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Specific features of the reactivity of organotellurium compounds

I D Sadekov, V I Minkin

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Abstract. The characteristic features of the reactivity of the principal classes of organic compounds of tellurium(II) and tellurium(IV) are examined and compared with the analogous compounds of sulfur and selenium. The factors determining the specific features of the chemical behaviour of organotellurium compounds are characterised. It is shown that the possibility of the convenient introduction of tellurium-containing functional groups, their structural modification, elimination, the low-temperature elimination of the tellurium atom as a result of the low energy of the C – Te bond, and the high nucleophilicity of the tellurolate anions and diorganyl tellurides together with other properties create preconditions for the development of a new methodology in organic synthesis. The bibliography includes 446 references.

I. Introduction

The first representative of organotellurium compounds — diethyl telluride — was obtained by Woehler[1] more than 150 years ago, but the principal data concerning the method of synthesis, reactivity, and structure of organic derivatives of tellurium have been obtained during the last 20 – 25 years. These compounds have been considered in monographs,[2–5] while individual classes of acyclic and cyclic tellurium-containing compounds have been the subject of review articles.[6–22] Together with profound analogies between the structure and reactivity of organic compounds of tellurium and [other] higher chalcogens, the studies which have been carried out have revealed significant characteristic features of the chemical behaviour of organotellurium compounds compared with their sulfur and selenium analogues. The present authors' previous review was devoted to the structure of the latter.[23] The present, more complete review takes into account new data which have accumulated during recent years. All the research results analysed are classified in terms of the specific features of organotellurium compounds which distinguish them from those of the other chalcogens and not in terms of the individual classes of such compounds, as was done in previous reviews.[23]

The specific structure and chemical behaviour of organic derivatives of tellurium are determined mainly by the following factors.

1. The increased nucleophilicity and halophilicity of the RTe^- and Te^{2-} anions compared with those of the other organochalcogen derivatives.

2. The reduced thermodynamic and kinetic stability of the tellanyl derivatives RTeX.

3. The ability of the tellurium atom in various coordination states to form extremely stable (compared with sulfur and selenium atoms) intramolecular coordinate bonds with electron-excess centres (oxygen, nitrogen), which play an important role in the stabilisation of the corresponding organotellurium compounds and which influence the stereochemistry of their reactions.

4. The unusual tendency of derivatives of dicoordinate tellurium — diorganyl tellurides R_2Te and diorganyl ditellurides R_2Te_2 — to enter into oxidative addition reactions with formation of structures containing tellurium in the Te(IV) and Te(VI) oxidation states.

5. The fact that the nucleophilicity of diorganyl tellurides is the highest in the series of diorganyl chalcogenides R_2M (M = O, S, Se, Te).

6. The high polarisation of the $Te=X \rightleftarrows Te^+ - X^-$ bonds (X = CR_2, NR, O) which is responsible for the specific reactions of π-telluranes.

7. The sharply increased stability of derivatives of tetracoordinate tellurium — σ-tellanes R_2TeX_2 and $RTeX_3$ as well as tetraorganyltellanes R_4Te — compared with the analogous selenium and sulfur derivatives.

8. The low energy of the C – Te bond (compared with those of the C – S and C – Se bonds).

These specific properties are responsible for the increasing application of organotellurium compounds in preparative organic chemistry (see the relevant reviews[24–31]).

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II. Nucleophilic and halophilic properties of tellurolate and telluride anions

The usual methods of synthesis of organic anions RM^- containing Group VIA elements (M = O, S, Se) from the corresponding hydride derivatives RMH are virtually impossible to apply in the case of their tellurium analogues. Until recently, only a few alkanetellurols had been described. These are thermally unstable and are extremely readily oxidised to ditellurides not only by atmospheric oxygen[2,3] but even by dilute H_2SO_4;[32] tellophenols have not been isolated in a pure form. (Trimethylsilyl)silanetellurol[33] $(Me_3Si)_3SiTeH$ and 2,4,6-trialkyltellurophenols[34] 2,4,6-$R_3C_6H_2TeH$ (R = Me, Pr^i, Bu^t), obtained by protonating the lithium salts of tellurols, are relatively stable by virtue of the presence of bulky organic groups. The organyltellurolate anions **1** are therefore usually obtained by reducing diorganyl ditellurides with alkali metal tetrahydroborates in alcohol or a benzene–alcohol mixture[2,3] and with alkali metals in liquid ammonia,[2,3,32,35–38] ether,[39] tetrahydrofuran (THF),[40,41] THF–dimethylformamide (DMF),[42] and hexamethylphosphoramide (HMPA)[43] or by the reactions of organolithium derivatives with elemental tellurium in ether or THF.[2,3] The tellurolate anions are oxidised extremely readily even by atmospheric oxygen and are therefore employed only in situ. These anions exhibit the highest nucleophilicity in the series of analogous derivatives of Group VIA elements. Although there are hitherto virtually no quantitative literature data on the nucleophilicity parameters of the tellurolate anions (such as the Swain–Scott parameter n[44] or the Ritchie parameter N_+[45]), the high basicity and polarisability of RTe^- guarantee that their nucleophilicity is even higher than the current record holders on these scales — the RS^- and RSe^- anions.

Quantitative kinetic data on the relative reactivities of the benzenechalcogenolate anions PhM^- (M = S, Se, Te) have been obtained only for $S_{RN}1$ reactions. In the interaction of 2-quinolinyl radicals, the relative rate constants increase in the sequence PhS^- (1.0) < $PhSe^-$ (5.8) < $PhTe^-$ (28.0),[46] while in the case of the 9-anthranyl radicals the increase is in the sequence PhS^- (1.0) < $PhSe^-$ (1.4) < $PhTe^-$ (3.2).[47]

By virtue of their high nucleophilicity, the tellurolate anions **1** readily add both to activated (α-ethynylcarbonyl compounds[43,48–55]) and nonactivated triple bonds,[43,50,52,53,55–58] which leads to the vinyl tellurides **2** and **3** in high yields.

$$R^1C{\equiv}CCOR^2 + ArTe^- \longrightarrow \underset{\mathbf{1}}{} \underset{TeAr}{R^1C{=}CHCOR^2} \quad \mathbf{2}$$

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

$$R^1C{\equiv}CH + R^2Te^- \longrightarrow R^1CH{=}CHTeR^2, \quad \underset{TeR^2}{R^1C{=}CH_2}$$

$\mathbf{3}$ $\mathbf{3a}$

R^1 = Alk, Ar, CH_2OH; R^2 = Ar, Me.

The addition of the tellurolate anions to activated triple bonds is regiospecific and is always accompanied by the formation of only type **2** compounds. In the case of the esters of ethyne-1-carboxylic acids, only the (*Z*)-isomers or mixtures of (*Z*)- and (*E*)-isomers with the former greatly predominating (more than 90%) are formed.[51] The preferential formation of (*Z*)-isomers was observed also in the reactions of activated ethynes, but these reactions are less regiospecific and, together with compounds **3**, the formation of the isomeric alkenes **3a** is observed.[53,55,58]

The addition of potassium telluride, generated from tellurium in a superbasic medium [KOH/HMPA(DMSO)/H_2O], first investigated by Trofimov et al.,[59] leads to vinyl telluride as the main product. (For further details about this and similar reactions, see the review of Gusarova et al.[12]) (*Z*)-Divinyl tellurides **4** have been synthesised in high yields by the reaction of Na_2Te (obtained by the reduction of tellurium with sodium tetrahydroborate in an aqueous alcoholic solution of NaOH) with monosubstituted ethynes.[58] In certain cases, the 1,1-disubstituted isomers **4a** are formed in yields up to 10% together with the tellurides **4**.[58]

$$RC{\equiv}CH + Na_2Te \longrightarrow \underset{\mathbf{4}}{(RCH{=}CH)_2Te}, \quad \underset{\mathbf{4a}}{(H_2C{=}CR)_2Te}$$

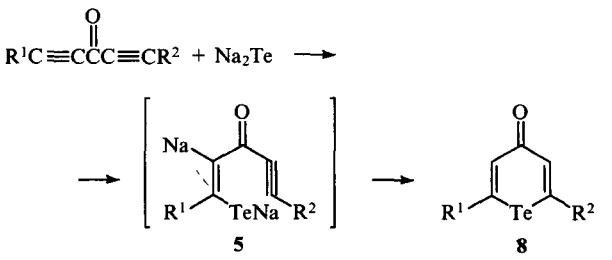
R = Ph, 4-ClC_6H_4, 4-BrC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$,

$HOCH_2CH{=}CMe$, $\overline{CH_2CH_2OCH_2CH_2NCH_2}$,

$\overline{CH_2(CH_2)_4CH{=}C}$, $\overline{CH_2(CH_2)_3OCHOCH_2}$.

The intramolecular nucleophilic addition reactions of the tellurolate anions **5**–**7**, formed as intermediates in the interaction of Na_2Te with the corresponding ethynes, have been used for the synthesis of certain tellurium-containing heterocycles which are difficult to obtain by other methods. 2,6-Diorganyltellurapyran-4-ones **8**,[60–64] 2-*H*-1,3-thiatellurols **9** (M = S),[65] 2*H*-1,3-ditellurols **9** (M = Te),[66] and 1-thia-4-telluracyclohexa-2,5-dienes **10**[67] have been obtained by this procedure (Scheme 1).

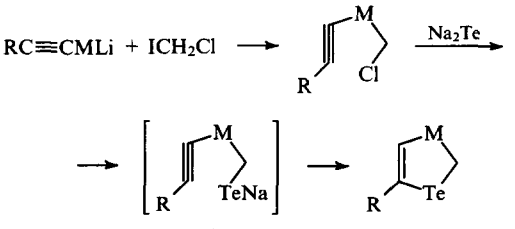
Scheme 1



$\mathbf{5}$ $\mathbf{8}$

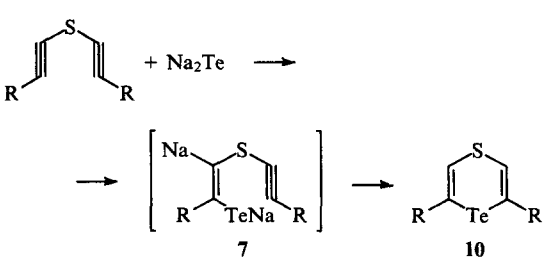
$R^1 = R^2$ = $SiMe_3$, Me, Bu^t, Ph; R^1 = Ph,

R^2 = $SiMe_3$, H, $(CH_2)_3OH$, 2-C_4H_3S, $(CH_2)_3OSiMe_2Bu^t$, 4-FC_6H_4, 2,5-$F_2C_6H_3$, 4-$MeOC_6H_4$.



$\mathbf{6}$ $\mathbf{9}$

M = S, R = Me, Et, Bu^t, Ph; M = Te, R = H, Me, Et, Ph.



$\mathbf{7}$ $\mathbf{10}$

R = H, Me, Bu^t.

In the last case, sodium telluride reacted much faster than sodium selenide and especially sodium sulfide.

The reactions involving nucleophilic addition of arenetellurolate anions to an activated double bond have been much less investigated.[57,68] A series of β-aryltellurapropionic

acids,[68] their esters,[57] and β-phenyltellurapropionitriles[57] have been synthesised with their aid in 31%–62% yield.

$$R^1CH{=}CHCOOR^2 + ArTe^- \longrightarrow ArTeCHCH_2COOR^2 \quad (R^1)$$

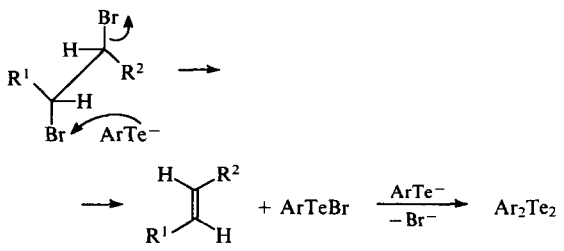
R^1 = H; R^2 = Na; Ar = Ph, 4-MeC_6H_4, 4-$EtOC_6H_4$;

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

$$RCH{=}CHCN + PhTe^- \longrightarrow PhTeCHCH_2CN \quad (R)$$

R = H, Me.

Organyltellurolate anions are not only more nucleophilic than other chalcogenolate anions but also exhibit more clearly expressed X-philic properties[69] (especially halophilic properties). As a result of this, sodium thiophenetellurolate debrominates vicinal dibromides, affording alkenes in 75%–100% yields.[70] This reaction, which proceeds with high *anti*-stereospecificity, is of definite preparative value, since it can be carried out catalytically in the presence of small amounts of ditelluride (1 mmol per 10 mmol of the halogen-containing substrate) and $NaBH_4$, which reduces the ditelluride obtained back to the tellurolate anion.

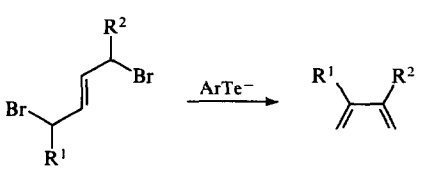


Ar = 2-C_4H_3S; R^1 = R^2 = Me, Ph, CO_2Et; R^1 = H; R^2 = C_8H_{17};

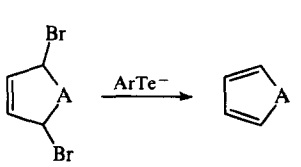
R^1 = CO_2H; R_2 = Me, Ph; R^1+R^2 = —$(CH_2)_4$—.

It is noteworthy that substituted 1,2-dibromocyclohexanes undergo similar debrominations also on treatment with sodium thiophenoxides.[71,72] However, in the case of 1,2-dihaloethanes only the products of the nucleophilic substitution of the halogen atoms by phenylthio-groups are formed.[73]

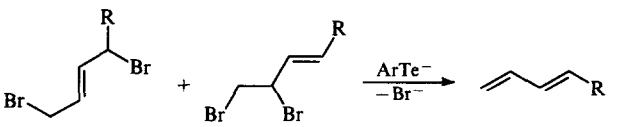
On the other hand, just as the debromination of the vicinal dibromo-derivatives described above is an example of β-halophilic elimination, the synthesis of 1,3-dienes from 1,4-dibromoalk-2-enes or their mixtures with 1,2-dibromoalk-3-enes on treatment with di(2-thienyl)ditelluride, used in catalytic amounts, and $NaBH_4$ is a δ-halophilic elimination reaction.[74] The reactions take place with high yields (60%–100%) and lead to mixtures of the (*E*)- and (*Z*)-isomers in proportions of ~9:1.



R^1 = R^2 = Me, Ph.



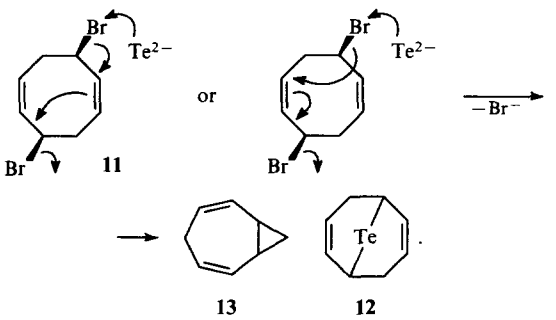
A = —$(CH_2)_2$—, —$(CH_2)_3$—, —$CH(CO_2Me)$—.



R = Et, Bu, C_6H_{13}, $(CH_2)_7OAc$, $(CH_2)_8OAc$, $C_{12}H_{25}$.

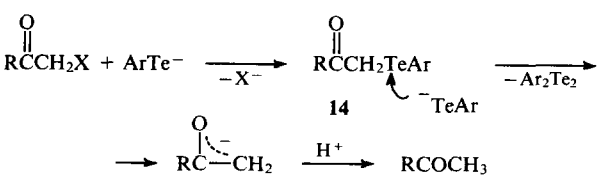
Examples of elimination of a similar kind are not known for the sulfur and selenium nucleophiles.[69]

An instance of ε-halophilic elimination is also known for the telluride anion.[75] Thus, when 3,7-dibromocycloocta-1,5-diene **11** reacts with Na_2Te, bicyclo[5.1.0]octa-2,5-diene **13** is formed together with the expected 9-tellurabicyclo[3.3.1]nona-2,6-diene **12** (yield 18%) in accordance with the following scheme:

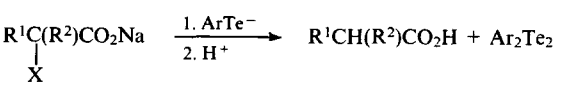


An analogous reaction is not observed when Na_2S is employed.

Another possible type of X-philic reaction — the reduction of C–Hal bonds — occurs when sodium (lithium) 2-thiophenetellurolate interacts with α-halocarbonyl compounds. For stoichiometric amounts of the reactants, the final reaction products are the corresponding ketones (or carboxylic acids) and ditellurides and not the products of the nucleophilic substitution, i.e. (2-thienyltelluro)carbonyl derivatives.[76] This is the result of the attack by the tellurolate anion on the tellurium atom of the intermediate tellurides **14**, which leads to the ditellurides and the corresponding enolates. This mechanism has been confirmed both by the isolation in certain cases of type **14** tellurides (R = $CH_2CONHPh$) and by the formation of the benzaldehyde chalcone (yield 48%) when the enolate (R = Ph) is used as the trapping agent.



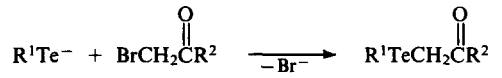
X = Cl, Br, I; R = Ph, 4-BrC_6H_4.



X = Cl, Br; R^1 = H, R^2 = Ph, 1-$C_{10}H_7$; R^1 = R^2 = Ph.

Similar results had been obtained earlier for the thiolate[77,78] and selenolate[78] anions. However, for these species the preferred mode of reaction (reduction or nucleophilic substitution) is determined primarily by the nature of the halogen. For stoichiometric amounts of the reactants and at reduced temperatures, α-chloro- and α-bromoketones afford mainly the products of nucleophilic substitution, while α-iodoketones give rise to the products of the reduction reactions. Tellurolate anions reduce all α-haloketones to ketones at room temperature.[76] However, at a very low temperature (−78 °C)

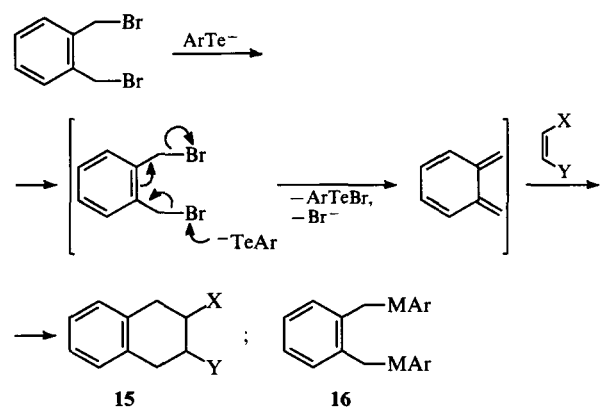
α-bromocarbonyl compounds afford the α-organyltellura-carbonyl compounds **14a** in fairly high yields (55%–92%) on interaction with tellurolate anions.[79] On the other hand, α-chloroketones are reduced even at −78 °C.



R^1 = Bu, Ph, CH_2=CH, BuC≡C, Me_3SiC≡C;

R^2 = OR^3 (R^3 = Li, Et, 4-$NO_2C_6H_4$).

The available data do not permit the quantitative characterisation of the halophilicities of S, Se, and Te organylchalcogenolate anions. However, bearing in mind the higher halophilicity of the methaneselenolate anion compared with the sulfur analogue (in the reaction with benzyl halides[80]) and the easy reduction of phenacyl phenyl sulfide by the thiophene-2-tellurolate anion,[76] one could postulate that the halophilicity increases from S to Te. The higher halophilicity of the tellurolate anions compared with the structurally related selenolate anions is indicated also by the result of the reactions of α,α′-dihalo-*o*-xylenes with these anions.[81] In the presence of an excess of the dienophile, the reactions of α,α′-dibromo(iodo)-*o*-xylenes with arenetellurolate anions (generated by the reduction of the corresponding diaryl ditellurides with $NaBH_4$) in boiling xylene, which proceed via the intermediate formation of *o*-quinodimethane, lead to the Diels–Alder adducts **15** in 20%–53% yields. The most probable mechanism of these reactions[81] is presented below.



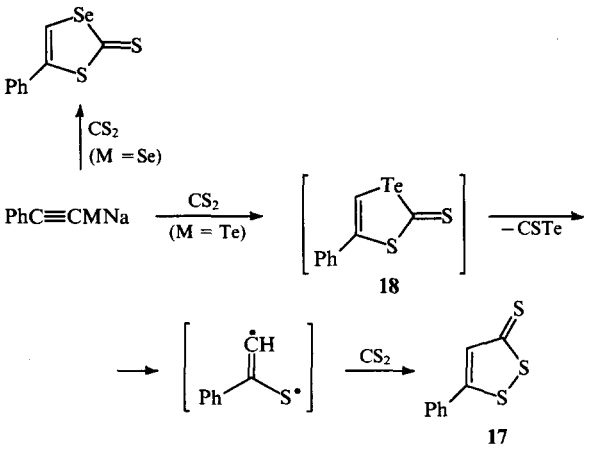
15 **16**

Ar = Ph, 3-MeC_6H_4, 3-ClC_6H_4, 4-$MeOC_6H_4$;

X = Y = CO_2Et; X = H, Y = CO_2Et, CN, Me.

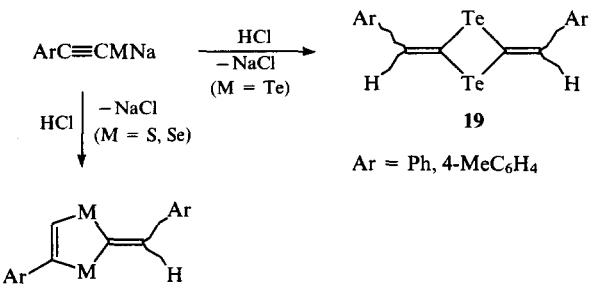
Under the same conditions, sodium benzeneselenolate gives rise to only the product of nucleophilic substitution at the C(sp^3) atoms — α,α′-bis(phenylseleno)-*o*-xylene **16** (M = Se) in 75% yield together with the product of nucleophilic addition to the double bond — ethyl phenylselenopropionate — when ethyl acrylate is employed as the dienophile.[81] Incidentally, the α,α′-bis(aryltello)-*o*-xylenes **16** (M = Te) are also formed in the reaction of arenetellurolate anions, since the product of the oxidation of compounds **16** — *o*-phthalic aldehyde — has been isolated in ~30% yield in all cases. The preferential formation of the telluride **16** (M = Te, Ar = 4-$EtOC_6H_4$) (yield 50%) has also been observed when the reaction was carried out at room temperature.[82]

The reactions examined below, the mechanisms of which are frequently obscure, are evidently not associated with the nucleophilic or halophilic properties of the organyltellurolate anions. However, the diversity of these reactions compared with the other RM^- (M = S, Se) anions makes it possible to consider them in the present section. In particular, a specific behaviour compared with ethynethiolate(selenolate) anions and geminal dithiolate (diselenolate) dianions, has been observed in certain reactions of their tellurium analogues. Thus, in contrast to sodium phenylethyneselenolate, which affords 5-phenyl-1,3-thiaselenole-2-thione on interaction with CS_2,[83] the product obtained in the similar reaction of sodium phenylethynetellurolate was 5-phenyl-1,2-dithiole-3-thione **17**.[84] The possible process mechanism, involving the dissociation of the C–Te bond in the intermediate 1,3-thiatellurole **18**, is presented below.[84]



18 **17**

Another example of the specific behaviour of the phenylethynetellurolate anion is its protonation (in solution in DMSO) by an ethereal solution of HCl. The only products of this reaction are the *cis*- and *trans*-1,3-ditelluretanes **19**[84–86] and not their isomers — benzylidene-4-aryl-2*H*-1,3-ditelluroles, which was suggested[87] when the reaction was first described. A mixture of the same compounds **19** is also formed in the reaction of phenylethyne with powdered tellurium under highly basic conditions.[88] On the other hand, the protonation of structurally similar thiolate and selenolate anions leads to the benzylidene-4-aryl-2*H*-1,3-dichalcogenoles **20**.[89]



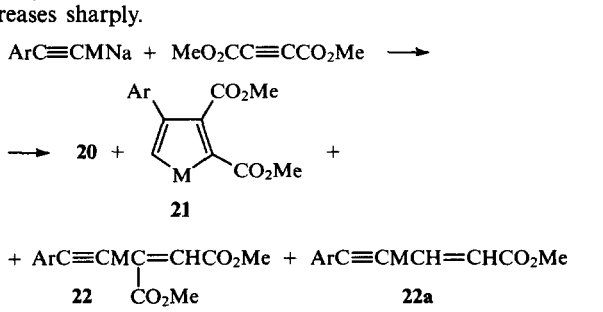
19

Ar = Ph, 4-MeC_6H_4

20

Ar = Ph

The interaction of phenylethynechalcogenolate anions with dimethyl ethynedicarboxylate results in the formation of a mixture of the corresponding chalcogenophenes **21**, the 1,3-dichalcogenoles **20**, and the products **22** and **22a** of the nucleophilic addition of the anions to the triple bond.[84,90] On passing from sulfur to tellurium, the yield of such adducts increases sharply.

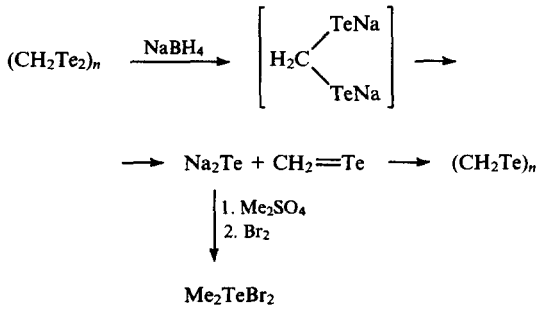


21

22 **22a**

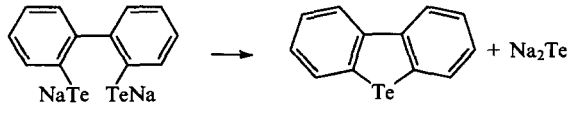
M = S, Se, Te

Significant differences have been observed also in the behaviour of geminal dichalcogenolate anions. Whereas the disodium salt of methanediselenol[91] is fairly resistant to heating and undergoes in solution the usual chemical reactions, its tellurium analogue, obtained by reducing poly(methylene ditelluride)[92] with $NaBH_4$ in ethanol, readily disproportionates to sodium telluride and telluromethanol, which polymerises subsequently to poly(methylene telluride).[93]

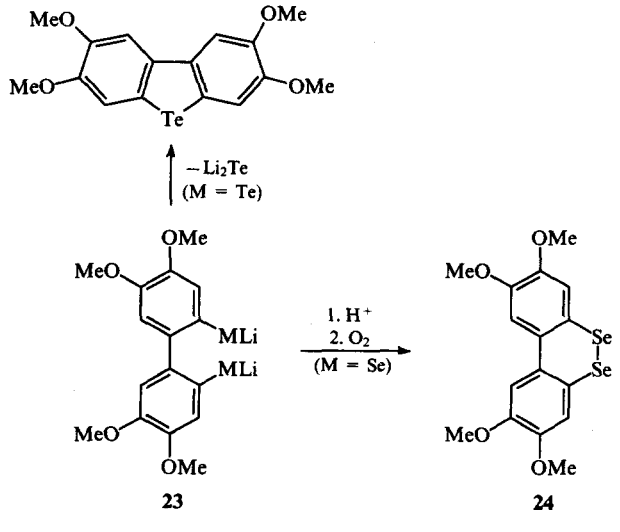


The mechanism of the formation of poly(methylene telluride) involving the reduction of poly(methylene ditelluride) with $NaBH_4$ in methanol and the subsequent alkylation of the ditellurolate dianion by methylene bromide (iodide) therefore appears erroneous.[94] Evidently, poly(methylene telluride) is formed via the disproportionation of the dianion, as described above, and not as a result of the alkylation reaction.

The sodium salt of bipyridyl-2,2'-ditellurol also undergoes a similar disproportionation with elimination of sodium telluride.[95] The second reaction product, isolated in a yield exceeding 90%, is dibenzotellurophene.



With the aid of this reaction, it is possible to account for the formation of various final products in the reactions of 2,2'-dilithio-4,4',5,5'-tetramethoxybiphenyl with tellurium and selenium.[96] In the former case, the product is the corresponding dibenzotellurophene, while the dilithio-derivative of the diselenole **23** (M = Se), which is incapable of undergoing the disproportionation reaction described above, is converted into the heterocyclic diselenide **24**, albeit in a very low yield.



23 **24**

III. Kinetic lability of organotellanyl halides

In contrast to the selenium and especially sulfur analogues, the tellanyl derivatives RTeX (X = Hal, OCOMe, SCN, N_3) are relatively unstable compounds, which readily decompose at room temperature both in the crystalline state and in solution.

Tellanyl halides, which are mainly aromatic derivatives, have been most thoroughly investigated among the tellanyl derivatives. The stability of arenetellanyl halides ArTeX increases in the sequence Cl < Br < I as the electronegativities of the atoms in the Te–X bonds approach equality. Thus the bromo-derivatives decompose fully at room temperature in 24 h, while arenetellanyl iodides in the crystalline state can be stored without decomposition for several weeks.[97] In the case of alkanetellanyl halides, the chloro-derivatives are more stable, while alkanetellanyl iodides decompose in several minutes.[98] The overall mechanism of the decomposition of aryltellanyl halides involves the formation of diorganyltellurium dihalides and elemental tellurium.[26,99]

$$2\,RTeX \longrightarrow R_2TeX_2 + Te$$

Such instability is predominantly kinetic in nature and is induced both by the relative ease (compared with other chalcogenyl halides) of dissociation of the chalcogen–halogen bond in solvating solvents and by the increased capacity of compounds of dicoordinate tellurium for associative oxidative addition reactions. Individual decomposition reactions of organyltellanyl halides are also facilitated by the comparative ease of elimination of the tellurium atom.

The principal methods for the stabilisation of organyltellanyl halides are associated either with the generation in their molecules of significant steric hindrance to the access of the reactants to the TeX groups or with the coordination of the Te(II) centre, which results in its transition to a more stable higher oxidation state. Thus the increased stability of biphenyl-2-tellanyl[100] and naphthalene-2-tellanyl[101] iodides, compared with other aryltellanyl halides, can be accounted for by the steric shielding of the TeI groups. The naphthalene derivative is thus the first arenetellurenyl iodide isolated in an analytically pure form. On the other hand, the first stable alkanetellanyl halides were tris(trimethylsilyl)methanetellanyl halides $(Me_3Si)_3CTeX$ (X = Cl, Br, I), obtained by oxidising the corresponding ditellurides with the halogen or SO_2Cl_2.[102] The stability of these compounds is undoubtedly associated with the bulky tris(trimethylsilyl)methyl group. However, the high stability of tris(trimethylsilyl)methanetellanyl pseudohalides $(Me_3Si)_3CTeX$ (X = CN, NCO, NCS, NCSe, N_3), obtained by the exchange reaction between tris(trimethylsilyl)methanetellanyl iodide and the corresponding AgX, is also noteworthy.[103]

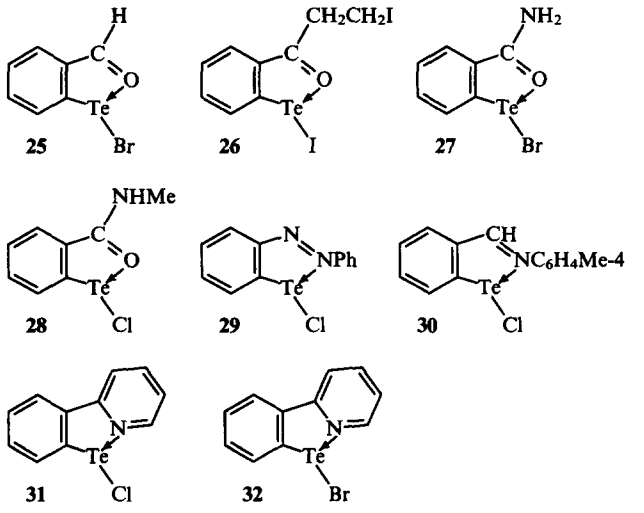
A second way of stabilising tellanyl halides involves the formation of complexes with neutral ligands,[2,3] the tellurium atom playing the role of the coordination centre.

IV. Intramolecular Te←O(N) coordination as a factor stabilising derivatives of dicoordinate tellurium

The most effective procedure for increasing the stability of tellanyl halides and other tellanyl derivatives involves the introduction in the *o*-position relative to the Te–Hal functional group of substituents capable of forming stable intramolecular Te←O(N) coordinate bonds involving their O or N atoms.[104–106] Compounds of this kind are also useful synthons in preparative organic chemistry and in the first place in the chemistry of tellurium-containing heterocycles.

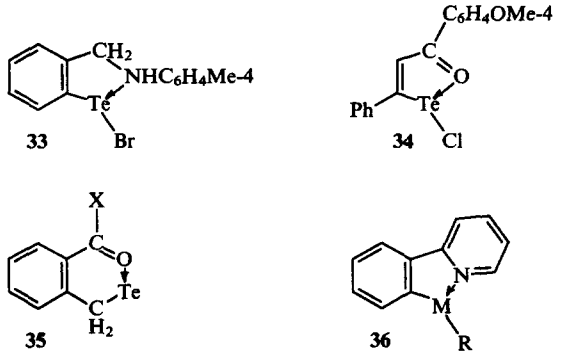
1. Tellanyl halides

Tellanyl halides are stabilised by substituents such as CHO,[107,108] COR,[51,109–118] $CONR_2$,[119,120] NO_2,[121] N=N,[122] CH=N [104,123–127] (this bond can also be part of the pyridine ring [128–130]), and CH_2NR_2.[127,131,132] The lengths *d* of the intramolecular Te←O and Te←N coordinate bonds, which belong to the class of three-centre four-electron (hypervalent) bonds, are in the range 2.21–2.37 Å (compounds **25**–**32**) and are much smaller than the sums of the van der Waals radii of the elements (3.60 Å for Te and O and 3.70 Å for Te and N),[133] approaching the lengths of the usual covalent bonds. The replacement of the sp^2-hybridised by the sp^3-hybridised nitrogen atom weakens somewhat the intramolecular coordination, which lengthens the Te–N bond (of the bond lengths in compounds **30** and **33**).



Compound	*d*(Te–O)/Å	Ref.	Compound	*d*(Te–N)/Å	Ref.
25	2.31	108	**29**	2.21	122
26	2.368	118	**30**	2.239	104, 124
27	2.237	119	**31**	2.236	130
28	2.25	119	**32**	2.236	130
34	2.19	51	**33**	2.375	129

The intramolecular Te←O coordinate bonds stabilise not only arenetellanyl halides but also vinyltellanyl (compound **34**)[51] and alkanetellanyl (compounds **35**)[134] halides.

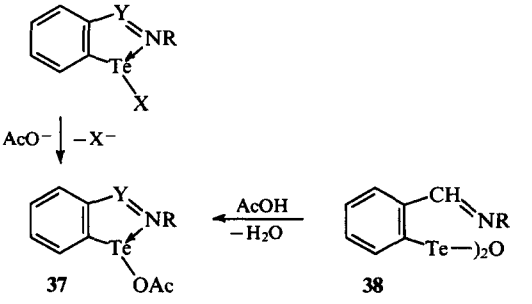


Comparison of the properties of compounds with the same structure of the organic ligand and of the chalcogen-containing groups is desirable for the quantitative characterisation of the relative strengths of the intramolecular O(N)→M coordinate bonds in the series M = S, Se, Te, the measure of which may be either the difference (Σ) between the van der Waals radii of M and O(N) [M···O(N)] or the Pauling bond order (*n*). Although there are comparatively few data, they make it possible to infer that the strength of bonds of this kind increases on passing from sulfur to tellurium. Thus comparison of the Se←N (2.813 Å)[135] and Te←N (2.695 Å)[129] bond lengths in *p*-ethoxyphenyl 2-(2-pyridyl)phenyl chalcogenides **36** with the sums of the van der Waals radii of selenium and nitrogen (3.55 Å)[133] and of tellurium and nitrogen (3.70 Å)[133] indicates the greater strength of the coordinate bonds involving a tellurium atom.

X-Ray diffraction data for benzoisotellurazole[136] and 1,2,5-telluradiazole[137] and their selenium analogues may serve as indirect evidence for the greater strength of the coordinate bonds with participation of tellurium atoms. Strong intermolecular Te···N bonds have been noted for tellurium-containing heterocycles in crystals. Their lengths are 2.40 Å for benzoisotellurazole and 2.764 Å for 1,2,5-telluradiazole (the sum of the van der Waals radii of Te and N is 3.70 Å).[133] The Se···N bonds have not been found in benzoisoselenazole, while in 3,4-diphenyl-1,2,5-selenazole they are much weaker than in telluradiazole. The anomalous physical properties of benzoisotellurazole and 1,2,5-telluradiazole compared with other chalcogen-containing heterocycles, namely the high melting points and sparing solubility in the usual organic solvents, are also explained by the presence of these intermolecular bonds.

2. Aryltellanyl acetates

Aryltellanyl acetates without intramolecular Te←O(N) coordinate bonds have not been obtained. However, stable tellanyl acetates **37** containing an azo-group or an azomethine group in the *o*-position relative to TeOAc group have been synthesised by the exchange reactions of the corresponding telluranyl halides with AcONa [138] or AgOAc [104,126] and also by the interaction of aryltellanic acids **38** with acetic acid.[126]



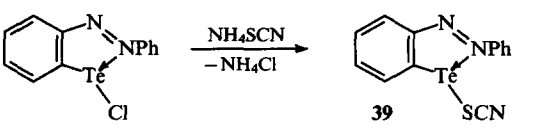
Y = N, R = Ph;

Y = CH; R = 4-MeC_6H_4, 4-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$.

The lengths of the coordinate bonds in compounds **37** (Y = N, R = Ph) and **37** (Y = CH, R = 4-MeC_6H_4) are 2.26 Å [138] and 2.297 Å [104] respectively.

3. Aryltellanyl thiocyanates

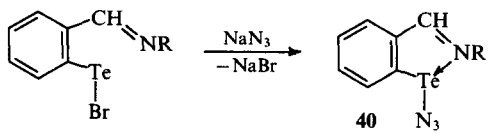
The interaction of equimolar amounts of diaryl ditellurides and thiocyanogen leads to unstable alkyltellanyl thiocyanates, which have been isolated in the form of complexes with thiourea, 2-picoline, and other nitrogen heterocycles.[139] However, the tellanyl thiocyanate **39**, containing the intramolecular Te←N coordinate bond (2.243 Å),[138] is extremely stable in the crystalline state.



It is noteworthy that the lengths of the intramolecular Te←O(N) coordinate bonds in the tellanyl derivatives ArTeX are in the range 2.130–2.375 Å (depending on the nature of X).[104–106] An increase in bond length for different X in the following sequence is then observed: Cl < Br < I < S_2CNMe_2, which agrees with the sequence based on decreasing electronegativity of the substituents X.

4. Arenetellanyl azides

The intramolecular Te←N coordination also ensures a high stability of the arenetellanyl azide **40**, obtained by the reactions of the corresponding arenetellanyl bromides with NaN_3.[126] The attempts to obtain the selenium analogues of these compounds from benzeneselanyl chloride and Me_3SiN_3 led actually only to diphenyl diselenide as a result of the rapid decomposition of the benzeneselanyl azide formed initially.[140] (By virtue of the steric hindrance due to the methyl groups, mesityleneselanyl azide is more stable and can be isolated on a preparative scale).[140] Bearing in mind that the selenyl derivatives ArSeX are in general always more stable than the analogous tellurium compounds, one must rule out the possibility of obtaining arenetellanyl azides from compounds in which the tellurium atom is not involved in intramolecular coordination.



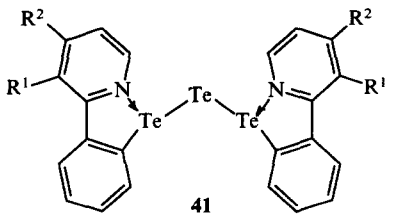
40

R = Ph, 4-MeC_6H_4.

5. Other derivatives of dicoordinate tellurium

Intramolecular Te←O(N) coordinate bonds increase the stability not only of the tellanyl derivatives RTeX but also certain other derivatives of dicoordinate tellurium: tritellurides, aryl cyclopentadienyl tellurides, and bis(organylthio)tellurides.

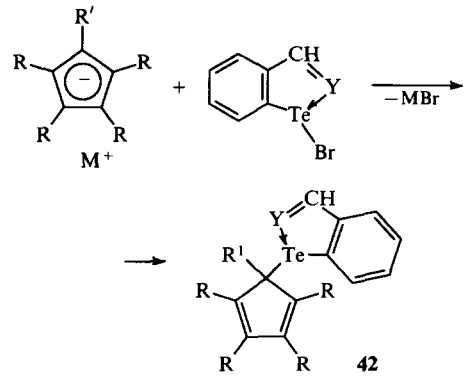
The first representative of tritellurides isolated in a pure form was bis[tris(trimethylsilyl)methyl] tritelluride $[(Me_3Si)_3C]_2Te_3$.[141] The stability of this compound is due to the presence of the bulky tris(trimethylsilyl)methyl group, which gives rise to steric hindrance to attack on the tritelluride bridge. On the other hand, the kinetic and thermal stabilities of type **41** tritellurides are associated with the intramolecular Te←N coordination in these compounds.[128,129] The Te←N bond length in bis[2-(2-pyridyl)phenyl]tritelluride **41** ($R^1 = R^2 = H$) is 2.554 Å.[128]



41

$R^1 = R^2 = H$; $R^1 + R^2$ = —(CH=CH)$_2$—.

Although aryl cyclopentadienyl sulfides and selenides are thermally stable, the attempts to obtain aryl cyclopentadienyl tellurides by the reaction of metal cyclopentadienides with benzenetellanyl bromide were unsuccessful.[142] However, the stable tellurides **42** have been obtained by the reactions of arenetellanyl bromides containing the *o*-formyl or *o*-aldimine groups, capable of forming strong intramolecular Te←O(N) coordinate bonds.

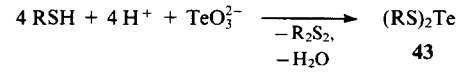


42

R = CO_2Me; R′ = CO_2Me; Y = O, NPh, 2-MeC_6H_4N;

R = CO_2Me; R′ = Me; Y = NPh, 4-$MeOC_6H_4N$.

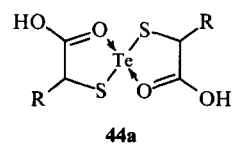
Yet another class of derivatives of dicoordinate tellurium, the stability of which is a consequence of the presence of the Te←O coordinate bonds comprises the bis(organylthiyl) tellurides **43**. Bis(benzenethiyl) telluride **43** (R = Ph) and bis(naphthalene-2-thiyl) telluride **43** (R = 2-$C_{10}H_7$), obtained by the interaction of the corresponding thiols with Na_2TeO_3, decompose very rapidly into diaryl disulfides and tellurium when they are kept in the crystalline state and especially in solutions.[143]



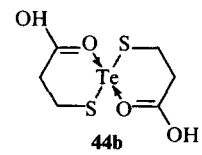
43

R = Ph, 2-$C_{10}H_7$.

Compounds **44a–c**, the carboxy-groups of which are capable of forming Te←O coordinate bonds, are much more stable.[143] According to the authors, two coordinate O←Te bonds are formed in their molecules.

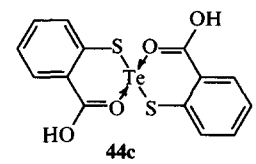


44a



44b

R = H, Me.



44c

According to IR spectroscopic data, a stronger Te←O bond and hence a more powerful stabilisation effect are manifested for five-membered chelates compared with six-membered ones.

V. Oxidative addition reactions of dicoordinate tellurium derivatives

One of the characteristic features of dicoordinate tellurium derivatives — diorganyl tellurides R_2Te and diorganyl ditellurides R_2Te_2 — is their ability to enter into oxidative addition reactions. Derivatives of dicoordinate sulfur and selenium undergo similar reactions. However, whereas in the case of tellurides (ditellurides) the reaction products are the stable σ-tellanes R_2TeX_2 or $RTeX_3$ with covalent Te–X bonds, the oxidation of the sulfides and selenides R_2M (M = S, Se) by the halogens X_2 results in the formation (depending on the nature of the chalcogens M and the halogens X) of either the charge-transfer complexes $R_2M\cdots X_2$

(M = S, Se, X = I; M = S, X = Br) or of σ-chalcogenanes R_2MX_2 (M = S, Se, X = F, Cl; M = Se, X = Br) (for a more detailed description see Section VIII).

Data on the most typical oxidation-reduction addition reactions of various types of organic derivatives of tellurium(II) are presented below.

1. Diorganyl tellurides

Diorganyl tellurides having different structures — dialkyl, aryl alkyl, and diaryl tellurides — readily combine with chlorine,[2,3] bromine,[2,3] iodine,[2,3] and fluorine (diluted with an inert gas)[144,145] under mild conditions (room or reduced temperatures), forming the corresponding σ-tellanes $R^1TeX_2R^2$. The latter are stable crystalline compounds which can be effectively purified by the usual recrystallisation. They are readily reduced to diorganyl tellurides in yields which are in many cases close to quantitative. Various reductants are employed: Na_2S, $K_2S_2O_5$ ($Na_2S_2O_5$), Na_2SO_3, $NaHSO_3$, $Na_2S_2O_3$, $Na_2S_2O_4$, $LiAlH_4$, $NaBH_4$, $N_2H_4 \cdot H_2O$,[2,3] thiourea dioxides,[146,147] zinc powder in benzene or acetic acid, $SnCl_2$, methyl (ethyl)magnesium iodide,[2,3] and lithium diethylamide.[148] The conversion of diorganyl tellurides into σ-tellanes with subsequent reduction of the latter is therefore employed for the isolation of diorganyl tellurides from reaction mixtures and for their purification.

One of the few compounds incapable of undergoing some of the reactions indicated above is $(CF_3)_2Te$.[149] Whereas the reactions of chlorine and bromine lead to the corresponding σ-tellanes, on interaction with iodine, a weaker oxidant, tellurium diiodide is not formed.

Thionyl chloride and sulfuryl chloride are used as oxidants instead of gaseous chlorine in the synthesis of tellurium dichloride.[2,3] Diorganyl tellurides may be oxidised also by certain metal salts: $FeCl_3$,[150] $HgCl_2$,[150] $CuCl_2$,[150–152] and $CuBr_2$.[152] It is noteworthy that, whereas diaryl tellurides are converted only into diaryltellurium dichlorides on treatment with $CuCl_2$,[150–152] the reaction of diethyl telluride with the same oxidant proceeds in a different manner:[153]

$$Et_2Te + CuCl_2 \longrightarrow Et_2TeCl_2 + Et_2Te \cdot CuCl.$$

Diorganyl tellurides are converted into the corresponding tellurium difluorides not only on treatment with fluorine[144,145] but also on reaction with SF_4,[154] XeF_2,[145,155,156] ClF,[156] Ph_2SF_2,[144] and $(4\text{-}MeC_6H_4)_3BiF_2$.[157–159]

$$Ar_2Te + XY \longrightarrow Ar_2Te\begin{matrix}X\\Y\end{matrix}$$

X = Y = NCS; X = Br, Y = I, CN; X = I, Y = Cl.

Diorganyl tellurides also enter into reactions involving the oxidative addition of thiocyanogen,[160–165] the interhalogens (ICl, IBr),[164] and halogen cyanides (BrCN, ICN),[164] forming the corresponding σ-tellanes in high yields.

The oxidation of diorganyl tellurides by lead tetraacetate, which occurs in benzene or toluene solutions at room temperature, leads to diorganyltellurium diacetates in high yields.[166–168]

$$R_2Te + Pb(OAc)_4 \xrightarrow[-Pb(OAc)_2]{} R_2Te(OAc)_2$$

R = Ar, Alk.

The reactions of diorganyl tellurides with certain oxidants, leading to σ-tellanes, proceed via the intermediate formation of telluroxides. Thus the interaction of diorganyl tellurides with benzoyl peroxide affords low yields of diorganyltellurium dibenzoates.[169,170] This mechanism is confirmed by the formation of diaryltellurium dicarboxylates in the reactions of diaryl telluroxides with percarboxylic acids[171,172] and their anhydrides.[171,173]

$$R_2Te + (PhCOO)_2 \xrightarrow[-(PhCO)_2O]{} [R_2TeO] \xrightarrow{(PhCO)_2O} R_2Te(OCOPh)_2$$

The results of the reactions of tellurides with dilute HNO_3, leading to diorganyltellurium dinitrates, have also been explained in terms of the 'telluroxide' mechanism.[2,3]

$$R_2Te + HONO_2 \longrightarrow [R_2TeO] \xrightarrow[-H_2O]{HONO_2} R_2Te(ONO_2)_2$$

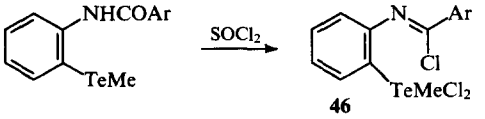
Finally, the interaction with one equivalent of *m*-chloroperbenzoic acid leads to the mixed σ-tellane **45**.[174] Taking into account the foregoing, the most probable mechanism of the formation of this σ-tellane can be represented as follows:

$$R^1R^2Te + ArCO_3H \xrightarrow[-ArCO_2H]{} [R^1R^2TeO] \xrightarrow{ArCO_2H} R^1R^2Te\begin{matrix}OCOAr\\OH\end{matrix}$$

45

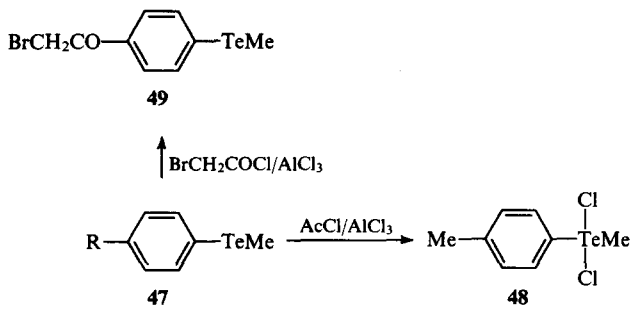
Ar = 3-ClC_6H_4.

The thermodynamic stability of σ-tellanes is the driving force of many of the reactions of diorganyl tellurides leading ultimately to σ-tellanes, while in the similar reactions of diorganyl sulfides, the formation of σ-sulfanes is not observed. Thus the arylation of diaryl ditellurides by arenediazonium salts in the presence of copper(II) halides[151,152] (see Section V) leads to diaryltellurium dihalides in high yields, while the arylation of diaryl disulfides under similar conditions results in the formation of only diaryl sulfides.[175,176] The synthesis of σ-tellanes is achieved by oxidising the diaryl tellurides formed initially with copper(II) salts.[152] Similarly the Sandmeyer reaction of 2-aminophenoxatellurane with CuCl terminates with the formation of 1,1,2-aminophenoxatellurane and not 2-chlorophenoxatellurane.[177] Another example is provided by the interaction of *N*-aroyl derivatives of *o*-methyltelluroaniline with $SOCl_2$.[178] This entails not only the conversion of the amide groups into the –N=C(Ar)Cl groups but also the oxidation of Te(II) to Te(IV), a consequence of which is the formation of the σ-tellanes **46**. These compounds are convenient synthons in the synthesis of 2-arylbenzotellurazoles.[178]



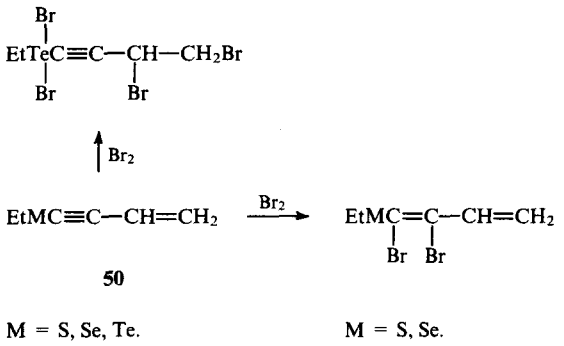
46

It is also of interest to note that the interaction of 4-methylphenyl methyl telluride **47** (R = Me) with acetyl chloride in the presence of $AlCl_3$ involves the oxidation of the initial telluride to the σ-tellane **48**[109] and not acetophenone, as in the case of the analogous selenium derivative.[179] Incidentally, the acylation of the telluroanisole **47** (R = H) by α-bromoacetyl chloride in the presence of $AlCl_3$ proceeds in the usual way, leading to the expected 4-methyltelluro-α-bromoacetophenone **49** in 52% yield.[180]



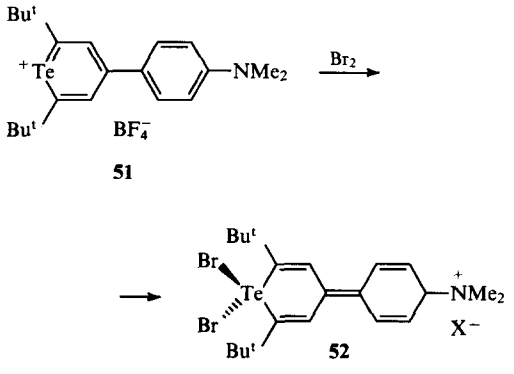
R = H, Me.

The vinylethynyl tellurides **50** behave differently in their reactions with bromine from their selenium and sulfur analogues. Whereas the latter readily combine with bromine only at the triple bond, the tellurides combine with two molecules of bromine: at the double bond and at the tellurium atom.[181]



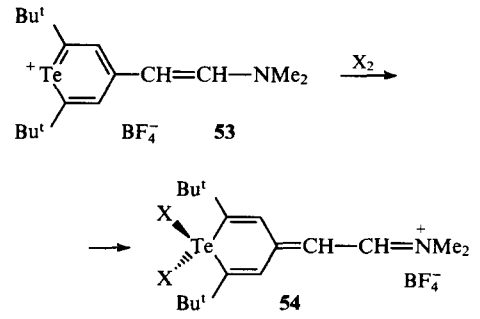
M = S, Se, Te. M = S, Se.

The reactions involving the oxidative addition of the halogens to the tellurium atom of tellurapyrylium salts containing a powerful electron donor (the dimethylamino-group) in the *p*-position relative to the heteroatom are of special interest. Bromine reacts under comparatively mild conditions with 4-(4′-dimethylaminophenyl)tellurapyrylium tetrafluoroborate **51**, which leads to the telluranes **52** in 90%–97% yields.[182] In the presence of an excess of bromine, the BF_4^- anions are exchanged for Br_3^-.

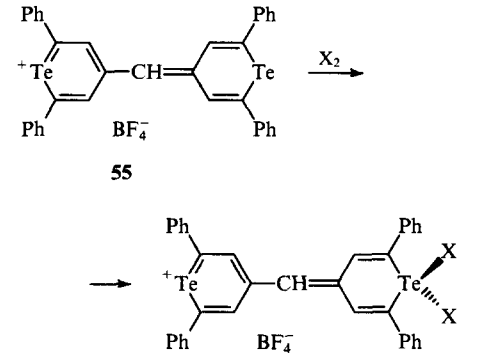


$X^- = BF_4^-, Br_3^-$.

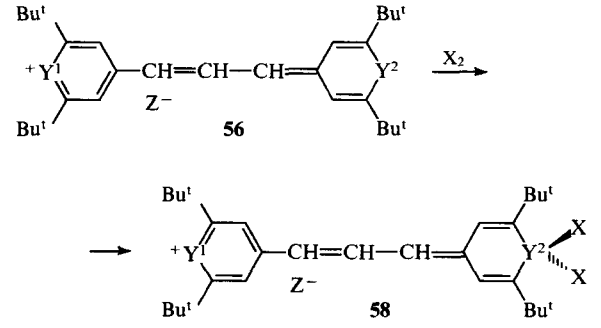
The analogous reactions with the tellurapyrylium dye **53** lead to the dibromo-derivative **54** (X = Br) and the diiodo-derivative **54** (X = I) in 67% and 91% yields respectively.[182]



The symmetrical tellurapyrylium monomethine dyes **55** and trimethine dyes **56** also enter into reactions in which the halogens undergo oxidative addition. The tellurapyrylium fragment is then retained in the σ-tellanes **57** and **58** formed.[182,183]



57, X = Cl, Br, I.



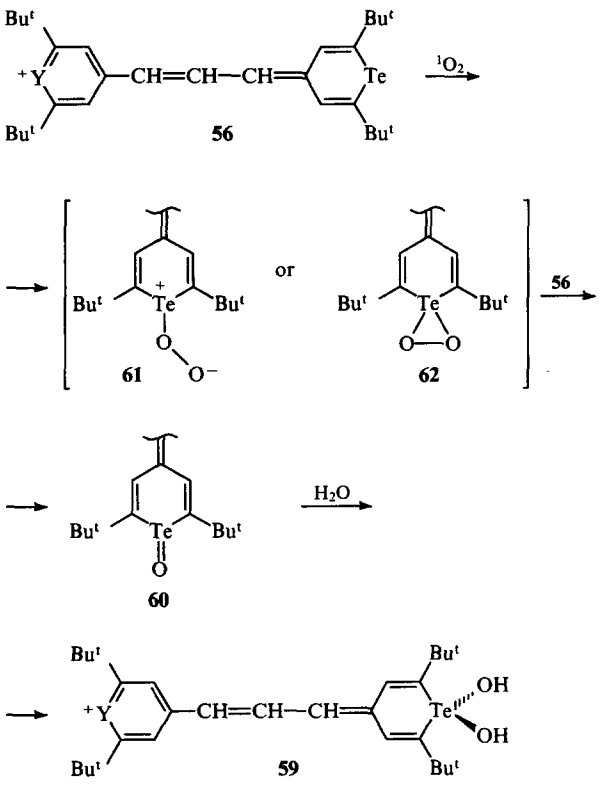
$Y^1 = Y^2 = Te$; X = Cl, Br, I;

$Z = BF_4^-, CF_3SO_3^-, PF_6^-$.

It is noteworthy that the trimethine pyrylium dyes of type **56** ($Y^1 = Y^2 = O$, S, Se) also enter into reactions with chlorine and bromine.[183,184] However, these are much slower than those involving the tellurapyrylium analogues and, which is most important, the trimethine bridges and not the heteroatoms are attacked.

Other examples of oxidative addition reactions, which take place only for the tellurapyrylium trimethine dyes **56** ($Y^1 = O$, S, Se, Te, $Y^2 = Te$) and are not characteristic of other structurally similar compounds without a tellurium atom, involve the oxidative addition of H_2O_2 or singlet oxygen in the presence of water, which results in the formation of the dihydroxytellanes **59**.[185–188] The latter reaction is carried out by the UV irradiation of solutions of the tellurium-containing dyes **56**, whereupon singlet oxygen is formed (the dyes **56** with Y = O, S, Se, or Te and $Y^2 = Te$ serve as effective photosensitisers for the singlet O_2 generation process) and oxidises compounds **56** to the tellur-oxides **60**. It has been suggested[185] that the latter are formed via the pertelluroxides **61** or telluradioxiranes **62**. The subsequent

hydration of the telluroxides **60** leads to the dihydroxytellanes **59**. Such hydration reactions are characteristic of dialkyl and alkyl aryl telluroxides.[2,3,189]

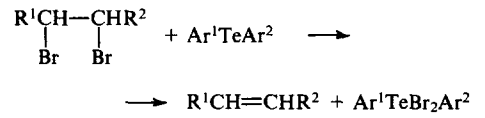


The interaction of other type **56** pyrylium cations, not containing tellurium atoms, with singlet oxygen is slower and the molecular π-skeletons are then involved in the reactions and not the heteroatoms.[186]

One of the characteristic properties of the dihydroxytellanes **59** is the relatively slow thermal reductive elimination of H_2O_2 in aqueous methanol solutions, which leads to the reformation of the initial compounds **56**. This can be used for the photochemical conversion of water and oxygen into H_2O_2.[187,188] Another possible application of the above reaction is photodynamic therapy: tellurapyrylium dyes function under these conditions as photosensitisers of the formation of singlet oxygen or the superoxide radical-anion, which are cytotoxic agents. A useful property of tellurapyrylium dyes is their ability to absorb in the near IR region, where biological tissues are transparent.

The ability of diorganyl tellurides to be converted by various oxidants into derivatives of tetracoordinate tellurium prevents in a number of instances the employment of reagents which are normally used for the conversion of the functional groups. Thus, in contrast to the sulfur and selenium derivatives, carboxylic acids containing telluride functional groups are converted into the corresponding acid chlorides on treatment with alkyl dichloromethyl ethers in the presence of anhydrous $ZnCl_2$,[51,54,56,111,113,117,190–192] whilst the use of PCl_5 or $SOCl_2$ for these purposes leads merely to the oxidation of tellurium(II) to tellurium(IV).

The appreciable 'affinity' of diorganyl tellurides for the halogens permitted the employment of these compounds as dehalogenating agents in the synthesis of alkanes from organic dihalides. Vicinal[193–195] and geminal[196] dibromo-derivatives are converted, with fairly high yields, into the corresponding alkenes on treatment with diaryl tellurides[193,195] or their cyclic analogue — phenoxatellurane.[194,196]

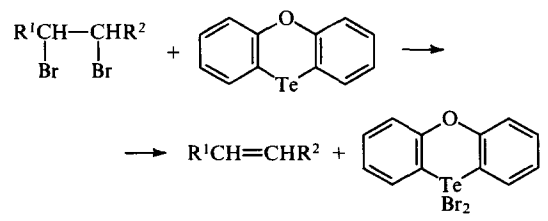


$R^1 = Ph$; $R^2 = CO_2H, CO_2Et, COPh$, 2-pyridyl;

$R^1 = R^2 = Ph$; $R^1 + R^2$ = cholesteryl,

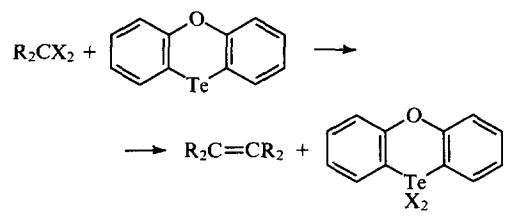
$Ar^1 = Ar^2 = Ph, 4\text{-}MeOC_6H_4$; $Ar^1 = 4\text{-}MeOC_6H_4$;

$Ar^2 = 1\text{-}C_{10}H_7, 2\text{-}C_{10}H_7$.



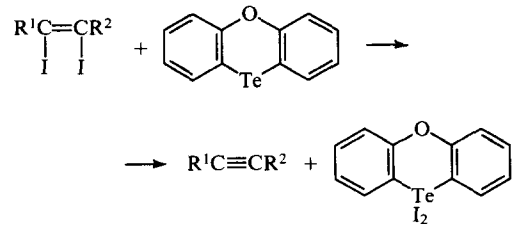
$R^1 + R^2$ = $-(CH_2)_3-$, $-(CH_2)_4-$, 1,8-naphthylidene;

$R^1 = Ph$; $R^2 = H, CO_2H, CO_2Et$; $R^1 = Me$; $R^2 = CO_2H$.



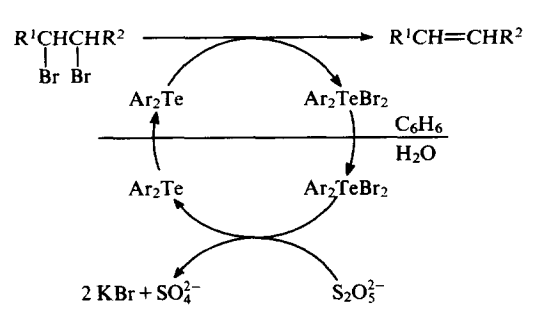
$R = Ph, CO_2Et$; $R + R = C_{12}H_8$, X = Cl, Br.

In terms of its dehalogenating capacity, phenoxatellurane is superior to diaryl tellurides, since it reduces not only 1,2-dibromoalkanes but also 1,2-diiodoalkenes, which leads to ethynes in yields exceeding 80%.[194]



$R^1 = Ph$, $R^2 = H, CO_2H$.

An important advantage of diaryl tellurides over other dehalogenating agents is the possibility of using them in catalytic amounts (the optimum amount is 5% of the mass of the halogen-containing substrates).[195] The reactions lead in this case to a two-phase system (benzene – water) and the tellurium dibromides formed are reconverted into the tellurides on treatment with potassium metabisulfite, which by itself does not reduce the vicinal dibromo-derivatives. The foregoing considerations can be illustrated by the following scheme:



2. Diorganyl ditellurides

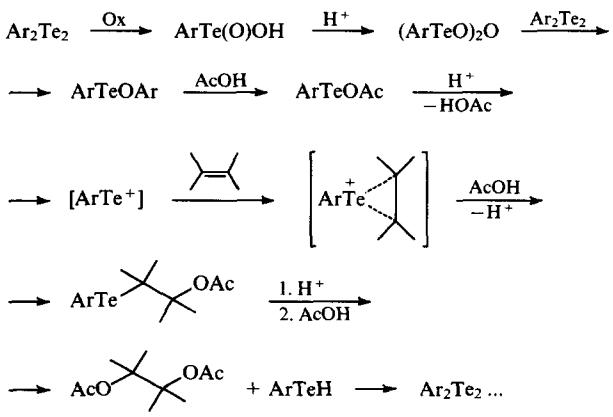
Like diorganyl tellurides, diorganyl ditellurides R_2Te_2 undergo oxidative addition reactions under mild conditions (at room or reduced temperature in the absence of catalysts). When solutions of these compounds are treated with the halogens [Cl_2($SOCl_2$, SO_2Cl_2), Br_2, I_2,[2-4] F_2, XeF_2,[197] or ClF [198]], the Te–Te bonds are ruptured and organyltellurium trihalides $RTeHal_3$ are formed in high yields. On treatment with various reductants, the latter can be reconverted into the corresponding ditellurides. The ease of the interconversions $R_2Te_2 \rightleftarrows RTeX_3$ is used (depending on the relative availability of these compounds) for their synthesis and purification. It has been shown in relation to aryltellurium triiodides that the halogen oxidative addition reactions proceed in stages.[199] The first stage of this process is the rapid formation of arenetelluranyl iodides, which are then converted into complexes **63** and finally into the triiodides **64**.

$$R_2Te_2 + I_2 \longrightarrow RTeI \rightleftharpoons \underset{\mathbf{63}}{RTeI \cdot I_2} \longrightarrow \underset{\mathbf{64}}{RTeI_3}$$

The reactions with other oxidants have been less thoroughly investigated. Thus, according to Pant's data,[166,167] the oxidation of diaryl ditellurides with lead tetraacetate affords, judging from the ^1H NMR spectra of the reaction mixture, aryltellurium triacetates. However, as a consequence of the ready hydrolysis of the latter, the attempts to isolate them from solutions were unsuccessful.

Diaryl ditellurides are catalysts of the oxidation of aromatic alkenes by various oxidants (O_2, Bu^tO_2H, H_2O_2, *m*-$ClC_6H_4CO_3H$) in methanol or acetic acid in the presence of H_2SO_4 to the vicinal dimethoxy- and diacetoxy-derivatives.[200] It has been suggested[200] that these reactions proceed via the intermediate formation of arenetellurinic acids ArTe(O)OH or their derivatives. This has been confirmed by the fact that, when the anhydrides of arenetellurinic acids $[ArTe(O)]_2O$[201] are refluxed with alkenes in acetic acid, they convert the latter into vicinal diacetates; the second reaction product is the corresponding ditelluride. The possible mechanism of these reactions[200,201] is presented in Scheme 2.

Scheme 2



Thus the intermediate formation of arenetellurinic acids or their anhydrides in the oxidation of diaryl ditellurides with Bu^tO_2H, H_2O_2, etc. under the conditions described above is evident; however, these reactions have not been investigated separately.

The ionisation potentials of the chalcogens (in eV) decrease in the sequence S(10.36) > Se(9.75) > Te(9.01).[202] As a result of this, diorganyl ditellurides are much stronger reductants than their sulfur and selenium anaogues and are capable of undergoing certain reactions which are not characteristic of the latter two classes of organochalcogen compounds.

The reducing properties of diaryl ditellurides have been used in preparative organic chemistry for the synthesis of alkenes from vicinal dibromo-derivatives.[203] Organic dibromo-derivatives convert diaryl ditellurides into arenetelluranyl bromides: under the reaction conditions (refluxing in toluene or acetic acid), the latter disproportionate to diaryltellurium dibromides and tellurium. Alkenes are obtained predominantly in the (*E*)-form in 68%–100% yields.

$$R^1\underset{Br}{CH}\!-\!\underset{Br}{CHR^2} + Ar_2Te_2 \longrightarrow$$

$$\longrightarrow R^1CH{=}CHR^2 + ArTeBr \longrightarrow Ar_2TeBr_2 + Te$$

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

Being strong one-electron reductants, diaryl ditellurides enter into reactions which cannot be carried out with the analogous sulfur derivatives. Thus the interaction of diaryl ditellurides with arenediazonium halides leads to a mixture of equimolar amounts of diaryltellurium dihalides and diaryl tellurides in accordance with the mechanism presented below:[152]

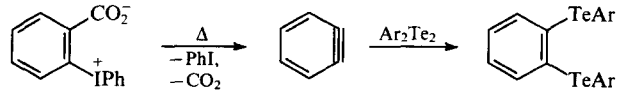
$$Ar^1_2Te_2 + Ar^2N_2X \xrightarrow[-N_2]{} Ar^1Te^{\cdot} + (Ar^2)^{\cdot} + Ar^1TeX,$$

$$Ar^1Te^{\cdot} + (Ar^2)^{\cdot} \longrightarrow Ar^1TeAr^2,$$

$$Ar^1TeX + Ar^2N_2X \xrightarrow[-N_2]{} Ar^1TeX_2Ar^2.$$

On the other hand, diaryl disulfides are arylated by arenediazonium halides only in the presence of copper(II) halides, which promote the formation of free aryl radicals.[175,176]

The M–M bond energy (kJ mol^{-1}) in the diorganyl dichalcogenides R_2M_2 decreases in the sequence S(264.0) > Se(202.0) > Te(149.8).[203] This is the reason for the strikingly manifested ability of diorganyl ditellurides to undergo other reactions (other than the reactions with the halogens) involving the dissociation of these bonds. Thus diaryl ditellurides containing electron-donating substituents in the *p*-positions in the arene rings add readily to dehydrobenzene, obtained by the thermal decomposition of 2-phenyliodonium benzoate, forming *o*-bis(aryltelluro)benzenes in 50%–64% yields.[205-206] Diphenyl disulfide does not enter into this kind of reaction.



Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$TeOC_6H_4$.

Mercury tellurophenoxides, which are stable under the usual conditions, are formed under extremely mild conditions—shaking of solutions of diaryl ditellurides with mercury at room temperature.[207-209] On heating, these compounds decompose into diaryl tellurides and HgTe.[209]

$$Ar_2Te_2 + Hg \longrightarrow (ArTe)_2Hg \xrightarrow{\Delta} Ar_2Te + HgTe$$

Ar = Ph, 4-$MeOC_6H_4$, 4-$EtOC_6H_4$.

It is probable that the interaction of diaryl ditellurides with powdered copper in boiling dioxane, leading to high yields of diaryl tellurides, also proceeds via the intermediate formation of copper(II) tellurophenoxides.[210-215] This reaction is frequently used as a preparative method of synthesis of diaryl tellurides and for the elimination of traces of diaryl ditellurides from the latter. In contrast to diaryl ditellurides, diaryl disulfides give rise to stable copper(I) thiophenoxides on heating with copper powder in *N,N*-dimethylacetamide.[216]

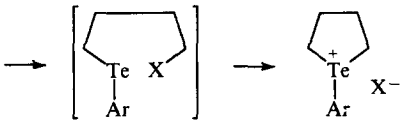
$$ArSCu \xleftarrow[M = S]{Cu/\Delta} Ar_2M_2 \xrightarrow[M = Te]{Cu/\Delta} Ar_2Te + CuTe$$

VI. Nucleophilic properties of dicoordinate tellurium derivatives

1. Diorganyl tellurides

Diorganyl tellurides of various types readily give rise to telluronium salts on interaction both with compounds containing activated neighbouring electron-accepting groups [esters of carboxylic α-bromoacids, α-bromoacetophenones, α-bromoacetone, chloro(bromo)acetonitriles] and with nonactivated alkyl halides.[2,3] The increased nucleophilicity of the tellurium atom, compared with the other chalcogens, in diorganyl tellurides results in the formation of telluronium salts on interaction of not only dialkyl and alkyl aryl tellurides but also diaryl tellurides with haloalkanes.[2,3] Furthermore, iodobenzene can be used as the halogen-containing substrate in relation to dimethyl telluride.[217] The interaction between these compounds leads to dimethylphenyltelluronium iodide in ~50% yield. In contrast to diaryl tellurides, diphenyl sulfide[218] and diphenyl selenide[219] form salts on treatment with haloalkanes only in the presence of Ag^+ cations. A similar difference between the reactivities has been observed also in the alkylation of chalcogen-containing heterocycles. Thus whereas benzo[*b*]tellurophene is alkylated by methyl bromide,[220] benzo[*b*]thiophenium and dibenzo[*b*]thiophenium salts have been obtained by the alkylation of the corresponding heterocycles only in the presence of $AgClO_4$ or $AgBF_4$.[221] The high nucleophilicity of the tellurium atom in diorganyl tellurides is also indicated by data[222] on the interaction of arenetellurolate anions with 1,4-dihalobutanes. 1-Aryl-1-telluroniacyclopentane halides **65** were obtained instead of the expected 1,4-bis(aryltelluro)butanes. These compounds are probably formed as a result of the intramolecular alkylation of the intermediate 1-aryltelluro-4-halobutanes **66**.

$$ArTe^- + XCH_2CH_2CH_2CH_2X \longrightarrow$$

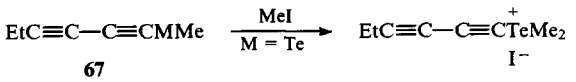


66 **65**

Ar = Ph, 4-$TeOC_6H_4$; X = Cl, Br.

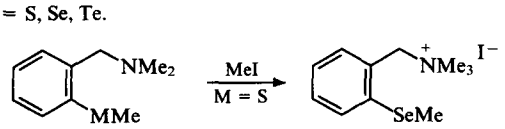
However, one should note that, according to the data of Hope et al.,[223] the main products of the reactions of lithium benzene- and methane-tellurolates with 1,4-dihalobutane are the corresponding tellurides and 1-telluracyclopentane.

Significant differences between the reactivities, determined by the nature of the chalcogen atoms, are observed also in the alkylation of alkylchalcogeno-1,3-diynes **67**[224] and 2-dimethylaminobenzyl methyl chalcogenides **68**.[116]

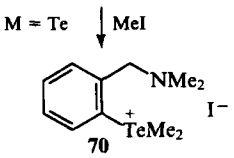


67

M = S, Se, Te.



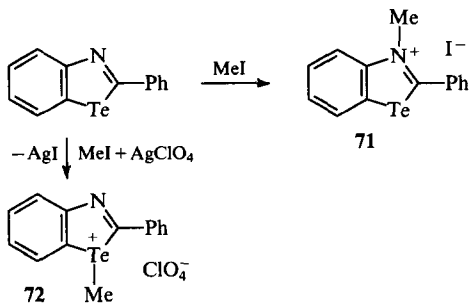
68 **69**



70

Among the methyl chalcogenides **67**, only the telluride is alkylated by methyl iodide, the telluronium salt being formed in this reaction in an almost quantitative yield.[224] More interesting data have been obtained on the alkylation of compound **68**. In the case of 2-dimethylaminobenzyl methyl selenide **68** (M = Se), the object of attack is the nitrogen atom; the iodide of methyl 2-*N*,*N*,*N*-trimethylammoniabenzyl selenide **69** is formed in an almost quantitative yield. On the other hand, the tellurium analogue is alkylated exclusively at the tellurium atom, which leads to the telluronium salt **70** in a high yield.[116]

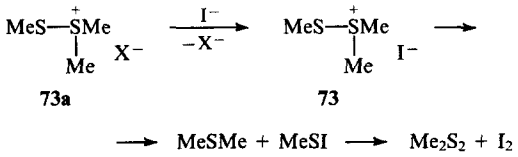
In relation to 2-phenylbenzotellurazole, it has been shown for the first time that the alkylation of N,Te-containing organic compounds can be achieved at different nucleophilic centres depending on the nature of the alkylating agents.[225,226] Refluxing of 2-phenylbenzotellurazole in an excess of MeI leads to the immonium salt **71** (yield 90%), while treatment of the same heterocycle with methyl iodide in the presence of an equivalent amount of $AgClO_4$ results in the formation of the telluronium salt **72** in an almost quantitative yield. Compound **72** is the first example of benzochalcogenazoles for which alkylation at the chalcogen atom has been achieved.



71 **72**

2. Diorganyl ditellurides

The alkylation of dialkyl disulfides by alkyl halides proceeds fairly effectively in the presence of HgI_2 or on treatment with trimethyloxonium 2,4,6-trinitrobenzenesulfonate.[227] We may note that *methylthio(dimethyl)sulfonium iodide* **73**, obtained by treating the sulfonate **73a** with the I^- ion, decomposes in accordance with the mechanism presented below:

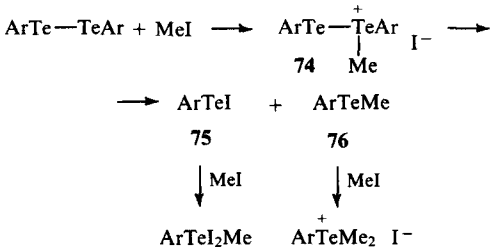


73a **73**

$$\longrightarrow MeSMe + MeSI \longrightarrow Me_2S_2 + I_2$$

X = 2,4,6-$(NO_2)_3C_6H_2SO_3$.

On the other hand, the alkylation of diaryl ditellurides evidently takes place under milder conditions in the presence of compounds similar to HgI_2 or the oxonium cation. Thus refluxing of di(*p*-anisyl) ditelluride in an excess of MeI leads to a mixture of *p*-anisylmethyltellurium diiodide and *p*-anisyl(dimethyl)telluronium iodide.[228,229] Evidently the intermediate *p*-anisyltelluro(methyl)*p*-anisyltelluronium iodide **74** decomposes, like the iodide **73**, to *p*-anisyltellanyl iodide **75** and *p*-anisyl methyl telluride **76**. The latter products react with the excess MeI, affording the observed products.



74 **75** **76**

The formation of type **74** telluronium salts is not ruled out also in the reactions of dialkyl ditellurides with phenylethyne and MeI under the conditions of phase transfer catalysis (PTC).[230,231]

VII. Reactions determined by the polarisation of the Te=X bonds (X = CR_2, NR, O)

π-Telluranes include telluronium ylides, tellurimides, and telluroxides:

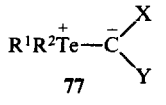
$$R_2Te{=}CR'_2 \longleftrightarrow R_2\overset{+}{T}e{-}\overset{-}{C}R'_2, \quad R_2Te{=}NR' \longleftrightarrow R_2\overset{+}{T}e{-}\overset{-}{N}R',$$

$$R_2T{=}O \longleftrightarrow R_2\overset{+}{T}e{-}\overset{-}{O}.$$

The reactivities and methods of synthesis of these compounds differ significantly from those of their sulfur (and to a lesser extent selenium) analogues. The principal factors responsible for the specific behaviour of π-telluranes compared with other π-chalcogenanes are the more intense polarisation of Te=X bonds (a greater contribution of the polar resonance structures Te^+-X^-) and hence the increased basicity of derivatives of tricoordinate tellurium. A characteristic feature of all π-telluranes without exception is their ability to be converted under the influence of different electrophiles into derivatives of tetracoordinate tellurium—the σ-telluranes R_2TeX_2.

The complete analogy of the electronic structures of organic derivatives of I(III) and Te(IV) should also be reflected in the similarity of the chemical properties of these compounds. The hypothesis[232] that organic derivatives of Te(IV), in particular π-telluranes, can be used in organic synthesis for the same purpose as organic derivatives of I(III) is therefore valid.[233]

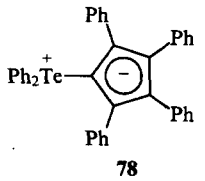
The number of telluronium ylides and imides described hitherto[7,10] is relatively small compared with their sulfur analogues. The doubly stabilised telluronium ylides **77**,[234–238] the diphenyltelluroniacyclopentadiene **78**,[239–241] and the diaryltelluronia-4,5-dicyanoimidazolylylidenes **79**[242] have been isolated on a preparative scale and characterised. The monostabilised and unstabilised telluronium ylides, compounds **80**[243–246] and **81**[247–249] respectively, have been used only in situ. Among tellurimides, only those which contain strongly electron-accepting groups at the nitrogen atom have been described.[250–256]



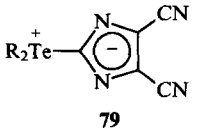
77

X+Y = $COCH_2CMe_2CH_2CO$, *o*-COC_6H_4CO;

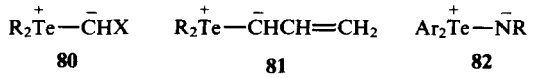
X = CO_2R; Y = CO_2R, CN, NO_2; X = Y = CN



78



79



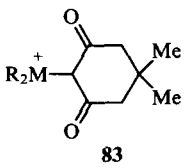
80 **81** **82**

X = CO_2R, CN, COR, $CONHBu^t$

X = SO_2R, COR (R = CCl_3, *m*-$O_2NC_6H_4$, *p*-$O_2NC_6H_4$).

We shall consider initially the properties and reactions common to all π-telluranes.

1. In contrast to dialkyl and alkyl aryl sulfoxides, the corresponding telluroxides are always isolated, by virtue of their high basicity, in the form of hydrates having the structure of σ-telluranes—diorganyltellurium dihydroxides $R_2Te(OH)_2$.[2,3,10,189] The basicity constants of the chalcogenoxides R_2MO[171,257–259] increase, like those of the telluronium ylides **83** (M = Te),[235] in the sequence M = S, Se, or Te. Thus the basicity constants of di(4-methoxyphenyl)chalcogenoxides $(4\text{-}MeOC_6H_4)_2MO$ have the following values in acetonitrile (the constants for the compounds with M = S or Se have been recalculated in relation to this solvent): S (4.2),[257] (5.4),[258] Se (9.1),[259] Te (14.9).[171] The telluroniadimedone ylides **77** (X+Y = $-COCH_2CMe_2CH_2CO-$) are somewhat weaker bases, comparable in strength to aromatic amines.[260] Indeed, $pK_a = 10.59$[235] for diphenyltelluroniadimedone ylide **83** (M = Te, $R^1 = R^2 = Ph$) is virtually identical with pK_a for aniline determined under identical conditions.[260] It follows from the pK_a for the diorganylchalcogenoniadimedone ylides **83**[235] that the basicity of the ylides increases sharply in the sequence S, Se, Te.

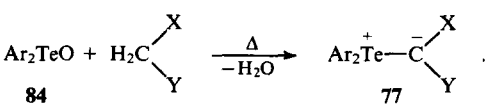


83

R = Me, M = S ($pK_a = 9.67$), Te ($pK_a = 12.07$);

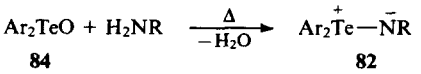
R = Ph, M = Se ($pK_a = 9.59$), Te ($pK_a = 10.59$).

By virtue of the high basicity of the oxygen atom in the diaryl telluroxides **84**, their reactions with reactive methylene compounds, leading to the telluronium ylides **77**,[236,237] do not require, in contrast to the synthesis of the corresponding sulfonium ylides, the use of any kind of dehydrating agents of the type of Ac_2O, PCl_5, $SOCl_2$, dicyclohexylcarbodiimide, etc.[7,10] The reactions are carried out by refluxing a mixture of equimolar amounts of the components in C_6H_6 or $CHCl_3$, the water formed in the reaction being simultaneously distilled away.



84 **77**

The syntheses of the tellurimides **82** from the diaryl telluroxides **84** and amides also take place under similar conditions.[251–253]



84 **82**

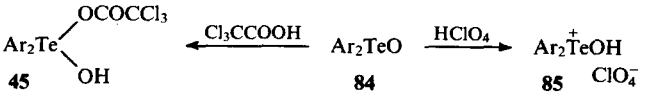
2. A characteristic feature of all π-telluranes is their interaction with protic acids accompanied by dissociation of the Te–M bond and the formation of the corresponding σ-tellanes.[171,172,261,262]



77, 82, 84

R^1 = Alk, Z = C(X)Y (**77**), NR^2 (**82**), O (**84**); X = F, Cl, Br, I, $OCOR^3$.

The reactions of diaryl telluroxides with acids proceed stepwise. For the equimolar reactant ratio, either type **45** hydroxytelluranes[171] (see above) or type **85** telluronium salts[171] are formed depending on the nature of the acids.



45 **84** **85**

In contrast to diaryl telluroxides, their sulfur analogues do not react with acids. On the other hand, the interaction of the doubly stabilised sulfonium ylides (dinitromethylides) with solutions of halides in organic solvents afford sulfides and not σ-sulfuranes.[263] Selenonium dinitromethylides occupy an intermediate position: depending on the nature of the hydrogen halides and the reaction conditions, either σ-selenanes or selenides are

formed.[264] The characteristic features of the reactions of the doubly stabilised chalcogenonium ylides with HHal noted above can be evidently attributed to the sharp increase in stability of the tetracoordinate derivatives of the chalcogens in the series S, Se, Te (for further details see Section VIII).

3. The diaryl telluroxides **84** [171–173] and tellurimides **82** [262] readily react with carboxylic acid anhydrides, affording the corresponding σ-tellanes, i.e. diaryltellurium dicarboxylates **86** and diacylamides (in the case of tellurimides).

$$\underset{\textbf{82, 84}}{Ar_2\overset{+}{T}e-\overset{-}{Z}} + (R^1CO)_2O \longrightarrow \underset{\textbf{86}}{Ar_2Te(OCOR^1)_2} + \underset{Z = NR^2}{Z(COR^1)_2}$$

Z = O (**84**), NR^2 (**82**); R^1 = Alk.

Diaryl sulfoxides do not react with anhydrides, while diaryl selenoxides behave similarly to diaryl telluroxides, giving rise to diarylselenium dicarboxylates.[171]

The reactions of π-telluranes and, in particular, of diaryl telluroxides with carboxylic acids and their anhydrides are important for the following two reasons.

a. They are convenient preparative methods of synthesis of diaryltellurium dicarboxylates, which make it possible to obtain virtually any compounds **86** in nearly quantitative yields. The methods for the formation of these compounds described earlier, namely the exchange reactions of diaryltellurium dihalides with silver salts of acids,[167,265] or the oxidation of diaryl tellurides by lead tetraacetate [166,167] require either the use of expensive silver salts or make it possible to obtain only diacetates. The interaction of diaryl tellurides and of the corresponding carboxylic acids with hydrogen peroxide (molar ratios 1:2:1) (yields 82%–92%) is a convenient preparative modification, which makes it possible to avoid the preliminary synthesis of diaryl telluroxides.[266]

$$Ar_2Te + H_2O_2 \xrightarrow[-H_2O]{} \underset{\textbf{84}}{[Ar_2TeO]} \xrightarrow[-H_2O]{RCOOH} \underset{\textbf{86}}{Ar_2Te(OCOR)_2}$$

b. In view of the ease of the interaction of acids with diaryl telluroxides, one cannot use for the synthesis of the latter the acid reagents widely employed in the preparation of sulfoxides from sulfides: HNO_3, H_2O_2 in acetic anhydride, peracids, etc.[267]

We may also note the ability of diaryl telluroxides to interact with acyl chlorides[171] (diaryl sulfoxides do not interact with the latter). For equimolar reactant ratios, a 1:1 mixture of diaryltellurium dichlorides and diaryl tellurium dicarboxylates **86** is formed.

$$\underset{\textbf{84}}{Ar_2TeO} + RCOCl \longrightarrow Ar_2TeCl_2 + \underset{\textbf{86}}{Ar_2Te(OCOR)_2}$$

However, in the presence of an excess of acyl chlorides, diaryltellurium dichlorides and carboxylic acid anhydrides are obtained in high yields.[171]

$$\underset{\textbf{86}}{Ar_2Te(OCOR)_2} + 2\,RCOCl \longrightarrow Ar_2TeCl_2 + 2\,(RCO)_2O$$

Later[268] this reaction was used as a preparative method of synthesis of acid anhydrides with different structures.

4. The telluronium ylides **77** [261] and imides **82** [262] react under mild conditions with the halogens, the reaction involving the cleavage of the Te–M bonds in the formation of σ-telluranes.

$$\underset{\textbf{77, 82}}{Ar_2\overset{+}{T}e-\overset{-}{Z}} + X_2 \longrightarrow Ar_2TeX_2 + X_2Z$$

Z = C(X)Y (**77**), NR′ (**82**); X = Cl, Br, I.

Sulfonium dinitromethylides give rise to dicoordinate sulfur derivatives, i.e. diorganyl sulfides, under analogous conditions.[263]

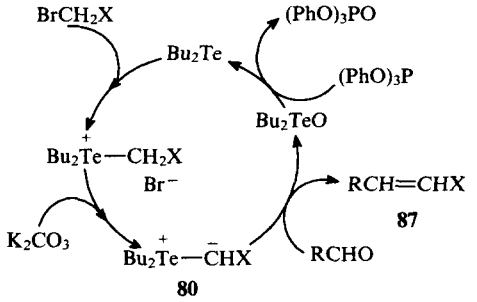
5. The monostabilised telluronium ylides **80**, generated by treating the corresponding telluronium salts with bases (Bu^tOK [243–245]) or NaH [244] and used in situ, are smoothly condensed with aldehydes and ketones, forming α,β-unsaturated esters (nitriles, ketones) **87** in fairly high yields. The (*E*)-isomers are formed preferentially in these reactions.

$$\underset{Y^-}{Bu_2\overset{+}{T}eCH_2X} \xrightarrow[-HY]{HB} \underset{\textbf{80}}{\left[Bu_2\overset{+}{T}e-\overset{-}{C}HX\right]} \xrightarrow[-Bu_2TeO]{R^1R^2C=O} \underset{\textbf{87}}{R^1R^2C=CHX}$$

X = CO_2Et, COPh, CN; Y = Cl, Br; R^1,R^2 = H, Alk, Ar.

On the other hand, the structurally similar sulfonium ylides do not react with aldehydes and ketones,[269,270] although they do react with α,β-unsaturated carbonyl compounds to form cyclopropanes.[269,270]

The ease of the synthesis of telluronium salts from dibutyl telluride and the ability of dibutyl telluroxide (or the corresponding dihydroxide), obtained as a result of the reaction, to be reduced back to the telluride by various reductants [$(PhO)_3P$, Na_2SO_3, $NaHSO_3$, $Na_2S_2O_3$] made it possible to carry out the latter reaction, as well as a series of other reactions involving organotellurium reagents described previously (see the reactions of arenetellurolate anions and diaryl tellurides) under catalytic conditions.[246] The alkenes **87** are formed stereoselectively in high yields when aldehydes and α-bromocarbonyl compounds are treated with catalytic amounts of dibutyl telluride in the presence of K_2CO_3 (as a base) and $(PhO)_3P$ (as a reductant) in accordance with the following mechanism:



X = CO_2Me, COPh, $COPr^i$.

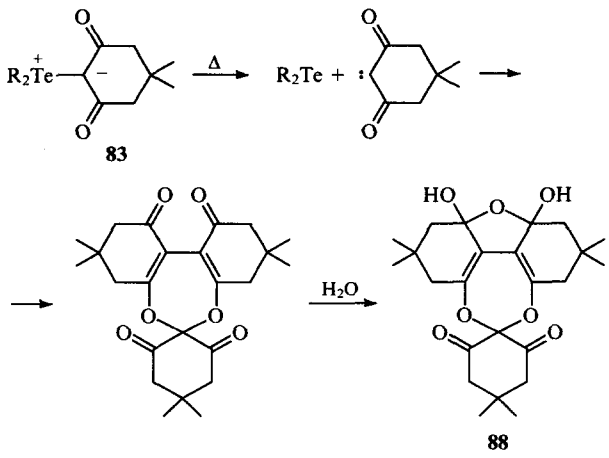
The fact that the alkenes **87** are obtained in high yields in the form of the (*E*)-isomers when aldehydes are condensed with telluronium salts in boiling THF in the absence of bases, i.e. under conditions which rule out the formation of ylides, is of special interest.[245,271]

$$ArCHO + \underset{Y^-}{Bu_2\overset{+}{T}e-CH_2X} \xrightarrow{\Delta} \underset{\textbf{87}}{ArCH=CHX}$$

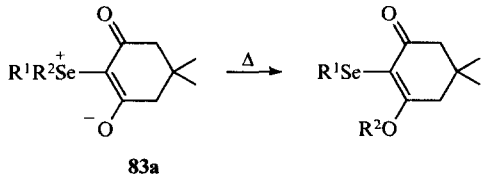
X = CO_2Me, CN, COPh; Y = Cl, Br.

However, the mechanism of these reactions remains unelucidated.

6. The thermolysis of the telluroniadimedone ylides **83** (M = Te) and their selenium analogues **83** (M = Se) proceeds in completely different ways. On heating in inert solvents, the former decompose with formation of tellurides and the product of trimerisation of the carbanionic fragment of compound **88**.[272]

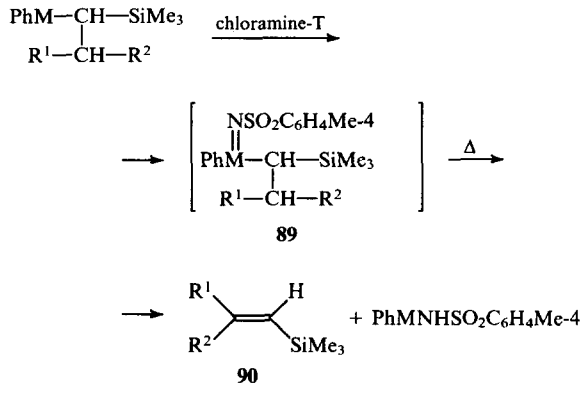


On the other hand, the selenoniadimedone ylides **83** undergo the Stevens thermal rearrangement under the same conditions.[273]



The different results of the thermolytic reactions can be accounted for by the smaller Te^+-C^- bond energy compared with that of Se^+-C^-. This is also confirmed by mass-spectrometric data for the type **83** telluronium[274] and selenonium[275] ylides. In the case of the telluronium ylides, the intensities of the M^+ molecular peaks are extremely low (0.1%–0.3% of the total ionic current), whereas for the selenonium ylides they are fairly intense.

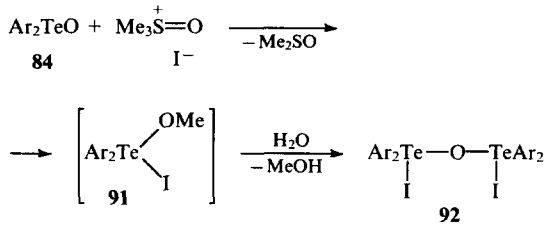
The thermolysis of the chalcogenonium imides **89**, containing S, Se, or Te, takes place in the same way and leads to the vinylsilanes **90** predominantly in the (*E*)-form.[276] The nature of the chalcogen affects only the reaction conditions: sulfur derivatives decompose at 100 °C, those of selenium decompose at room temperature, and those of tellurium decompose in boiling THF.



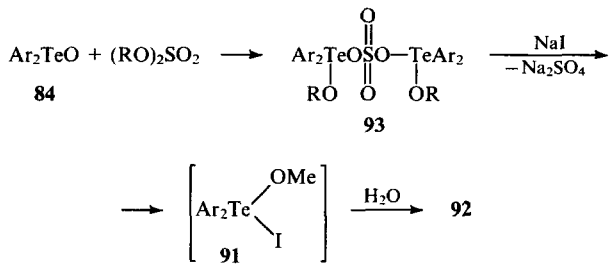
M = S, Se, Te; $R^1 = C_9H_{19}, C_{11}H_{23}, C_{13}H_{27}, C_{15}H_{31}$; R^2 = H.

7. Extremely significant differences are observed in the reactions of diaryl telluroxides and sulfoxides with alkylating agents. Depending on the nature of the alkylating agents, the sulfoxides undergo both *O*- and *S*-alkylation.[277] On the other hand, the interaction of diaryl telluroxides with various alkylating agents (trimethylsulfoxonium iodide,[278,279] dialkyl sulfates,[279,280] and methyl iodide[279,281]) leads evidently to *O*-alkylation only (it has been suggested that the structure of the intermediates corresponds to the σ-tellanes **91**). However, in most cases the compounds isolated were formed as a result of further reactions of these intermediates, the structure and composition of which are determined by the nature of the groups linked to the tellurium atom and the reaction conditions.

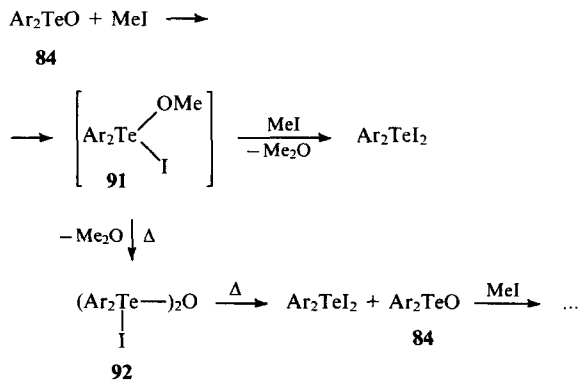
The interaction of the diaryl telluroxides **84** with trimethylsulfoxonium iodide leads ultimately to the bis(diaryliodotellurium) oxides **92**, probably via the intermediate *O*-alkylation product **91**.[278,279]



Treatment of diaryl telluroxides with dialkyl sulfates involves the formation of the σ-tellanes **93**,[279,282] which are converted into the oxides **92** on treatment with NaI $2H_2O$.



Telluroxides and sulfoxides behave quite differently in their reactions with methyl iodide. While dimethyl sulfoxide affords the *S*-alkylation product — trimethylsulfoxonium iodide — on refluxing in an excess of MeI,[277] diaryl telluroxides give rise to diaryltellurium diiodides in high yields under the same conditions.[279,281] The formation of the latter can be explained by the mechanism presented below,[279] which indicates two alternative paths leading to the conversion of diaryl telluroxides into diaryltellurium diiodides.

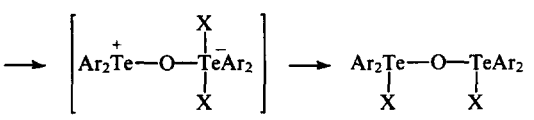


The possibility of the formation of tellurium diiodides via the bis(diaryliodotellurium) oxides **92** has been confirmed by the fact that the oxides **92** obtained by independent methods[282] decompose into diaryltellurium diiodides and diaryltelluroxides on heating in solution.

8. The diaryl telluroxides **84** react readily with the σ-tellanes Ar_2TeX_2, forming bis[diarylhalo(acetoxy)tellurium oxides **92** in high yields.[282]

$Ar_2TeO + Ar_2TeX_2 \longrightarrow$

84



92

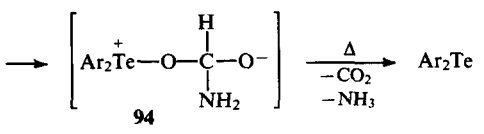
X = F, Cl, Br, I, OCOMe.

Such a reaction is evidently impossible for organosulfur compounds because of the instability of σ-sulfanes — analogues of Ar_2TeX_2.

9. The high nucleophilicity of the diaryl telluroxides **84**, which promotes the formation of the intermediate **94**, results in the ready reduction of compounds **84** to tellurides on heating in an excess of formamide at 120–140 °C. The yields of the tellurides are almost quantitative.[283]

$Ar_2TeO + HCONH_2 \longrightarrow$

84

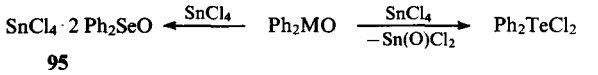


94

The same reagent has been used for the reduction of diaryl selenoxides,[283] whereas diaryl sulfoxides, which are the least basic among the chalcogenoxides, do not react with formamide.

Evidently formamide has significant advantages as a reductant over bis(trimethylsilyl) chalcogenides[284] and phenylselenotrimethylsilane.[285] Indeed, the above reagents, which are in addition synthesised only in moderate yields, have an unpleasant smell and are extremely sensitive to moisture and air. Furthermore, their employment entails the formation of side products [the chalcogens, $(Me_3Si)_2O$, or Ph_2Se_2 and $(Me_3Si)_2O$], which hinders the isolation and purification of diaryl tellurides.

10. The striking tendency of various organotellurium compounds to be converted into tetracoordinate tellurium derivatives is probably responsible for the different results of the reactions of diphenyl telluroxide and diphenyl selenoxide with $SnCl_4$. Whereas Ph_2TeO gives rise to the corresponding σ-tellane, i.e. Ph_2TeCl_2,[286] diphenyl selenoxide affords complex **95** under the same conditions.[287]



95

M = Se, Te.

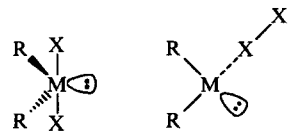
VIII. The increased stability of tetracoordinate tellurium derivatives

The most thoroughly investigated derivatives of tetracoordinate tellurium are σ-tellanes: diorganyltellurium dihalides R_2TeX_2 and organyltellurium trihalides $RTeX_3$. These compounds are at the same time important synthons for the preparation of various derivatives of di-, tri-, penta-, and hexa-coordinate tellurium.[2–5] Tetraorganyltellanes R_4Te have been less thoroughly investigated and the first tellurone reliably described (and so far the only one) is di(4-methoxyphenyl) tellurone.[288]

σ-Tellanes and tetraorganyltellanes exhibit an increased stability compared with the analogous sulfur and selenium derivatives. These compounds have a trigonal-bipyramidal structure; the equatorial and axial bonds, even those with identical substituents, have different lengths. The axial bonds are hypervalent,[289,290] their three-centre orbitals being occupied by four electrons: two from the *p*-orbitals of the chalcogen atoms and one each from the axial substituents. As a result of this, the axial bonds are appreciably lengthened compared with the usual two-centre two-electron covalent bonds. Thus the average lengths of the $Te-C_{eq}$ bonds are 2.127 Å for tetramethyltellane Me_4Te[291] and 2.13 Å for the tetraphenyltellane solvate $Ph_4Te \cdot 0.125C_6H_6$;[292] on the other hand, the $Te-C_{ax}$ bond lengths are 2.292 and 2.29 Å respectively. In the case of nonequivalent substituents, the axial positions are always occupied by the more electronegative ligands in which there is a possibility of delocalisation of the electrons from the nonbonding L^1-M-L^2 orbital (L is the substituent and M the chalcogen). The increased stability of σ-tellanes compared with other σ-chalcogenanes can be explained by the higher energy level of the *p* orbital of tellurium, which favours bonding.[289,290]

1. The σ-tellanes R_2TeX_2 and $RTeX_3$

Depending on the nature of the chalcogen and halogen atoms, the compounds R_2MHal_2 (M = S, Se, Te; Hal = F, Cl, Br, I) have either a covalent structure with a trigonal-bipyramidal configuration of the bond (TBP) at the central atom (compounds **96**) or are charge-transfer complexes (CTC) of type **97**.[293–297] In the latter, the chalcogen atom is coordinated to only one halogen atom and the M···X–X angle is close to 180°.



96 **97**

The formation of compounds of one type or another is determined primarily by the effective electronegativities (EO) of the chalcogen and halogen atoms. In general, if the electronegativity of the halogens is much higher than that of the chalcogens, covalent type **96** TBP structures are formed. Otherwise, the formation of type **97** CTC is to be expected. This rule agrees well with results of X-ray diffraction in other studies on R_2MX_2, the results of which for the structures of the compounds R_2MHal_2 are presented below:

M	F	Cl	Br	I
S	TBP	TBP	CTC	CTC
Se	TBP	TBP	TBP	CTC
Te	TBP	TBP	TBP	TBP

However, one should note that variation of the electronic nature of the groups R linked to the chalcogen atoms can alter the effective electronegativity of the latter, which may affect in its turn the structure of the R_2MHal_2. Thus diorganylselenium dibromides are usually σ-selenanes,[293–296] whereas, judging from the ^{13}C NMR spectra, dibromoselenoxanone[295,296] as well as the diarylselenium dibromides Ar_2SeBr_2 (Ar = 4-NCC_6H_4, 4-$O_2NC_6H_4$, 3,5-$Cl_2C_6H_3$, 2-ClC_6H_4) and $Ar^1Ar^2SeBr_2$ (Ar^1 = 2,6-$Cl_2C_6H_3$, Ar^2 = Ph)[298] are molecular complexes. This is due to the increase in the effective electronegativity of the selenium atom as a consequence of its conjugation with strongly electron-accepting groups.

It follows from the data presented that, regardless of the nature of the chalcogens, the true σ-chalcogenanes are the difluorides and dichlorides. The former are thermally stable for any M, while the stability of the dichlorides increases sharply in the sequence S, Se, Te. Some data on the thermal stabilities of the σ-chalcogenanes R_2MCl_2 as well as $RMCl_3$ and MCl_4 are presented below.

The σ-tellanes R_2TeX_2 are readily reduced to diorganyl tellurides R_2Te by various reductants (see above) and can be converted into telluronium salts, telluroxides, telluronium ylides,

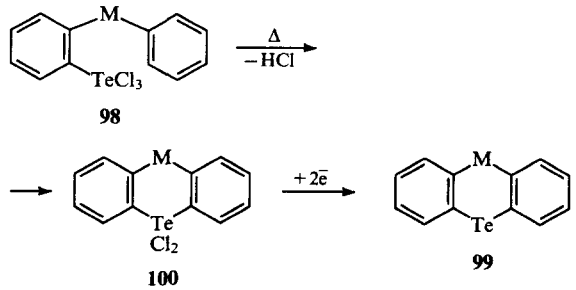
SCl_4 decomposes at -31 °C[299]	$SeCl_4$ melts without decomposition at 305 °C[299]	$TeCl_4$ melts without decomposition at 224 °C[299]
The compounds $RSCl_3$ decompose even at temperatures in the range 5–25 °C[300,301]	The compounds $RSeCl_3$ are stable at room temperature; on heating, they decompose readily into RSeCl and Cl_2[302–305]	The compounds $RTeCl_3$ are stable up to their melting points[2–5]
The compounds R_2SCl_2 decompose at temperatures below 0 °C; at room temperature, they exist only under a dry chlorine atmosphere[306–310]	The compounds R_2SeCl_2 are stable up to their melting points[299,305]	The compounds R_2TeCl_2 are stable up to their melting points[2–5]

and tetraorganyltellanes.[2–5] On interaction with $TeCl_4$, diaryltellurium dichlorides are converted into aryltellurium trichlorides.[311]

Like other organyltellurium trihalides $RTeX_3$, aryltellurium trichlorides (the most thoroughly investigated representatives of σ-tellanes of this type) are readily reduced to diorganyl ditellurides, hydrolysed to aryltellurium oxide halides, and are converted into diaryltellurium dichlorides (symmetrisation reaction).[311] They also readily form the pertelluranes $[RTeX_4]^-$ and $[RTeX_3Y]^-$ containing a pentacoordinate tellurium atom.[2–5]

Aryl(organyl)tellurium trihalides $RTeHal_3$ are electrophiles, but their reactivity is inferior to that of the corresponding tellurium tetrahalides. The electrophilicity of the aryltellurium trihalides $ArTeHal_3$ (Hal = Cl, Br, I) decreases in the sequence Cl, Br, I.[312] Aryltellurium trichlorides therefore add comparatively readily to double and triple bonds and undergo electrophilic substitution reactions with activated strong electron donors, aromatic substrates, and aliphatic compounds containing activated methyl or methylene groups (ketones, acetic anhydride, etc.).[2–5] The method of synthesis specific to tellurium-containing heterocycles, involving the intramolecular electrophilic cyclisation of the aryltellurium trichlorides **98** having the appropriate structure, is in fact based on the electrophilic nature of the trichlorotelluro-groups.

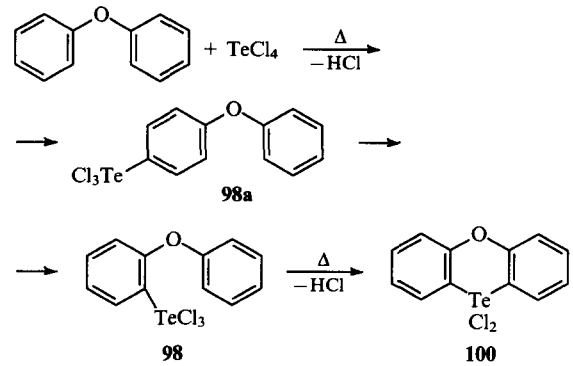
This reaction has been most often employed to synthesise tricyclic tellurium-containing systems **99** with two heteroatoms. The reaction leads to the formation of the corresponding tellurium dichlorides **100**, which are smoothly converted into the heterocycles **99** on treatment with various reductants.



M = CH_2, NH, O, S.

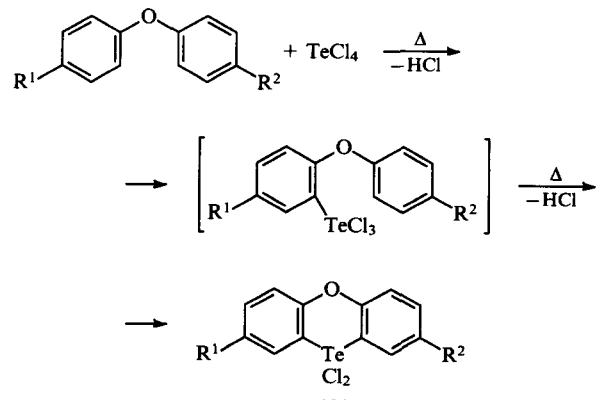
The synthesis is usually carried out by heating the trichloride **98** in suitable solvents or without them. The cyclisation temperatures are determined primarily by the electronic nature of the heteroatoms. As the electron-donating properties of these atoms become more pronounced, the temperature at which the process takes place is reduced. Thus the cyclisation of 2-(phenylamino)phenyltellurium trichloride **98** (M = NH) takes place on refluxing in acetic acid,[313] whereas the cyclisation of the diphenyl ether **98** (M = O) and diphenyl sulfide **98** (M = S) requires heating to 200 °C[314] and 240–250 °C[315] respectively. The weak electron-donating properties of the methylene bridge are evidently the reason why 10,10-dichlorotelluraxanthene **100** (M = CH_2) could not be obtained by heating 2-benzylphenyltellurium trichlorides **98** (M = CH_2).[316] The synthesis of this heterocycle was found to be possible only by carrying out the reaction in the presence of $AlCl_3$, which increases the electrophilicity of the trichlorotelluro group as a result of the formation of the complex $[ArTeCl_2]^+[AlCl_4]^-$.[316,317]

It is of interest to note that 10,10-dichlorophenoxatellurane **100** (M = O) can be obtained in approximately 50% yield by the prolonged heating of equimolar amounts of $TeCl_4$ and diphenyl ether.[314] The primary product of this reaction, isolated in an analytically pure form, is *p*-phenoxyphenyltellurium trichloride **98a**, because, like other electron releasing groups,[2,3,318,319] the OPh group directs the electrophile to the *para*-position. However, on further heating of this compound, the $TeCl_3$ group migrates to the *ortho*-position and the *o*-phenoxyphenyltellurium trichloride thus obtained is converted further into the heterocycle **100** (M = O).



A similar migration of the $TeCl_3$ groups with subsequent cyclisation occurs on heating *p*-(phenylamino)phenyltellurium trichloride (obtained from *p*-chloromercuriodiphenylamine and $TeCl_4$[313]) in acetic acid and by heating $TeCl_4$ in an excess of Ph_2S at 190–200 °C.[196] The yields of the heterocycles **99** (M = NH, S) are, however, extremely low and amount to 7% and 6% respectively.

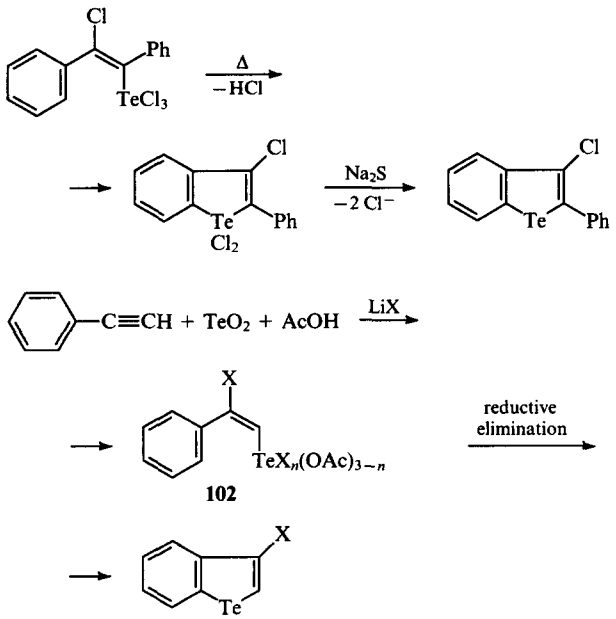
Similar reactions have been used also to synthesise 2,8-disubstituted 10,10-dichlorophenoxatelluranes **101**. The latter are obtained in 14%–50% yields on heating melts of mixtures of 4,4′-disubstituted diphenyl ethers and $TeCl_4$.[177,320–324]



$R^1 = R^2$ = Me,[321] Cl,[322] F;[323]

R^1 = Me, R^2 = H,[320] Cl,[320] F,[324] CO_2H;[320] R^1 = F, R^2 = Cl.[177]

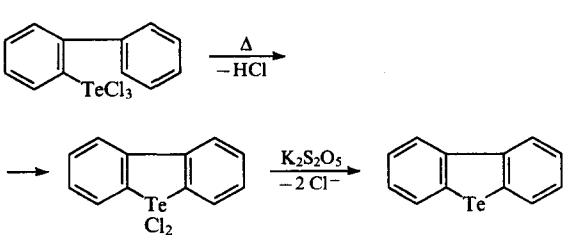
The synthesis of five-membered tellurium-containing heterocycles — substituted benzo[*b*]tellurophenes and dibenzotellurophenes — has also been achieved with the aid of cyclisation reactions of the corresponding aryltellurium trichlorides. Thus the first representative of benzo[*b*]telluro-phenes — 1,1,3-trichloro-2-phenylbenzo[*b*]tellurophene — has been obtained in a yield exceeding 50% by heating 2-chloro-1,2-diphenylvinyltellurium trichloride[325] (the product of the electrophilic addition of $TeCl_4$ to diphenylethyne[326]). A series of 3-halobenzo[*b*]tellurophenes have been synthesised in 21%–92% yields by treating phenylethyne with tellurium dioxide in acetic acid in the presence of LiX.[327,328] The latter reaction evidently proceeds via the intermediate formation of the σ-tellanes **102**, the cyclisation of which leads to the required heterocycles.



102

X = Cl, Br, I.

Brief heating at 210 °C of 2-trichlorotelluriobiphenyl (obtained from 2-chloromercuriobiphenyl and $TeCl_4$) leads to 1,1-dichlorodibenzotellurophene in almost quantitative yield.[329]



Evidently, these reactions, like those examined above, could not be used to obtain the sulfur and selenium heterocycles because the corresponding arylsulfur trichlorides and arylselenium trichlorides are thermally unstable. However, benzo[*b*]thiophene[330] and benzo[*b*]selenophenes[331] as well as dibenzothiophene[332] and dibenzoselenophene[333] have been obtained by the thermal cyclisation of arylchalcogen monohalides ArMX (M = S, Se; X = Cl, Br, I).

2. Tetraorganyltellanes R_4Te and tetraalkoxytellanes $(RO)_4Te$

As in the case of the σ-tellanes R_2TeX_2 and $RTeX_3$ as well as their sulfur and selenium analogues, significant differences between the thermal stabilities of tetraaryltellanes Ar_4Te **103** and other tetraarylchalcogenanes Ar_4M (M = S, Se) are observed. The latter exist only in solutions at very low temperatures [thus the formation of tetrakis(pentafluorophenyl)sulfane in solution on reaction between SF_4 and C_6F_5Li has been detected by the ^{19}F NMR method at −80 °C[334]], decomposing to biaryls and diaryl chalcogenides on raising the temperature. In contrast to them, the tetraaryltellanes **103** are stable crystalline compounds under the usual conditions, melting above 100 °C.[335–338] It is noteworthy that the tetraalkyltellanes **103**, which have been obtained comparatively recently, are thermally stable but are extremely sensitive to air and light.[339–341] The most general method of synthesis of compounds **103** involves the interaction of organolithium or organomagnesium derivatives with $TeCl_4$[335–338,340,341] [Ph_4Te has also been obtained from PhLi, Ph_2TeCl_2, and Ph_3TeCl,[335] whilst $(CF_3)_4Te$ has been synthesised by the reaction of $(CF_3)_2TeCl_2$ with $(CF_3)_2Cd$.[339]]

$$RM + TeCl_4 \xrightarrow[-MCl]{} R_4Te$$

103

M = Li, MgX; R = Ph,[335,337,338] C_6D_5,[338] 4-MeC_6H_4,[337,338] C_6F_5,[336] Me,[340,341] Bu,[341] Me_3SiCH_2,[341] $CH_2{=}CH$,[340] $CH_2{=}CHCH_2$.[341]

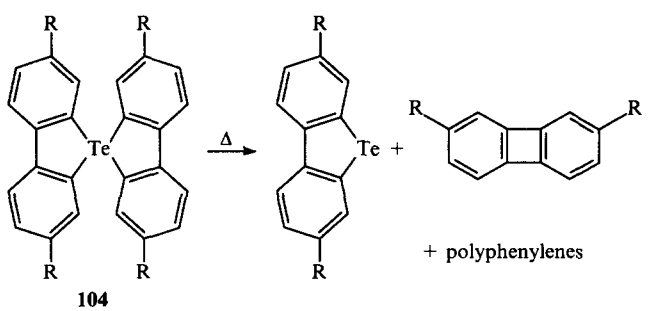
Tetraaryltellanes, which are stable under the usual conditions, decompose smoothly to diaryl tellurides and biaryls on heating.

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

103

The decomposition of tetraalkyltellanes, especially $(CF_3)_4Te$, proceeds in a more complex manner, considerable amounts of secondary reaction products being formed in addition to dialkyl tellurides and the corresponding hydrocarbons.

The highly stable cyclic tetraaryltellanes **104**[250,255,342,343] (with melting points above 200 °C) decompose on thermolysis similarly to the acyclic tetraaryltellanes **103**: the principal decomposition products are dibenzotellophene and biphenylene.



104

R = H, Me.

The high thermal stability of the recently synthesised hexamethyltellurium Me_6Te is also noteworthy;[344] this compound does not decompose on heating in solution in C_6D_6 in a sealed tube at 140 °C in the course of 4.5 h (for comparison, we may note that tetramethyltellane Me_4Te decomposes fully in 4 h at 120 °C).[344]

The thermal stabilities of tetraalkoxychalcogenanes $(OR)_4M$ (M = S, Se, Te) are also very different. Among the sulfur derivatives, only those which contain perfluorinated alcohol residues are stable.[345] Tetraalkoxyselenanes are stable only below 0 °C,[346,347] decomposing rapidly to dialkyl selenites and dialkyl ethers when the temperature is raised.[346,347]

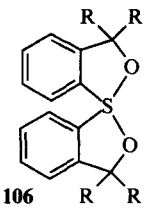
$$(RO)_4Se \xrightarrow{\Delta} (RO)_2Se{=}O + R_2O$$

105

The tetraalkoxytellanes $(RO)_4Te$ (R = Me, Et, Pr^i, Bu)[347–349] are thermally more stable than their sulfur and selenium analogues and can be vacuum distilled without decomposition. Their thermolysis proceeds in a different way from that of

the selenium derivatives. Thus tetraethoxytellane decomposes on heating to ethanol, acetaldehyde, and tellurium.[350]

We may also note that dialkoxydiorganyltellanes $R^1_2Te(OR^2)_2$, obtained by means of exchange reactions of diorganyltellurium dihalides with sodium alkoxides, are thermally stable regardless of the nature of the alkoxy-groups.[351] On the other hand, only those sulfur analogues which contain perfluoroalkoxy-groups, for example $Ph_2S[OC(CF_3)_2Ph]_2$,[306,352] or have the cyclic structure **106**[306] are stable under the usual conditions.



R = H, Me, CF_3.

106

IX. Reactions involving the dissociation of C–Te bonds

The C–Te bonds have the lowest energy among carbon–chalcogen bonds. The bond energies of the latter as well as the M–M bond energies (kJ mol^{-1}) in diorganyl dihalides RM–MR[204] are presented below.

	S	Se	Te
C_{prim}–M	287.0	246.9	213.4
C_{sec}–M	285.8	245.6	302.0
M–M	264.0	202.0	149.8

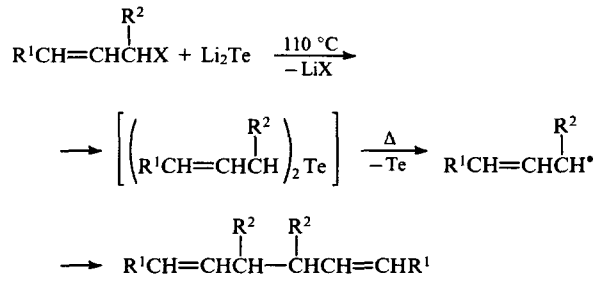
As a result of the significant decrease in the carbon–chalcogen bond energies in the sequence S, Se, Te, certain reactions, which in the case of organosulfur and organoselenium compounds take place with retention of the C–M bonds, in the case of organotellurium compounds are accompanied by the dissociation of the C–Te bonds. Because of this, certain reactions leading to particular types of acyclic and cyclic sulfur and selenium compounds are inapplicable to the synthesis of the structurally similar tellurium-containing derivatives. On the other hand, the application of organotellurium compounds in preparative organic chemistry is based precisely on the ease of dissociation of the C–Te bond accompanied by elimination of the Te atom. This section deals with the reactions of derivatives of dicoordinate tellurium, principally of diorganyl tellurides of various types, which proceed with dissociation of one or two C–Te bonds (elimination of the Te atom). (Analogous reactions of certain derivatives of tricoordinate tellurium were examined in Section VII, while those of derivatives of tetracoordinate tellurium and the telluroxide elimination reactions have been considered in other reviews.[10,26,27,29,30])

The dissociation of the C–Te bonds in organotellurium compounds in general and in diorganyl tellurides in particular takes place as a result of pyrolysis or photolysis and also on treatment with Raney nickel, transition metals (primarily palladium and its compounds), nontransition metal salts, Group IV element hydrides, as well as a series of oxidants, electrophiles, and nucleophiles.

The gas-phase pyrolysis of dialkyl tellurides[2,3,353,354] is accompanied by the dissociation of both C–Te bonds and makes it possible to obtain ultrapure tellurium. It is believed[2,3,355] that these reactions take place via a radical mechanism. The pyrolysis of dimethyl telluride (330–380 °C) is four times faster than that of Me_2Se.[353] The decomposition in the gas phase of mixtures of volatile dialkyl tellurides and alkyl derivatives of metals (Zn, Cd, Hg, etc.)[356,357] is used for the synthesis of the tellurides of these metals, which have found an application as semiconductors, in the preparation of opto- and acousto-electronic systems, etc.

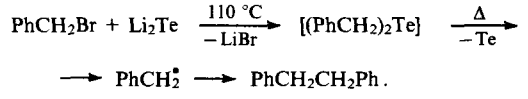
The synthesis of benzo[*b*]thiophene and of its selenium analogue (in yields of 85% and 40% respectively),[358] as well as selenophene, mixed with benzo[*b*]selenophene,[359] can be achieved by means of the high-temperature reactions of diphenyl disulfide and diselenide with ethyne and propargyl alcohol respectively. On the other hand, diphenyl ditelluride decomposes in similar reactions with liberation of metallic tellurium; for example, benzo[*b*]tellurophene is detected in only trace amounts (1%–2%).[358] The different compositions of the final products of the reactions of 2-iodothiophene with dimethyl selenide and telluride and the formation of considerable amounts of metallic tellurium[360] are also a result of the decrease in the carbon–chalcogen bond energy on passing from selenium to tellurium.

Reactions involving the pyrolytic dissociation of the C–Te bonds have been used in a number of instances for the preparative synthesis of various hydrocarbons. Allyl and benzyl halides interact with lithium telluride, affording 1,5-dienes (yield 60%–93%)[361] and bibenzyl (yield 37%)[24,361] as the main products. These hydrocarbons are the products of the coupling of the allyl(benzyl) radicals arising following the elimination of the tellurium atom from the intermediate diallyl(benzyl) tellurides.



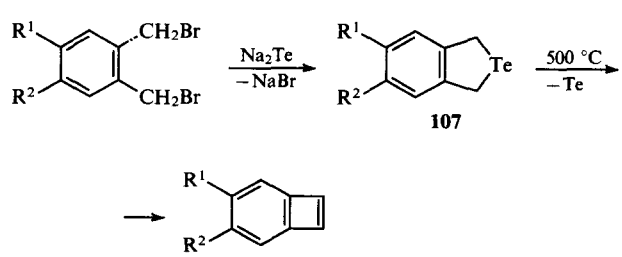
$R^1 + R^2 = -(CH_2)_4-$, $-(CH_2)_5-$, $-(CH_2)_6-$;

$R^1 = R^2 = Me$; R^1 = Ph, $CH_2=CH$, Pr, R^2 = H; X = Cl, Br.



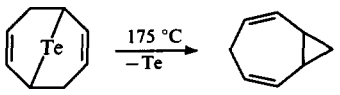
Such reactions, which constitute a new method of synthesis of 1,5-dienes are characteristic of tellurium derivatives only. Indeed, whereas treatment of 3-bromocyclohexene with lithium telluride gives 2,2′-bicyclohexenyl in 81%–86% yield, only the corresponding selenide is formed in the analogous reaction with Li_2Se.[361] However, one should note that the interaction of allyl and benzyl halides with sodium and lithium tellurides at room temperature makes it possible to obtain symmetrical diallyl or dibenzyl tellurides in 50%–100% yields.[341,355,362–366]

The pyrolysis of the cyclic tellurides **107** (the mechanism of their synthesis is presented below) and **12** (see over; the synthesis of this compound was described in Section II) is also accompanied by the elimination of the tellurium atom and the formation of derivatives of cyclobutene[367] and bicyclo[5.1.0]octa-2,5-diene respectively.[75]



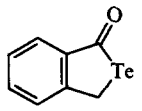
107

$R^1 = R^2 = H$; $R^1 + R^2 = (-CH=CH-)$.



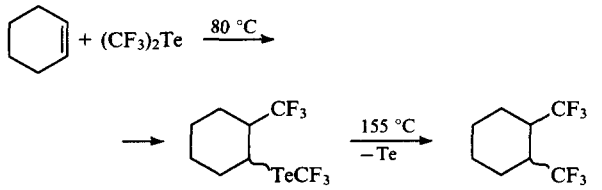
12 13

On the other hand, the attempts to obtain benzocyclobutenone by the vacuum flash photolysis of tellurophthalide **108** were unsuccessful;[134] the elimination of the tellurium atom was not observed under these conditions.



108

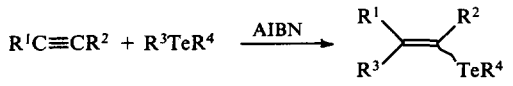
As the electron-accepting properties of the groups linked to the tellurium atom are enhanced, the temperature at which the tellurium atom is eliminated probably decreases. Thus at 80 °C bis(trifluoromethyl) telluride adds to cyclohexene, forming a mixture of *cis*- and *trans*-1-trifluoromethyltelluro-2-trifluoroethylcyclohexanes **109**; the tellurium atoms are eliminated from these compounds at 155 °C.[368]



109

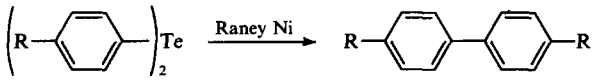
According to the data of Naumann and Wilkes,[368] bis(trifluoromethyl) telluride is superior to CF_3I and $(CF_3)_2Hg$ in terms of its trifluoromethylating capacity in both thermal and photochemical reactions.

Whereas the carbotelluration of cyclohexene (preceding reaction) takes place at 80 °C, the carbotelluration of alkynes is achieved when benzene solutions of equimolar mixtures of alkynes and diorganyl tellurides are refluxed in the presence of catalytic amounts of 2,2′-azobisisobutyronitrile (AIBN).[369,370]



The reaction proceeds via a radical mechanism and leads to a mixture of (*E*)- and (*Z*)-vinyl tellurides in yields ranging from 40% to 100%. The $C(sp^3)$–Te bonds are dissociated exclusively in alkyl phenyl tellurides; the C_{tert}–Te bonds are cleaved more readily than the C_{prim}–Te bonds.[370]

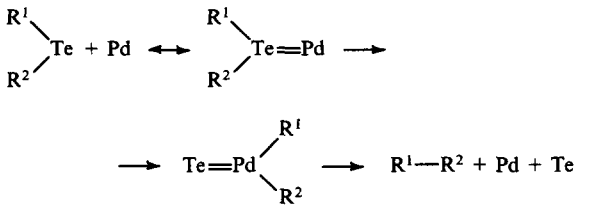
The synthesis of symmetrical biaryls from diaryl tellurides catalysed by Raney nickel is of definite interest for preparative organic chemistry.[371] The reactions are carried out by refluxing diaryl tellurides with a 20-fold molar excess of freshly prepared Raney nickel in 2-methoxyethyl ether for many hours and make it possible to obtain biaryls in 72%–90% yields.



R = OEt, OMe, Me, H, Br.

However, one should note that, according to Horner and Doms,[372] Ph_2Te is reduced under the influence of Rany nickel to benzene. Tellurium is then evidently converted into nickel telluride because on treatment with inorganic acid after the reaction H_2Te is evolved.

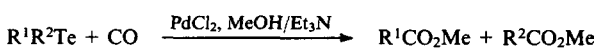
A more general method of synthesis of hydrocarbons of different composition (yield 76%–100%), based on the elimination of tellurium atoms from diorganyl tellurides, involves treatment of the tellurides R^1TeR^2 with palladium generated in situ from $Pd(OAc)_2$ and Et_3N.[373]



R^1 = 4-$MeOC_6H_4$; R^2 = 4-$MeOC_6H_4$, Ad^1, $C_{15}H_{31}$;

$R^1 = R^2 = PhCH_2CH_2$; $R^1 = PhCH_2CH_2$, $R^2 = CH_2Ph$.

Palladium(II) salts promote the insertion of carbon monoxide in the Te–C bonds of diorganyl tellurides, which leads to either carboxylic acids[43,374] or their methyl esters[53] depending on the conditions. The most convenient procedure for carrying out these reactions involves treatment of solutions of diorganyl tellurides in $MeOH/Et_3N$ at room temperature with carbon monoxide in the presence of stoichiometric amounts of palladium(II) salts.[53] The reactions can also be carried out in the presence of catalytic amounts of $PdCl_2$ when the reaction mixtures contain oxidants, the most effective of which is $CuCl_2$.[53] It is believed[43,53] that the reactions proceed via the intermediate formation of the monomeric complexes $(R_2Te)_2PdCl_2$ or dimeric complexes $[R_2TePdCl_2]_2$ with subsequent migration of the organic groups from Te to Pd, the insertion of CO in the Pd–C bond, and the hydrolysis of the acylpalladium intermediates.

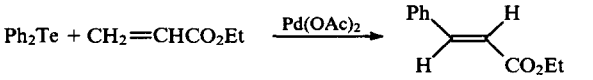


R^1 = Ph;

R^2 = PhCH=CH, EtO_2CCH=CH, PhC≡C, $C_6H_{13}C$≡C, Ph, $C_{12}C_{25}$.

It is noteworthy that, when the salts of other transition metals capable of forming complexes with diorganyl tellurides [Rh(III), Ru(III), Ir(III)] are used, the carbonylation reactions have very low yields (for $RhCl_3 \cdot 3H_2O$) or do not occur at all. The ability of triorganyl chalcogenides R_2M to enter into the reactions considered above increases sharply in the following sequence of the elements M: S ≪ Se < Te.[43,53] Thus Ph_2S does not enter into the reaction, Ph_2Se forms methyl benzoate in 14% yield, whereas in the reaction involving Ph_2Te the yield of the ester increases to 86%.

The arylation of alkenes by diorganyl tellurides also proceeds via arylpalladium intermediates formed when phenyl groups migrate from Te to Pd.[375] Thus the interaction of diphenyl telluride with ethyl acrylate in the presence of $Pd(OAc)_2$ leads to the formation of (2*E*)-phenyl acrylate in a yield exceeding 90% (biphenyl is a side product of the reaction).



It is noteworthy that Ph_2Se undergoes a similar reaction, but its rate is much slower than that of the reaction with Ph_2Te.

Under comparatively mild conditions, one or both C–Te bonds in diorganyl tellurides are cleaved by the triorganyl-substituted hydrides of Group IVA elements R_3XH (X = Si, Ge, Sn; R = Et, Bu, Ph).[376–382] The composition of the final reaction product (dissociation of one or two bonds) then depends on the nature of the hydride. Thus Et_3SiH and Et_2Te afforded compounds **110** and **111** in comparable yields at 200 °C,

Et_3GeH gave rise to the analogous compounds at 140 °C, but the reaction of Et_3SnH (even at 20 °C) led to the formation of only bis(triethylstannyl) telluride **111** (X = Sn).[376,377]

$$R_3XH + Et_2Te \xrightarrow[-C_2H_6]{} \underset{\mathbf{110}}{R_3X{-}TeEt} + \underset{\mathbf{111}}{R_3X{-}Te{-}XR_3}$$

The mild conditions in the reactions of diorganyl tellurides with triorganyltin hydrides and the high yields of the hydrocarbons makes it possible to employ diorganyl tellurides in the synthesis of the latter.[378–382] Ph_3SnH or Bu_3SnH are usually employed in these reactions. Diorganyl selenides are reduced to hydrocarbons in high yields (heating with Ph_3SnH at 120 °C).[378] However, organic sulfides are inert to Ph_3SnH.[378] The reduction of tellurides and selenides by tin hydrides probably proceeds via a S_H2 mechanism;[378,383] the rate of reduction of tellurides is then higher than that of selenides.

$$R_3SnH \longrightarrow R_3Sn^{\bullet} + H^{\bullet}$$

$$R_3Sn^{\bullet} + R^1_2Te \longrightarrow R_3Sn{-}TeR^1 + R^{1\bullet}$$

$$R^{1\bullet} + R_3SnH \longrightarrow R^1H + R_3Sn^{\bullet}$$

The dissociation of one (more rarely two) C–Te bond is observed in the protodetelluration and halodetelluration reactions of diorganyl tellurides. These reactions are most characteristic of alkyl aryl tellurides containing in the *ortho*-position functional groups capable of being coordinated to the Te atom; the weaker of the two C–Te bonds, namely $C(sp^3)$–Te, is then cleaved. Thus treatment of alkyl *o*-carbonylaryl tellurides by hydrogen halides (usually HBr) affords high yields of the *o*-halotellurocarbonyl compounds **112** stabilised by strong intramolecular O→Te coordinate bonds.[107,114,116,384]



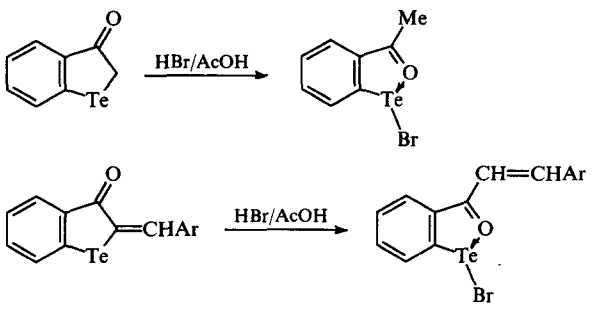
112

X = Cl, Br, I; $R^1 = R^3 = H$; $R^2 = CH_2CO_2Et, CH_2CH(OEt)_2$;[107]

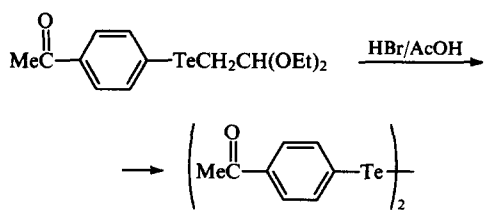
$R^1 = R^2 = Me$; R^3 = H, 4-Cl, 4-Me, 5-Me;[116]

R^1 = Me,[384] Ph;[114] R^2 = Bu; R^3 = H; X = Br.

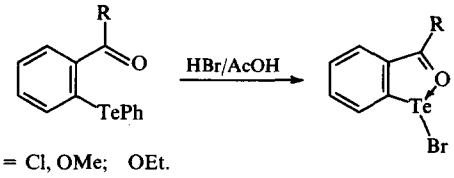
The $C(sp^3)$–Te bonds in telluroindoxyl[112] and telluroaurones[110] dissociate under similar conditions.



The presence of the COR groups in the *ortho*-positions relative to the TeR groups is a necessary condition for the formation of arenetellurenyl halides. Indeed, in the case of the diethyl acetal of *p*-acetylphenyltelluraacetaldehyde the hydrolysis leads only to the corresponding ditelluride.



It is of interest to note that not only the $C(sp^3)$–Te bond but also the C_{Ar}–Te bonds are cleaved by HBr when coordinating groups are present in the *ortho*-position in the molecules. Treatment of derivatives of 2-carboxyphenyl phenyl telluride (but not the acid itself) with HBr in acetic acid leads to tellanyl bromides in high yields.[113] Bearing in mind the ease of the reduction of the tellanyl bromides obtained to ditellurosalicylic acid, this reaction can be regarded as a convenient preparative method of synthesis of the latter.



R = Cl, OMe; OEt.

The $C(sp)$–Te bonds in the ethynes **113**[385,386] and **114**[387] and in alkylchalcogenovinylethynes **50a**[386,388] are very readily cleaved by acids in the presence (or absence) of Hg^{2+} salts.

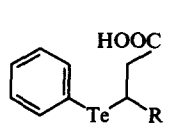
$RC{\equiv}CMMe$	$MeMC{\equiv}CMMe$	$CH_2{=}CHC{\equiv}CMMe$
113	**114**	**50a**

R = Me, Ph.

Whereas phenyl(methyl)thio- and phenyl(methyl)seleno-ethynes are hydrated with formation of the methyl esters of phenyl(methyl)thio(seleno)acetic acids, their tellurium analogues afford only the products of the cleavage of the $C(sp)$–Te bonds ($PhC{\equiv}CH$) and the product of partial dehydration — PhCOMe in the case of compound **113** (R = Ph, M = Te).[385] Whereas bis(methylseleno)ethyne **114** (M = Se) gives rise to a small yield of the addition product of the triple bond in its reaction with acetic acid in the presence of Hg^{2+} salts, its tellurium analogue undergoes only protodetelluration.[387] The product of the addition of acetic acid to the triple bond can be obtained under mild conditions from 1-methyltellurobut-3-en-1-yne **50a** (M = Te) in a low yield.[388] However, under more severe conditions this telluride is protodetellurated,[388] although the sulfur and selenium compounds having analogous structures are entirely stable under these conditions.[388]

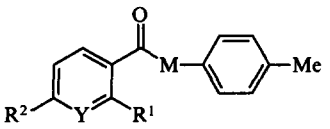
The ease with which protodetelluration takes place prevents in many instances the application in the synthesis of tellurium-containing compounds of reactions such as those employed in the chemistry of their sulfur and selenium analogues. Thus 3-phenyltelluropropionic acid **115** (R = H)[191] and its phenyl analogue **115** (R = Ph)[109] do not cyclise on treatment with perfluoroacetic acid (PFA) under the conditions employed to obtain selenachromanones,[389] but decompose with liberation of metallic tellurium. Similarly the attempts to synthesise telluro-chromanone by the pyrolysis of β-(*o*-carboxyphenyltelluro)-propionic acid or by the Dieckmann condensation of its diester were unsuccessful: the reactions occurred with cleavage of the $C(sp^3)$–Te bonds and led to ditellurosalicylic acid.[191]

Here it is appropriate to mention that one of the methods of synthesis of thia- and selena-xanthones — the photocyclisation of the esters **116** (M = S, Se) is inapplicable to the synthesis of telluraxanthones. UV irradiation of solutions of the telluroesters **116** (M = Te) leads to a complex mixture of products as a consequence of the cleavage of the C–Te bonds.[114,390,391]



115

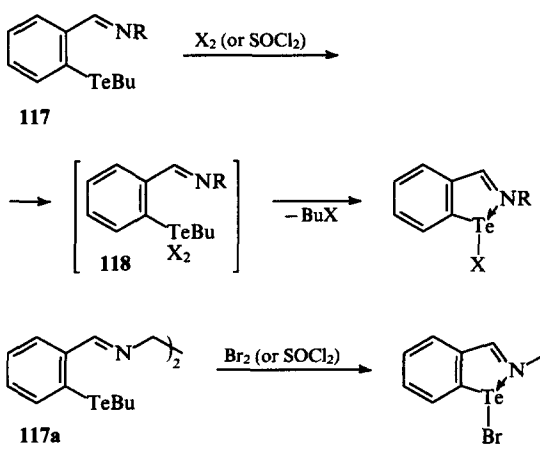
R = H, Ph



116

M = S, Se, Te; $R^1 = R^2 = H$; R^1 = H, R^2 = OMe; R^1 = Cl, SMe, OMe, SO_2Me; R^2 = H, Y = N, CH.

Reactions involving the oxidative addition of the halogens to alkyl aryl tellurides (see Section V and also Refs. 2–4) usually lead to stable alkylaryltellurium dihalides. However, when the *o*-tellurated azomethines **117**[104,123,124,126] and **117a**[125] react with the halogens or SO_2Cl_2, the C(sp^3)–Te bonds are cleaved, which leads to the formation of the corresponding tellanyl halides in high yields. The reactions evidently proceed via the σ-tellane intermediates **118**, the existence of which in solutions at a low temperature has been demonstrated with the aid of ^{1}H NMR spectra.[104] When the temperature is raised to room temperature, butyl halide molecules are eliminated.

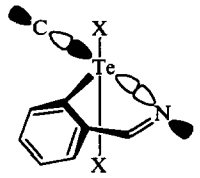


117

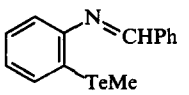
118

117a

The driving force of these reactions is, as in the protodetelluration reactions examined above, the marked stabilisation of tellanyl halides (which are 10-Te-3-telluranes according to the N–X–L nomenclature[392]) as a result of the coordination of the N(O) atoms to the tellurium atoms. In addition, there are favourable steric conditions for the N–Te and *n*(N) → σ*(Te–Bu) electron delocalisations in the intermediates **118**. As can be seen from the orbital interaction model **118a**, such delocalisation weakens the Te–C bond, which forms an angle of approximately 180° with the Te←N bond.

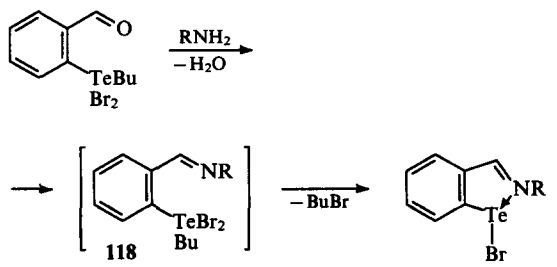


118a

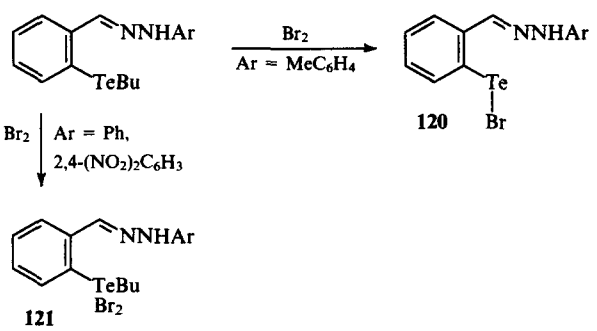


119

There are many examples of reactions facilitating the dissociation of the C–X bonds, which occurs when the interacting fragments are arranged in such a way that appreciable overlap of the *n*(O)–σ*(X–C) or *n*(N)–σ*(X–C) orbitals and hence partial population of the antibonding σ*(X–C) orbitals are ensured. In fact, benzylidene-2-methyltelluroaniline **119**, in which there is no N → Te coordination, gives rise to stable tellurium dihalides. The interaction of *o*-dibromo(butyl)tellurobenzaldehyde with primary amines gives rise to *o*-halotellurobenzylideneamines and not the σ-tellanes **118**.[104,124]



Thus, regardless of the nature of the substituents in the *N*-aryl rings of the azomethines **118**, their halogenation always leads to arenetellanyl halides. On the other hand, similar reactions with the arylhydrazones of 2-butyltellurobenzaldehyde proceed differently.[393] Electron-donating substituents in the arylhydrazone rings (Ar = MeC_6H_4) favour the cleavage of the C(sp^3)–Te bond on bromination, which leads to the formation of the tellanyl bromide **120**; when Ar = Ph or 2,4-$(NO_2)_2C_6H_3$, the arylhydrazones of 2-dibromo(butyl)tellurobenzaldehyde **121** are formed.

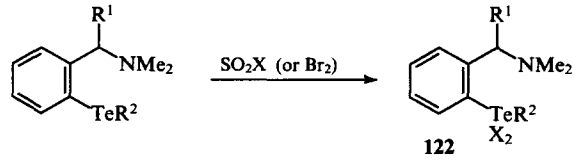


120

121

The reactions examined above, involving the halogenolysis of *o*-butyltellurobenzylideneamines and the arylhydrazones of 2-butyltellurobenzaldehyde are excellent illustrations of the influence of intramolecular N→Te coordinate bonds on the reactivity of organotellurium compounds (for other examples, see Section X).

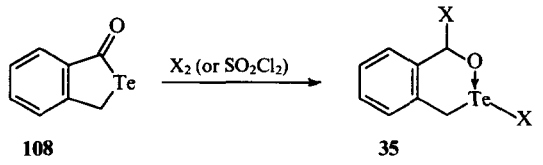
It is noteworthy that, when 2-alkyltellurobenzyldimethylamines are treated with SO_2Cl_2[131] or Br_2,[131,132] the stable σ-tellanes **122** are formed. This is evidence that the coordinate bonds involving an sp^3-hybridised nitrogen atom are weaker than those involving an sp^2-hybridised nitrogen atom.



122

R^1 = H; R^2 = Me, Et, Bu; $R^1 = R^2$ = Me; X = Cl, Br.

The cleavage of the C(sp^3)–Te bond at low temperatures takes place also in the halogenolysis of tellurophthalide **108**.[134] The tellanyl halides **35** formed in this reaction are the first examples of stable alkanetellanyl halides, their stability being due to the presence of the O→Te coordinate bonds.



108 35

X = Cl, Br, I.

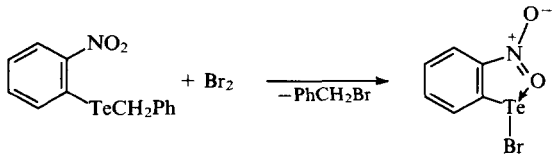
The halogenolysis of aryl benzyl tellurides, accompanied both by the dissociation of the C(sp^3)–Te bonds and by an increase in the coordination number of the tellurium atom, proceeds fairly specifically under the influence of $SOCl_2$ or SO_2Cl_2.[364,394]

$$RTeCH_2Ph \xrightarrow{X} RTeCl_3 + PhCH_2Cl$$

R = 4-MeOC$_6$H$_4$, 2-C$_{10}$H$_7$; X = $SOCl_2$, SO_2Cl_2.

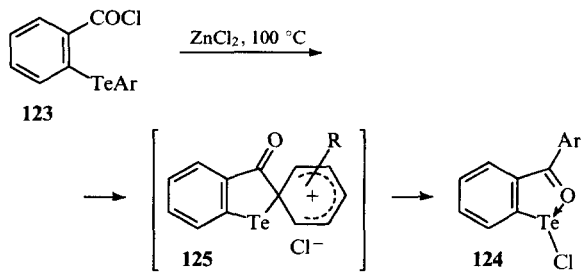
$$(PhCH_2)_2Te \xrightarrow{Br_2} PhCH_2Br + TeBr_4$$

Treatment of benzyl 2-nitrophenyl telluride with bromine entails the formation not of a tribromotelluro-derivative but of a tellanyl bromide stabilised by the O→Te coordinate bond.[121]



The C–Te bond dissociates also on interaction of bis(pentafluorophenyl)telluride with an excess of ClF, which results in the formation of considerable amounts of $C_6F_5TeF_4Cl$ and TeF_5Cl together with $(C_6F_5)_2TeF_4$.[156]

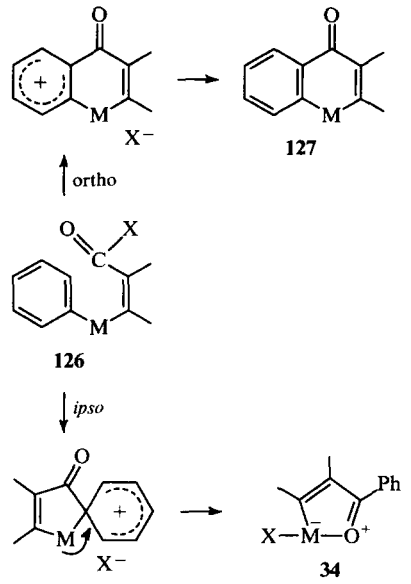
The cleavage of the C–Te bonds with simultaneous rearrangement has been achieved by treatment with certain Lewis acids. Thus heating of aryl 2-chlorocarbonylphenyl tellurides **123** in the presence of $ZnCl_2$ results in their rearrangement to 2-aroylbenzenetellanyl chlorides **124**,[111,113] which are probably stabilised by the formation of the intermediates **125**.



Ar = Ph, 4-MeC$_6$H$_4$, 2-C$_4$H$_3$S.

The selenium analogues of compound **123** undero a similar rearrangement, whilst the corresponding sulfur and oxygen analogues cyclise the thioxanthones and xanthones.

Another similar example illustrating the influence of the nature of the chalcogen atoms on the mode of reaction is the cyclisation of β-arylchalcogenopropenoyl chlorides **126** [51,54,115] or the corresponding acids.[115] The electrophilic cyclisation of these compounds can be achieved either by *ortho*-acylation, which leads to six-membered heterocycles — chalcogenochromones (flavones) **127**, or via *ipso*-acylation accompanied by the formation of five-membered heterocycles — 1,2-oxachalcogenolium chlorides **34**.



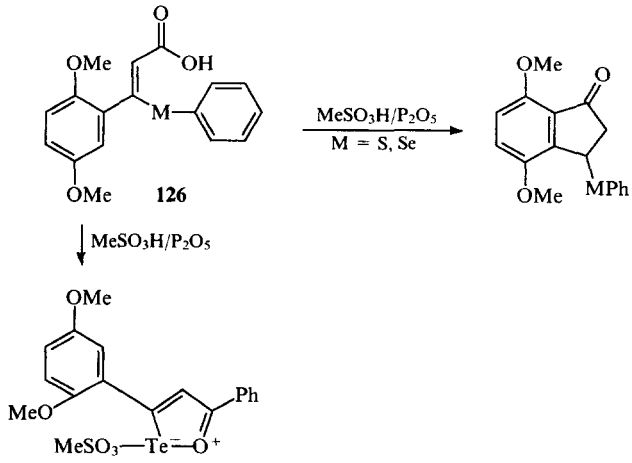
X = Cl, OH; M = S, Se, Te.

Regardless of the nature of substituents in the arene ring, the sulfur derivatives **126** (M = S) are only *o*-acylated, which leads to the thiochromones **127** (M = S).[115,395–398] Only *ipso*-acylation and the formation of the heterocycles **34** (M = Te) is characteristic of the *para*-substituted β-aryltelluropropenoyl chlorides **126** (M = Te).[51,54,115] This is probably due to both the increased polarisability of the tellurium atom and to its relatively low electronegativity compared with other chalcogenes. Depending on the nature of the substituents in the selenoaryl rings, the selenium compounds **126** (M = Se) can cyclise either to the heterocycles **127** (M = Se)[399–401] or to 1,2-oxaselenolium chlorides **34** (M = Se).[115] Mixtures of the two heterocycles are formed in some cases.

However, one should note that, by varying the nature and positions of the substituents in telluroaryl rings of compound **126** (M = Te), it is possible to activate the *ortho*-positions in these rings to electrophilic attack, i.e. to drive the interaction towards the preferential formation of tellurochromones (flavones).[54,115]

Furthermore, whereas the cyclisation of β-thio(seleno)arylcinnamic acids **126** (M = S, Se) on treatment with the $MeSO_3H-P_2O_5$ system leads to benzocyclopentenones,[401] the analogous reaction with the tellurium analogues affords 1,2-oxatellurolium methanesulfonates[54] (Scheme 3).

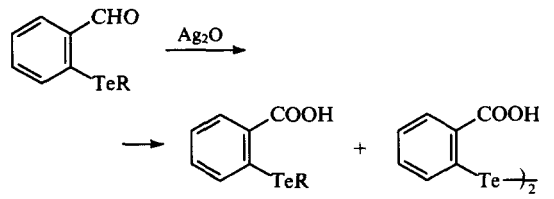
Scheme 3



The dissociation of the C–Te bond in diorganyl tellurides can also take place in the presence of other than halogen-containing ($SOCl_2$, SO_2Cl_2) oxidants. Thus, according to Balfe and coworkers,[169,170] on reaction with O_2 or H_2O_2 dialkyl tellurides

are converted into complexes of different compositions, one of the components of which is tellurinic acids RTe(O)OH. These old data probably require additional confirmation. Incidentally, the formation of alkanetellurinic acids, the structure of which has been established by spectroscopic methods, has also been noted in the oxidation of 1-alkyltellurobut-3-en-1-ynes of type **50**.[402] The C(*sp*)–Te bonds are dissociated during the reaction and vinylethyne is formed together with the trimers.

The oxidation of 2-alkyltellurobenzaldehydes by Ag_2O in an alkaline medium affords, apart from the expected 2-alkyltellurobenzoic acid **128**, the product of the cleavage of the C(sp^3)–Te bond — ditellurosalicylic acid.[190] In the case of *o*-methyltellurobenzaldehyde, the acid **128** is obtained in a yield of about 60%.



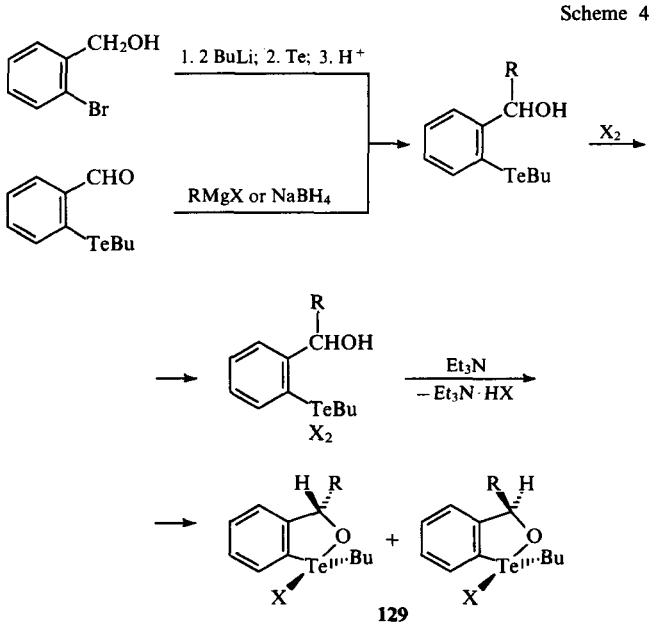
128

R = Me, Bu.

On the other hand, the oxidation of aryl benzyl tellurides by atmospheric oxygen gives rise to the corresponding benzaldehydes.[81,364,366,394]

The ready dissociation of the C–Te bonds under the influence of oxidants is the reason why some of the usual oxidation reactions in organic chemistry cannot be employed for the synthesis of organotellurium compounds. Thus the oxidation of the secondary alcohol 1-(2-methyltellurophenyl)ethanol (in order to obtain 2-methyltelluroacetophenone) by DMSO in acetic acid[109] or of the methyl group in 2-methyltellurotoluene (in order to synthesis 2-methyltellurobenzaldehyde)[190] is accompanied by the elimination of the tellurium atom. The recently developed method of synthesis of tellurium-containing carbonyl compounds from 3*H*-2,1-benzoxatelluroles **129**, the synthesis of which is illustrated in Scheme 4, is of definite interest in the chemistry of such tellurium-containing carbonyl compounds.[403,404]

Scheme 4

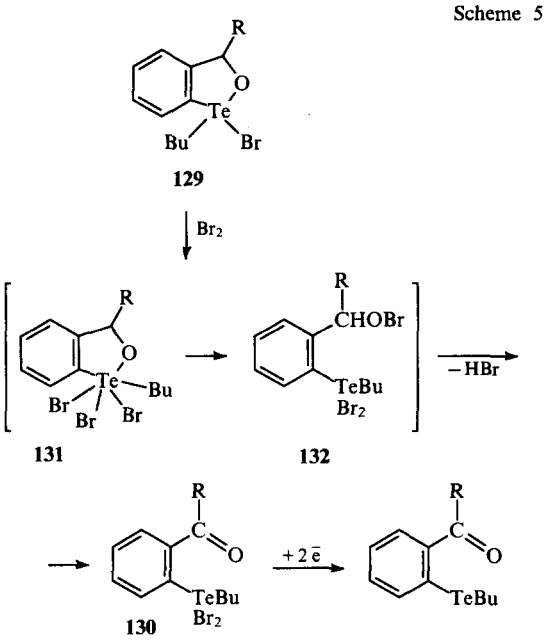


129

X = Cl, Br, I; R = H, Me, Ph, 4-MeC$_6$H$_4$.

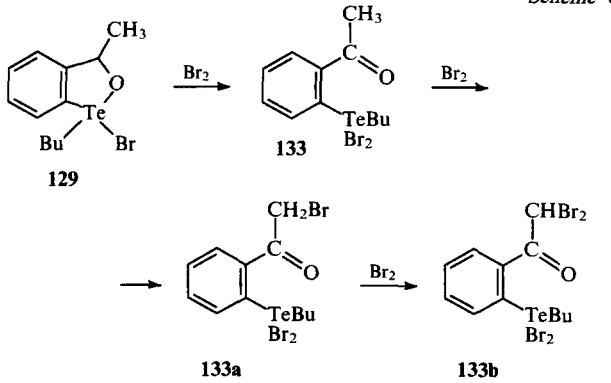
On treatment with bromine, the O–Te bond in the heterocycles **129** is cleaved, giving rise to aldehydes or ketones **130**, depending on the nature of the substituents in the 3-position in the heterocycle, with the Te(Bu)Br$_2$ group in the *o*-position. The reaction probably proceeds via intermediate **131** with a hexacoordinate tellurium atom, which rearranges to compound **132**. Yields of the carbonyl derivatives **130** are 70%–90% (Scheme 5).

Scheme 5

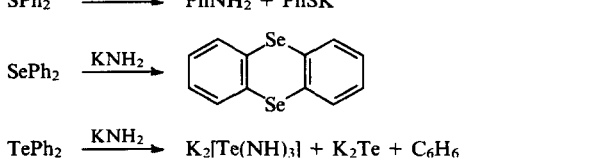


Bearing in mind that 3-R benzoxatelluroles **129** can be obtained from 2-butyltellurobenzaldehyde, the above sequence of reactions can be regarded as a new method for the conversion of *o*-alkyltellurobenzaldehyde into ketones and of *o*-alkyltellurobenzyl alcohols into aldehydes, which is specific to organotellurium compounds. In the case of the 3-methyl derivative **129** (R = Me), the acetophenone derivative **133** formed initially is brominated at the methyl group with formation of compounds **133a** and **133b** (Scheme 6).[404]

Scheme 6



Finally, the cleavage of the Te–C bonds by various nucleophiles is possible. Thus the nature of the chalcogen atoms in diphenyl chalcogenides determines the different results of their reactions with potassium amide in liquid ammonia presented below.[405] The reaction with Ph_2Te is accompanied by the complete dissociation of the C_{Ar}–Te bonds.



On treatment with lithium in liquid NH_3 or with $LiNH_2$, the bonds between the chalcogens and the unsaturated groups in the alkylseleno(telluro)alkenynes of type **50** are ruptured, whereas in their thio-analogues both these bonds and the C(sp^3)–S bonds are cleaved.[406]

$$CH_2{=}CHC{\equiv}CLi + RMLi$$

$LiNH_2$; M = S, Se, Te; R = Me, Bu

$$CH_2{=}CHC{\equiv}CMR \xrightarrow[M = S,\ R = Me]{LiNH_2} CH_2{=}CHC{\equiv}CSLi + RLi$$

50

On the other hand, in contrast to the sulfur and selenium derivatives **50**, which combine with RMgX at the triple bond[407] with formation of chalcogen-containing allenes, their tellurium analogues react with dissociation of the C(sp)–Te bond and the formation of dialkyl tellurides. The cleavage of the C–Te bonds in compound **50** (M = Te) is also observed in the reaction with EtSH.[408]

Lithium in liquid NH_3 also ruptures the C(sp^2)–Te bonds; on subsequent alkylation of ethynetellurolate by alkyl halides, alkyl vinyl tellurides are formed.[409]

$$(CH_2{=}CH)_2Te \xrightarrow[2.\ RX]{1.\ Li/NH_3} CH_2{=}CHTeR$$

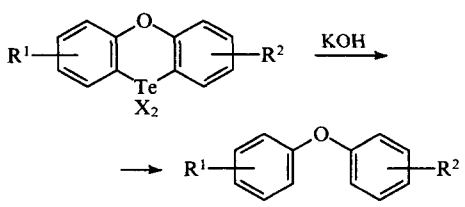
R = Me, Et, Pr.

On the other hand, the cleavage of the Te–C bonds in bis(perfluoroalkyl)tellurides by aqueous solutions of alkalies takes place at room temperature and leads to perfluoroalkanes.[410]

$$(R_F)_2Te \xrightarrow{KOH} R_FH$$

$R_F = CF_3, C_2F_5$.

Elimination of the tellurium atom is also observed on heating phenoxatelluranes, 10,10-dichlorophenoxatelluranes, and 10,10-dinitratophenoxatelluranes in aqueous K_2CO_3 or KOH solutions;[18,21] diaryl ethers are then formed in high yields. These reactions have been used to identify the products of electrophilic substitution of phenoxatellurane (nitration, bromination).



X = Cl, ONO_2.

Much attention has been devoted in recent years to the reactions of diorganyl tellurides with organolithium compounds. Like the Grignard reagents, these compounds cleave the C–Te bond in dialkyl,[411–413] alkyl aryl,[411,413–416] and even diaryl tellurides.[411,417–420] The reactions of butyllithium with organyl vinyl and divinyl telluride are accompanied by the dissociation of the C(sp^2)–Te bonds and lead to vinyllithium derivatives,[58,411,413,421] the latter being formed with retention of the configuration. The C(sp)–Te bonds are ruptured just as readily by organolithium and organomagnesium compounds [the C(sp)–Te bonds[411,413,422,423] are also cleaved by $NaBH_4$].[422,424] It has been shown by ^{13}C NMR spectroscopy that the reactions of organolithium compounds with diorganyl tellurides proceed via the intermediate formation of complexes **134** containing a tricoordinate Te atom. The latter decompose with formation of the thermodynamically more stable organolithium derivative (for example, R^1Li) and a new diorganyl telluride.

$$R^1TeR^2 + R^3Li \longrightarrow \left[R^1{-}\underset{\displaystyle R^3}{\underset{|}{Te}}{-}R^2\right]^- Li^+ \longrightarrow$$

134

$$\longrightarrow R^1Li + R^2TeR^3$$

The comparatively readily available diorganyl tellurides have therefore been used as effective sources of alkyl-, alkenyl-, alkynyl-, aryl-, acyl(aroyl)-,[425] and carbamoyl-lithium compounds.[426] They can be synthesised from organyl halides without the preliminary isolation of the telluride, in accordance with the following scheme:

$$R^1X + R^2TeLi \xrightarrow[-LiX]{} R^1TeR^2 \xrightarrow[-R^2TeR^3]{R^3Li} R^1Li$$

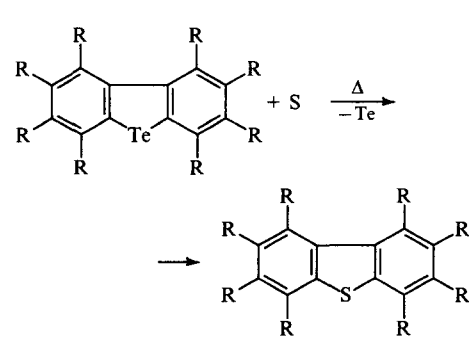
The interaction of diaryl and alkyl aryl tellurides with Grignard reagents (for alkyl aryltellurides the group R in RMgX must be the same as one of the groups in ArTeR) in the presence of catalytic amounts of nickel or cobalt compounds [$NiCl_2(PPh_3)_2$, $NiCl_2(Ph_2PCH_2CH_2PPh_2)_2$, $CoCl_2(PPh_3)_2$] also takes place with dissociation of the C–Te bonds. This leads to the formation of a mixture of cross- and homo-coupling products.[50,52]

$$ArTeR + RMgBr \xrightarrow{Cat} Ar{-}R + Ar{-}Ar + R{-}R$$

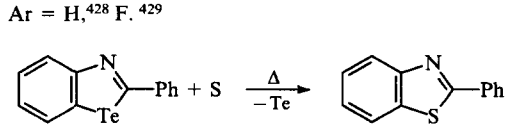
On heating with elemental sulfur, the tellurium atom in certain organotellurium compounds is substituted by a sulfur atom. These reactions are undergone both by diaryl tellurides[336,427] and by tellurium-containing heterocycles: dibenzotellurophenes,[428,429] 2-phenylbenzotellurazole,[178] phenoxatelluranes,[177,321–324,430] phenothiatellurane,[196] and phenotellurazines.[431] The only example of the substitution of the tellurium atom by selenium involves the formation of phenoxaselenane on heating phenoxatellurane with powdered selenium.[430]

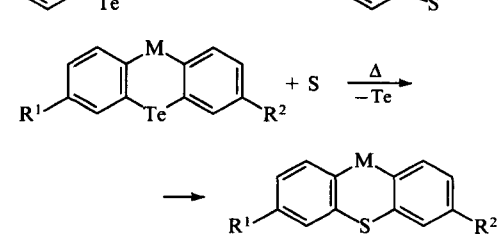
$$Ar_2Te + S \xrightarrow[-Te]{\Delta} Ar_2S$$

Ar = Ph,[427] C_6F_5.[336]



Ar = H,[428] F.[429]



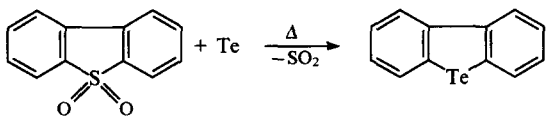


M = O; $R^1 = R^2$ = H,[430] Me,[321] Cl,[322] F;[323]

R^1 = F, R^2 = Me,[177] Cl;[324]

M = S; $R^1 = R^2$ = H;[196] M = NEt; $R^1 = R^2$ = H, Me[431].

This property of organic tellurium derivatives is evidently due both to the higher C–S bond energy compared with that of C–Te and the more pronounced aromaticity of the sulfur heterocycles compared with their tellurium analogues.[15] On the other hand, the greater aromaticity of tellurium-containing heterocycles compared with heterocyclic sulfones leads to the possibility of the substitution of the SO_2 group by a Te atom.[432]



X. Intramolecular Te←N(O) coordination and the reactivity of organotellurium compounds

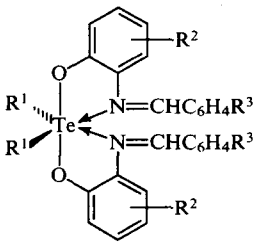
Intramolecular Te←N and Te←O coordinate bonds are one of the principal factors ensuring the stability of certain classes of organotellurium compounds (see Section IV) and exerting a significant influence on the reactivity and structure of organic tellurium derivatives.[104–106] Data concerning the influence of intramolecular coordination on reactivity are qualitative; one of the examples of the influence of the N→Te coordination on the halogenolysis of 2-butyltellurobenzylideneanilines was examined previously (see Section IX).

1. Reduction of C=N bonds

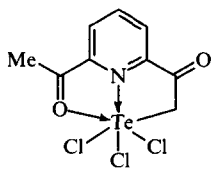
In contrast to the C=N bonds of the tellurium-free aromatic azomethines, which are readily reduced by $NaBH_4$ in ethanol, 2-butyltellurobenzylidene-4′-methylaniline does not change even after prolonged refluxing with this reductant.[126] On the other hand, both the C=N bond and the $TeBr_3$ group are reduced (the latter to TeBr) in 2-tribromotellurobenzylidene-4′-methylaniline on treatment with $NaBH_4$, leading to a secondary amine.[127] Replacement of the 4-methyl group by the more bulky *tert*-butyl groups in the 2-, 4-, and 6-positions inhibits both these reactions.

2. Reactions of σ-telluranes

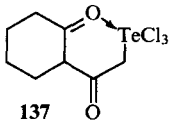
The presence of the Te←N and Te←O coordinate bonds in the molecules of σ-telluranes increases significantly their hydrolytic stability. The diorganyl (diaryloxy)telluranes **135** with Te←N bonds are not hydrolysed on prolonged contact with water,[433,434] whereas diaryl(dialkoxy)telluranes which do not contain such bonds are rapidly hydrolysed even by atmospheric moisture.[351] A similar behaviour is characteristic also of the tellurium trichlorides **136–138**,[435] which are inert to water [the usual trichlorides are rapidly hydrolysed by water with formation of the tellurium oxide chlorides RTe(O)Cl].[2,3]



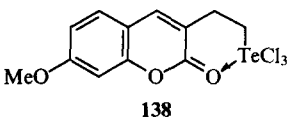
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136



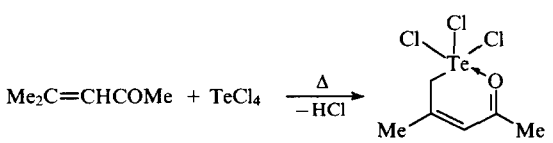
137



138

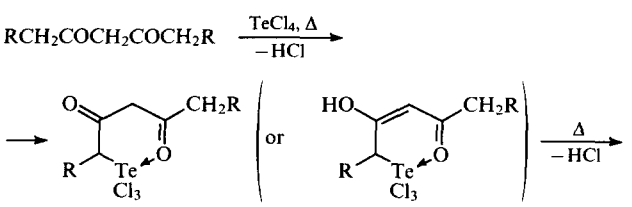
The electrophilic nature of the $TeCl_3$ groups coordinated to N and O atoms is less pronounced than that of noncoordinated trichlorotelluro-groups. Thus, whereas acetophenone and its derivatives afford σ-telluranes of the type $(ArCOCH_2)_2TeCl_2$ on interaction with $TeCl_4$,[436–439] the reactions of 2,6-diacetylpyridine, 2-acetylcyclohexanone, and 3-acetyl-7-methoxycoumarin with $TeCl_4$ give rise to only σ-telluranes of the type $RTeCl_3$ (compounds **136–138**) even in the presence of a twofold molar excess of the carbonyl component.[435]

The reaction of mesityl oxide with $TeCl_4$ in $CHCl_3$ is also instructive. It leads to 2-methylpent-2-en-4-onetellurium trichloride **139**,[440,441] i.e. involves the methyl group adjoining the double bond and not that linked to the carbonyl group, as happens in the analogous reactions of acetophenones and other methyl ketones.[436–439] The possible reaction mechanism involves the initial electrophilic attack by $TeCl_4$ on the COMe group with the subsequent rearrangement of the resulting tellurium trichloride to compound **139**. The driving force of the reaction is the marked stabilisation of the trichloride **139** with the Te←O coordinate bond (the bond length is 2.44 Å).[441]

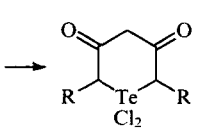


139

This is probably the reason[440] why in the reactions of 1,3-diketones with $TeCl_4$ the latter attacks the terminal carbon atom, which results in the formation of 1-telluracyclohexane-3,5-dione 1,1-dichlorides **140**.[18,21] When the hydrogen atoms at the terminal carbon atoms are substituted, there is a possibility of the formation of the tellurium trichlorides **141**, which are stabilised by the Te←O coordination.

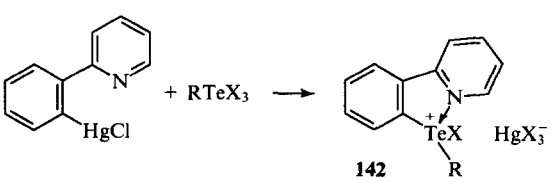


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140

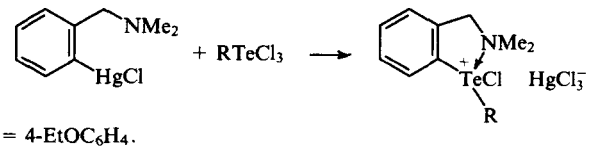
The interaction of organyltellurium dichlorides and tribromides $RTeHal_3$ with RHgHal leads readily to diorganyltellurium dihalides R_2TeHal_2 and $HgHal_2$.[2,3] However, when the formation of coordinate bonds involving the Te atom becomes possible in the final product, the reactions of $RTeHal_3$ with ArHgCl lead to 2-(2-pyridyl)phenylhalo-tellurium trihalomercurates **142**.[129,442]



142

X = Cl, Br; R = 4-$EtOC_6H_4$.

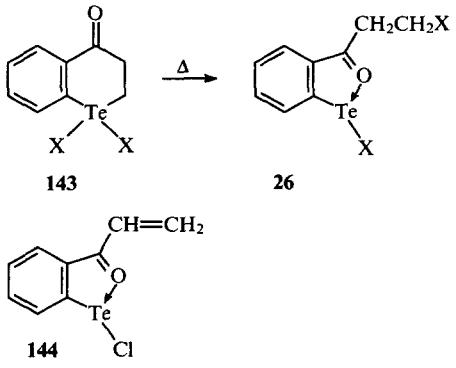
The products of the interaction of 2-chloromercuriobenzyldimethylamine with $ArTeCl_3$ have an analogous structure.[131]



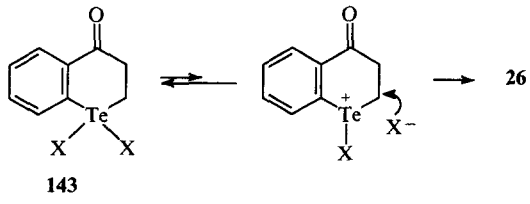
R = 4-EtOC$_6$H$_4$.

3. Rearrangement of dihalotellurochromanones

Dihalotellurochromanones **143** undergo on heating a rearrangement, not described previously, which involves the dissociation of the C(sp^3)–Te bond and the formation of 2-(β-halopropionyl)benzenetellurenyl halides **26**.[118] In the case of the chloro-derivative **143** (X = Cl), the ketone **144** was isolated as the final product, evidently as a consequence of the elimination of HCl from compound **26** (X = Cl) formed initially. The rearrangement is achieved by heating solutions of dihalotellurochromanones in $CHCl_3$, C_6H_5Br, or $C_6H_5NO_2$ for 20–30 h.

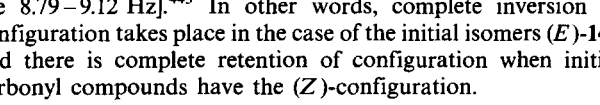


As in the series of reactions considered above, the driving force of the rearrangement is the marked stabilisation of the tellanyl halides **26** with the Te←O coordinate bonds [the length of the bond in 2-(β-iodopropionyl)benzenetellanyl iodide **26** (X = I) is 2.368 Å][118] and the possible mechanism involves the predissociation of the Te–X bond with subsequent attack by the halide anion on the β-carbon atom.



4. Stereochemistry of reactions involving the substitution of chlorine atoms in β-chlorovinylcarbonyl compounds by arenetellurolate anions

The reactions involving the nucleophilic substitution of chlorine atoms in β-chlorovinylcarbonyl compounds **145** by arenetellurolate anions leads in all cases to the formation of only (*Z*)-isomers by β-aryltellurovinylcarbonyl compounds **146** [the spin–spin coupling constants for the ketones **146** ($R^1 = R^2 = H$) are 8.79–9.12 Hz].[443] In other words, complete inversion of configuration takes place in the case of the initial isomers (*E*)-**145** and there is complete retention of configuration when initial carbonyl compounds have the (*Z*)-configuration.

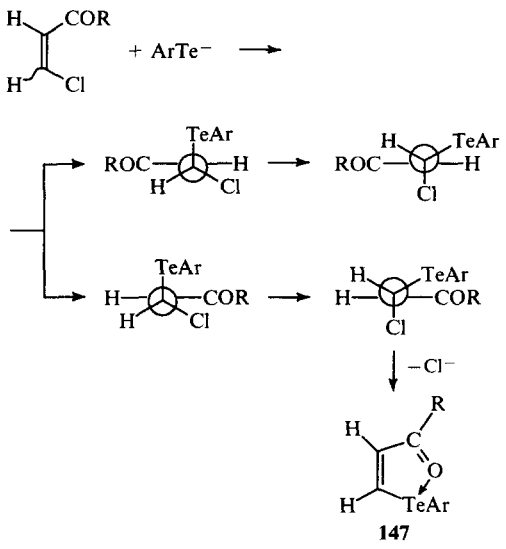


$R^1 = R^2 = H$; R^3 = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$, 4-BrC$_6$H$_4$;

R^1 = Ph, $R^2 = R^3 = H$; $R^1 + R^2 = -(CH_2)_4-$, $R^3 = H$;

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

The stereochemical result obtained may be interpreted in terms of a 2-stage nucleophilic substitution mechanism (addition–elimination).[444] The first stage of the process is the addition of the arenetellurolate anions to the double bond activated by the strongly electron-accepting carbonyl group. Among the possible conformers arising on rotation of the C–C single bond in the carbanion formed, the most stable is evidently the conformer stabilised by the intramolecular Te←O coordinate bond. In the second stage, the elimination of the chloride ions from this conformer leads to the formation of the (*Z*)-isomers **147** which are additionally stabilised by the formation of the Te←O coordinate bonds.[443]



Apparently 2-(4′-ethoxyphenyltelluro)-1-formylcyclohexene **146** [Ar = Ph; $R^1 + R^2 = -(CH_2)_4-$, $R^3 = H$], which is a cyclohexene derivative, is also a (*Z*)-isomer with an intramolecular Te←O coordination bond. Judging from the ^{1}H NMR spectrum, the aldehyde **146** (Ar = R^1 = Ph, $R^2 = R^3 = H$) exists in solution in only one form. On the basis of the mechanism proposed above and the marked stabilisation of tellurium(II) derivatives by intramolecular coordinate bonds, the hypothesis that this form has the (*Z*)-structure in which the Te and O atoms are coordinated is evident.

* * *

The specific features of the chemical behaviour of organotellurium compounds considered in the present review give rise to interesting additional possibilities for a rapidly developing aspect of organic synthesis — the methodology of the use of organoelement synthons incorporating heavy elements of the main groups of the Periodic Table. The organoiodine[233] and organoselenium[445] methodologies, based on the extensive possibilities for the introduction, modification, and elimination of the corresponding groups accompanied by the formation of new carbon–carbon bonds, have come to be widely used.

The possible employment of phenyl derivatives of bismuth(V) for the *C*- and *O*-phenylation of various organic compounds is being developed.[446] It is so far too early to speak of an organotellurium methodology, but the foundations for its establishment have already been laid in the specific reactions of organotellurium compounds which have been presented.

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