltelluro)-4-bromobutane **31**.[109]



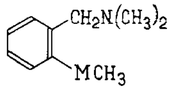
31 **30** (80%)

Sharp differences in the reactivity brought about by the enhanced nucleophilicity of the tellurium center in diorganyl tellurides with respect to similar sulfides and selenides are observed in the alkylation reactions of the alkylchalcogenodiynes **32**[110] and the (*o*-methylchalcogenobenzyl)dimethylamines **33**.[111]

$C_2H_5C{\equiv}CC{\equiv}CMCH_3$

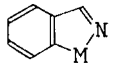
32

M = S,Se,Te



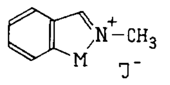
33

M = Se, Te



34

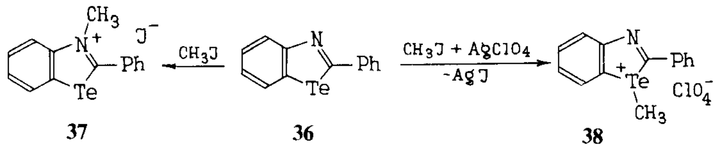
M = Se, Te



35

M = Se, Te

In the case of the compounds **32**, only the telluride affords the corresponding telluronium salt in almost quantitative yield (95%) upon alkylation with methyl iodide. Even more indicative is the alkylation of the compounds **33**. (o-Methylselenobenzyl)dimethylamine (**33**, M = Se) in this reaction affords the *N,N,N*-trimethylammonium compound (≃ 100%), whereas in the case of the respective tellurium derivative there is produced the telluronium rather than ammonium salt. At the same time, benzisotellurazole (**34**, M = Te) with methyl iodide only forms an immonium salt (**35**, M = Te)[112] whose structure was established by determination of the $^4J_{HH}$ spin couplings (1.4–1.5 Hz) of the *N*-methyl and H-3 protons. However, in the case of 2-phenylbenzotellurazole **36**[113] the direction of the alkylation reaction depends on the nature of the alkylating agent. Treatment of **36** with excess methyl iodide leads to the immonium salt **37** (90%), but when methyl iodide acts upon **36** in the presence of an equimolar amount of $AgClO_4$, the telluronium salt **38** is formed in almost quantitative yield.

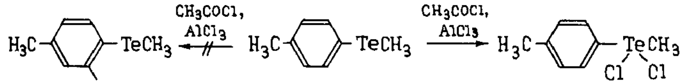


37 **36** **38**

Being prone as noted above to oxidative addition reactions, diorganyl tellurides readily transform to the tetracoordinated σ-telluranes. A broad variety of oxidizing agents such as Hal_2, SO_2Cl_2, $SOCl_2$, $(SCN)_2$, HalCN, PCl_5, SF_4, HNO_3, H_2O_2, $(RCOO)_2$, $Pb(OCOCH_3)_4$, salts of Cu(II), Fe(III), Hg(II), etc. may be employed in this reaction.[2-4] The σ-telluranes formed can be easily purified by recrystallization. Since by means of various reducing agents such as Na_2S, Na_2SO_3, $K_2S_2O_5$, powdered Zn in ethanol, and hydrazine hydrate[2-4] they can be readily reduced to the initial diorganyl tellurides, the reaction

$$R_2Te \longrightarrow R_2TeX_2 \longrightarrow R_2Te$$

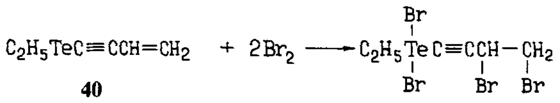
sequence is in some cases utilized for the purification of diorganyl tellurides. The thermodynamic stability of tetracoordinated tellurium compounds serves as a driving force of many reactions occurring with diorganyl tellurides and ending in the formation of telluranes, whereas sulfuranes are rarely accessible via the respective sulfide reactions, e.g., in the above-mentioned (Section 3.3.) arylation of diorganyl ditellurides[91,92] with aryldiazonium salts in the presence of copper(II) halides the reaction products are diaryltellurium dihalides, while arylation of diaryl disulfides under similar conditions affords diaryl sulfides.[93] The formation of diaryltellurium dihalides occurs by oxidation of the initially formed diaryl tellurides by copper(II) halides.[92] Similarly, the Sandmeyer reaction of 2-aminophenoxatellurine produces not 2-chlorophenoxatellurine, but 2,10,10-trichlorophenoxatellurine.[114] Interestingly, the interaction of 4-methylphenyl methyl telluride with acetyl chloride in the presence of $AlCl_3$ leads not to the acetophenone derivative as in the case of the analogous selenium derivative,[115] but to the oxidation of Te(II) to Te(IV) resulting in the formation of the tellurane **39**.[68]



39

On the other hand, methyl phenyl telluride with α-bromoacetyl chloride in the presence of $AlCl_3$ gives the expected 4-(methyltelluro)-α-bromoacetophenone (52% yield).[116]

Alkyl vinylacetylenyl tellurides such as **40** in the reaction with bromine behave differently from their sulfur and selenium analogs. Whereas the latter readily add bromine to the triple bond, the former adds two equivalents of bromine, one to the double bond and the second to tellurium.[117]

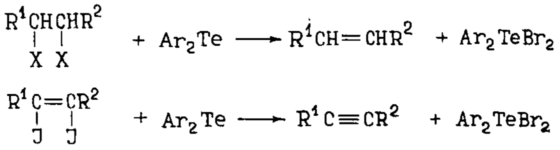


40

$$C_2H_5TeC{\equiv}CCH{=}CH_2 + 2Br_2 \longrightarrow C_2H_5\overset{Br}{\underset{Br}{Te}}C{\equiv}C\underset{Br}{CH}{-}\underset{Br}{CH_2}$$

The ability of diorganyl tellurides to transform under the action of various oxidizing reagents into σ-telluranes requires more than in the case of sulfides and selenides a careful selection of the reagents usually employed for the transformation of functional groups. E.g., in the synthesis of acyl chlorides bearing a dicoordinated tellurium group neither PCl_5 nor $SOCl_2$ (which convert Te(II) into Te(IV)) can be employed. Therefore, the synthesis of such acyl chlorides is performed with either dichloromethyl alkyl ethers in the presence of $ZnCl_2$ [28,71,118-122] or with oxalyl chloride.[123,124]

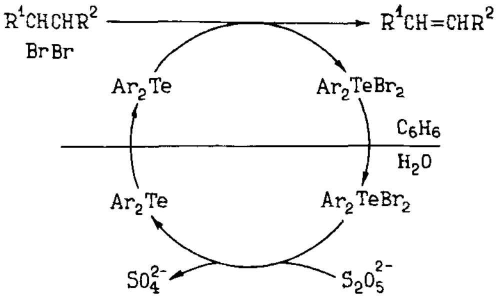
The facility of the Te(II) ⇄ Te(IV) interconversion suggests the use of diorganyl tellurides and phenoxatellurine in the synthesis of olefins and acetylenes from vicinal[125,126] and geminal[127] dibromides and diiodides by dehalogenation.



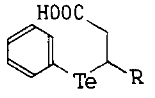
$$\underset{X}{R^1CH}\underset{X}{CHR^2} + Ar_2Te \longrightarrow R^1CH{=}CHR^2 + Ar_2TeBr_2$$

$$\underset{J}{R^1C}{=}\underset{J}{CR^2} + Ar_2Te \longrightarrow R^1C{\equiv}CR^2 + Ar_2TeBr_2$$

The cyclic diaryl telluride phenoxatellurine[126,127] surpasses in its reductive properties, i.e. its tendency to form telluranes, the acyclic diaryl tellurides.[125] The important advantage of diaryl tellurides as well as of some other telluriumorganic compounds such as tellurolate anions (see Section 2.2.) over other dehalogenating reagents consists in the possibility to use them in approximately 5% of the amount of the bromine-containing substrate in a phase transfer catalytic reductive cycle. It conforms to the following scheme:[128]

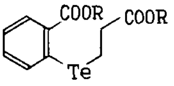


It has already been pointed out that the ease of the carbon-chalcogen bond cleavage is enhanced in the order S < Se < Te. For this reason, a number of reactions yielding heterocyclic compounds of sulfur and selenium fail to produce similar tellurium-containing heterocyclic compounds due to the fission of C_{sp^3}–Te bonds. Thus, β-(phenyltelluro)-β-phenylpropionic acid **41** (R = Ph) does not convert to telluroflavanone[69] under conditions analogous to those used for the synthesis of thio- and selenoflavanones. Similarly, β-(phenyltelluro)propionic acid (**41**, R = H) is decomposed by polyphosphoric acid while β-(*o*-carboxyphenyltelluro)propionic acid (**42**, R = H) or its ethyl ester (**42**, R = Et) do not undergo the Dieckmann cyclization yielding, because of cleavage of the C_{sp^3}–Te bond, ditellurosalicylic acid instead of the expected tellurochromanone[121]



41

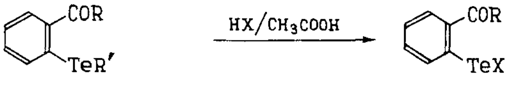
R = H, Ph



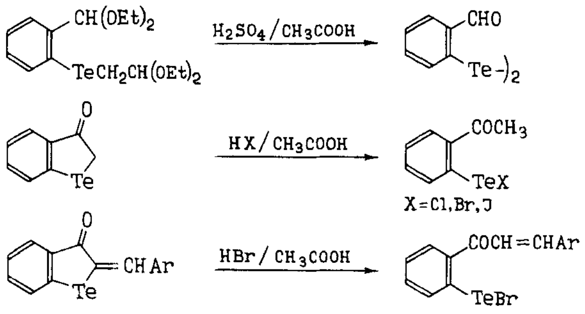
42

R = H, Et

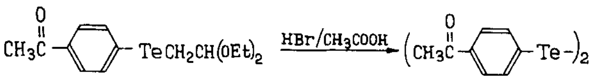
The C_{sp^3}–Te bonds in the *o*-carbonyl derivatives of alkyl aryl tellurides,[64,68,72] telluroindoxyl[70] and telluroaurones[69] are readily cleaved by strong acid. The result of the bond cleavage depends on the kind of the acid employed. Either tellurenyl halides or diaryl ditellurides, stemming from the oxidation of intermediate tellurols, can be obtained as shown below



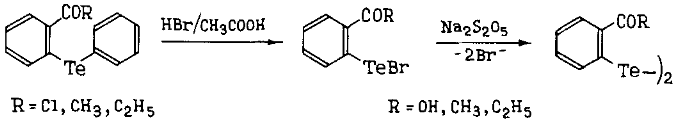
R = H, R' = $CH_2CH(OEt)_2$, X = Cl, Br, J; R = CH_3, R' = C_4H_9, CH_2COOEt, X = Br; R = CH=CHPh, R' = CH_3, X = Br



It appears that the formation of tellurenyl halides in the above reactions is due to their stabilization by intramolecular Te...O interactions. In fact, in the case of treatment with HBr of alkyl aryl tellurides bearing a carbonyl function in the *p*-position produces under analogous conditions not tellurenyl bromides, but diaryl ditellurides.[64]



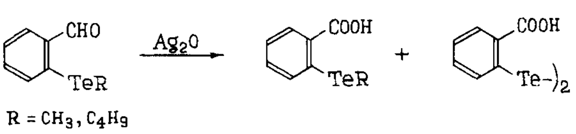
Not only C_{sp^3}–Te, but C_{Ar}–Te bonds as well are cleaved under the action of HBr. E.g., upon treatment of derivatives of 2-carboxydiphenyl telluride (but not of the parent compound) with HBr the corresponding tellurenyl bromides are formed in high yields.[71] Since they can be readily reduced to ditellurosalcylic acid, the reaction serves as a convenient preparation of ditellurosalicyclic acid.



Some cases are known of facile cleavage of the C_{sp^3}–Te bonds under the action of lithiumorganic compounds and oxidants. Thus, the reaction of alkyllithium in tetrahydrofuran at −78 °C with bis(phenyltelluro)methane results in the rupture of one of the CH_2–Te bonds leading to alkyl phenyl tellurides and (phenyltelluro)methyllithium.[129]

$$(C_6H_5Te)_2CH_2 \xrightarrow[-C_6H_5TeR]{RLi} C_6H_5TeCH_2Li$$

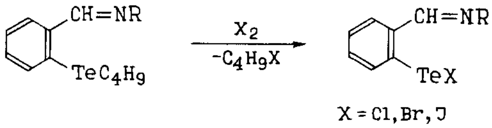
Oxidation of alkyl 2-formylphenyl tellurides with silver oxide in alkaline medium leads in addition to the expected alkyl 2-carboxyphenyl tellurides to the product of the cleavage of C_{sp^3}–Te bonds, viz. to ditellurosalicylic acid.[118] In the case of 2-formylphenyl methyl telluride the only product of the oxidation is ditellurosalicylic acid (60% yield).



Rupture of carbon-tellurium bonds is also observed in the halogenolysis of aryl benzyl tellurides with bromine, SO_2Cl_2 or $SOCl_2$. Instead of the corresponding arylbenzyltellurium dihalides, as in the case of other diorganyl tellurides,[2-4] aryltellurium trihalides and benzyl halides are formed.[130]

$$ArTeCH_2Ph \xrightarrow{X_2} ArTeX_3 + PhCH_2X$$

Ready cleavage of the C_{sp^2}–Te bonds facilitated by the formation of the Te←N coordinative bonds occurs under very mild conditions in the reactions of *N*-arylimines of butyl *o*-formylphenyl telluride with halogens or SO_2Cl_2. This reaction gives rise not to the expected σ-telluranes, but rather to *N*-arylimines of *o*-formylbenzene tellurenyl halides[76,77] in 60–90% yield.



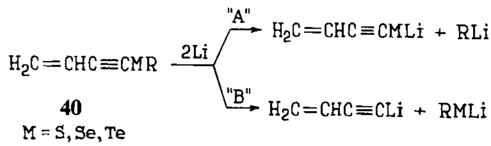
Cleavage of C_{sp}–Te bonds occurs easily in alkyl ethynyl tellurides.[131-135] Phenylethynyl methyl telluride **43** (M = Te) with water in the presence of mercury(II) salts forms a mixture of phenylethyne and acetophenone and not the methyl ester of phenyltelluroacetic acid, as might be expected in analogy with its selenium analog.[131] Similar behavior is shown by (alkyltelluro)alkynes and (alkyltelluro)vinylethynes.[132]

$$PhC{\equiv}CTeCH_3$$

43

The structure of the tellurium-containing products formed in this reaction has not been specified.

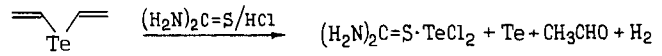
Tellurium-containing enynes **40** do not add organomagnesium compounds to the triple bonds as in the case of their sulfur and selenium analogs, but convert to dialkyl tellurides, products of C_{sp}–Te bond cleavage.[133] The latter occurs in compounds **40** under the action of ethanethiol,[134] while in compounds **32** it is initiated by treatment with acetic acid.[135]



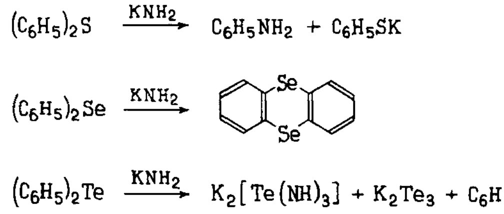
Interaction of alkyl vinylethynyl chalcogenides **40** with lithium in liquid ammonia is also accompanied by rupture of the C_{sp^2}–M ("A") or C_{sp}–M ("B") bond, the direction of the reaction being determined by the nature of the chalcogen. In the case of derivatives of selenium and tellurium, the reactions proceed only in the direction "B" whereas for the sulfur analogs the products of the "A" and "B" reactions are isolated in approximately 1:1 ratio.[136]

Unlike divinyl sulfide which gives with thiourea catalysed by acid 2*H*,6*H*-2,6-

dimethyl-4-amino-1,3,5-dithiazine,[137] divinyl telluride under the same conditions suffers cleavage of both C_{sp^2}–Te bonds to form $TeCl_2$ complexes of thiourea.[138]

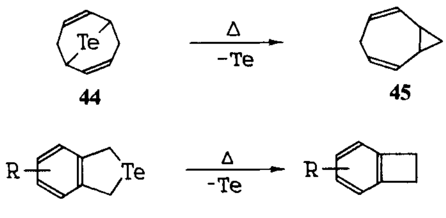


The nature of the chalcogen atom in diphenyl chalcogenides determines the course of their reactions with potassium amide in liquid ammonia.[139] Some reactions of derivatives



of dicoordinate tellurium resulting in cleavage of both C–Te bonds are utilized for the synthesis of a number of cyclic hydrocarbons and 1,5-dienes.

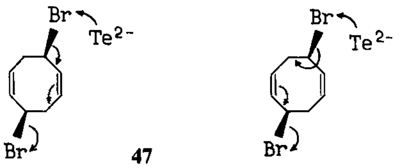
The pyrolysis of 9-tellurabicyclo[3.3.1]nona-2,6-diene **44** gives in almost quantitative yield bicyclo[5.1.0]octa-2,5-diene **45**[140] while thermal decomposition of 1,3-dihydrobenzo[*c*]tellurophene **46** (R = H) and 1,3-dihydronaphtho[2,3-*c*]tellurophene (**46**, R = 3,4-C_4H_4) produces benzocyclobutene and naphtho[*b*]cyclobutene.[141]



44 **45**

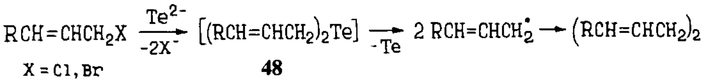
46 R = H, 3,4-C_4H_4

Noteworthy is that **45** is obtained in 20% yield together with the tellurium-containing bicyclic derivative **44** (18%) in the reaction of 3,7-dibromocycloocta-1,5-diene **47** with sodium telluride under conditions prohibiting thermal extrusion of tellurium from **44**.[40] No such reaction occurred when sodium telluride was substituted by sodium sulfide.



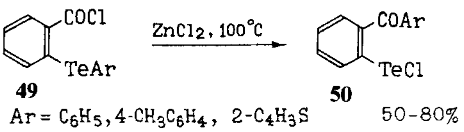
47

A promising method for high-yield syntheses of 1,5-dienes is based on the easy extrusion of tellurium from bis(allyl) tellurides **48**.[142] The latter compounds are intermediates in the reactions of allyl halides with lithium telluride and very rapidly decompose to Te and allyl radicals. Recombination of the latter affords 1,5-dienes. Selenium analogs of **48** are quite stable, giving under similar conditions 1,5-dienes in very low yields (< 2%).[142]

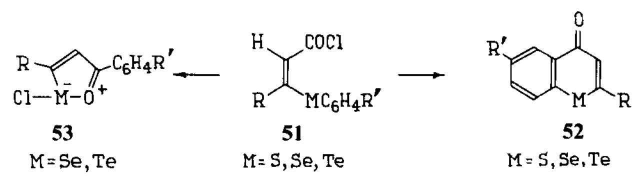


$$\underset{X = Cl, Br}{RCH{=}CHCH_2X} \xrightarrow[-2X^-]{Te^{2-}} \underset{\mathbf{48}}{[(RCH{=}CHCH_2)_2Te]} \xrightarrow[-Te]{} 2\,RCH{=}CH\dot{C}H_2 \longrightarrow (RCH{=}CHCH_2)_2$$

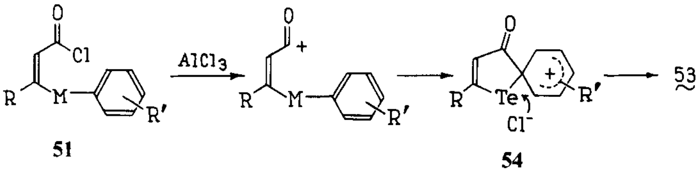
Different results depending on the type of the chalcogen atom M were achieved in attempts to cyclize *o*-chloroformyldiaryl chalcogenides **49**. While the cyclization of **49** (M = Te) affords in the presence of $ZnCl_2$ not the expected telluroxanthones, but rearranged products, 2-aroylbenzenetellurenyl chlorides **50**,[71,119] their sulfur analogs (**49**, M = S) produce thiaxanthones in good yield.



An interesting example illustrating the role of the chalcogen atom in cyclizations of *β*-(arylchalcogeno)propenoyl chlorides **51** is given by Detty.[123,124] Thermal or catalytic ($AlCl_3$) cyclization of these compounds gives rise either to six-membered heterocycles (chalcogenochromones or -flavones **52**) via *ortho*-cyclization or five-membered heterocycles, i.e. 1,2-oxachalcogenol-1-ium chlorides **53** via *ipso*-acylation.[124] The Te-O distances (2.18–2.20 Å) in **53** (M = Te) are much less than the sum of the tellurium and oxygen van der Waals radii.[123] On this ground Detty[123] assigned to these compounds the mesoionic heterocyclic structure **53**.



Compounds **51** (M = S), regardless of R and R′ can be converted to the thiaflavones **52** (M = S) in high yield (70–85%). In the case of *β*-(arylseleno)propenoyl chlorides **51** (M = Se), the direction of the cyclization depends on the aryl substituent. With R′ = H only selenoflavones (**52**, M = Se, R′ = Ph) are obtained, while introducing R′ = 4-OCH_3 results in the exclusive formation of 1,2-oxaselenol-1-ium chlorides (**53**, M = Se, R = CH_3, Ph). With R′ = 4-F a mixture of both **53** (M = Se, R = CH_3, yield 36%) and **52** (M = Se, R = CH_3, yield 36%) was obtained. On the other hand, regioselective *ipso*-acylation to form 1,2-oxatellurol-1-ium chlorides (in 50–95% yield) occurs in the case of *p*-substituted *β*-(aryltelluro)propenoyl chlorides **51** (M = Te).[123,124] The spirocyclic *σ*-complex **54** is assumed as an intermediate[123,124]



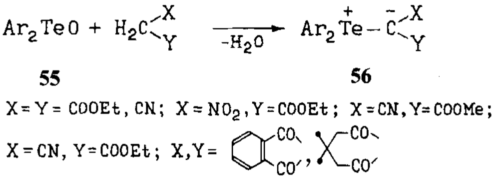
51 **54**

It should, however, be noted that by appropriate choice of substituents in the aryltellurium moiety which activate the *ortho*-positions towards electrophilic attack and inhibit *ipso*-acylation the cyclization of β-(arytelluro)propenoyl chlorides can be directed toward predominant formation of the telluraflavones **52** (M = Te). Thus, with R′ = 3-F there is formed a mixture of **52** (yield 5%) and **53** (yield 78%), while in the case of R′ = 3,5-$(OCH_3)_2$ only the telluroflavone **52** (M = Te) is produced in 90% yield.[124]

4. DERIVATIVES OF TRICOORDINATE TELLURIUM

Apart from telluronium salts $R^1R^2R^3Te^+X^-$ this group of compounds comprises telluronium ylides $R_2Te{=}CR'_2 \leftrightarrow R_2Te^+{-}C^-R'_2$, tellurimides $R_2Te{=}NR' \leftrightarrow R_2Te^+{-}N^-R'$ and telluroxides $R_2Te{=}O \leftrightarrow R_2Te^+{-}O^-$ all known under the common name of π-telluranes.[143,144] Since some reactions involving telluronium salts have been considered in Sections 2.2 and 3.4, this Section deals mainly with π-telluranes. It is their reactivity and methods of preparation which are different from those of the respective tricoordinate sulfur (and, to a lesser extent, selenium) analogs. The chief factors responsible for the unusual behaviour of π-telluranes in contrast to other π-chalcogenuranes are a stronger polarization of the Te=X bonds (larger contribution of the $Te^+{-}X^-$ resonance structure) and an enhanced basicity as well as a sharply pronounced propensity of tricoordinate tellurium compounds to nucleophilic addition reactions converting them to σ-telluranes. First, reactions common to all groups of π-telluranes will be considered.

1. Unlike alkyl phenyl and dialkyl sulfoxides, the corresponding telluroxides are always isolated as hydrates possessing, apparently, the σ-tellurane structure $R_2Te(OH)_2$[2,3,18,143]. Because of the high basicity of the oxygen atom in diaryl telluroxides **55** their reaction with activated methylene compounds leading to telluronium ylides **56**[145,146] does not require, in contrast to the preparation of the corresponding sulfonium and selenonium ylides, strong dehydrating agents such as acetic anhydride, dicyclohexyl carbodiimide, phosphoric acid anhydride, thionyl chloride etc.[143] These reactions proceed in benzene or chloroform solution of equimolar amounts of the reaction components the water formed being distilled off azeotropically.[145,146]



There is no need for dehydrating agents either in the synthesis of tellurimides **57** from diaryl telluroxides **55** under equally mild conditions[147,148]

$$\underset{\mathbf{55}}{Ar_2TeO} + H_2N{-}R \xrightarrow[-H_2O]{} \underset{\mathbf{57}}{Ar_2\overset{+}{Te}{-}\overset{-}{N}{-}R}$$

$$R = ArSO_2,\ CCl_3CO,\ 4\text{-}NO_2C_6H_4C(O),\ 3\text{-}NO_2C_6H_4C(O)$$

2. The reactions of ylides and imides with halogens proceed smoothly with cleavage of the Te–M (M = CR_2, NR) bonds and formation of σ-telluranes.[149,150] In the reactions of analogous sulfur derivatives there are formed compounds of dicoordinate sulfur, the diorganyl sulfides.[151]

$$R_2\overset{+}{Te}{-}\overset{-}{M}R' + X_2 \longrightarrow R_2TeX_2 + X_2MR'$$

56 **57**

$M = C, N$; $X = Cl, Br, J$

3. The reaction of π-telluranes with proton acids with cleavage of the Te–M bond in π-telluranes and formation of the corresponding σ-telluranes is a general property of π-telluranes.[2,3,149,150,152–155]

$$R_2\overset{+}{Te}{-}\overset{-}{M}R' + 2HX \longrightarrow R_2TeX_2 + H_2MR'$$

55–57

$M = C, N, O$; $X = F, Cl, Br, J, OCOR$

Diaryl sulfoxides on the other hand, do not react with acids at all, while stabilized sulfonium ylides such as dinitromethylides, when treated with solutions of hydrogen halides in organic solvents, give not σ-sulfuranes, but sulfides.[151] In the case of selenonium dinitromethylides, depending on the hydrogen halide and the reaction conditions, either selenides or σ-selenuranes may be obtained.[156] Such a tendency in the reaction considered is obviously explained by the gradient in the stability of tetracoordinate chalcogen compounds: Te(IV) > Se(IV) > S(IV).

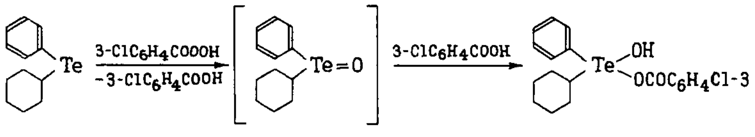
4. Diaryl telluroxides **55**[153,154,157] as well as tellurimides **57**[150] react readily with carboxylic acid anhydrides to form σ-telluranes, i.e. diaryltellurium dicarboxylates and diacyl amides.

$$R_2Te{-}MR' + (R''CO)_2O \longrightarrow R_2Te(OCOR'')_2 + R'M(COR'')_2$$

55, **57**

$MR' = O, NCOCF_3$

Some reactions of π-telluranes, particularly of diaryl telluroxides, with carboxylic acids and their anhydrides are important for two reasons: a) They serve as convenient methods for the synthesis of diaryltellurium dicarboxylates. Other synthetic procedures, such as nucleophilic substitution of halogens in diaryltellurium dihalides by acyloxy groups upon treatment with silver carboxylates[158] and oxidation of diaryl tellurides with lead tetraacetate,[159] are of limited scope. b) Because of the ease the reactions of acids with diaryl telluroxides procedures for the preparation of the latter must avoid reagents such as nitric acid, hydrogen peroxide in acetic anhydride, etc. widely utilized in the synthesis of sulfoxides from sulfides.[160] Thus, it was found that the oxidation of phenyl cyclohexyl telluride by 3-chloroperbenzoic acid yielded the tetracoordinate tellurium derivative **58**.[161] Obviously, the primary product of this reaction is phenyl cyclohexyl telluroxide **59** whose subsequent reaction with the 3-chlorobenzoic acid formed simultaneously leads to **58**. Similar compounds were earlier obtained by treatment of diaryl telluroxides with carboxylic acids[153]



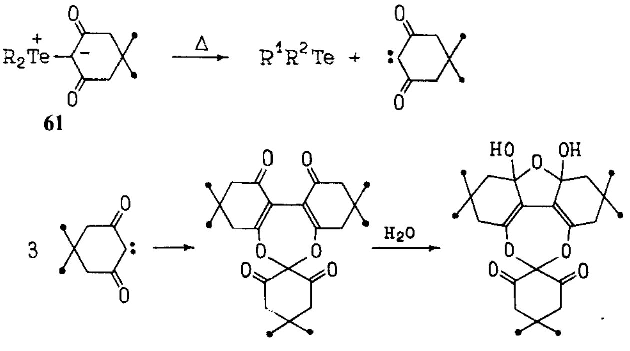
59 **58**

5. Only one group of telluronium ylides containing a single acceptor substituent at the carbanionic center has been described to date, namely the dialkyltelluronium carbethoxymethylides **60**.[162] Reactions of these ylides with aldehydes and ketones lead in high yields to α,β-unsaturated esters. α,β-Unsaturated carbonyl compounds also form the respective esters. The corresponding sulfonium ylides do not react with aliphatic and aromatic aldehydes and ketones, while with α,β-unsaturated carbonyl compounds they form cyclopropanes.[163]

$$R_2\overset{+}{Te}-\overset{-}{C}HCOOEt + R^1R^2C=O \xrightarrow[-R_2TeO]{} R^1R^2C=CHCOOEt$$

60

6. Quite different are the results of thermolysis of the stable telluronium and selenonium ylides **61**. Upon heating in inert solvents, the telluronium ylides decompose into diorganyl tellurides and a trimer of the initially formed cyclic carbene, **62**.[164]



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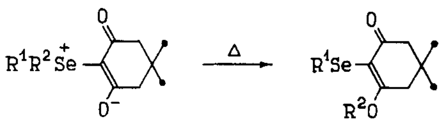
62

On the other hand, selenonium ylides **61** under the same conditions undergo a thermal Stevens rearrangement.[165]

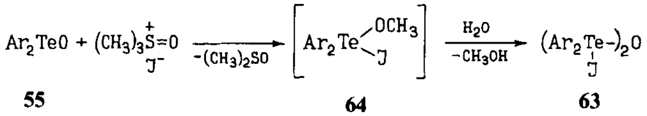


61

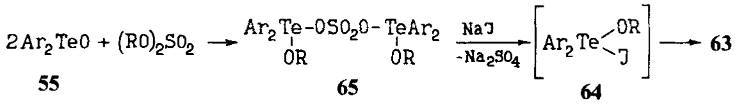
These findings were explained[164] in terms of the fact that the rupture of the Te$^+$–C$^-$ bond requires less energy than that of the Se$^+$–C$^-$ bond. This is borne out by mass spectrometric studies of the intensities of the molecular peaks M$^+$ of the telluronium[166] and selenonium ylides.[167] They are extremely low (0.1–0.3% of the total ionic current) for the telluronium ylides **61**, whereas with the selenonium ylides **61** the M$^+$ peaks are quite intensive.[167]

7. Substantial differences are observed in the reactivity of diaryl telluroxides and diaryl sulfoxides towards alkylating agents. Sulfoxides undergo either *O*- or *S*-alkylation,[168] depending the reaction partners. By contrast, only *O*-alkyltelluronium salts were found to be the primary products of the reactions of diaryl telluroxides **55** with various alkylating agents such as trimethylsulfoxonium iodide,[169] dialkyl sulfates[170] and methyl iodide.[171] Their further transformations are strongly affected by the nature of the groups attached to the tellurium center as well as by the reaction conditions.

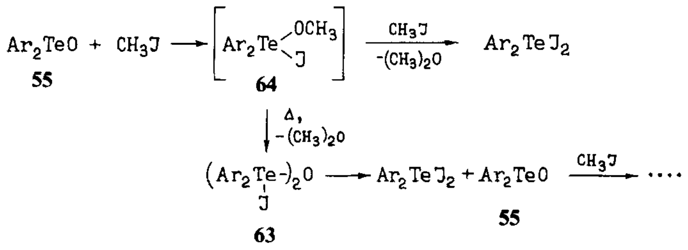
Interaction of diaryl telluroxides **55** with Me$_3$SO$^+$ I$^-$ leads to bis(diaryliodotellurium) oxides **63**,[169] probably via an intermediate *O*-alkylation product **64**



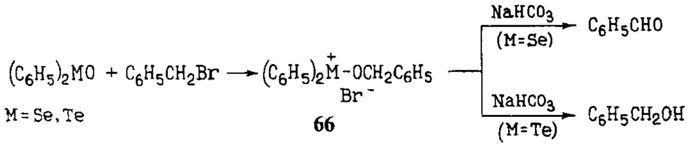
Treatment of diaryl telluroxides **55** with dialkyl sulfates affords rather stable σ-telluranes, bis(diaryl-alkoxytellurium)sulfates **65**[170] which with NaI·2H$_2$O are converted to **63**:



The difference in the reactivity of telluroxides and sulfoxides manifests itself in their reactions with methyl iodide. Whereas dimethyl sulfoxide upon reflux in methyl iodide solution gives rise to the product of *S*-alkylation, trimethylsulfoxonium iodide,[168] diaryl telluroxides under the same conditions form diaryltellurium diiodides.[171]



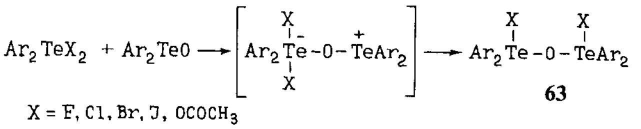
Diphenylbenzyloxychalcogenonium salts **66** are assumed to be the primary products of the reaction of diphenyl chalcogenoxides Ph_2MO (M = Se, Te) with benzyl bromide.[172] Further transformations depend on the chalcogen atom. Diphenylbenzyloxyselenonium bromide, when treated with base, is converted to benzaldehyde in over 50% yield whereas its telluronium analog under the same conditions affords benzyl alcohol as the main product.



$$(C_6H_5)_2MO + C_6H_5CH_2Br \longrightarrow (C_6H_5)_2\overset{+}{M}\text{-}OCH_2C_6H_5\ Br^- \ (\mathbf{66}) \quad \xrightarrow[(M=Se)]{NaHCO_3} C_6H_5CHO; \quad \xrightarrow[(M=Te)]{NaHCO_3} C_6H_5CH_2OH \qquad M = Se, Te$$

In the light of the distinctive behavior of diaryl sulfoxides and diaryl telluroxides in their alkylation reactions, of specific interest would be the results of a comparative study of the corresponding reaction of diaryl selenoxides.[173] It has been assumed that diphenyl selenoxide with potent alkylating agents such as methyl iodide (in the presence of HgI_2), trimethyloxonium tetrafluoroborate or methyl triflate forms the unstable diphenylalkoxyselenonium salts, but that have not been isolated and no definite spectral proof of their formation has been yet presented.

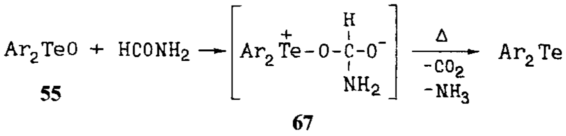
8. Diaryl telluroxides **55** promptly react with σ-telluranes Ar_2TeX_2 containing electronegative groups X = Hal, OCOR at the tellurium atom to form **63** in high yield.[174]



$$Ar_2TeX_2 + Ar_2TeO \longrightarrow \left[Ar_2\overset{X}{\underset{X}{\overset{|}{\underset{|}{Te}}}}{}^{-}\text{-}O\text{-}\overset{+}{Te}Ar_2\right] \longrightarrow Ar_2\overset{X}{\overset{|}{Te}}\text{-}O\text{-}\overset{X}{\overset{|}{Te}}Ar_2 \ (\mathbf{63}) \qquad X = F, Cl, Br, J, OCOCH_3$$

Such a reaction is, apparently, prohibited in the case of organosulfur compounds because of the instability of the corresponding σ-sulfuranes.

9. The high nucleophilicity of diaryl telluroxides **55** facilitates the formation of **67** and enhances their reduction to tellurides proceeding in quantitative yield upon heating them in formamide at 120–140 °C[175]



$$Ar_2TeO\ (\mathbf{55}) + HCONH_2 \longrightarrow \left[Ar_2\overset{+}{Te}\text{-}O\text{-}\overset{H}{\underset{NH_2}{\overset{|}{\underset{|}{C}}}}\text{-}O^-\right] (\mathbf{67}) \xrightarrow[-CO_2,\ -NH_3]{\Delta} Ar_2Te$$

This reaction can also be employed for the reduction of diaryl selenoxides,[175] while the less nucleophilic diaryl sulfoxides do not react with formamide in this way.

10. The propensity of tellurium derivatives to be converted to their tetracoordinate forms is, probably, responsible for the different results of the reactions of diphenyl telluroxide and diphenyl selenoxide with $SnCl_4$. Whereas the telluroxide forms the corresponding σ-tellurane, viz. Ph_2TeCl_2,[176] diphenyl selenoxide gives rise to the complex $2\ Ph_2SeO \cdot SnCl_4$.[177]

5. DERIVATIVES OF TETRACOORDINATE TELLURIUM

To the most studied compounds of this type belong the diorganyltellurium dihalides R_2TeX_2 and the organyltellurium trihalides $RTeX_3$ which are involved in important synthetic procedures for various derivatives of di-, tri-, and pentacoordinate tellurium.[2-4] Tetraaryltelluranes and, particularly, diaryl tellurones Ar_2TeO_2 are little-studied substances, the first reliably characterized tellurone, bis(4-methoxyphenyl) tellurone having being reported only in 1982.[178]

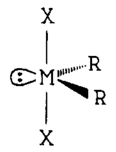
5.1. *σ-Telluranes* R_2TeX_2 *and* $RTeX_3$

These tetracoordinate tellurium derivatives with electronegative substituents X are stable well-crystallized compounds. Some of their properties (compared to those of analogous derivatives of selenium and sulfur) are listed in Table 1.

Table 1. Some properties of chalcogen tetrachlorides and their organyl derivatives

SCl_4 decomposes at −31°C [179]	$SeCl_4$ melts withough decomposition at 305°C [179]	$TeCl_4$ melts without decomposition at 225°C[179]
$RSCl_3$ decompose even at very low temperature[180,181]	$RSeCl_3$ stable at room temperature, upon heating decompose readily into RSeCl and Cl_2[182,183]	$RTeCl_3$ stable up to the melting point[2,3,179]
R_2SCl_2 decompose at temperatures below 0°C, at room temperature they exist only in a dry chlorine atmosphere[184-188]	R_2SeCl_2 stable up to the melting point[179]	R_2TeCl_2 stable up to the melting point[2,3,179]

The principal structure of the compounds R_2MHal_2 ($M = S, Se, Te$) changes depending on the chalcogen and the halogen from covalent with trigonal-bipyramidal configuration **68** (TBP) to the charge-transfer complexes **69** (CT) in which the chalcogen atom is coordinated to only one halogen atom with the angle M···X–X close to 180°.[189-191]



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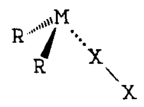


69

In general, structure **68** is characteristic of compounds in which a sufficiently large difference between the electronegativities of the chalcogen and halogen atoms exists. If this difference is small, the structure **69** is favored. This rule stemming from the hypervalent nature of the bonding in **68** explains the predominance of the σ-chalcogenurane structure **68** (M = S, Se, Te) in the case of their fluorine derivatives. Data concerning the structures of compounds $R^1R^2MHal_2$ (Hal = F, Cl, Br, I; $R^1 = R^2 = CH_3$; $R^1 = CH_3$, $R^2 = C_6H_5$; R^1, $R^2 = (CH_2)_5$) are summarized in Table 2.[189-191]

Table 2. The structure of the chalcogenuranes R_2MHal_2

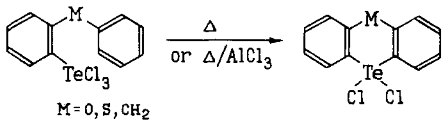
M	Hal = Cl	Hal = Br	Hal = I
S	TBP* (**68**)	CT* (**69**)	CT
Se	TBP	TBP	CT
Te	TBP	TBP	TBP

TBP - trigonal bipyramidal structure; CT - charge-transfer complex.*

It is to be noted, however, that structural variations in R may affect the predicted (see Table 2) structure of R_2MHal_2. E.g., diorganylselenium dibromides are usually σ-selenuranes,[189-191] but dibromoselenoxanthone, judging from its ^{13}C NMR spectrum, possesses structure **69**.[191] This may be caused by an enhanced effective electronegativity of the selenium atom brought on by conjugation with the carbonyl group. However, all tellurium derivatives R_2TeX_2 exist as true tetracoordinate compounds **68**.

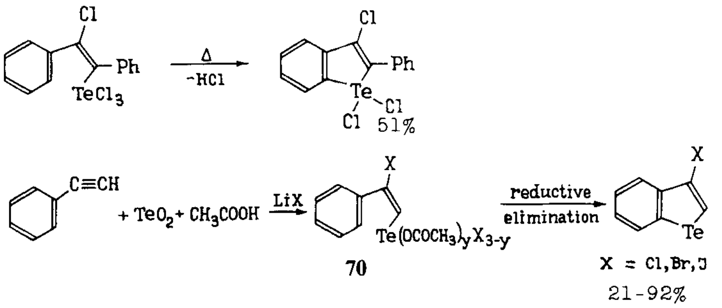
σ-Telluranes R_2TeX_2 can be reduced to diorganyl tellurides R_2Te, converted to telluronium salts, telluroxides, and telluronium ylides.[2-4] By treatment with tellurium tetrachloride diaryltellurium dichlorides are transformed into aryltellurium trichlorides $ArTeCl_3$.[192] Aryltellurium trichlorides as well as other organyltellurium trihalides $RTeX_3$ can be reduced to diorganyl ditellurides R_2Te_2[2-4] and transformed, through symmetrization reactions, to σ-telluranes Ar_2TeCl_2.[192] They can be also converted to pertelluranes $RTeX_5^-$ containing a pentacoordinate tellurium atom.[2,3] The strong electrophilicity of the $TeCl_3$ group facilitates intramolecular electrophilic substitution in aromatic compounds containing this substituent. A variety of six- and five-membered tellurium-containing heterocyclic compounds have been synthesized by this reaction. In some similar reactions ArMX compounds (M = S, Se) are used as starting material as well.[193-196] But, in distinction to the chemistry of telluriumorganic compounds, they have a limited scope. Originally this approach was utilized to obtain 10,10-dichlorophenoxatellurine from 2-phenoxyphenyltellurium trichloride.[197] Later on, a number of substituted 2-phenoxyphenyltellurium trichlorides were used in this reaction.[114,198-203] The method was also extended to the synthesis of 10,10-dichlorothiophenoxatellurine,[127,204] and 10,10-dichlorotelluroxanthene.[205,206] 10,10-Dichlorothiophenoxatellurine has been prepared by reaction of diphenyl ether with $TeCl_4$ at elevated temperature. The initially formed 4-phenoxyphenyltellurium trichloride rearranges into its 2-isomer which then cyclizes. Similarly, 4,4′-disubstituted diphenyl ethers afford 2-tellurium trichlorides in a one-pot reaction with $TeCl_4$. However, in the cases of 4-substituted diphenyl ethers, diphenyl sulfide, and diphenylmethane the use of previously prepared tellurium trichlorides is preferable. The synthesis of 10,10-dichlorotelluroxanthene is possible only in the presence of an equimolar amount of $AlCl_3$[205,206]

which enhances the electrophilicity of the $TeCl_3$ group due to the formation of the intermediate ionic complex $[RTeCl_2H]^+ [AlCl_4]^-$ whose structure is analogous to that of the complex $[TeCl_3]^+ [AlCl_4]^-$.[207]

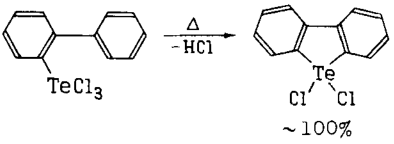


M = O: $R^1 = R^2 = H$ (50%)[197], Cl (43%)[201], F (37%)[202], $R^1 = H$: $R^2 = CH_3$ (80%)[199], F (30%)[203], M = S: $R^1 = R^2 = H$ (42%)[204]; M = CH_2: $R^1 = R^2 = H$ (80%)[205,206]

The cyclization of phenylvinyltellurium trichlorides is extensively used for the synthesis of benzoannelated five-membered heterocyclic compounds. For instance, the first benzo[*b*]tellurophene derivative, 1,1,3-trichloro-2-phenylbenzo[*b*]tellurophene, was obtained by thermal cyclization of 2-chloro-1,2-diphenylvinyltellurium trichloride.[208] Similarly, 3-halobenzo[*b*]tellurophenes have been prepared via cyclization of intermediate **70**.[209,210]



The thermal cyclization of 2-trichlorotelluriumbiphenyl resulted in the formation of 1,1-dichlorodibenzotellurophene.[211]



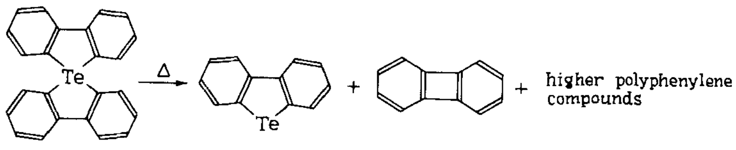
5.2. *Tetraaryltelluranes Ar_4Te*

Whereas tetraarylsulfuranes and tetraarylselenuranes formed by treatment of the respective chalcogen tetrahalides with aryllithiums exist only in solution at very low temperature, tetraaryltelluranes are quite stable crystalline compounds.[212,213] However, they decompose into diaryl tellurides and biaryls upon melting or heating in solution.

$$Ar_4Te \xrightarrow{\Delta} Ar_2Te + Ar\text{-}Ar$$

$$Ar = C_6H_5,\ 4\text{-}CH_3C_6H_4$$

The spirocyclic tellurane **71** decomposes under these conditions giving rise to dibenzotellurophene, biphenylene, and higher polyphenylene compounds.[214,215]



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Widely different stabilities are also observed with the tetraalkoxychalcogenuranes $M(OR)_4$ **72** (M = S, Se, Te). The sulfuranes are not known at all with the exception of perfluoro derivatives. The existence of tetramethoxy- and tetraethoxyselenurane at low temperature (−35 °C) may be inferred from the ^{77}Se NMR spectra,[216] but with rising temperature they rapidly decompose into dialkyl selenites and dialkyl ethers.[216,217]

$$\underset{\substack{\mathbf{72}\\ R = CH_3, C_2H_5}}{(RO)_4Se} \xrightarrow{\Delta} (RO)_2SeO + R_2O$$

On the other hand, tetramethoxy- and tetraethoxytellurane are stable compounds which can be distilled *in vacuo* without decomposition.[216,218,219]

6. OUTLOOK

In this brief review we have focused on the most characteristic properties and reactions of telluriumorganic compounds providing some new aspects of their reactivity in comparison with the sulfur and selenium analogs. Special emphasis has been put on preparative applications of the featured reactions of telluriumorganic compounds.

Promising synthetic results can be expected from further development of dehalogenation reactions of various halogen-containing substrates promoted by catalytic amounts of dicoordinate telluriumorganic compounds and tellurolate anions. Of special interest is also a search for novel applications of facile tellurium extrusion reactions which may provide convenient routes to some otherwise not readily accessible structures and of *ipso*-substitutions of organotellurium(IV) groups in aromatic rings. The particular reactivity of organotellurium compounds with intramolecular coordinative Te ← X (X = O, N, S) bonds may be appropriately used for promoting reactions requiring the cleavage of Te–C bonds. A rapid growth of interest in tellurium-containing heterocyclic compounds leads to further development of methods for their preparation. Among the most promising approaches deserving elaboration are methods such as intramolecular nucleophilic additions of tellurolate anions to triple bonds leading, for example, to 1,3-ditelluroles and 1-thia-4-chalcogenacyclohexanes as well as intramolecular electrophilic cyclizations of relevant organyltellurium trichlorides.

We expect that further development of the above-mentioned and other, still undiscovred, selective aspects of organotellurium methodology may lead to significant progress both in syntheses of novel groups of telluriumorganic compounds and in synthetic applications of telluriumorganic compounds.

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