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Synthesis, reactions and structures of telluronium salts

A V Zakharov, I D Sadekov, V I Minkin

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Abstract. The published data on the synthesis, structures and properties of triorganyltelluronium salts are generalised and systematised. Special attention is given to the applications of these compounds in preparative organic synthesis. The bibliography includes 163 references.

I. Introduction

Triorganyltelluronium salts comprise compounds of the general formula $R^1R^2R^3TeX$. Depending on the nature of the electronegative group X, solvent and the structure of the crystal lattice, the degree of ionicity of the Te – X bond varies from purely ionic to covalent. Whereas the first organotellurium compound, diethyl telluride, was synthesised in 1840,[1] the first representatives of telluronium salts, *viz*., trimethyl- and triethyltelluronium iodides, were obtained only 25 years later.[2]

At present, triorganyltelluronium salts are widely used in preparative organic chemistry as starting materials for the synthesis of alkenes, alkylidene(or arylmethylidene)malonates, benzylic, propargylic and allylic alcohols. The trifluoromethyl derivatives are used as trifluoromethylating reagents, whereas triphenyltelluronium salts are used as catalysts in the liquid-phase oxidation of alkenes. It is recommended to use triphenyltelluronium salts as analytical reagents for Co^{2+} and Bi^{3+} ions (Refs 3 and 4); their trialkyl analogues are inhibitors of acid corrosion of iron and steel.[5, 6] Telluronium ylides generated *in situ* from telluronium salts are used in the synthesis of epoxides,[7] cyclopropanes [7, 8] and alkenes containing electronegative substituents at the double bond.[7]

Separate chapters in the monographs [9, 10] of 1974 and 1983 are devoted to telluronium salts. However, a considerable number of papers on the synthesis and, particularly, on reactions and structures of telluronium salts have been published later. This review is intended to complement the published reviews and to analyse the state of the art of the problem. The main attention is given to acyclic salts; the data on cyclic telluronium salts are reviewed in the monograph by Detty and O'Regan [11] devoted to heterocyclic tellurium derivatives, so they are mainly not included here.

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II. Synthesis of telluronium salts

The reaction of tellurium tetrachloride with organoelement compounds is one of the main preparative methods for the synthesis of symmetrical triorganyltelluronium salts $R_3Te^+X^-$ (**1**). Diethylzinc was the first to be used for this purpose; however, it was organomagnesium (RMgHal) and organolithium (RLi) compounds that came in practice later.[9, 10, 12, 13] An attempt to obtain a triorganyltelluronium salt with the use of organocadmium compound is also reported.[14] The reaction of tellurium tetrachloride with organoelement compounds is usually carried out under mild conditions and is followed by fast acid hydrolysis.

$$TeCl_4 + RM \xrightarrow[2)\ HX]{1)\ Et_2O,\ 0\ ^\circ C} R_3Te^+X^- \quad \mathbf{1}\ (15\% - 79\%)$$

M = MgHal, Li; X = Cl, Br, I; R = Alk, Ar.

In the majority of cases, salts **1** were isolated as poorly soluble iodides upon treatment of the reaction mixture with an aqueous solution of potassium iodide. It should be noted that under these conditions the reaction of 2,4,6-tris(*tert*-butyl)phenyllithium with $TeCl_4$ affords the corresponding telluride $(2,4,6\text{-}Bu^t_3C_6H_2)_2Te$ instead of the expected telluronium salt.[13]

Recent studies have shown [15] that depending on the procedure for quenching of the reaction mixture, the reaction of 2,6-dimethoxyphenyllithium with $TeCl_4$ in ether yields telluronium salts **2** or **3**. The former were isolated after hydrolysis with hot water, while the latter were isolated upon treatment of aqueous filtrates with 6 M HCl. In the latter case, bis(2,6-dimethoxyphenyl) telluride was formed as a side product (yield 15%).[15]

$$TeCl_4 + ArLi \xrightarrow{1)\ Et_2O} \begin{cases} \xrightarrow{2)\ \Delta,\ H_2O} (Ar_3Te^+Cl^-)\cdot n\,H_2O \quad \mathbf{2}\ (60\%) \\ \xrightarrow{2)\ H_2O,\ HCl} [(Ar_3Te^+)(HCl_2^-)]\cdot 0.5\,H_2O \quad \mathbf{3}\ (65\%) \end{cases}$$

Ar = 2,6-$(MeO)_2C_6H_3$; n = 2 – 2.5.

Reactions of diaryltellurium dihalides Ar_2TeY_2 (Y = Cl [9,10,13]; Br, I [9,10]) with arylmagnesium bromides or aryllithium compounds represent a general method for the synthesis of triaryltelluronium salts. This method was used for the preparation of both symmetrical telluronium salts ($Ar_3Te^+X^-$) (**1**) and their non-symmetrical analogues, $Ar^1_2Ar^2Te^+X^-$ (**4**).

$$Ar^1_2TeY_2 + Ar^2M \xrightarrow[2)\ \Delta,\ H_2O,\ HX]{1)\ Et_2O} \underset{\mathbf{1,4}}{Ar^1_2Ar^2Te^+X^-}$$

M = MgBr, Li.

This reaction can obviously be used for the preparation of non-symmetrical telluronium salts of the type $Ar^1Ar^2Ar^3Te^+X^-$ from diaryltellurium dihalides $Ar^1Ar^2TeY_2$ and Ar^3M (M = MgHal, Li). However, no data on such a synthesis are available so far.

In the reactions of arenes with $TeCl_4$, salts **1** or their mixtures with diaryltellurium dichlorides **5** are formed.[10,16] Cresol derivatives of this type were obtained earlier with the use of $TeOCl_2$; however, these results seem doubtful now.[9]

$$TeCl_4 + ArH \xrightarrow{(a\ \text{or}\ b)} \underset{\mathbf{1a-c}}{Ar_3Te^+Cl^-} + \underset{\mathbf{5b,c}}{Ar_2TeCl_2}$$

(*a*) $AlCl_3$, Δ (for **a**); (*b*) 110–130 °C (for **b**, **c**);
Ar = Ph (**a**, 60%), 2-OH-5-MeC_6H_3 (**b**), 4-OH-2-MeC_6H_3 (**c**).

A new method for the synthesis of various types of telluronium salts has been developed recently.[17] It is based on the reactions of electrophilic intermediates **6** (formed upon the reaction of diaryltellurium difluorides with $BF_3\cdot Et_2O$) with silyl derivatives **7**–**9**. For example, these intermediates reacted with *O*-trimethylsilyl ethers **7** and **8** at room temperature to give 2- (**10**) and 3-oxoalkyldiaryltelluronium salts **11** in 85%–100% yields. Similarly, allyldiphenyltelluronium tetrafluoroborate **12** was obtained from allyltrimethylsilane (**9**) in quantitative yield under very mild conditions.[17]

$$Ar_2TeF_2 + BF_3\cdot OEt_2 \xrightarrow{CH_2Cl_2} \underset{\mathbf{6}}{[Ar_2TeF]^+BF_4^-} \longrightarrow$$

$CH_2{=}C(R)OSiMe_3$ (**7**), 20–25 °C → $Ar_2Te^+CH_2COR\ \ BF_4^-$ (**10**)
Ar = Ph: R = Bu^t, Pr^i, Ph;
Ar = 4-MeC_6H_4: R = Bu^t, Ph;
Ar = 4-$MeOC_6H_4$, R = Ph.

(**8**) → $Ph_2Te^+CH_2CH_2COBu^t\ \ BF_4^-$ (**11**)

$CH_2{=}CHCH_2SiMe_3$ (**9**), −50 °C, Ar = Ph → $Ph_2Te^+CH_2CH{=}CH_2\ \ BF_4^-$ (**12**)

The use of tributyl(organyl)stannanes in a similar reaction enabled the synthesis of the telluronium salts $Ar_2RTe^+\ BF_4^-$ containing Te–C(sp^3), Te–C(sp^2) and Te–C(sp) bonds, *viz.*, compounds **13** (R = Alk), **14** and **15**, respectively, as well as of non-symmetrical triaryltelluronium salts of the type **4** (Ar = Ph, R = 4-$MeOC_6H_4$).[17]

$$Ar_2TeF_2 + BF_3\cdot OEt_2 + Bu^n_3SnR \xrightarrow[-Bu^n_3SnF]{CH_2Cl_2,\ 20-25\ ^\circ C} \underset{\mathbf{4,\ 13-15}}{Ar_2RTe^+\ BF_4^-}$$

Compound	Ar	R	Yield (%)
4	Ph	4-$MeOC_6H_4$	95
13	Ph, 4-$MeOC_6H_4$	Bn	88–100
14	Ph	$Me_2C{=}CH$	87
15	Ph, 4-$MeOC_6H_4$	$PhC{\equiv}C$	94–96

The method for the synthesis of telluronium salts described in Ref. 17 has a number of advantages. First, it enables preparation of diaryl(organyl)telluronium salts containing various substituents at the tellurium atom. Second, telluronium salts that are difficult to obtain by other methods are produced in high yields under mild conditions. And finally, nearly pure salts can be isolated upon evaporation of the solvent, since side reaction products, fluorotriorganylsilanes(stannanes), are volatile compounds.

Telluronium salts are synthesised from organic derivatives of boron [18] and iodine.[19,20] Thus treatment of diphenyltellurium difluoride with 4-methoxyphenylboronic acid in the presence of $BF_3\cdot Et_2O$ and subsequent addition of an aqueous solution of $NaBF_4$ to the reaction mixture results in non-symmetrical triaryltelluronium salts **4** (Ar^1 = Ph, Ar^2 = 4-$MeOC_6H_4$) in a nearly quantitative yield.[18] Hex-1-enyl(diphenyl)telluronium tetrafluoroborate **14** [Ar = Ph, R = (*E*)-hex-1-enyl] was prepared using a similar approach.[18]

$$Ph_2TeF_2 \xrightarrow[-BF(OH)_2]{1)\ RB(OH)_2,\ BF_3\cdot OEt_2,\ CH_2Cl_2,\ 20\ ^\circ C;\ 2)\ NaBF_4,\ H_2O}$$

R = 4-$MeOC_6H_4$ → $Ph_2(4\text{-}MeOC_6H_4)Te^+\ BF_4^-$ (**4**) (100%)

R = (*E*)-$Bu^nCH{=}CH$ → Bu^n, H, H, Te^+Ph_2, BF_4^- (**14**) (97%)

Alkenyl(diphenyl)telluronium salts **14** [Ar = Ph: R = $Me_2C{=}CH$, $(CH_2)_5C{=}CH$] were also synthesised by the reaction of β,β-dialkylvinyl(phenyl)iodonium tetrafluoroborates with diphenyl telluride in the presence of diisopropylethylamine at room temperature.[19] This reaction proceeds through intermediate alkylidene carbenes.

$$\underset{\mathbf{14}}{\begin{matrix}R\\R\end{matrix}\!\!>\!\!\!\!\!\!\begin{matrix}BF_4^-\\I^+Ph\end{matrix}} \xrightarrow[20\ ^\circ C]{CH_2Cl_2,\ Pr^i_2NEt} \left[\begin{matrix}R\\R\end{matrix}\!\!>\!\!=\!\!:\right] \xrightarrow{Ph_2Te} \underset{\mathbf{14}}{\begin{matrix}R\\R\end{matrix}\!\!>\!\!\!\!\!\!\begin{matrix}BF_4^-\\Te^+Ph_2\end{matrix}}$$

R = Me (68%); R–R = $(CH_2)_5$ (89%).

The reaction of alkynyl(phenyl)iodonium tetrafluoroborates with diphenyl telluride was accompanied by transfer of the alkynyl group to the tellurium atom.[20] This reaction occurred under mild conditions (mixing of the reactants in CH_2Cl_2 at room temperature) and yielded alkynyldiphenyltelluronium tetrafluoroborates **15**.

$$Ph_2Te + RC{\equiv}CI^+Ph\ \ BF_4^- \longrightarrow \underset{\mathbf{15}\ (85\%-100\%)}{RC{\equiv}CTe^+Ph_2\ \ BF_4^-}$$

R = H, Me, Pr^i, Bu^t, n-C_8H_{17}, Me_3Si, Ph.

Reactions of diorganyl tellurides (including those containing aromatic substituents) with alkyl halides represent the most general method for the synthesis of trialkyl-, dialkylaryl- and alkyldiaryltelluronium salts.

$$R^1R^2Te + AlkHal \longrightarrow R^1R^2AlkTe^+Hal^-$$

R^1, R^2 = Alk, Ar.

In the case of dialkyl tellurides, exothermic reactions occurred even upon mechanical mixing of the reactants.[2,9,10,21–48] Alkyl aryl tellurides were found to be less reactive.[9,10,49–57] Reactions of diaryl tellurides with alkyl halides usually required long-term refluxing of the reaction mixtures.[9,10,58–60] It is noteworthy that reactions of diphenyl sulfide [61] and diphenyl selenide,[62] which are

less nucleophilic than diaryl tellurides, with alkyl halides yielded onium salts only in the presence of Ag(I) salts.

Divinyl telluride,[63,64] ethynyl phenyl, *tert*-butyl ethynyl, ethynyl vinyl, ethynyl propylthio and hexa-1,3-diynyl methyl tellurides[10] as well as di(methyltellurio)acetylene[65] also yielded telluronium salts upon reactions with alkyl iodides.

Dimethyl sulfate, together with organic bromides and iodides of various structures, *viz*., alkyl halides, allyl bromides, propargyl bromides, benzyl halides, α-bromo ketones, α-bromocarboxylic acids, esters and *N*-substituted amides, bromoacetonitrile, alkyl-mono- and dibromomalonates and 1,2-dibromoethane, are used as alkylating reagents. Among chloro derivatives, only chloroacetonitrile gives telluronium salts in reactions with dialkyl tellurides.[27,29,36]

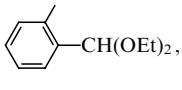
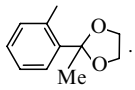
Because of their very unpleasant odour and easy oxidation by atmospheric oxygen, dialkyl tellurides are sometimes prepared *in situ*. Thus the reduction of readily available dialkyltellurium diiodides with sodium sulfite and subsequent reaction with alkyl iodides were used in the synthesis of triorganyltelluronium iodides.[9,10]

$$R^1_2TeI_2 \xrightarrow{H_2O,\ Na_2SO_3,\ Na_2CO_3} [R^1_2Te] \xrightarrow{R^2I} R^1_2R^2Te^+I^- \quad (41\%-62\%)$$

$R^1 = R^2 = Me, Pr^n$; $R^1 = Bu^n$, $R^2 = Me$; $R^1 = Me$, $R^2 = Ph$.

An alternative approach to the synthesis of these compounds is based on the treatment of lithium tellurolates with an excess of an alkylating reagent (methyl iodide) without preliminary isolation of the intermediate dialkyl(alkylaryl) tellurides.[9,10,26]

$$RTeLi + MeI \xrightarrow[-LiI]{} [RTeMe] \xrightarrow{MeI} RMe_2Te^+I^-$$

R = Me, , .

Strong alkylating reagents, such as methyl fluorosulfonate and alkyl trifluoromethanesulfonate,[66,67] easily form dimethyl(organyl)telluronium salts **16** and **17** from dimethyl telluride in Freon solutions in the cold.

$$Me_2Te + ROSO_2X \xrightarrow[Freon]{0-20\ ^\circ C} Me_2RTe^+OSO_2X^-$$

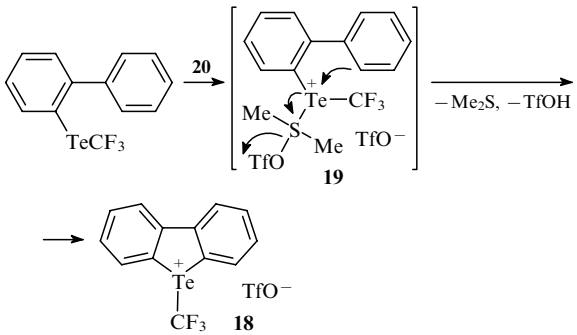
16, **17**

X = F, R = Me (**16**); X = CF_3, R = Me, Et (**17**).

5-Trifluoromethyldibenzotellurophenonium trifluoromethane sulfonate (**18**) was prepared by the reaction of trifluoromethanesulfonic anhydride (Tf_2O) with biphenyl-2-yl trifluoromethyl telluride in DMSO.[68,69] This reaction presumably occurs *via* intermediate **19** resulting from addition of sulfonium salt **20** to the tellurium atom.

$$Me_2SO + Tf_2O \longrightarrow MeS^+(OTf)Me\ TfO^-$$

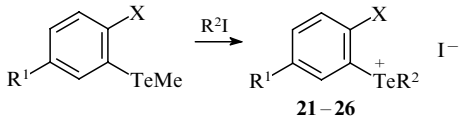
20



19

18

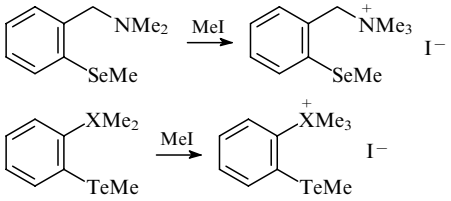
Interesting results suggestive of high nucleophilicity of the tellurium atom in alkyl aryl tellurides were obtained while studying the alkylation, by methyl iodide[50,59,70] or aryl iodides (PhI, *p*-$MeOC_6H_4I$ or *p*-$EtOC_6H_4I$),[59] of aromatic compounds containing various nucleophilic substituents, *viz*., dimethylaminomethyl-,[50] dimethylamino-,[59,70] 2-(4,4-dimethyloxazolino)-[50] or methylthio(seleno) groups[70] in the *ortho*-position relative to organyltellurium groups. These reactions yield telluronium salts **21**–**26**.



21–**26**

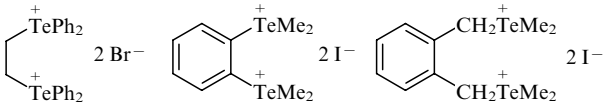
$R^1 = H$, $R^2 = Me$: X = CH_2NMe_2 (**21**), NMe_2 (**22**), SMe (**23**), SeMe (**24**), 4,4-dimethyl-4,5-dihydrooxazol-2-yl (**25**); X = NMe_2, $R^1 = Me$, R^2 = 4-YC_6H_4 [Y = H (**26a**), OMe (**26b**), OEt (**26c**)].

At the same time, dimethyl(2-methylselenobenzyl)amine is methylated at the nitrogen atom;[50] dimethyl(2-methyltellurophenyl)phosphine, -arsine and -stibine react with methyl iodide to give phosphonium, arsonium and stibonium salts, respectively.[70]



X = P, As, Sb.

Bis(telluronium) salts were synthesised by the reaction of 1,2-dibromoethane with diphenyl telluride (product **27**)[9,10] or by alkylation of compounds containing two telluromethyl groups with methyl iodide [salts **28a** (see Ref.70) and **28b** (see Ref. 57)].



27 **28a** **28b**

It is of note that reactions of tellurides containing three tellurium atoms with MeI yield tris(telluronium) salts **29**.[71]

$$Te(CH_2CH_2CH_2TeR)_2 + MeI \xrightarrow[1\ h,\ 20\ ^\circ C]{Me_2CO} MeTe^+(CH_2CH_2CH_2Te^+(Me)R)_2\ \ 3I^-$$

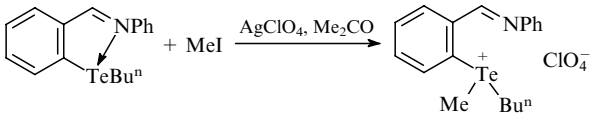
29

R = Me, Ph.

Tellurides containing electron-withdrawing perfluoroalkyl groups at the tellurium atom are alkylated only in the presence of silver tetrafluoroborate.[10]

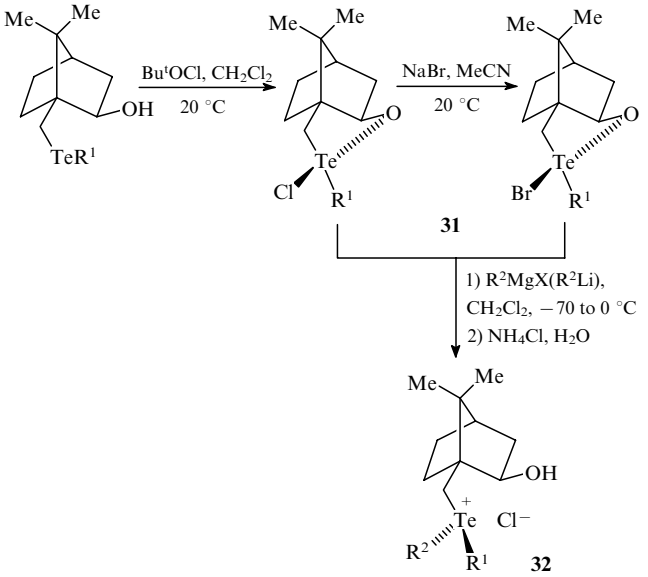
$$n\text{-}C_3F_7TePh + MeI \xrightarrow[-AgI]{AgBF_4,\ CH_2Cl_2} n\text{-}C_3F_7MePhTe^+BF_4^-$$

Telluronium salt **30** was prepared from *N*-(2-butyltellurobenzylidene)aniline containing the intramolecular coordination bond N → Te in the presence of silver perchlorate.[72,73]



30

Scheme 1

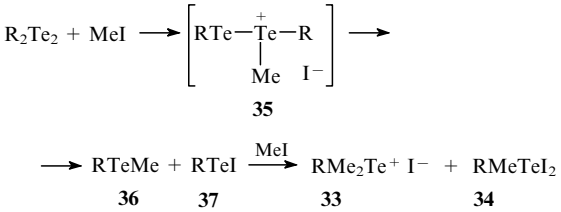


X = Cl, Br;
R^1 = Me, Et, Bu^n, n-C_6H_{13}, Ph; R^2 = Me, Et, Bu^n, Bn, $CH_2CH=CH_2$ (All).

A novel approach to the synthesis of trialkyl- and dialkylaryltelluronium salts containing a (1*S*)-2-*exo*-10-bornyl substituent has been developed (Scheme 1).[74–76] Reactions of halooxatelluranes **31** with organomagnesium or -lithium compounds and subsequent treatment of the reaction mixtures with aqueous NH_4Cl afforded optically pure triorganyltelluronium chlorides **32** in 60%–97% yields (for an alternative method for the preparation of chiral telluronium salts, see Section III). The structures of diastereomeric salts **32** (R^1 = Me, R^2 = Et; R^1 = Et, R^2 = Me) were confirmed by X-ray diffraction analysis.[75]

The pyramidal inversion barrier of tricoordinated tellurium atoms in these compounds exceeds 30 kcal mol^{-1}. Thus 5-h refluxing of salts **32** in chloroform or methanol did not result in their epimerisation.[75]

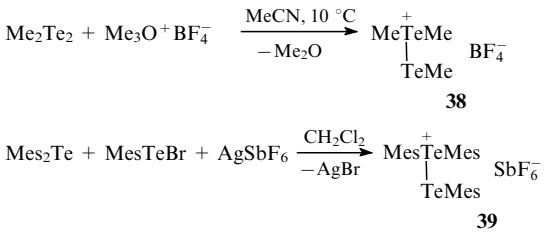
Organyldimethyltelluronium iodides **33** were formed, along with organylmethyltellurium diiodides **34** (molar ratio 1 : 1), upon treatment of diorganyl ditellurides with an excess of methyl iodide.[9, 10, 77] The methylation of ditelluride, which obviously represents the first step in these reactions, gives intermediate organyltelluro(methyl)organyltelluronium iodides **35**. Spontaneous decomposition of these salts results in methylorganyl tellurides **36** and organyltellurenyl iodides **37**; their subsequent reactions with methyl iodide yield compounds **33** and **34**, respectively.



R = Me, Et, Pr^i, Bu^t; 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$.

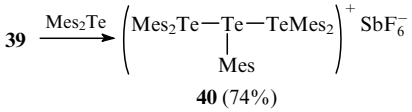
The reaction of diorganyl ditellurides with phenylacetylene in the presence of methyl iodide also seems to occur *via* salts of the type **35** and affords alkyl phenylethynyl tellurides.[77, 78]

Tellurotelluronium salts with BF_4^- and SbF_5^- anions were isolated in the individual state, *e.g.,* compound **38**[79] and mesityl derivative **39**.[80, 81]

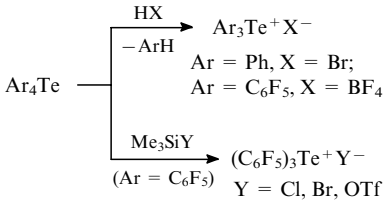


Mes = 2,4,6-$Me_3C_6H_2$.

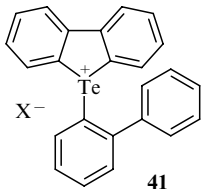
Heating of salt **39** with a small excess of dimesityl telluride yielded telluronium salt **40**, which contained a chain of three tellurium atoms.[80, 81]



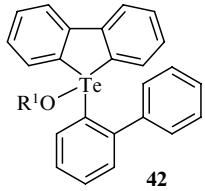
The triaryltelluronium salts $Ph_3Te^+Br^-$ and $(C_6F_5)_3Te^+X^-$ (X = Cl, Br, OTf) were prepared in high yields by the reaction of tetraphenyltellurane Ph_4Te (see Refs 9 and 10) and tetrakis(pentafluorophenyl)tellurane $(C_6F_5)_4Te$ (Ref. 82) with mineral acids[9, 10, 82] or trimethylsilyl derivatives.[82]



Reactions of a cyclic spirotetraaryltellurane, *viz.*, bis(2,2′-biphenylene)tellurane, with mineral[9, 10] and organic acids[83] and phenols[84, 85] were accompanied by the cleavage of one of the Te–C bonds. The corresponding reaction products (compounds **41** and **42**) were formed in 47%–95% yields.



41

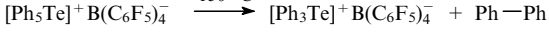


42

X = Cl, I, BPh_4;
R^1 = MeCO, PhCO, 4-$R^2C_6H_4$ (R^2 = H, Me, Cl, MeO_2C, Ac, NO_2), 2,4,6-$Cl_3C_6H_2$.

The preparative significance of these reactions is relatively low. Tetraaryltelluranes and bis(2,2′-biphenylene)tellurane are usually prepared by reactions of aryllithium derivatives with the corresponding tellurium dichlorides, which, as was shown above, can directly be converted into telluronium halides. Exchange reactions of the latter (see Section III) afford various triaryltelluronium salts including the derivatives of the type **41** and **42**.

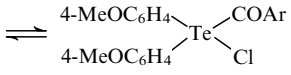
The synthesis of triphenyltelluronium tetrakis(pentafluorophenyl)borate by thermal decomposition of a pentaphenyltelluronium-containing salt presents purely theoretical interest.[86]



Refluxing of equimolar amounts of bis(4-methoxyphenyl) telluride and 3,5-dinitrobenzoyl chloride in neutral solvents (CH_2Cl_2 or benzene) yielded a compound with a tentative structure of telluronium salt **43a**.[87]

$$(4\text{-MeOC}_6H_4)_2Te + ArCOCl \longrightarrow (4\text{-MeOC}_6H_4)_2Te^+COAr \; Cl^- \rightleftharpoons$$

43a



43b

Ar = 3,5-$(O_2N)_2C_6H_3$.

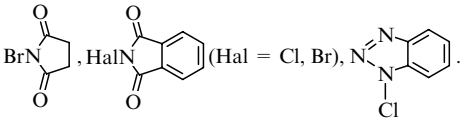
However, low melting point of this compound and low electric conductivity of its 10^{-3} M solution in acetonitrile are in favour of the covalent structure **43b** containing a tetracoordinated tellurium atom.

Triorganyltelluronium derivatives **44** containing two Te–C bonds and one Te–N bond are worthy of note. These salts are prepared by oxidation of diaryl tellurides by compounds that are sources of positively charged halogens (*e.g.*, *N*-halosuccinimides [88, 89]). Derivatives **44** are high-melting crystalline compounds poorly soluble in common organic solvents.

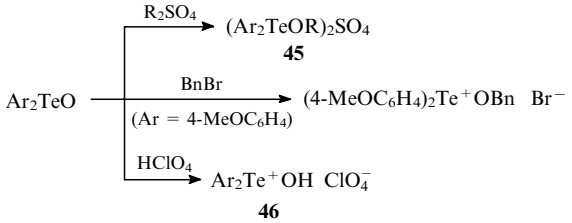
$$Ar^1TeAr^2 + R^1R^2NX \longrightarrow \underset{Ar^2}{\overset{Ar^1}{\overset{+}{Te}}}—NR^1R^2X^-$$

44

Ar^1, Ar^2 = Ph, 4-$MeOC_6H_4$; R^1R^2NX = PhCONHBr,



Diaryltellurium oxides manifest the highest basicity in the series of diarylchalcogen oxides Ar_2EO (E = S, Se, Te) and are therefore easily alkylated at the oxygen atom by dialkyl sulfates [60, 90] and benzyl bromide [91] resulting in diaryl(alkoxy)telluronium salts **45**. The reaction of diaryltellurium oxides with perchloric acid yields diaryl(hydroxy)telluronium perchlorates **46**.[60, 92]



45

46

Compound	R	Ar	Ref.
45	Me	4-DC_6H_4, 4-$Pr^iC_6H_4$	90
	Me	2,6-$(MeO)_2C_6H_3$	60
	Et	Ph, 4-DC_6H_4, 4-$Pr^iC_6H_4$	90
46		4-$MeOC_6H_4$	92
		2,6-$(MeO)_2C_6H_3$	60

III. Reactions of telluronium salts

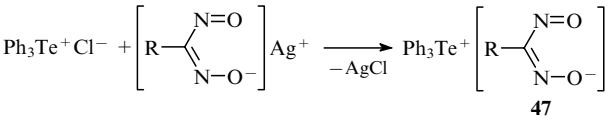
Anion-exchange reactions (see the monographs [9, 10] and references cited therein, as well as Refs 12, 25, 28, 93–106) are among the most important preparative methods for the synthesis of triorganyltelluronium salts. The direction of the exchange is determined by the relative solubilities of the original and final salts, which depend on the nature of the anion. By virtue of the large radius of the tellurium atom and its low electronegativity, the telluronium cation can be regarded as a mild acid. In accordance with the HSAB principle,[93] the salts containing hard anions (F^-, Cl^-, OH^-, NO_3^-, CrO_4^{2-}, $Cr_2O_7^{2-}$, BF_4^-, BPh_4^-, ClO_4^-, *etc.*) should possess better solubilities in comparison with the salts containing soft anions (Br^-, I^-, N_3^-, CN^-, SCN^-, *etc.*). In particular, the solubilities of telluronium halides $R_3Te^+Hal^-$ decrease in the order: F > Cl > Br > I; therefore, the exchange can be carried out in aqueous media under the action of alkali metal halides. Compounds with solubilities exceeding those of the starting compounds are prepared using the corresponding silver salts. In this case, the direction of the exchange is determined by the relative solubilities of silver halides. The exchange reactions were used in the synthesis of many telluronium salts containing various anions.

$$R^1_2R^2TeX + MY \underset{-MX}{\longrightarrow} R^1_2R^2Te^+Y^-$$

M is an alkali metal or silver.

Anion-exchange reactions were also used in the synthesis of telluronium salts containing doubly charged anions.

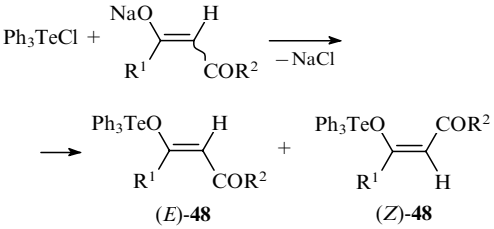
Reactions of triphenyltelluronium chloride with silver nitrosolates afforded the corresponding triphenyltelluronium nitrosolates **47**.[107]



47

R = Me (65%), Ph (25%).

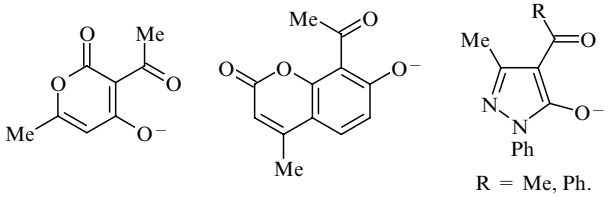
Reactions of aqueous triphenyltelluronium chloride with an excess of sodium β-diketonates resulted in triphenyltelluronium β-diketonates **48** (yields 52%–90%).[108] The ^1H NMR spectra suggest that these compounds exist as mixtures of *E*- and *Z*-isomers.



(*E*)-**48** (*Z*)-**48**

$R^1 = R^2$ = Me, Ph; R^1 = Me, R^2 = Ph; $R^1 = CF_3$: R^2 = Ph, 2-thienyl.

Similarly,[109] enolates of heterocyclic β-diketones



R = Me, Ph.

gave triphenyltelluronium derivatives.

The exchange reactions of triphenyltelluronium chloride with sodium alkoxides gave triphenyltelluronium alkoxides **49** in high yields.[110]

$$Ph_3TeCl + RONa \underset{-NaCl}{\overset{ROH}{\longrightarrow}} Ph_3TeOR$$

49

R = Me, Et, Pr^i.

Triphenyltelluronium organylchalcogenolates **50a–c** [X = S (**a**), Se (**b**), Te (**c**)] were synthesised from triphenyltelluronium chloride.[111–113]

$$Ph_3TeCl + RXNa \underset{-NaCl}{\overset{MeOH,\ EtOH,\ -60\ ^\circ C}{\longrightarrow}} Ph_3TeXR$$

50a–c

X = S: R = Et, Pr^i, Bu^t, Bn, Ph, 4-$MeOC_6H_4$, 4-ClC_6H_4, 2-Py, 4-Py;
X = Se, R = 4-MeC_6H_4; X = Te: R = 4-MeC_6H_4, 4-$MeOC_6H_4$.

However, the reactions of $Ph_3Te^+Cl^-$ with sodium aryltellurolates in THF yielded diphenyl and aryl phenyl tellurides as the final products.[113] Obviously, the latter were formed as a result of decomposition of intermediate compounds of the type **50c**.

$$Ph_3TeCl + ArTeNa \xrightarrow[-NaCl]{THF} [\mathbf{50c}] \longrightarrow Ph_2Te + PhTeAr$$

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

Treatment of triphenyltelluronium alkoxides **49** with carboxylic acids resulted in the corresponding carboxylates **51**.[97] Similar compounds were synthesised by reactions of triorganyltelluronium hydroxides with carboxylic acids[97] and of triorganyltelluronium halides with silver salts of organic acids.[58, 94, 97]

$$R^1_3TeOR^2 + R^3CO_2H \xrightarrow[-R^2OH]{} \underset{\mathbf{51}}{R^1_3TeOCOR^3}$$

R^1 = Ph, R^2 = Me; R^1 = Me, R^2 = H; R^3 = Me, $CHCl_2$, CCl_3, Ph.

$$R^1_2R^2TeHal + AgOCOR_3 \xrightarrow[-AgHal]{} \underset{\mathbf{51}}{R^1_2R^2TeOCOR^3}$$

R^1, R^2 = Me, Ph; R^3 = Me, Ph, 2-$MeOC_6H_4$, 3-$O_2NC_6H_4$.

Triphenyltelluronium xanthates **52** were prepared by the insertion of carbon disulfide into the Te–O bond of triphenyltelluronium alkoxides **49**.[110]

$$\underset{\mathbf{49}}{Ph_3TeOR} + CS_2 \xrightarrow{CH_2Cl_2,\ \Delta,\ 15\ min} \underset{\mathbf{52}\ (63\%-91\%)}{Ph_3TeSC(S)OR}$$

R = Me, Et, Pr^i.

However, the exchange reactions between triorganyltelluronium chlorides and the corresponding sodium (less frequently, ammonium) salts represent the most general method for the synthesis of xanthates **52**,[95, 110, 114–116] thioxanthates **53**,[95, 110] dithiocarbamates **54** (Refs 95, 114, 117–119) and dithiophosphates **55**.[112, 114, 120]

$$R^1_3TeCl + NaSC(S)XR^2 \xrightarrow[-NaCl]{} \underset{\mathbf{52,\ 53}}{R^1_3TeSC(S)XR^2}$$

X = O (**52**), S (**53**); R^1 = Me, Ph; R^2 = Me, Et, Pr^n, Pr^i, Bu^i, Bu^t, cyclo-C_6H_{11} (Cy).

$$R^1_3TeCl + NaSC(S)NR^2R^3 \xrightarrow[-NaCl]{} \underset{\mathbf{54}}{R^1_3TeSC(S)NR^2R^3}$$

R^1 = Me: R^2 = R^3 = Me, Et, Ph; R^1 = Ph: R^2 = R^3 = Me, Et, Pr^i, Ph, $(CH_2)_2OH$; R^1–R^2 = $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$.

$$R^1_3TeCl + NaSP(S)(OR^2)_2 \xrightarrow[-NaCl]{} \underset{\mathbf{55}}{R^1_3TeSP(S)(OR^2)_2}$$

R^1 = Me, Ph; R^2 = Me, Et, Pr^i, Ph.

Compounds **55** were also synthesised by the reaction of methoxytriorganyltelluranes with dialkyl dithiophosphates.[120]

$$R^1_3TeOMe + HSP(S)(OR^2)_2 \xrightarrow[-MeOH]{} \underset{\mathbf{55}}{R^1_3TeSP(S)(OR^2)_2}$$

R^1 = Me, Ph: R^2 = Me, Pr^i, Ph.

Dithiophosphinates **56** were prepared using a similar approach, *i.e.*, by the reaction of methoxytriorganyltelluranes with diorganyldithiophosphinic acid $HSP(S)R_2$ (Ref. 120) or the corresponding chlorides with sodium (ammonium) dithiophosphinates $MSP(S)R_2$ (Refs 120 and 121) (M = Na, NH_4).

$$R^1_3TeX + MSP(S)R^2_2 \longrightarrow \underset{\mathbf{56}}{R^1_3TeSP(S)R^2_2}$$

X = OMe, Cl; M = H, Na, NH_4; R^1 = Me, Ph; R^2 = Me, Pr^i, Ph.

The phosphorus analogues of triorganyltelluronium dithiocarbamates **57** were formed in the reaction of triphenyltelluronium chloride with dialkylphosphines and carbon disulfide in the presence of triethylamine.[122] Treatment of compounds **57** with equimolar amounts of sulfur was accompanied by the insertion of the sulfur atom into the Te–S bond resulting in derivatives **58**. At the same time, the reaction with excess sulfur in benzene at room temperature gave triphenyltelluronium diphenyldithiophosphinate **56**.[122]

$$Ph_3TeCl + R_2PH + CS_2 \xrightarrow[20\ ^\circ C]{MeOH,\ Et_3N} \underset{\mathbf{57}}{Ph_3TeSC(S)PR_2} \longrightarrow$$

S_8 (1 equiv.) → $Ph_3TeS{-}SC(S)PR_2$ **58** (77%–90%)

S_8 (excess), (R = Ph) → $Ph_3TeSP(S)Ph_2$ **56** (40%)

R = Pr^i, Bn, Ph.

Triphenyltelluronium dichalcogenoimidodiphosphinates **59** were prepared by the exchange reaction of triphenyltelluronium chloride with tetraorganyl dichalcogenoimidodiphosphinates.[121, 123]

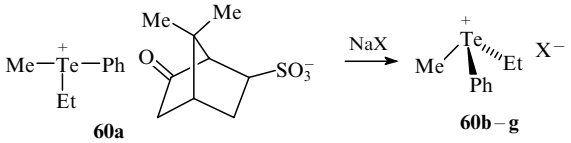
$$Ph_3TeCl + M[N(XPR^1_2)(YPR^2_2)] \xrightarrow[-MCl]{} \underset{\mathbf{59}}{Ph_3Te[N(XPR^1_2)(YPR^2_2)]}$$

M = Na, K; X = O, S; R^1, R^2 = Me, Ph.

The salts **59** containing diphenylphosphine residues (R^1 = R^2 = Ph) were isolated from the reaction mixture and characterised by X-ray diffraction analysis. The existence of other salts in solution was established only by ^1H, ^{13}C and ^{31}P NMR spectroscopy.[123]

The exchange reaction of methyl(phenyl)(*p*-tolyl) telluronium iodide (*p*-TolPhMeTe$^+$I$^-$) with silver D-α-bromocamphorsulfonate (D-BCS) and subsequent crystallisation resulted in compound [*p*-TolPhMeTe]$^+$[D-BCS]$^-$ with molecular rotation $[M]^{18}_{5461}$ = +262° in ethyl acetate (*cf.* Lowry, cited in Refs 9 and 10). This salt undergoes fast mutarotation in various solvents.

Enantiometrically pure telluronium salts **60a** containing the camphorsulfonate anion were prepared by fractional crystallisation of a diastereomeric mixture.[54–56, 124] The absolute configurations of both isomers were established by X-ray diffraction analysis. Anion-exchange reactions of (*R*)-camphorsulfonate were used for the synthesis of the enantiomerically pure (*R*)-telluronium salts **60b–g** with various anions.[54–56, 124]



60a **60b–g**

X = ClO_4 (**b**), BF_4 (**c**), BPh_4 (**d**), *p*-$ClC_6H_4SO_3$ (**e**), 2,4,6-$(O_2N)_3C_6H_2SO_3$ (**f**), bornane-10-sulfonate (**g**).

In contrast to the methyl(phenyl)(*p*-tolyl)telluronium salt with the D-BCS anion described above, perchlorate **60b** is resistant against pyramidal inversion; no racemisation occurred even upon refluxing in methanol for 3 days.

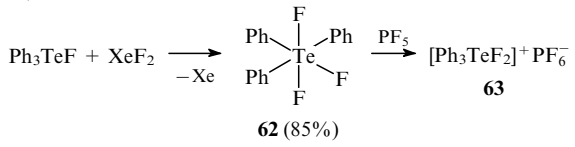
Some reactions of telluronium salts consist of conversions of the anionic fragments of the molecules. Thus reactions of triphenyltelluronium halides with halogens yield salts **61**, which contain the trihalide anion.[10]

$$Ph_3TeX + Y_2 \xrightarrow{CHCl_3} \underset{\mathbf{61}}{Ph_3Te^+[XY_2]^-}$$

X = Cl: Y = Br, I; X,Y = Br, I.

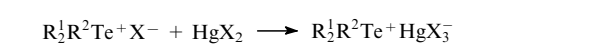
When xenon difluoride was used instead of halogens, it was the tellurium atom that underwent the attack. For example, the

reaction of XeF_2 with triphenyltelluronium fluoride yielded *mer*-Ph_3TeF_3 **62**, a hexacoordinate tellurium derivative; this reacted with PF_5 to give the pentacoordinate tellurium derivative **63**.[125,126]



62 (85%)

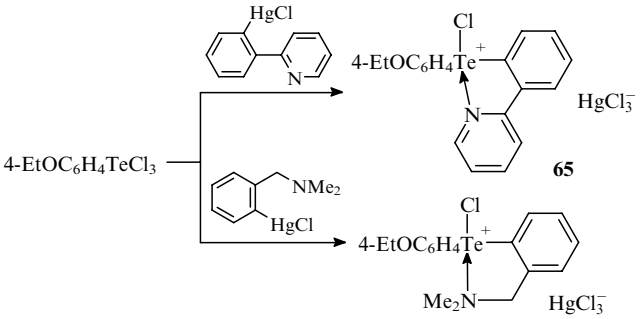
Telluronium salts form 1 : 1 adducts with mercuric halides[9,10,127] to which the structures of triorganyltelluronium trihalomercurates **64** were ascribed based on the data from elemental analysis and IR spectroscopy.[127] However, according to X-ray structural data, the reaction product of Ph_3TeCl with $HgCl_2$ has a dimeric structure, *viz*., $(Ph_3Te^+)_2[Hg_2Cl_6^{2-}]$.[128]



64

X = Cl, Br, I; R^1 = Ar, R^2 = Alk, Ar.

A new type of telluronium salts the tellurium atom in which is covalently bound to two organic radicals and one chlorine atom has been described.[129–131] Reactions of aryltellurium trichlorides with arylmercury chlorides usually yield diaryltellurium dichlorides, Ar_2TeCl_2.[132] However, the reactions of *p*-ethoxyphenyltellurium trichloride with 2-[(2-pyridyl)phenyl]mercury chloride[129,130] and 2-dimethylaminobenzylmercury chloride[131] unexpectedly gave telluronium salts **65** and **66**.

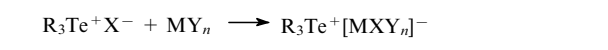


65

66

The molecules of salts **65** and **66** contain relatively short intramolecular coordination bonds N—Te. The length of this bond in salt **65** is equal to 2.31 Å,[130] whereas the sum of the van der Waals radii of tellurium and nitrogen is 3.65 Å.[133]

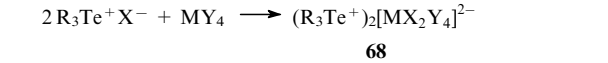
Triorganyltelluronium halides form 1 : 1 adducts **67** with boron, aluminium, tin, arsenic and antimony halides and organyltellurium trihalides, which have the structure of telluronium salts containing complex anions.[9,10,24,96]



67

X, Y = Hal; R = Me, Et, Ph; M = B, Al, As, Sb, Te, Sn; *n* = 3, 4.

As for the reactions of triorganyltelluronium halides with Lewis acids, for example $SnBr_4$, $SnCl_4$, $TeBr_4$, $TeCl_4$ and $TiBr_4$ (molar ratio 2 : 1), they yield adducts **68**.[24,96]



68

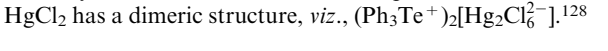
R = Et, Ph; X, Y = Cl, Br; M = Sn, Te, Ti.

Complexes of telluronium salts with organic donors are poorly studied. It is known[10] that the triphenyltelluronium halides $Ph_3Te^+X^-$ (X = Cl, Br) yield 1 : 1 adducts with dihexyl sulfoxide. Similar products were formed upon reaction of $Ph_3Te^+Cl^-$ with 1-R-4,4,6-trimethyl-3,4-dihydro-1*H*-pyrimidine-2-thiones (R = Ph, 4-$MeOC_6H_4$, 4-$O_2NC_6H_4$, Bu^n, NH_2). It is noteworthy that it is the thionic form of the sulfur atom that is involved in the complexation.[134]

Reaction of trimethyltelluronium iodide with phosphines occurs as demethylation of the original salt and results in high yield of dimethyl telluride.[26]

R = Bu^n, Ph.

The dealkylation of telluronium salts is usually performed by heating in a solid state or in high-boiling solvents.[9,10,49,135]



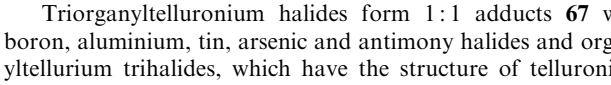
X = Br, I; R^1 = Alk; R^2, R^3 = Alk, Ar.

In some cases, heating of salts was carried out in the presence of alkyl halide acceptors, *e.g*., pyridine or dimethylaniline,[9,10] resulting in *N*-alkylpyridinium and alkyldimethylphenylammonium salts, respectively. The thermal decomposition of telluronium salts has not been studied systematically so far. It was only noted[10] that thermal stabilities of trimethyltelluronium salts depend on the anion and increase in the series $F^- < Cl^- < SO_4^{2-} < Br^- < I^-$; however, there are still no data on the effects of the leaving group, the anion and the solvent on the direction of dealkylation.

The thermal decomposition of triorganyltelluronium ethers[110] and esters,[97] pseudohalides[10] and xanthates[110] as well as dithiocarbamates,[117] -phosphates and -phosphinates[120] proceeds according to the same scheme as the decomposition of triorganyltelluronium halides. It is noteworthy that heating of $Ph_2MeTeNCS$ yielded Ph_2Te and MeSCN.[10]

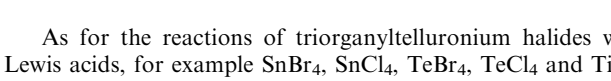
R^1 = Me: X = $OCOR^2$ (R^2 = Me, $CHCl_2$, CCl_3, Ph), $SP(S)R_2^2$ (R^2 = Me, Pr^i, Ph, OMe, OEt, OPr^i, OPh);
R^1 = Ph: X = OR^2 (R^2 = Me, Et, Pr^i), $OCOR^2$ (R^2 = Me, $CHCl_2$, CCl_3, Ph), CN, NCO, NCS, NCSe, $SC(S)NR_2^2$ (R^2 = Me, Pr^i, Ph), $SP(S)R_2^2$ (R^2 = Me, Pr^i, Ph, OPh).

The decomposition of triphenyltelluronium thioxanthates upon heating is somewhat different.[110]



R = Et, Pr^i.

Heating of tris(2,6-dimethoxyphenyl)telluronium chloride in 0.1 M HCl at 80 °C gave bis(2,6-dimethoxyphenyl)tellurium dichloride in 60% yield.[15] Presumably, the thermolysis proceeded as follows:



No such conversion is reported for other telluronium salts.

In contrast to aryltellurium trihalides and diaryltellurium dihalides, which are converted into diaryl ditellurides and diaryl tellurides, respectively, under the action of sodium sulfide, heating of telluronium salts with Na_2S affords mixtures of tellurides and aromatic derivatives. The compositions of the latter depend on the structures of the original salts.[9,10]

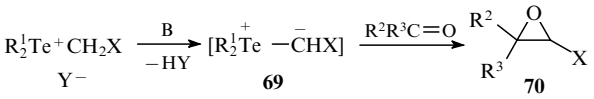
Other reactions of telluronium salts employed for the preparation of various classes of organic compounds are considered in the next Section.

IV. The use of telluronium salts in organic synthesis

Telluronium salts are widely used as precursors of non-stabilised and monostabilised telluronium ylides. The latter are prepared by treatment of the original salts with basic reagents and are introduced *in situ* into reactions with carbonyl compounds. Depending on the structure of the original salt, *i.e.,* the nature of the ylide generated, and the type of the carbonyl derivative, various classes of organic compounds are formed.[7,8]

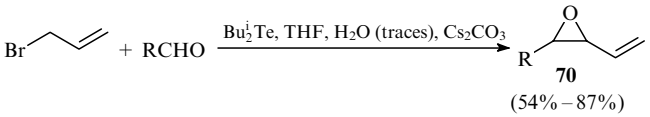
Diphenyltelluronium methylide **69** (R^1 = Ph, X = H) prepared from methyldiphenyltelluronium tetraphenylborate under the action of lithium 2,2,6,6-tetramethylpiperidide (LiTMP) reacted with carbonyl compounds to give epoxides **70** (R^1 = Ph, X = H) in 55% – 74% yields.[100] A similar reaction was used [23,34] in the synthesis of α,β-unsaturated epoxides **70** (X = CH = CH_2). Dialkyltelluronium allylides **69** (X = CH = CH_2) were generated by treatment of triorganyltelluronium bromides with potassium *tert*-butoxide [23] or KOH.[34] The best results were achieved in reactions of the ylide prepared from allyl(diisobutyl)telluronium bromide with carbonyl compounds. The yields of vinyl epoxides did not depend on the nature of the dehydrobrominating reagent and amounted to 58% – 98% for aromatic aldehydes; the yields are lower for aliphatic derivatives. Compounds **70** (X = CH = CH_2) are prepared as mixtures of *cis*- and *trans*-isomers, the former being slightly predominant.

Trimethylsilylvinyl (**70**, X = CH = $CHSiMe_3$, yields 83% – 89% [40]) and trimethylsilylethynyl epoxides (**70**, X = C≡$CSiMe_3$, 80% – 96% [38,39]) were obtained in reactions of ylides **69** (R^1 = Bu^i: X = CH = $CHSiMe_3$, C≡$CSiMe_3$) with aldehydes and ketones. Ylides **69** were prepared by dehydrobromination of the corresponding telluronium salts under the action of LiTMP and used *in situ*. Trimethylsilylvinyl(or ethynyl) epoxides **70** are predominantly represented by *cis*-isomers.



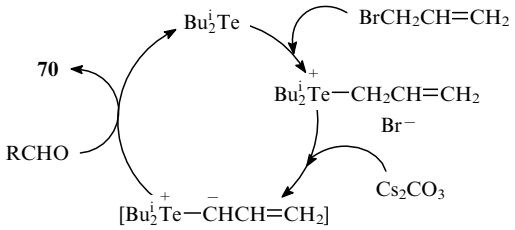
B (base) = LiTMP, Bu^tOK, KOH, *etc.*
Y = BPh_4, Br; X = H, CH = CH_2, CH = $CHSiMe_3$, C≡$CSiMe_3$;
R^1 = Bu^t, Ph; R^2 = H, Ph; R^3 = Me, n-C_5H_{11}, n-C_6H_{13}, n-C_9H_{19}, Cy, $R^4_nC_6H_{5-n}$ [R^4_n = H, 4-F, 2-Cl, 3-Cl, 4-Cl, 4-Br, 4-O_2N, 2-Me, 4-Me, 2,4,6-Me_3, 4-Ph, 2-MeO, 4-MeO, 3,4-$(MeO)_2$, 3,4-(OCH_2O), 6-Br-3,4-(OCH_2O)], 2-Py, 3-Py, 1-naphthyl, 2-naphthyl;
R^2 – R^3 = $(CH_2)_5$.

Vinyl derivatives **70** (X = CH = CH_2) were synthesised by catalytic epoxidation without preliminary preparation of telluronium salts.[33] Allyl bromides reacted with aldehydes in the presence of catalytic amounts of diisobutyl telluride (20 mol.%) at 50 °C.

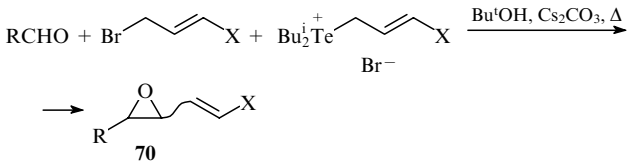


R = Cy, 4-XC_6H_4 (X = H, F, Cl, Br, NO_2, Ph), 2-naphthyl, 2-Py.

The sequence of steps resulting in epoxides **70** can be presented as a catalytic cycle. The reaction of telluride with allyl bromide yields a telluronium salt; treatment of the latter with Cs_2CO_3 leads to the generation of diisobutyl allylide, which reacts with the aldehyde to give the epoxide and Bu^i_2Te.

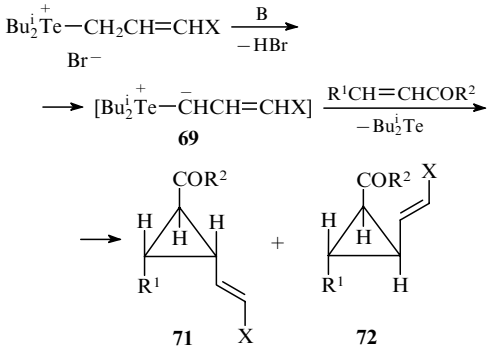


A more efficient (in comparison with diisobutyl telluride) catalyst has been proposed.[136] Vinyl epoxides **70** (X = CH = CH_2) were prepared by refluxing a mixture of an aldehyde, allyl bromide and catalytic amounts of a telluronium salt in the presence of solid Cs_2CO_3. Allyl(diisobutyl)telluronium bromide proved to be the catalyst of choice; the amount required was 10 times smaller (2 mol.%) than that of diisobutyl telluride (20 mol.%). However, this reaction is not stereoselective (the *cis*,*trans*-isomer ratio is ~1 : 1).



X = H: R = 4-ClC_6H_4; X = $SiMe_3$: R = n-C_9H_{19}, Cy, YC_6H_4 (Y = H, 4-Cl, 2-Cl, 4-O_2N, 4-Me), 2-naphthyl.

Telluronium ylides of the type **69** proved to be convenient synthons for the preparation of substituted cyclopropanes. Trimethylsilylvinylcyclopropanes **71** and **72** (X = $SiMe_3$, R^1 = OMe, OEt) were synthesised for the first time in > 90% yields by the reaction of diisobutyltelluronium allylide **69** (X = $SiMe_3$), generated by deprotonation of the corresponding telluronium salt under the action of LiTMP, with α,β-unsaturated esters.[41] The reactions of ylides **69** (X = $SiMe_3$) with β-aryl-substituted esters are characterised by high stereoselectivities and gave exclusively alkyl *trans*-2-trimethylsilylvinyl-*trans*-3-substituted cyclopropane carboxylates **71**. Reactions with methyl *trans*-but-2-enoate and methyl methacrylate are less stereoselective: mixtures of the isomers **71** and **72** were formed in 1.5 : 1 and 1 : 1 ratios, respectively.[41] Later, this reaction was extended to other ylides of the type **69** (X = H,[137,138] Me,[137] $SiMe_3$ [137–139]) and α,β-unsaturated esters [137–139] and amides.[137,138] Alkali metal bis(trimethylsilylamides), $MN(SiMe_3)_2$ (M = Na, K),[137] lithium diisopropylamide (LDA) [138] and LiTMP [139] were used as the bases.



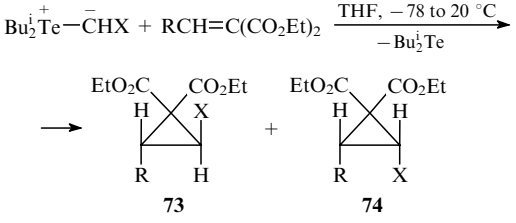
B = $MN(SiMe_3)_2$ (M = Na, K), LDA, LiTMP;
X = H, Me, $SiMe_3$;
R^1 = Me, 2-furyl, $R^3C_6H_4$ (R^3 = H, 4-F, 4-Me, 2-MeO, 4-MeO);
R^2 = OMe, OEt, $N(CH_2)_4$, $N(CH_2)_5$.

All the reactions give high yields; the stereochemistry of the reaction product is determined primarily by the nature of the base. *trans*,*trans*-Isomers **71** are formed exclusively in the presence of lithium cations. In other cases, the stereoselectivity of the reaction changes towards the predominant formation of *trans*,*cis*-isomers **72**. By varying the nature of the base, the ratio of the isomers **71** : **72** can be changed from 1 : 99 to 99 : 1. Thus the **71** : **72** isomer ratio in the reaction of diisobutyltelluronium salt (X = $SiMe_3$) with methyl cinnamate under the action of $KN(SiMe_3)_2$ was < 1 : 99, whereas that in the presence of the $LiBr-NaN(SiMe_3)_2$ system as a base was > 99 : 1.[137] According to the reported data,[137, 138] the effect of the lithium cation is determined by its chelation with the carbonyl oxygen atom and the ylide carbanion and formation of a stable six-membered ring. The addition to the reaction mixture of hexamethylphosphoramide (HMPA) able to coordinate the lithium cation and to inhibit the formation of lithium chelates resulted in the formation of *trans*,*cis*-isomers **72** in good yields and with high selectivity.[138]

The reaction of ylide **69** (X = $SiMe_3$) with diethyl fumarate and dimethyl maleate also resulted in isomers **71** ($R^1 = CO_2Et$, $R^2 = Et$; $R^1 = CO_2Me$, $R^2 = Me$).[41]

Ylide **69** (X = $SiMe_3$) generated from the corresponding telluronium salt under the action of LiTMP [139] was introduced into the reaction with (−)-8-phenylmenthyl esters of α,β-unsaturated acids. This resulted in the formation of *trans*-2-trimethylsilylvinyl-*trans*-3-substituted cyclopropyl carboxylates in high yields and with high diastereoselectivities.

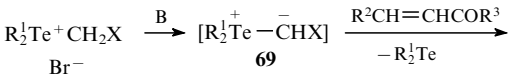
Diisobutyltelluronium ylides **69** generated by deprotonation of telluronium salts with potassium (or sodium) bis(trimethylsilylamide) reacted smoothly with diethylalkylidene- and arylmethylidenemalonates to give vinylcyclopropane-1,1-dicarboxylates **73** and **74** in high yields (81% – 93%) and with high *trans*-selectivities (the **73** : **74** ratio was in the range from 71 : 29 to 98 : 2).[140] The addition of lithium bromide to the reaction mixture increased slightly the percentage of *trans*-isomer **73**.

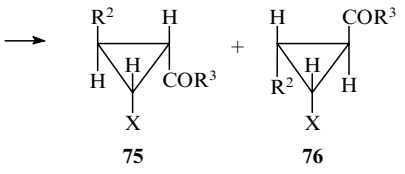


X = CH = $CHSiMe_3$: R = n-C_6H_{13}, CH = CHPH, Ph, 4-MeC_6H_4; R = Ph: X = CH = CH_2, CH = CHMe, Ph.

Cyclopropanes of yet another type are formed in the reaction of telluronium ylides **69** with α,β-unsaturated ketones. The ylides generated by treatment of the corresponding telluronium salts with solid NaOH in THF,[42] $KN(SiMe_3)_2$ (for X = Ar) [141] or Cs_2CO_3 in 1,2-dimethoxyethane (DME) containing traces of water,[45] $KN(SiMe_3)_2$,[141] Bu^tOK [141] (for X = CH = CHR where R = $SiMe_3$, H, Me, Ph) gave rise to cyclopropyl ketones **75** and **76** (yields 52% – 95%). This reaction is highly stereoselective: ketones **75** are the main products (> 90% in the mixture) where the keto group and the X fragment lie on the same side relative to the plane of the cyclopropane ring.

In contrast to α,β-unsaturated esters and amides, the stereochemistry of reactions of telluronium ylides with α,β-unsaturated ketones does not depend on the presence of lithium cation. Moreover, the presence of lithium salts in reaction mixtures decreases the yields of cyclopropanes and favours the formation of epoxides.[45, 141] The use of α,β-unsaturated aldehydes in such reactions results in complex mixtures of reaction products.[45]



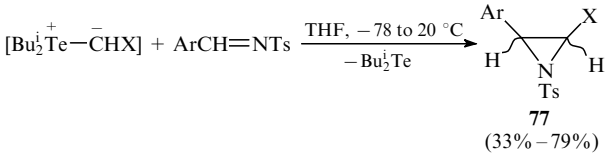


X = CH = CH_2, CH = $CHSiMe_3$, CH = CHMe, CH = CHPh, Ph, 4-ClC_6H_4; R^1 = Bu^n, Bu^i; $R^2 = R^4C_6H_4$ (R^4 = H, 4-Cl, 4-Br, 4-Me, 4-Me_2N, 3-O_2N, 4-O_2N); R^3 = Bu^t, Ph, CH = CHPh.

It is of note that triphenylarsonium allylides react with α,β-unsaturated ketones to give high yields of cyclopropyl ketones with an opposite configuration of substituents in comparison with the products generated from telluronium ylides.[141]

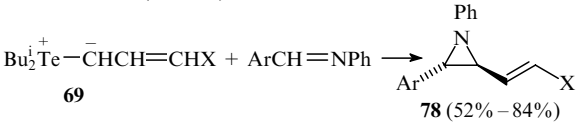
A one-pot synthesis of cyclopropanes without preliminary generation of telluronium ylides has been developed for reactions with chalcones.[45] This approach is based on the use of a biphasic system Cs_2CO_3 – THF (with traces of water) in the presence of catalytic amounts of diisobutyl telluride (20 mol.%).

Similar to sulfonium ylides, telluronium ylides react with *N*-sulfonylimines to give aziridines **77**.[142, 143] Ylides **69** (X = CH = CHR,[142] C ≡ $CSiMe_3$ [143]) generated from the corresponding telluronium salts under the action of potassium bis(trimethylsilylamide) in THF at low temperature react with *N*-tosylimines of aromatic aldehydes to give vinyl(or ethynyl)aziridines **77** with low stereoselectivity (the *trans* : *cis* ratio is 33 : 67 – 58 : 42).[142, 143]



Ar = 4-ClC_6H_4: X = CH = CH_2, CH = $CHSiMe_3$;[142]
Ar = Ph: X = C ≡ $CSiMe_3$.[143]

Sulfonium allylides afford aziridines only in reactions with arylimines activated by *N*-sulfonyl [142] or *N*-diphenylphosphinoyl groups,[144] while more reactive telluronium allylides enter into aziridination reactions with less reactive imines. Thus treatment of telluronium allylides **69** (X = $SiMe_3$) prepared by deprotonation of the telluronium salt with $LiN(SiMe_3)_2$ in the presence of HMPA (toluene, −78 °C) with aryl imines gave aziridines **78**.[145] This reaction was highly stereoselective and yielded almost exclusively *trans*-isomers (> 96%).

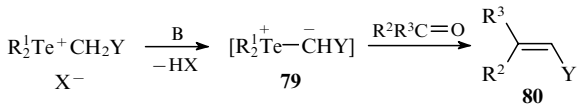


X = H, Ar = Ph; X = $SiMe_3$: Ar = Ph, 4-ClC_6H_4, 4-$CF_3C_6H_4$, 4-$MeOC_6H_4$, 2-$MeOC_6H_4$.

The reaction of diisobutylallylide **69** (X = H) with benzylideneaniline results in aziridine **78** (X = H), however, in a lower yield (37%) and with lower stereoselectivity (the *trans* : *cis* ratio is 80 : 20) than in the case of the trimethylsilyl analogue **69** (X = $SiMe_3$).[145]

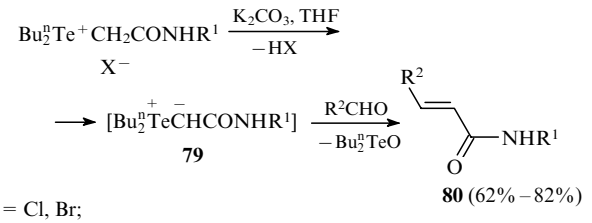
In contrast to their sulfonium analogues, stabilised telluronium ylides containing electronegative substituents at the anionic carbon atom react with aldehydes and ketones to give alkenes.[22, 29, 30] For the first time this was demonstrated in the example of dialkyltelluronium ethoxycarbonylmethylides **79** (R^1 = Me, Bu^n; Y = CO_2Et).[22] Ylides **79** were generated from (ethoxycarbonylmethyl)dialkyltelluronium bromides under the action of potassium *tert*-butoxide and coupled *in situ* with various carbonyl compounds. This resulted in α,β-unsaturated esters **80** (Y = CO_2Et, yields 52% – 90%), predominantly in the *E*-form.[22] Later, dibutyltelluronium methylide derivatives Bu^n_2TeCHY (Y = COPh,[29] CN, [29] CONHBu^i, see Ref. 30) were employed in

a similar reaction. The ylides were generated by deprotonation of telluronium halides under the action of Bu^tOK [29] or NaH;[30] their *in situ* reactions with aldehydes and ketones gave good yields (36%–83% for Y = CN, 74%–81% for Y = COPh, and 40%–71% for Y = CONHBu^i) of alkenes **80** with *E*-configurations of the double bonds.



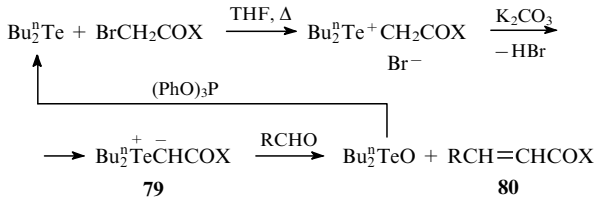
X = Br, Cl; Y = CN, CO_2Et, COPh, CONHBu^i;
R^1 = Me, Bu^n; R^2, R^3 = Alk, Ar.

The reaction of dibutyltelluronium alkylcarbamoyl methylides **79** (Y = CONHR) prepared by treatment of (alkylcarbamoylmethyl)dibutyltelluronium halides with potassium carbonate in THF, with aldehydes gave α,β-unsaturated amides **80** (Y = CONHR) with high *E*-stereoselectivity and in good yields.[146]



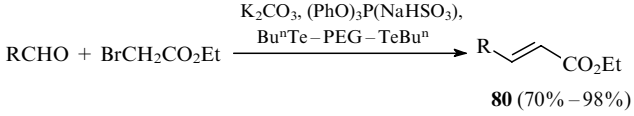
X = Cl, Br;
R^1 = Pr^i, Bu^i; R^2 = 4-$R^3C_6H_4$ (R^3 = H, Cl, Me, MeO), CH=CHPh.

The synthesis of alkenes **80** from α-bromo esters or α-bromo ketones in the presence of dibutyl telluride can be carried out as a cyclic catalytic process using triphenyl phosphite as a reducing agent for the liberating Bu^n_2TeO.[31] Catalytic amounts of dibutyl telluride react with α-bromo esters or ketones to give telluronium salts, which are converted into ylides under conditions of phase-transfer catalysis (solid K_2CO_3, THF containing traces of water). The reaction of the ylide with aldehydes occurs in the presence of $(PhO)_3P$ and yields alkenes and Bu^n_2TeO. The latter is reduced to the original dibutyl telluride, which again reacts with the bromo derivatives. Na_2SO_3, $NaHSO_3$ and $Na_2S_2O_5$ can also be used as reducing agents for dibutyltellurium oxide.[31]



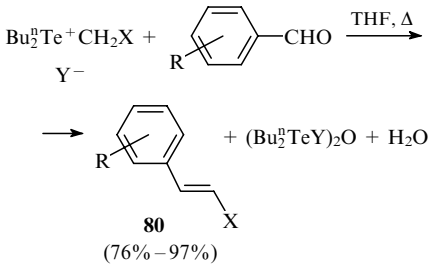
X	R	Yield (%)
OMe	Cy, Ph, 4-ClC_6H_4, 4-MeC_6H_4, PhCH=CH_2, 2-furyl	74–98
Pr^i	Ph, 2-Py, n-C_9H_{19}	78–98
Ph	Bu^n, 4-ClC_6H_4, 2-furyl	72–91

This catalytic reaction requires 20 mol.% of dibutyl telluride. The yields of alkenes decreased with a decrease in the amount of the catalyst even with the increase in the reaction time. Poly(ethylene glycol) (PEG) telluride, $Bu^nTe-PEG-TeBu^n$ (Refs 48 and 147), manifested higher catalytic activity in the olefination reaction. It was prepared by the reaction of *O*-tosyl-PEG with Bu^{n}TeLi (yield 83%).[48, 147] Reactions of aromatic and aliphatic aldehydes with ethyl bromoacetate in THF or toluene in the presence of potassium carbonate as a base, $(PhO)_3P$ or $NaHSO_3$ as a reducing agent and only 2 mol.% of $Bu^nTe-PEG-TeBu^n$, give α,β-unsaturated esters **80**, mainly with the *E*-configured double bond (> 99% in the mixture).



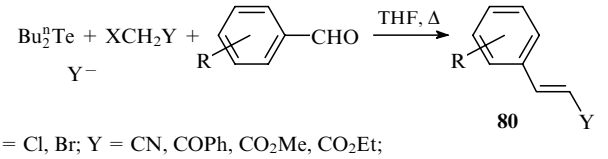
R = n-C_9H_{19}, Cy, PhCH=CH, 4-XC_6H_4 (X = H, Cl, NO_2, CF_3, Me, MeO), 2-furyl.

Due to relatively low energy and high polarity of the Te–C bonds, telluronium salts enter into the reactions that do not occur with their sulfur or selenium analogues. Thus coupling of telluronium salts with aromatic aldehydes to give alkenes without the intermediate formation of ylides occurs upon refluxing in THF.[27, 29] In some cases, the yields of *E*-alkenes **80** are even higher than the yields attained in reactions with pre-formed ylides.



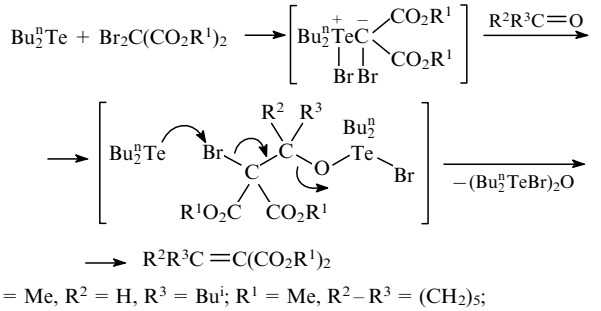
Y = Cl, Br; X = CN, CO_2Me, COPh; R = 4-Cl, 4-Br, 3-NO_2, 4-NO_2.

As telluronium salts are easily formed upon reactions of dibutyl telluride with α-bromo esters (or ketones) or chloroacetonitrile, the synthesis of alkenes **80** can be carried out by refluxing of equimolar amounts of dibutyl telluride, the halogen-containing substrate and the aldehyde in THF.[27] The yields of alkenes **80** are only slightly lower than with the use of the *in situ* prepared telluronium salts.



X = Cl, Br; Y = CN, COPh, CO_2Me, CO_2Et;
R = 4-Cl, 4-Br, 3-NO_2, 4-NO_2.

The reaction of dibromomalonates with carbonyl compounds in the presence of dibutyl telluride (2 equiv.) is a convenient alternative to the Knoevenagel reaction.[37]

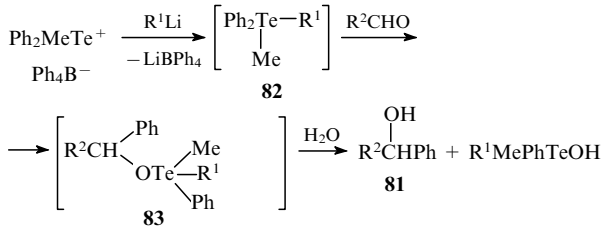


R^1 = Me, R^2 = H, R^3 = Bu^i; R^1 = Me, R^2-R^3 = $(CH_2)_5$;
R^1 = Et, R^2 = H: R^3 = n-C_9H_{19}, $R^4C_6H_4$ (R^4 = H, 2-Cl, 4-Cl, 4-NO_2, 4-MeO), 2-Py, 2-(3-bromothienyl).

This reaction proceeds under mild conditions (heating of the reaction mixture in THF at 50 °C) and results in alkylidene- and arylmethylidene α,β-unsaturated malonates in 84%–98% yields. A tentative mechanism of the reaction is reported.[37]

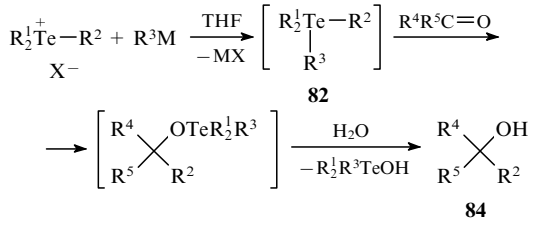
It was already mentioned that the deprotonation of methyldiphenyltelluronium tetraphenylborate under the action of

LiTMP gave the ylide [$Ph_2Te^+H_2C^-$] which reacted with carbonyl compounds to yield epoxides of the type **70**.[100] The reaction of the same salt with organolithium compounds and subsequent addition of aldehydes to the reaction mixture gave quite different results, *viz.*, secondary alcohols **81** (yields 55%–85%) were formed as the reaction products.[99] This can be attributed to the formation, from original telluronium salts and organolithium compounds, of unstable tetraorganyltelluranes **82** [similar to the formation of thermostable Ph_4Te from Ph_3TeCl and PhLi or thermally unstable tetrabutyltellurane Bu^n_4Te from Bu^n_3TeI and Bu^nLi (Refs 9, 10)]. The reactions of telluranes **82** with carbonyl compounds are accompanied by migration of one of the radicals bound to the tellurium atom to the carbonyl carbon atom resulting in intermediates **83**. In the case of methyldiphenyltelluronium tetraphenylborate, this reaction yields arylbenzyl alcohols **81** due to the preferential migration of the phenyl radical.[99]



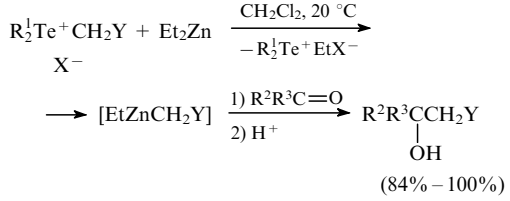
R^1 = Me, Bu, Bu^t, Ph; R^2 = 4-$R^3C_6H_4$ (R^3 = H, Br, Cl, F, Me, MeO), 2-naphthyl, 2-Py.

The Bn and $CH_2C{\equiv}CSiMe_3$ groups in tetraorganyltelluranes **82** (R^1 = Bn,[35] $CH_2C{\equiv}CSiMe_3$ [39]) formed upon reaction of the corresponding telluronium salts with organolithium (or -magnesium) derivatives migrate to the carbonyl carbon atom. This yields alcohols **84** containing a benzyl[35] or a trimethylsilylethynylmethyl[39] group at the α-carbon atom. A large series of β-hydroxy nitriles **84** (R^2 = CH_2CN) were synthesised from dibutyl(cyanomethyl)telluronium chloride using a similar approach.[36]



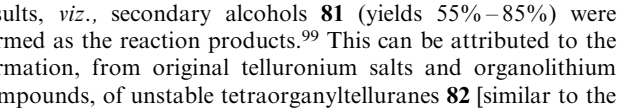
X = Cl, Br; R^1 = Bu^n, Bu^i; R^2 = Bn, $CH_2C{\equiv}CSiMe_3$, CH_2CN;
R^3M = MeLi, Bu^nLi, Bu^tLi, PhLi, 4-MeC_6H_4Li, MeMgI;
R^4 = H, Me, Ph; R^5 = Alk, Ar, Het; R^4–R^5 = $(CH_2)_5$, $(CH_2)_3CH{=}CH$.

Yet another example of the use of telluronium salts in the synthesis of alcohols is the tellurium–zinc exchange reaction between telluronium salts and diethylzinc. This reaction proceeds under mild conditions (in CH_2Cl_2 at room temperature).[148] The diorganylzinc derivatives formed *in situ* reacted with carbonyl compounds (aldehydes, ketones, phenacyl chlorides) and afforded secondary and tertiary alcohols in high yields after hydrolysis.[148]



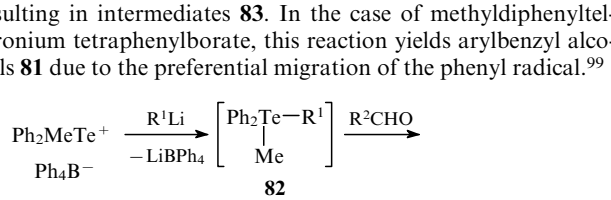
X = Cl, Br, I, BPh_4; Y = $CH{=}CH_2$, $C{\equiv}CSiMe_3$, Ph;
R^1 = Bu^n, Bu^i; R^2 = H, Ph; R^3 = n-$C_{11}H_{23}$, CH_2Cl, $CH{=}CHPh$, Ph, 4-ClC_6H_4.

Allyl(dialkyl)telluronium bromides are efficient reagents for the allylation of phenols. The reactions of these salts with phenols in the presence of solid NaOH in THF yielded allyl aryl ethers (yields 81%–95%).[43]



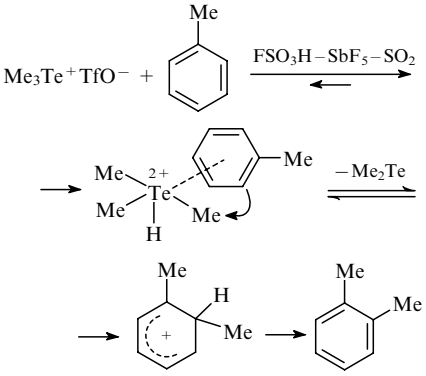
R^1 = R^2 = H, Me; R^1 = H, R^2 = 4-ClC_6H_4; Ar = Ph, $R^3C_6H_4$ (R^3 = 4-Cl, 2-Me, 4-Bu^t), 1-naphthyl, 2-naphthyl.

The reaction of telluronium salt **11** with sodium phenylsulfinate yielded the corresponding alkyl phenyl sulfone.[17]



However, in contrast to their iodonium [*e.g.*, $PhI^+CH{=}CR^1R^2BF_4^-$ (Ref. 149)] and bismuthonium [$Ph_3Bi^+CH_2CORBF_4^-$ (Ref. 150)] analogues, telluronium salts **10** and **14** do not enter into this reaction. It was thus concluded [17] that the nucleofugicity of the diphenyltelluronium group is lower than those of the phenyliodonium and triphenylbismuthonium groups.

In the presence of a superacid (*e.g.*, the $FSO_3H–SbF_5–SO_2$ system), trimethyltelluronium trifluoromethanesulfonate alkylated toluene under very mild conditions (−78 °C) resulting in the predominant formation of *o*-xylene (yield 25%); *m*- and *p*-isomers were formed as minor products (93 : 6 : 1).[67]



Dibenzotellurophenonium trifluoromethanesulfonate **18**, like its selenium and sulfuric analogues, can serve as a trifluoromethylating reagent with respect to various enolates including trimethylsilyl enolates, anilines and sodium alkanethiolates. Their trifluoromethylating activities increase in the following order: Te < Se < S.[69] Trifluoromethyldibenzotellurophenonium-3-sulfonate [151] is the most convenient trifluoromethylating reagent of this class as regards the ease of isolation of the reaction products, since dibenzotellurophene-3-sulfonic acid formed is readily soluble in water.

Among other important practical applications of telluronium salts, special mention should be made of the use of triphenyltelluronium tetrafluoroborate and phosphate as catalysts of liquid-phase oxidation of alkenes.[152]

V. Crystal structures of telluronium salts

The molecular and crystal structures of over 60 telluronium salts were studied using X-ray diffraction analysis. The Te–C and Te–heteroatom bond lengths, C–Te–C bond angles, coordination numbers (CN) of tellurium atoms and references are given in Table 1, the data being sorted in accordance with the type of the anion X.

Table 1. Bond lengths and bond angles in triorganyltelluronium salts $R^1R^2R^3Te^+X^-$.

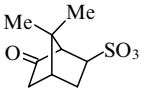
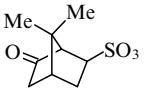
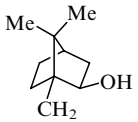
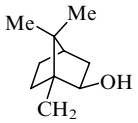
Example	X	R^1	R^2	R^3	Bond lengths /Å		Bond angle C–Te–C /deg	CN of Te atom	Ref.
					Te–C	Te–heteroatom			
85a	BPh_4	Me	Me	Me	2.113–2.163		90.4–93.0	3	10
85b	BPh_4	Me	Ph	Ph	2.123–2.132		91.5–97.7	3	46
85c	BPh_4	Bu	$Bu^tO_2CCH_2$	$PhO(CH_2)_3$	2.098–2.205	2.926 (Te···OPh), 3.282 (Te···O=$COBu^t$)	88.7–93.4	4	48
30	ClO_4	Me	Bu^n	2-(PhN=CH)C_6H_4	2.121–2.148	2.75 (Te···N), 3.31, 3.448, 3.558 (Te···O)	92.5–97.8	4	72, 73
64a	$HgCl_3$ [a]	Cl	4-$EtOC_6H_4$	2-(2-Py)C_6H_4	2.05–2.11	2.43 (Te–Cl), 2.31 (Te···N)	101.0	4	130
86	$B(C_6F_5)_4$	Ph	Ph	Ph	2.103–2.117	3.363 (Te···F)	97.1–99.2	3	86
10a	BF_4	Bu^tCOCH_2	Ph	Ph	2.109–2.130	2.892 (Te···O), 3.065 (Te···F)	94.8–98.9	4(5)	17
87a	SbF_6	Mes	Mes	Mes	2.131–2.137		104.4–109.3	3	81
87b	SbF_6 [b]	Mes	Mes	Br	2.116–2.139	2.479, 2.509 (Te–Br), 2.62, 2.66, 2.93, 3.24 (Te···F)	106.4–106.8	4	81
88	$AuCl_4$	Ph	Ph	Ph	2.112–2.122	3.064–3.400 (Te···Cl)	96.5–98.7	6	106
89	$PtCl_6$	Ph	Ph	Ph	2.095–2.131	3.331–3.843 (Te···Cl)	93.5–100.9	4	106
90	$IrCl_6$	Ph	Ph	Ph	2.094–2.139	3.13–3.743 (Te···Cl)	94.1–100.9	4	106
91	Hg_2Cl_6	Ph	Ph	Ph	2.097–2.119	3.337, 3.489, 3.574 (Te···Cl)	94.4–101.3	6	128
92	$TeCl_6$	Ph	Ph	Ph	2.120	3.527 (Te···Cl)	97.72	6	153
93	$MeTeI_4$	Me	Me	Me	2.007–2.127	3.84, 3.88, 3.97, 4.00 (Te···I)	90.7–98.6	3(4)	10
94	Ag_4I_5 [c]	Et	Et	Et	2.11–2.16	3.822, 4.051, 4.166, 4.231 (Te···I)	91.0–96.0	3(4)	154
(*R*)-**60a**		Me	Et	Ph	2.117–2.170	2.88, 3.05 (Te···O)	93.7–96.6	5	54–56, 124
(*S*)-**60a**		Me	Et	Ph	2.09–2.200	3.00, 3.01, 3.03 (Te···O)	92.0–100.8	6	56, 124
95	OTf	C_6F_5	C_6F_5	C_6F_5	2.062–2.142	2.61–2.68 (Te···O)	91.1–106.1	4	82
1a	Cl	Me	Me	Me	2.108–2.114	3.318 (Te···Cl)	93.9–96.2	5	28
1b	Cl	Et	Et	Et	2.15	3.448 (Te···Cl)	85.8	6	25
(*S*)-**32a**	Cl	Me	Et		2.082–2.165	see [d]	92.9–96.5	–	75
(*R*)-**32a**	Cl	Et	Me		2.092–2.150	see [d]	92.0–96.5	–	75

Table 1 (continued).

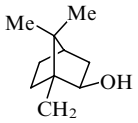
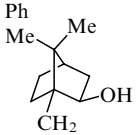
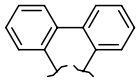
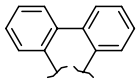
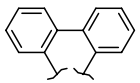
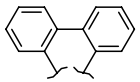
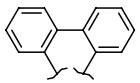
Example	X	R^1	R^2	R^3	Bond lengths /Å		Bond angle C–Te–C /deg	CN of Te atom	Ref.
					Te–C	Te–heteroatom			
32b	Cl	Et	$PhCH_2$		2.132–2.161	3.153 (Te···Cl), 2.841 (Te···O)	80.1–95.8	5	74
1c	Cl	Ph	Ph	Ph	2.115–2.144	3.142, 3.234 (Te···Cl)	93.4–97.1	5	28, 155
1d	Cl	C_6F_5	C_6F_5	C_6F_5	2.108–2.207	2.670, 3.47 (Te···Cl)	87.8–102.3	5	156
1e	Br	Et	Et	Et	2.14	3.564 (Te···Br)	89.3	6	24
1f	Br	Bu^i	Bu^i	Ph	2.113–2.122	3.293 (Te···Br)	92.8–93.7	4	46
32c	Br	Me	$PhCH_2$		2.122–2.161	see [d]	93.6–97.4	5	47
1g	Br [e]	C_6F_5	C_6F_5	C_6F_5	2.13–2.21	2.834, 3.570 (Te···Br)	89.2–102.0	5	82
1h	I	Me	Me	Me	2.120–2.129	3.698, 3.731, 3.813 (Te···I)	92.2–95.7	6	28
1i	I	Et	Et	Et	2.11–2.16	3.813, 3.861, 4.494 (Te···I)	96.6–101.2	5	25
1j	I	Me	Me	Ph	2.128–2.132	3.659, 3.758 (Te···I)	93.7–95.4	5	57
1k	I [f]	Me	Me	C≡CTeMe	2.069–2.136	3.58, 3.76 (Te···I), 3.45, 3.70 (Te^+···I), 3.77 (Te^+···Te)	92.07–97.09	6	65
1l	I	Mes	Mes	Mes	2.134–2.148	4.128 (Te···I)	103.7–110.5	3	13
96	ONO_2	Me	Me	Me	2.107–2.112	3.002, 3.018, 3.138 (Te···O)	94.6–95.7	6	28
42a	OCOPh	2-PhC_6H_4			2.110–2.133	2.469 (Te–O), 3.182 (Te···O=C)	80.9–99.3	5	83
42b	OCOMe	2-PhC_6H_4			2.116–2.153	2.491 (Te–O), 3.181 (Te···O=C)	80.3–97.2	6	83
42c	OPh	2-PhC_6H_4			2.104–2.175	2.294 (Te–O)	79.7–103.9	4	84
42d	$OC_6H_4NO_2$-4	2-PhC_6H_4			2.102–2.150	2.461 (Te–O)	80.2–99.1	4	85
42e	$OC_6H_2Cl_3$-2,4,6	2-PhC_6H_4			2.108–2.159	2.762 (Te–O), 2.787 (Te–O)	81.3–96.5	5	85

Table 1 (continued).

Example	X	R^1	R^2	R^3	Bond lengths /Å		Bond angle C–Te–C /deg	CN of Te atom	Ref.
					Te–C	Te–heteroatom			
50c	TeC_6H_4Me-4	Ph	Ph	Ph	2.132–2.187	3.32, 3.38, 3.53, 3.60 (Te···Te)	91.1–96.3	5	113
50c	TeC_6H_4OMe-4	Ph	Ph	Ph	2.122–2.171	3.40, 3.44, 3.45, 3.48 (Te···Te)	90.9–98.5	5	14
50b	SeC_6H_4Me-4	Ph	Ph	Ph	2.119–2.179	3.15, 3.28, 3.31, 3.34 (Te···Se)	90.8–94.9	5	113
50a	SC_6H_4Cl-4	Ph	Ph	Ph	2.120–2.170	3.02–3.64 (Te···S)	90.8–96.7	5	112
97	$OC_6H_2(NO_2)_3$-2,4,6	Me	Me	CF_3	2.111–2.192	2.496 (Te–O), 3.134, 3.138 (Te···O)	89.9–95.1	6	98
98a	OCN	Me	Me	Me	2.110–2.121	2.983, 3.103 (Te···N), 3.095 (Te···O)	93.3–95.4	6	104
98b	OCN	Ph	Ph	Ph	2.102–2.156	2.783, 3.005, 3.171 (Te···N), 2.891, 3.028 (Te···O)	92.8–99.0	5, 6	105
99a	SCN	Me	Me	Me	2.113–2.120	3.185 (Te···N), 3.390, 3.488 (Te···S)	92.7–96.7	6	104
99b	SCN	Ph	Ph	Ph	2.100–2.150	2.963, 3.153, 3.182 (Te···N), 3.256, 3.348, 3.527 (Te···S)	92.3–100.0	5, 6	10
100a	SeCN	Me	Me	Me	2.107–2.124	3.252 (Te···N), 3.471, 3.553 (Te···Se)	93.3–96.6	6	104
100b	SeCN [g]	Ph	Ph	Ph	2.120–2.139	3.125 (Te···N), 3.442, 3.541 (Te···S)	93.4–99.9	6	104
101a	N_3	Me	Me	Me	2.107–2.143	2.938, 3.006, 3.018, 3.032, 3.037 (Te···N)	92.5–94.7	6	104
101b	N_3 [g]	Ph	Ph	Ph	2.120–2.146	2.772, 2.867, 2.946, 3.00, 3.027 (Te···N)	92.7–98.8	6	104
102a	$Ag(CN)_2$	Me	Me	Me	2.100–2.109	3.154, 3.270, 3.407 (Te···N)	93.6–95.9	6	104
102b	$Ag(CN)_2$	Ph	Ph	Ph	2.119–2.121	3.162, 3.346, 3.501 (Te···N)	94.4–99.5	6	104
54a	$SC(S)NPr_2$ [g]	Ph	Ph	Ph	2.128–2.163	3.095, 3.145 (Te···S)	92.0–97.3	5	119
52a	SC(S)OMe	Ph	Ph	Ph	2.123–2.188	3.174–3.270 (Te···S)	91.7–97.9	5	115
52b	$SC(S)OBu^n$ (see [g])	Ph	Ph	Ph	2.142–2.172	3.123–3.535 (Te···S)	88.4–97.8	5	115
56a	$SP(S)Ph_2$	Ph	Ph	Ph	2.129–2.139	3.331–3.655 (Te···S)	94.4–101.2	5	121
55a	$SP(S)(OEt)_2$	Ph	Ph	Ph	2.134–2.136	3.150–3.286 (Te···S)	95.2–96.9	5	112
59a	$N\{P(O)Ph_2\}_2$	Ph	Ph	Ph	2.111–2.131	2.654, 2.926 (Te···O)	94.1–97.0	5	123
59b	$N\{P(S)Ph_2\}_2$	Ph	Ph	Ph	2.121–2.143	3.264, 3.451 (Te···S)	96.8–97.4	5	121
59c	$N\{P(O)Ph_2\}\{P(S)Ph_2\}$	Ph	Ph	Ph	2.113–2.137	2.771 (Te···O), 3.282 (Te···S)	94.5–96.3	5	123

[a] The C–Te–Cl angles lie in the range 88.5–91.7° (Ref. 130); [b] the salt contains two independent ionic pairs; the C–Te–Br angles are equal to 91.6–101.8° (Ref. 81); [c] the salt was unexpectedly isolated in an attempt to obtain triethyltelluronium diethyl thiophosphate by the exchange reaction of triethyltelluronium iodide with silver diethyl thiophosphate;[158] [d] the data on secondary bonds are absent; [e] the solvate with benzene (1 : 1); [f] the bonds of the non-charged Te atom: Te–$C(sp)^3$ and Te–C(sp) are 2.149 and 2.067 Å, respectively (Ref. 65); [g] the solvate with chloroform (1 : 0.5).

The nature of the Te–X bonds in the telluronium salts R_3TeX in the crystalline state varies from purely ionic to covalent and is largely determined by the nature of the electronegative group X and, to a lesser extent, by the nature of the organic radicals bound to the tellurium atom. Like other tellurium derivatives,[157,158] telluronium salts form secondary bonds with various elements, which allows the CN of tellurium atoms to acquire values from 3 to 6. Besides, a significant role in the structures and reactivities of organotellurium compounds is played by intramolecular coordination bonds (ICB) O → Te, N → Te, *etc.*[159,160] The nature of these bonds is mainly determined by the donation of the unshared electron pair (UEP) of a heteroatom in such group as CHO, COR, CO_2R, NO_2, N=N, CH=N, CH_2NR_2, *etc.*, to the antibonding molecular orbital (σ^*-MO) of the Te–X bond. The intramolecular coordination bonds O(or N) → Te should always be taken into consideration in determining the CN for the tellurium atom, since these bond lengths are much smaller than the sum of the van der Waals radii of the elements involved in the interaction.

Salts **85a–c**, **86** containing tetraphenylborate anion and its perfluorinated analogue, as well as perchlorate **30** and trichloromercurate **64a** exist in the form of discrete cations and anions; in the majority of cases, they are not involved in significant secondary interactions with one another. The lengths of the Te···F bond in salt **86** (3.36 Å[86]) and of the Te···O bond in salt **30** (average value of 3.45 Å[72,73]) are close to the sum of the van der Waals radii for the Te, F (3.53 Å[133]) and Te, O (3.60 Å[133]) pairs and are not taken into consideration in the calculation of CN for the Te atom. The bonds at the Te atom in R_3Te^+ cations have a trigonal-pyramidal configuration; the CN of Te in compounds **85a**,**b** and **86** is 3. At the same time, the bonds at the Te atoms in salts **85c**, **30** and **64** acquire a trigonal-bipyramidal configuration as a result of which the CN increases to 4 due to the occurrence, in these salts, of ICB O → Te, N → Te. Their lengths are 0.7–1.3 Å smaller than the sum of the van der Waals radii of the corresponding elements. Tetrafluoroborate **10a** contains, together with ICB O → Te (2.892 Å[17]), an interionic secondary Te···F bond the length of which (3.06 Å[17]) is nearly 0.5 Å smaller than the sum of the van der Waals radii of Te and F (3.53 Å[133]). With regard to this interaction, the CN of the tellurium atom increases to 5.

Secondary interionic Te···Hal bonds usually occur in salts containing complex halogen anions $MHal_n$ (Hal = F, Cl); it is noteworthy that these bonds are shorter than the sum of the van der Waals radii of the elements. Hexafluoroantimonate **87a** containing three bulky mesityl groups is an exception, it exists in the form of discrete non-interacting ions. The Te atom in this compound has the trigonal-pyramidal configuration, and its CN is 3. However, CN of the tellurium atom in bromodimesityltelluronium salt **87b** containing the shortest Te···F contacts is 4.[81] It is of note that secondary bonds Br···F in this compound are relatively short (2.69–2.80 Å), *i.e.*, 0.5–0.6 Å shorter than the sum of their van der Waals radii (3.32 Å[133]). In salt **88**, each Te atom forms secondary Te···Cl bonds with the chlorine atoms of three $AuCl_4^-$ anions[106] and, as a consequence, the CN of the tellurium atom is 6. Salts **89**, **90** containing the doubly charged anions MCl_6 (M = Pt, Ir) manifest three secondary interactions Te···Cl.[106] However, only the shortest bonds are taken into consideration in determining the type of the coordination polyhedron of the tellurium atom (the trigonal bipyramid with allowance for the UEP of the Te atom[106]) and its CN (equal to 4). Bis(triphenyltelluronium) di-μ-chlorobis(dichloromercurate) **91** contains symmetrical Cl-bridging dimeric $Hg_2Cl_6^{2-}$ anions.[128] Due to three secondary Te···Cl bonds, which are 0.24–0.47 Å shorter than the sum of the van der Waals radii, the CN of the Te atom is equal to 6.[128] The coordination number of the onium tellurium atom in bis(triphenyl)telluronium hexachlorotellurate **92** is also equal to 6.[153] In this salt, each of the two tellurium atoms in the triphenyltelluronium cations is linked to the $TeCl_6^{2-}$ anion by three secondary Te···Cl bonds, the average length of the bonds being 3.527 Å. The $TeCl_6^{2-}$ anion has an octahedral structure; the average length of the Te···Cl bonds is 3.545 Å.[153] Trimethyltelluronium methyltetraiodotellurate **93**[10] and triethyltelluronium tetraargentatopentaiodide **94**[154] are made up of trigonal-pyramidal cations, Alk_3Te^+ and square-pyramidal anions $MeTeI_4^-$ or tetracoordinate Ag atoms constituting the $[Ag_4I_5]^-$ anions.[154] Considering that the shortest Te···I bonds in both salts are only 0.2 Å shorter than the sum of the van der Waals radii of Te and I (4.04 Å[133]), the CN of the tellurium atom in these compounds can be taken equal to 3 and 4, respectively.

It is of note that the *R*- and *S*-diastereomers of ethyl(methyl)phenyltelluronium camphor-10-sulfonate **60a** differ from one another not only in the lengths of their Te–C bonds and the C–Te–C bond angles, but also in the number of secondary interactions between the tellurium atom and the oxygen atoms of the sulfonate group. The *R*-isomer in the crystalline state was found to contain two secondary bonds Te···O (2.88 and 3.05 Å[54–56,124]), which points to the square-pyramidal geometry of the Te atom (CN 5). At the same time, the *S*-isomer contains three Te···O bonds (3.00, 3.01 and 3.03 Å[56,124]) with an octahedral configuration around Te (CN 6). Telluronium salt **95** containing a trifluoromethanesulfonate anion has only one Te···O bond (2.61–2.68 Å); the CN of the Te atom in this salt is equal to 4.[82]

Presumably,[56] the difference in the type of secondary interactions between the optical isomers is determined by the peculiarities of the crystal packing of their molecules. It should be noted that the lengths of the Se···O bonds (3.03 and 3.32 Å) in (*R*)-ethyl(methyl)phenylselenonium camphor-10-sulfonate[161] exceed those in its tellurium analogue (*R*)-**60a** despite the fact that the van der Waals and the covalent radii of selenium are smaller than those of tellurium. This suggests that the cation–anion interactions in telluronium salts are stronger than in selenonium salts.

The crystalline states of the salts containing nucleophilic halide anions are represented by several structural types. Each tellurium atom in triethyltelluronium bromide **1e** is involved in three secondary interactions with the bromine atoms (the average length of the Te···Br bonds is 3.56 Å;[24] the sum of the van der Waals radii of the elements is 3.91 Å[133]). This favours the formation of cubane-like tetramers where the Te and Br atoms alternately occupy the vertices of the Te_4Br_4 backbone. The presence of three primary Te–C bonds and three secondary Te···Br bonds at tellurium atoms results in the distorted octahedral environment of Te (CN 6). Triethyltelluronium chloride **1b** has a similar structure: the average length of the Te···Cl bonds is 3.45 Å,[25] while the sum of the van der Waals radii of Te and Cl is 3.81 Å.[133] Trimethyltelluronium iodide **1h** was found to contain three secondary Te···I bonds with the average bond length of 3.75 Å[28] (the sum of the van der Waals radii being 4.04 Å[133]); the CN of the Te atom is also equal to 6.

Triethyltelluronium iodide **1i** has a different structure.[25] Its cations form centrosymmetrical dimers linked together by bridging iodine atoms (the average length of the Te···I bonds is 3.84 Å). In contrast to the halides considered above, each tellurium atom is included into two secondary interactions, which is favourable for the square-pyramidal environment of the tellurium atom (CN 5). The same configurations of the bonds were found in trimethyl- (**1a**),[28] triphenyl- (**1c**)[28,155] and tris(pentafluorophenyl)telluronium (**1d**) chlorides,[156] in tris(pentafluorophenyl)telluronium bromide (**1g**)[82] and dimethylphenyltelluronium iodide (**1j**).[57] The CN (5) of the Te atom in the *S*-diastereomer of the optically active telluronium salt **32b** is determined by the presence of two secondary bonds: Te···Cl (3.153 Å) and Te···O (2.842 Å),[74] their lengths are much smaller than the sum of the van der Waals radii of the corresponding elements. All the three nitrogen atoms in tris(2-dimethylaminobenzyl)telluronium chloride (not included into the Table) are coordinated by the tellurium atom, which favours the formation of the octahedral environment of the latter[14] (CN 6). The length of ICB N → Te in this compound slightly exceeds that in salts **30** and **64a,** which contain sp^2-hybridised nitrogen atoms. Chlorine atoms are not involved in secon-

dary interactions [the shortest distance Te···Cl is 4.72 Å, which exceeds the sum of the van der Waals radii of Te and Cl (3.81 Å)[133] by 0.9 Å]. Each iodine atom in (methyltelluroethynyl)dimethyltelluronium iodide (**1k**) forms secondary bonds with four tellurium atoms.[65] The Te^{+}···I bonds (3.45 and 3.70 Å) are shorter than the MeTe···I bonds (3.58 and 3.76 Å). The crystals of **1k** were found to contain relatively short Te^{+}···Te bond; their lengths (3.77 Å) are about 0.4 Å smaller than the sum of the van der Waals radii of the elements (4.12 Å).[133] The CN of the onium Te atom with consideration of these interactions is 6, that for the tellurium atom bound to C(sp^3)- and C(sp)-atoms is 5.[65]

The presence of bulky mesityl radicals in trimesityltelluronium iodide (**1l**) may account for the fact that this salt is not characterised by any significant secondary interactions involving the tellurium atom. The length of the Te···I bond is 4.13 Å,[13] *i.e.,* exceeds the sum of the van der Waals radii of Te and I (4.04 Å)[133] by nearly 0.1 Å.

Biphenyl-2-yl(dibenzotellurophenium) benzoate (**42a**)[83] has a trigonal-bipyramidal structure characteristic of σ-telluranes R_2TeX_2 (X = Hal, OCOR, ONO_2, *etc.*[162]) containing covalent bonds Te–X. The apical positions are occupied by the O atom and one of the Te–C bonds of the dibenzotellurophene fragment (the angle between the apical substituents is 159.9°). The length of the Te–O bond (2.469 Å) is 0.3 Å greater in comparison with diphenyl telluroacetate $Ph_2Te(OCOCH_3)_2$ (2.16 Å[163]). The secondary Te···O bond between the tellurium atoms and the carbonyl oxygen atom of this molecule (3.182 Å) is about 0.4 Å smaller than the sum of the van der Waals radii of the elements. With consideration of this bond, the CN of the Te atom is 5. Benzoate **42a** exists as a monomer in the crystalline state, while the acetate **42b** is a dimer due to the presence of secondary Te···O bonds with carbonyl oxygen atoms of not only its own molecule (2.491 Å), but also the adjacent molecule (3.181 Å).[83] If these bonds are taken into consideration, the CN of the Te atom becomes equal to 6. The difference between the structures of benzoate **42a** and acetate **42b** can be attributed to the effects of steric factors, *i.e.*, the different sizes of the OCOPh and OCOMe groups.[83]

2,2′-Biphenylene(biphenyl-2-yl)telluronium phenolates **42c**[84] and **42d**[85] have identical structures. The coordination polyhedra of the tellurium atom in these compounds are distorted trigonal bipyramids the apical positions in which are occupied by the oxygen atoms and by one of the Te–C bonds of dibenzotellurophene (the angles between the apical substituents in both compounds are equal to 159.6°). The Te–O bond in 4-nitrophenoxy derivative **42d** (2.461 Å) is nearly 0.2 Å longer than that in the unsubstituted derivative **42c** (2.294 Å). The lack of secondary interactions in the crystals of compounds **42c**,**d** makes the CN of the Te atom equal to 4. In contrast to the monomeric phenoxy derivatives **42c**,**d**, salt **42e** containing a 2,4,6-trichlorophenoxy substituent exists in the form of a dimer.[85] In the latter case, the lengths of the primary Te–O bonds (2.762 Å) and secondary Te···O bonds between the tellurium atom and the oxygen atom of the adjacent molecule (2.787 Å) are virtually identical, the tellurium atom has a distorted square-pyramidal configuration of the bonds (CN is 5). Presumably,[85] the gradual increase in the lengths of the Te–O bonds in phenolates **42c**–**e** reflects the gradual changes in the nature of the Te–X bonds from predominantly covalent to ion-like.

Similarly to phenolate **42e**, triphenyltelluronium chalcogenolates **50b**–**c** exist as dimers with virtually planar cyclic fragments Ar_8Te_4 and $Ar_8Te_2Se_2$.[113] The average lengths of four secondary interactions Te···Te are 3.451 (**50c**, X = TeC_6H_4Me-4) and 3.441 Å (**50c**, X = TeC_6H_4OMe-4), *i.e.,* much smaller than the sum of the van der Waals radii of the Te atoms (4.40 Å[133]). The lengths of the Te···Se bonds in selenolate **50b** (3.269 Å) are about 0.2 Å smaller than the Te···Te bonds and 0.7 Å smaller than the sum of the van der Waals radii of Te and Se (3.96 Å[133]). Thus, the CN of the Te atom in the above tellurolates and selenolates is equal to 5. At the same time, it is suggested[112] that triphenyltelluronium 4-chlorophenylthiolate **50a** exists in a solid state as a tetramer each tellurium atom in which forms two secondary bonds with sulfur atoms (the CN of Te is 5); the Te···S distances lie in the range 3.02–3.64 Å.

The structure of dimethyl(trifluoromethyl)telluronium 2,4,6-trinitrophenolate (**97**) differs from those of **42c**–**e** and **50a**–**c**.[98] The coordination polyhedron of the tellurium atom in **97** (with consideration of the UEP) represents a distorted pentagonal bipyramid. The apical positions are occupied by the trifluoromethyl group (the lengths of the Te–C bonds reach 2.192 Å) and the phenol oxygen atom (the length of the Te–O bonds is 2.496 Å), whereas two methyl groups (the average length of the Te–C bonds is 2.113 Å), two oxygen atoms of the nitro groups of two neighbouring molecules (the lengths of secondary Te···O bonds are equal to 3.134 and 3.138 Å) and the UEP of the tellurium atom occupy the equatorial positions. Thus, the CN of the Te atom in phenolate **97** is 6.

With consideration of secondary interactions, salts **98a**, **99a**, **100a**,**b** containing the chalcogenocyanate anions XCN (X = O, S, Se) are characterised by the octahedral environment of the bonds around the Te atom (CN = 6).[104] As the XCN anions are ambident, both Te···N and Te···X interactions take place in the crystals of these compounds. In salts **99a** and **100a**,**b** containing soft S and Se atoms,[93] two bonds of these atoms with soft Te atom take place along with one secondary Te···N bond. Only one secondary Te···O bond (3.10 Å) and two secondary Te···N bonds (2.98 and 3.10 Å) are found in trimethyltelluronium cyanate (**98a**) containing a harder oxygen atom. Triphenyltelluronium cyanate (**98b**)[105] and thiocyanate (**99b**)[10] were found to contain secondary Te···X bonds (X = O, S) and Te···N bonds of approximately the same lengths as in the corresponding trimethyltelluronium salts.[104] Cyanate **98b** contains discrete tetramers two Te atoms in which have distorted square-pyramidal environment (CN = 5), while the other two have distorted octahedral environment (CN = 6). Triphenyltelluronium thiocyanate **99b** is made up of dimers containing Te atoms with CN = 5, and tetramers the Te atoms in which are penta- and hexacoordinate.

In trimethyltelluronium (**101a**)[104] and triphenyltelluronium (**101b**)[104] azides, the tellurium atoms are linked to terminal nitrogen atoms of nearly linear azido groups, resulting in a distorted octahedral environment of the Te atom (CN = 6). The average length of secondary Te···N bonds is 3.0 Å, *i.e.*, 0.65 Å less than the sum of the van der Waals radii of Te and N. Such a coordination of tellurium atoms was observed in triorganyltelluronium dicyanoargentates **102a**,**b**.[104] The Te atoms form two shorter secondary Te···N bonds (3.15 and 3.27 Å in the trimethyltelluronium salt **102a** and 3.16 and 3.35 Å in its phenyl analogue **102b**) and one more extended Te···N bond (3.41, 3.50 Å, respectively). The latter are only 0.15–0.25 Å shorter than the sum of the van der Waals radii of Te and N.

Telluronium salts containing 1,1-dithio ligands SC(S)X (X = NR_2, OR) (**52a**,**b**, **54a**) are represented by two major structures. Triphenyltelluronium dithiocarbamate (**54a**)[119] and triphenytelluronium alkyl xanthate (**52a**)[115] are dimeric in the crystalline state due to the formation of secondary Te···S bonds. This results in the distorted octahedral (with consideration of UEP) environment of the Te atom (CN = 5). The lengths of the Te···S bonds in salts **52a** and **54a** vary from 3.10 to 3.27 Å. In contrast to these salts, triphenyltelluronium isobutyl xanthate (**52b**) is monomeric.[115] The xanthate fragment is chelated by only one tellurium atom. The length of one of the two secondary Te···S bonds (3.535 Å) exceeds that of the other bond (3.123 Å) by nearly 0.4 Å. The difference in the structures of methyl and isobutyl xanthates seems to be due to the steric hindrance created by the isobutyl groups in the dimer formation.

Salts **55a**, **56a** and **59a**–**c** with various phosphorus-containing ligands are always monomeric. The tellurium atom in compounds **55a** and **56a** containing dithiophosphoric substituents [$SP(S)(OEt)_2$[112] and $SP(S)Ph_2$[121]], is pentacoordinate and has a distorted square-pyramidal environment. In addition to three

primary Te–C bonds, each tellurium atom forms two secondary Te···S bonds. It is noteworthy that the Te···S bonds (3.15 and 3.29 Å) in salt **55a** are somewhat shorter than those in salt **56a** (3.33 and 3.66 Å).

Six-membered chelate rings TeX_2P_2N (X = O,[123] S [121]) and $TeOSP_2N$ [123] are formed in triphenyltelluronium dichalcogenoimidodiphosphinates **59a–c**.[123] The distorted square-pyramidal geometry of the bonds at the tellurium atom (CN = 5) is determined by secondary bonds Te···O (2.65–2.93 Å) and Te···S (3.26–3.45 Å).

Hence, the structural diversity of telluronium salts suggests the existence of different types of interactions of tellurium atoms in crystalline states.

VI. Conclusion

The reviewed data suggest that the chemistry of telluronium salts has advanced considerably in the past two decades. This is manifested in the development of novel efficient methods for the synthesis of telluronium derivatives and preparation of hitherto unknown types of telluronium salts. Considerable progress has been achieved in the application of telluronium salts in preparative organic chemistry. Telluronium ylides prepared by deprotonation of telluronium salts and used *in situ* react with various carbonyl compounds and compounds with multiple bonds to give cyclopropanes, aziridines, oxiranes, alkenes, benzylic and propargylic alcohols and β-hydroxy nitriles. The majority of these reactions proceed in good yields and with high stereoselectivity. Of special interest is the synthesis of alkenes containing electron-withdrawing substituents (CO_2R, COR, CN) at the double bond by the reaction of dialkyl tellurides with the corresponding organobromine derivatives and aldehydes. Such reactions have no analogies in the chemistry of sulfonium and selenonium salts. X-ray diffraction analysis of more than 60 telluronium salts revealed that the coordination number of the tellurium atom varies from 3 to 6 due to its ability to form secondary bonds with various heteroatoms.

Further progress in the chemistry of telluronium salts seems to be associated with the development in three major areas, *viz.*, (i) development of novel preparative methods for telluronium salts from organoelement compounds, in the first place, from organomercury, organosilicon and organotin derivatives and highly electrophilic organotellurium intermediates; (ii) search for novel reactions aimed at the synthesis of various organic derivatives based on telluronium salts. This task is attainable due to the ease of cleavage of $C-Te^+$ bonds. Special attention should be given to further improvement of one-pot processes where catalytic amounts of telluronium salts or their precursors (diorganyl tellurides) can be used. And finally, (iii) the continuation of X-ray diffraction studies of telluronium salts containing various types of intramolecular coordination bonds ($O \rightarrow Te$, $N \rightarrow Te$) may result in the discovery of novel structural types of these compounds.

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