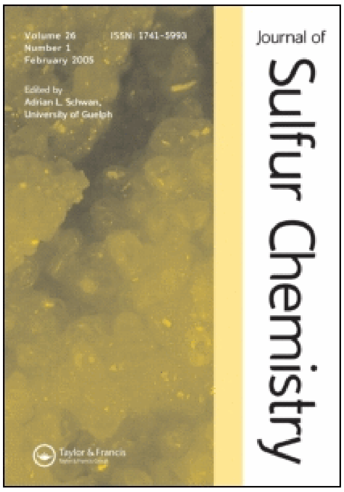

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SYNTHESIS AND REACTIONS OF DIORGANYL TELLURIDES

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Literature data concerning the synthesis and reactions of diorganyl tellurides, viz., dialkyl, alkyl aryl and diaryl tellurides are systematized and generalized in this review.

Key words: Alkyl aryl tellurides, dialkyl tellurides, diaryl tellurides.

CONTENTS

1. INTRODUCTION

Diorganyl tellurides R^1TeR^2 ($R^1 = R^2$ = alkyl, aryl; R^1 = alkyl, R^2 = aryl) with their relatively facile transformation into derivatives of tri- (telluronium salts, π-telluranes, viz., telluronium ylides, tellurimides and telluroxides), tetra- (σ-telluranes R_2TeX_2 where X is an electron acceptor group, and diaryl tellurones) and even of hexacoordinated tellurium are synthetically important organotellurium compounds. However, in contrast to vinyl and alkynyl tellurides which have been reviewed quite recently,[1,2] the data available from monographs[3,4] and surveys[5,6] and concerning diorganyl tellurides which include C_{sp^3}-Te and $C_{arom.}$-Te bonds are considerably out of date. At the same time the fast growth in the number of publications devoted to the preparation and reactivity of these compounds as well as to the elaboration of novel reagents and the synthesis of new types of diorganyl tellurides made it necessary to systematize and generalize the data accumulated in this area.

Diorganyl tellurides of the types mentioned are also of special interest as ligands for coordination compounds[7] and as synthons in preparative organic chemistry.[8–14] These applications of diorganyl tellurides, particularly the last one, are discussed mainly in Chapter 3 of this review. Also mentioned are the preparation of ultrapure tellurium[15] as well as of semiconducting metal tellurides[16–18] by means of gase-phase pyrolysis of neat dialkyl tellurides themselves or their admixtures with appropriate metalalkyls. In addition, there are a number of publications concerning the use of diorganyl tellurides as components of light sensitive materials.[19–21]

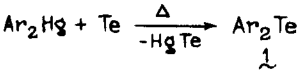
2. SYNTHESIS OF DIORGANYL TELLURIDES

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

2.1. *From Elemental Tellurium*

The use of elemental tellurium for the synthesis of diorganyl tellurides is based on its reactions with mercury- and thallium-organic derivatives as well as with rhodium complexes and with radicals.

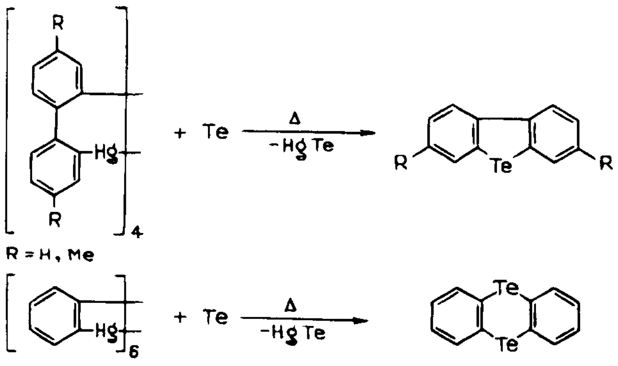
Diarylmercury derivatives were the first class of elementoorganic compounds used for this purpose.[22] Tellurium when heated with a diarylmercury to a high temperature gives rise to the appropriate diaryl telluride **1** in 50–100% yield.[22–29]



Ar = Ph,[22,24,26–28] 4-MeC_6H_4,[23,26] 3-MeC_6H_4,[26] 2-MeC_6H_4,[23,26] 4-MeOC_6H_4,[26] $2,5\text{-Me}_2C_6H_3$,[26] C_6F_5,[29] $1\text{-C}_{10}H_7$[25,26]

It should be noted that, in contrast to bis(pentafluorophenyl)mercury,[29] the replacement of mercury by tellurium in bis(2-nonafluorobiphenyl)mercury is accompanied by cyclization of the telluride formed to octafluorodibenzotellurophene (10% yield).[30]

The same method has been employed for the synthesis of some heterocyclic tellurium-containing systems. Thus, dibenzotellurophene and its 4-methyl homolog have been prepared in 82% and 79% yield, respectively, by heating of the appropriate tetrameric orthobiphenylenemercury with tellurium at 260–270 °C (230 °C).[31-33] Analogously the reaction of hexameric *o*-phenylenemercury and tellurium at 250 °C leads to the corresponding telluranthrene in 72% yield.[34]

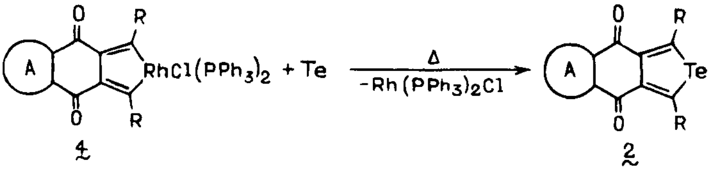


It should be noted that the preparation of telluranthrene from tetraphenyltin and tellurium at 310 °C described in an earlier report[35] could not be confirmed in later publications.[34,36]

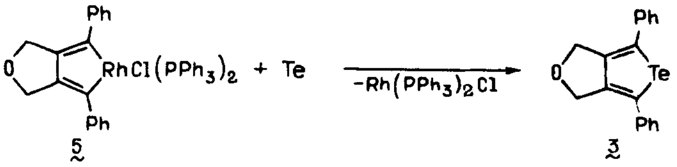
Bis(pentafluorophenyl)thallium bromide is the only representative of this class of compounds which has been allowed to react with tellurium. Three-day heating of the reaction mixture at 190 °C gave rise to bis(pentafluorophenyl) telluride in 18% yield.[37]

$$(C_6F_5)_2TlBr + Te \xrightarrow[-TlBr]{\Delta} (C_6F_5)_2Te$$

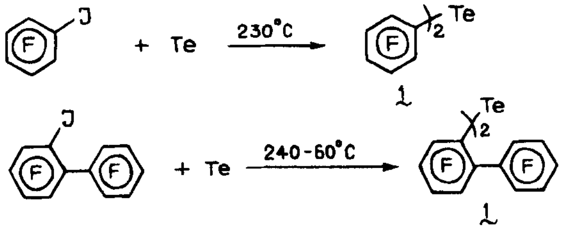
Another variant of the use of elemental tellurium which permits to prepare cyclic tellurides, i.e. tellurophenes **2** and **3**, consists of the boiling of the rhodium complexes **4** and **5** with an equimolar amount of tellurium in toluene or xylene. The heterocycles **2** and **3** which are difficult to access otherwise were obtained in 10–63% yield.[38-40]



R = Ph: A = 1,2-benzo, 2,3-naphtho, 3,4-(2,5-dimethyl)thieno, 2,3-benzothieno
R = 4-MeC_6H_4: A = 1,2-benzo, 2,3-naphtho

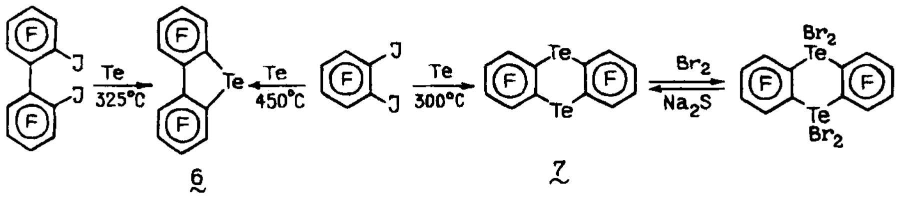


The reaction of iodopolyfluoroarenes with tellurium metal is a specific method of synthesis of polyfluorinated diaryl tellurides and their cyclic analogs. Thus, bis(pentafluorophenyl) **1**[29] and bis(2-nonafluorobiphenylyl) telluride **1**[30] have been prepared in 100% and 35% yield, respectively, by means of the reactions presented below.



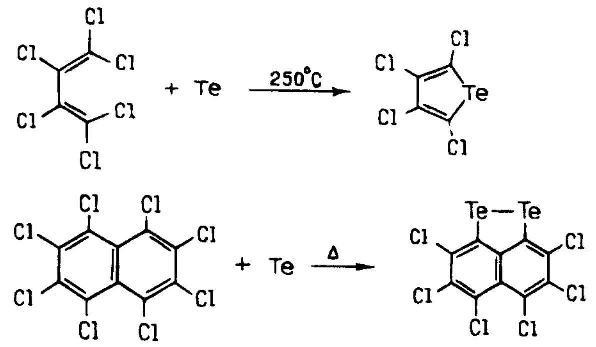
However, heating of methyl iodide[41] and its homologs[42,43] with tellurium in a sealed tube give rises to dialkyl tellurium diiodides. Probably the strong electron acceptor properties of perfluoroalkyl groups weakening the Te-I bonds in the intermediate σ-telluranes as well as the high reaction temperature result in the decomposition of the σ-telluranes to diaryl tellurides **1** and iodine.

Interestingly the reaction temperature determines the structure of the products formed upon heating of tellurium with 1,2-diiodotetrafluorobenzene. According to[30,36] the products are octafluorodibenzotellurophene **6** at 450 °C (17% yield) and octafluorotelluranthrene **7** at 300 °C, purified by transformation into the corresponding tetrabromo derivatives and subsequent reduction with sodium sulfide. This method, i.e. oxidation of diorganyl tellurides with halogens to the corresponding σ-telluranes (usually dichlorides or dibromides) which can be easily purified by recrystallization and then reduced under mild conditions in almost quantitative yield to the initial telluride is widely used for the purification of diorganyl tellurides.



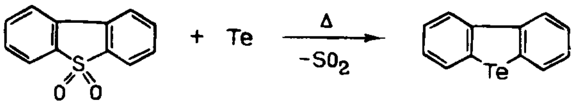
2,2′-Diiodooctafluorobiphenyl when heated with tellurium gives rise to the heterocycle **6** in 66% yield.[29]

Furthermore the synthesis of some tellurium-containing heterocycles has been performed by high-temperature reaction of tellurium metal with polychlorinated hydrocarbons. Thus, the first representatives of tellurophenes and naphtho[1,8-*c*,*d*]1,2-ditelluroles have been prepared by heating of tellurium and hexachlorobutadiene[44] or octachloronaphthalene,[45] respectively.



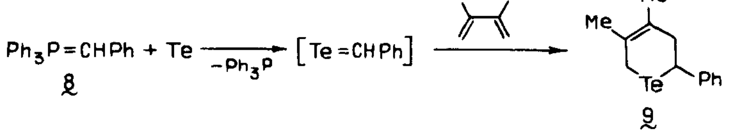
Radicals generated by thermal decay of various organic compounds react with tellurium mirrors. Dimethyl,[3] diphenyl,[3] and bis(trifluoromethyl) telluride[46] have been isolated as products of such processes. However, these reactions are without preparative importance because the corresponding ditellurides are formed together with the tellurides.[46]

At high temperature tellurium replaces the SO_2 group in dibenzothiophene *S*,*S*-dioxide giving rise to dibenzotellurophene in about 10% yield.[47]

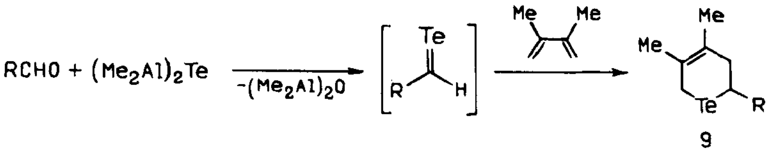


It would be interesting to investigate the synthetic possibilities of this reaction by extending it to other cyclic and acyclic sulfones.

A novel approach to the application of tellurium for the preparation of cyclic diorganyl tellurides was proposed recently.[48] Interaction between the phosphorane **8** and tellurium results in telluroaldehyde formation. This intermediate reacts *in situ* with 2,3-dimethylbutadiene leading to 3,6-dihydro-4,5-dimethyl-2-phenyl-2*H*-telluropyran **9** in 11% yield.



By generation of telluroaldehydes and telluroketones from the appropriate carbonyl compounds and bis(dimethylaluminium) telluride[49] higher yields of **9** and its analogs can be achieved. This reaction is analogous to one used earlier to prepare sulfur- and selenium-containing heterocycles of type **9**.[50]



9

R = Pr, *t*-Bu, Ph

2.2. *From Tellurium Di- and Tetrahalides*

Symmetric diaryl tellurides **1** have been obtained by reaction of tellurium dihalides with Grignard reagents.[51–65] Biaryls, diaryl ditellurides and elemental tellurium are by-products of this reaction. These by-products are the result of partial disproportionation of tellurium dihalides to tellurium and tellurium tetrahalides.[3,66] The following reaction of a magnesiumorganic reagent with tellurium and a tellurium tetrahalide leads to the corresponding diaryl ditelluride and tetraaryltellurane Ar_4Te, respectively. The latter derivative undergoes thermal decomposition to diaryl telluride and biaryl (cf. 2.5.7.).

$$ArMgX + TeX_2 \xrightarrow[-MgX_2]{} Ar_2Te$$

Ar = $2\text{-}C_4H_3S$,[64] $4\text{-}ClC_6H_4$,[57*] $4\text{-}BrC_6H_4$,[57*] C_6H_5,[51] $4\text{-}MeC_6H_4$,[52,65] $3\text{-}MeC_6H_4$,[55] $2\text{-}MeC_6H_5$,[52,65] $4\text{-}MeOC_6H_4$,[56] $3\text{-}MeOC_6H_5$,[61] $2\text{-}MeOC_6H_4$,[62] $4\text{-}EtOC_6H_4$,[60,64] $2\text{-}EtOC_6H_5$,[58] $2,5\text{-}Me_2C_6H_3$,[53] $2,4\text{-}Me_2C_6H_3$,[53] $2,4,6\text{-}Me_3C_6H_2$,[54] $2\text{-}C_{10}H_7$[59]

Later lithiumorganic reagents were used in the corresponding reaction with tellurium diiodide. This allowed to raise the yields of diaryl tellurides to more than 60%.[67–69]

$$RC_6H_4Li + TeI_2 \xrightarrow[-LiI]{} (RC_6H_4)_2Te$$

R = D, 4-*i*-Pr, $2\text{-}CHOCH_2CH_2O$

Tellurium diiodide has been successfully used also in cases where the lithioarenes were generated by an exchange reaction between an aryl halide and butyllithium. Since diaryl tellurides form telluronium salts with alkyl halides with difficulty, the butyl halide liberated in the exchange reaction does not impede the progress of the reaction.

As judged from the data of[67–69] tellurium diiodide in contrast to $TeCl_2$ and $TeBr_2$ is the synthetic equivalent of Te(II). Indeed, the reaction of TeI_2 prepared by alloying of equimolar

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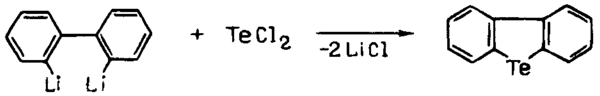
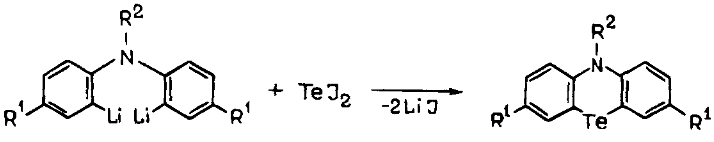
* Di(4-chlorophenyl) and di(4-bromophenyl) telluride have been isolated as the corresponding *Te,Te*-dibromides

amounts of powdered Te and I_2 with lithioarenes leads to more than 60% yield of the corresponding diaryl telluride. Biaryls and ditellurides are only isolated in trace amounts.

Interaction between 2,2′-dilithium derivatives and tellurium dihalides allows to prepare cyclic diorganyl tellurides. Thus, treatment of 2,2′-dilithiobiphenyl with $TeCl_2$ gives dibenzotellurophene in 52% yield.[31,32]



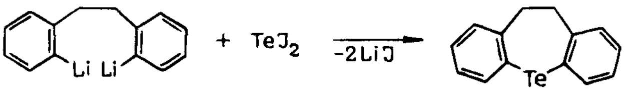
Analogously interaction between TeI_2 and 2,2′-dilithio-*N*-alkyldiarylamines, prepared by exchange reaction of the corresponding dibromodiarylamines and butyllithium, gave in more than 50% yield *N*-alkylphenotellurazines **10**.[70–72]



10

R^2 = Me: R^1 = Me, Br; R^2 = Et: R^1 = H, Me,Br

The same reaction was recently employed in the synthesis of dibenzo[*b,f*]tellurepane (32% yield).[73]



The use of tellurium dihalides for the synthesis of unsymmetric diorganyl tellurides is of no preparative interest because a mixture of three possible diorganyl tellurides is the result of the reaction.[74,75]

$$4\text{-}R^1C_6H_4MgX + TeX_2 + R^2MgX \xrightarrow[-MgX_2]{} 4\text{-}R^1C_6H_4TeR^2$$

R^2 = Me: R^1 = H,[74,75] Ph[75]

Tellurium tetrahalides, usually the tetrachloride, have also been employed in the synthesis of diorganyl tellurides. The treatment of $TeCl_4$ with 4–5-fold excess of Grignard reagent gives symmetric diorganyl tellurides in high yield.[65,76–84]

$$RMgX + TeCl_4 \xrightarrow[-MgXCl]{} R_2Te$$

R = Me_3SiCH_2,[84] $CH_2{=}CHCH_2$,[84] *t*-Bu,[83,84] C_6F_5,[65] C_6H_5,[65,76–79] 4-MeC_6H_4,[80] $PhCH_2$,[65] 4-$MeOC_6H_4$,[81] 1-$C_{10}H_7$[76,82]

Lithiumorganic derivatives behave analogously.[29,30,84,85]

$$RLi + TeCl_4 \xrightarrow[-LiCl]{} R_2Te$$

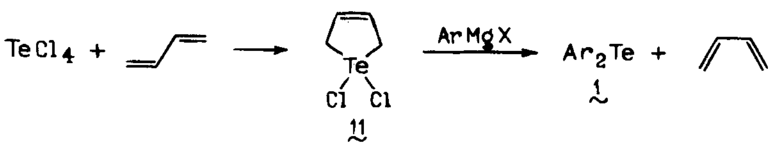
R = Bu,[84,85] t-Bu,[84] C_6F_5,[29] 2-$C_6F_5C_6F_4$[30]

Taking into consideration the large excess of magnesiumorganic reagent used and the formation of appreciable amounts of biaryls, the reaction possibly proceeds via intermediate formation of tetraalkyl(aryl)telluranes and their subsequent thermal decomposition.

$$RM + TeCl_4 \xrightarrow[-MCl]{} R_4Te \xrightarrow{\Delta} R_2Te + R\text{-}R$$

M = Li, MgX

The basic shortcoming inherent in this method is the necessity of a considerable amount of the magnesiumorganic reagent. Use of 2,5-dihydrotellurophene 1,1-dichloride **11**, readily generated in 60% yield from $TeCl_4$ and butadiene,[86] instead of $TeCl_4$ allows to eliminate this shortcoming. Treatment of **11** with two equivalents of an arylmagnesium halide gives rise to symmetrical diaryl tellurides **1** in more than 70% yield.



Ar = Ph, 4-MeC_6H_4, 2-C_4H_3S

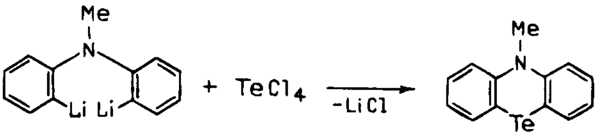
Bis(phenylethynyl) telluride was recently proposed as a synthetic equivalent of Te(II).[87] The use of this reagent for this purpose is based on the facile rupture of C_{sp}−Te bonds by nucleophiles. The interaction between lithioarenes (2.2 eq.) and this telluride in THF at −78 °C leads to symmetric diaryl tellurides in excellent yields (75–100%).

$$(PhC{\equiv}C\text{-})_2Te + 2\,ArLi \xrightarrow[\sqrt{-PhC\equiv CLi}]{} \underset{\mathbf{1}}{Ar_2Te}$$

Ar = 2-C_4H_3S, 2-thianaphthenyl, Ph, 4-HOC_6H_4, 4-$F_3CC_6H_4$, 3-MeC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$, 4-$Me_2NC_6H_4$, 2,5-$Me_2C_6H_3$, 2,4,6-$Me_3C_6H_2$

Tellurium tetrakis(diethyldithiocarbamate) was also used instead of $TeCl_4$ for the preparation of diaryl tellurides. With a large excess of phenylmagnesium bromide it gave diphenyl telluride almost quantitatively[88].

In a number of cases $TeCl_4$ has been employed in the synthesis of tellurium-containing heterocycles. Thus, N-methylphenotellurazine **10** has been prepared in low (18%) yield by treatment of 2,2′-dilithio-N-methyldiphenylamine with tellurium tetrachloride,[89] and the tellurospirane **12** (44% yield [31,32,90]) and octafluorodibenzotellurophene **6** (17% yield [29]) by reaction of $TeCl_4$ with 2,2′-dilithiobiphenyl and 2,2′-dilithiooctafluorobiphenyl, respectively.



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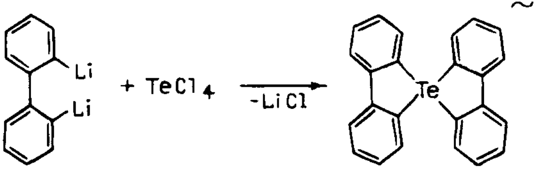

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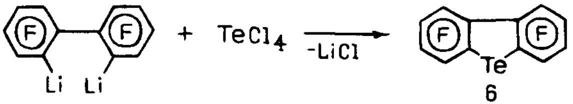


6

Other applications of $TeCl_4$ in the synthesis of diorganyl tellurides have only been demonstrated in single instances. After interaction between phenyldiazonium tetrafluoroborate and $TeCl_4$ in the presence of zinc dust in acetone (molar ratio 1:1:1) diphenyl telluride was isolated in low yield in the shape of Ph_2TeBr_2.[91] 4-Methylphenyldiazonium tetrafluoroborate reacts in the same way.[91]

By reaction of tellurium tetrabromide with trifluoromethyl radicals generated from hexafluoroethane in the plasma state or with bis(trifluoromethyl)mercury the synthesis of bis(trifluoromethyl) telluride has been achieved in 20%[92] and 92%[93] yield, respectively. Use of $TeCl_4$ instead of $TeBr_4$ in the latter reaction reduces the yield to 50%.[94]

$$(CF_3)_2Hg + TeBr_4 \xrightarrow{155^\circ C} (CF_3)_2Te \xleftarrow{250^\circ C} (CF_3)_2Hg + TeCl_4$$

Whereas the above-mentioned reactions of tellurium tetrahalides with a dialkylmercury lead to telluride, the interaction between tellurium tetrachloride and diarylmercury derivatives in boiling dioxane gives rise to diaryltellurium dichlorides.[95] A possible explanation of the unusual outcome of these reactions is the strong electron acceptor character of the CF_3 group which weakens the Te-Hal bonds in the intermediate $(CF_3)_2TeHal_2$, the high temperature inducing the decomposition of these σ-telluranes into telluride and free halogen. The formation of bromotrifluoromethane together with the desired telluride, probably a result of the side reaction of $Hg(CF_3)_2$ with bromine, confirms this assumption.[93]

2.3. *From Sodium Telluride and Hydrogen Telluride*

The alkylation of alkali metal tellurides is the most common and widely used method of preparation of symmetric dialkyl tellurides. This reaction marked the beginning of telluriumorganic chemistry since the first such compound, diethyl telluride, was synthesized by Wöhler more than one and a half century ago[96] by simple alkylation of K_2Te with diethyl sulfate. Since then a wide series of symmetric dialkyl tellurides **13** have been prepared as shown in the scheme below. Lithium, sodium and potassium telluride have been used and the yields range from moderate to excellent.[84,97-124]

$$2\,RX + M_2Te \xrightarrow[-MX]{} \underset{\mathbf{13}}{R_2Te}$$

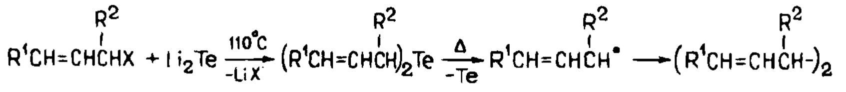
M = Na, Li, K

R = Me,[101,107,117] Et[103,105,106,108,116,121] $CH_2{=}CHCH_2$,[84,120,122,124] Pr,[103,121] *i*-Pr,[105] $CH_2{=}C(Me)CH_2$,[122] Bu[99,116,121] *s*-Bu,[116]$MeOCH_2CH_2$,[121] CH_2SiMe_3,[110,111] $CH_2{=}C(Me)CH_2CH_2$,[122] C_5H_{11},[100,116] *i*-C_5H_{11},[116,119]$CH_2CH_2CH_2SiMe_3$,[110,111] 2-methylenetetrahydrofuryl,[113] $PhCH_2$,[97,98,104,109,115] C_7H_{15},[110] C_8H_{17},[116,119] $PhCH_2CH_2$,[110,112,114] CH_2SiMe_2Ph,[110] 4-$CH_2{=}CHC_6H_4CH_2$,[123] $C_{11}H_{23}$,[119] $CH_2(CH_2)_3CHO(CH_2)_5CH_2$,[119] $C_{12}H_{25}$,[118] $C_{16}H_{33}$,[102,112]

It must be noted that the action of phenacyl halides on sodium telluride does not lead to bis(phenacyl) tellurides in spite of the high mobility of the halogen atom in these alkylating agents.[125,126] However, bis(phenacyl) tellurides have been prepared by reduction of the corresponding *Te*,*Te*-dichlorides with $Na_2S_2O_5$ under PTC conditions[125,127] (cf. 2.5.6.). Quite recently the preparation of diphenacyl telluride has also been performed when bis(triphenylstannyl) telluride was employed instead of Na_2Te as its synthetic equivalent.[128]

$$PhCOCH_2Br + Na_2Te \not\rightarrow (PhCOCH_2)_2Te \xleftarrow[-Ph_3SnBr]{(Ph_3Sn)_2Te,\,CsF} PhCOCH_2Br$$

The interaction between allyl or benzyl halides and sodium[97,98,104,109,120,122-124] or lithium telluride[84,129] gives different results depending on the reaction temperature. At room temperature[84,97,98,109,120,122,123] or upon heating of short duration to 70 °C[104] symmetric diallyl or dibenzyl tellurides are isolated in 50–100% yield. However, at 110 °C (oil bath), the main products of the reaction are 1,5-dienes (yield 60–93%[129]) or dibenzyl (yield 37%[129,130]), respectively. Most probably, these hydrocarbons are formed by recombination of allyl (benzyl) radicals generated by extrusion of tellurium from the intermediate diallyl (dibenzyl) telluride.



$$R^1CH{=}CH\overset{R^2}{C}HX + Li_2Te \xrightarrow[-LiX]{110°C} (R^1CH{=}CH\overset{R^2}{C}H)_2Te \xrightarrow[-Te]{\Delta} R^1CH{=}CH\overset{R^2}{C}H^{\bullet} \longrightarrow (R^1CH{=}CH\overset{R^2}{C}H\text{-})_2$$

X = Cl, Br; $R^1 + R^2 = (CH_2)_4$, $(CH_2)_5$, $(CH_2)_6$; R^1 = Ph, R^2 = H*; $R^1 = CH_2{=}CH$, R^2 = H*; $R^1 = R^2$ = Me; R^1 = Pr, R^2 = H*;

$$PhCH_2Br + Li_2Te \xrightarrow[-LiBr]{110°\,C} (PhCH_2)_2Te \xrightarrow[-Te]{} PhCH_2^{\bullet} \longrightarrow PhCH_2CH_2Ph$$

Such a transformation is observed only in the case of tellurium derivatives and allows a

---

* A mixture of stereoisomers is formed

novel approach to C-C bond formation. Thus, treatment of 3-bromocyclohexene with Li_2Te leads to 2,2′-bicyclohexenyl in 81–86% yield whereas the same reaction with Li_2Se gives rise only to the corresponding selenide.[129]

Now we shall take a brief look at the preparations of the sodium (or lithium) telluride employed in the synthesis of diorganyl tellurides. The "rongalite" method, first introduced by Chugaev[97] and most widely used until recently, consists of the reduction of elemental tellurium with sodium formaldehyde sulfoxylate (rongalite) in alkaline medium.[97–101,107,109,131–141]

$$Te + HOCH_2SO_2Na + 3\,NaOH \longrightarrow Na_2Te + CH_2O + Na_2SO_3 + 2\,H_2O \tag{1}$$

Later the alkali metal tellurides required for these preparations had been generated by interaction between Te and Na (Li) in (2) liquid ammonia;[102,105,106,108,142] (3) tetrahydrofuran in the presence of naphthalene;[84,120,121] (4) *N,N*-dimethylformamide,[125,143] hexamethylphosphotriamide[143] or *N*-methylpyrrolidone;[143,144] by reduction of Te with (5) sodium dithionite $Na_2S_2O_4$;[104,145] (6) sodium (potassium) tetrahydroborate;[110–114,122,125,139,146–153] (7) lithium triethylborohydride;[129,151,154–156] (8) sodium hydride;[118,126,141,144,157–160] (9) tin (II) chloride in alkaline medium;[117,161–166] (10) hydrazine hydrate in alkaline aqueous *N,N*-dimethylformamide;[116,167] (11) thiourea *S,S*-dioxide;[119,145] (12) by disproportionation of tellurium in strongly alkaline solution[168,169] and by (13) electrochemical reduction of tellurium.[115]

$$Te + 2\,Na \longrightarrow Na_2Te \tag{2)-(4}$$

$$Te + Na_2S_2O_4 + 4\,NaOH \longrightarrow Na_2Te + 2\,Na_2SO_3 + 2\,H_2O \tag{5}$$

$$Te + 2\,NaBH_4 \longrightarrow Na_2Te + 2\,BH_3 + H_2 \tag{6}$$

$$Te + 2\,LiBEt_3H \longrightarrow Li_2Te + 2\,BEt_3 + H_2 \tag{7}$$

$$Te + 2\,NaH \longrightarrow Na_2Te + H_2 \tag{8}$$

$$Te + SnCl_2 + 6\,KOH \longrightarrow K_2Te + K_2SnO_3 + 2\,KCl + 3\,H_2O \tag{9}$$

$$2\,Te + N_2H_4 + 4\,NaOH \longrightarrow 2\,Na_2Te + N_2 + 4\,H_2O \tag{10}$$

$$Te + 2\,(H_2N)_2CSO_2 + 2\,NaOH \longrightarrow Na_2Te + 2\,(H_2N)_2CSO_3H \tag{11}$$

$$3\,Te + 6\,KOH \longrightarrow 2\,K_2Te + K_2TeO_3 + 3\,H_2O \tag{12}$$

There are two methods of generation of telluride anions which have not found wide use for the synthesis of diorganyl tellurides. Thus, dibutyl telluride was isolated in 95% yield when tellurium was treated with tetrabutylammonium tetrahydroborate.[170] In this reaction, the ammonium salt plays the part of a reducing agent as well as that of an alkylating one.

$$2\,Bu_4N^+BH_4^- + Te \longrightarrow Bu_2Te + 2\,Bu_3N{\cdot}BH_3 + H_2$$

However, among the tetraalkylammonium salts only the butyl derivative is a sufficiently strong reducing agent to attack elemental tellurium.[170]

Furthermore, the telluride anions have been generated in THF from bis(*t*-butyldimethylsilyl) telluride and tetrabutylammonium fluoride and subsequently added to 1,5-diphenyl-1,4-pentadiyn-3-one.[155]

$$(t\text{-}BuMe_2Si)_2Te + 2\,Bu_4N^+F^- \xrightarrow[-\,t\text{-}BuMe_2SiF]{} (Bu_4N)_2Te$$

Sodium telluride prepared by the rongalite method[137,141] or by reactions (4)[143] or (8)[118,141,144] can not only be alkylated but also arylated with appropriate aryl halides giving rise to the corresponding diaryl tellurides **1** in varying yields. It should be particularly noted that even aryl halides which are not activated by strongly electronegative substituents are useful for such arylation.

$$ArX + Na_2Te \xrightarrow[-NaX]{} \underset{\mathbf{1}}{Ar_2Te}$$

Ar = C_6F_5 (56%[144]), C_6H_5 (35%,[43] 42%,[118] 71%,[137] 77%[144]), 4-MeC_6H_4 (42%,[144] 81%[137]), 3-MeC_6H_4 (84%[137]), 2-MeC_6H_4 (55%[144]), 4-$MeOC_6H_4$ (58%,[144] 74%[137]), 2,4-$Me_2C_6H_3$ (94%[137]), 2,4,6-$Me_3C_6H_2$ (77%[137]), 1-$C_{10}H_7$ (59–70%[141]), 2-$C_{10}H_7$ (61%,[141,144] 30%[143]), substituted naphthalenes (41–89%[141,144]), 2-fluorenyl (48%[141]), 2-pyrenyl (60%[141])

Although the overall arylation amounts formally to nucleophilic substitution of X^- by Te^{2-} anion, the authors of ref. 141 are inclined to consider this process as proceeding according to an $S_{RN}1$ mechanism. The reductive dehalogenation of the substrates which accompanies the above reaction corroborates this supposition. Thus, in the case of 9-iodo-9-phenylanthracene which is able to form a highly stable radical ion, all attempts to arylate this substrate resulted only in reduction.[141] Usually the best yields of diaryl tellurides **1** are achieved when sodium telluride generated by the rongalite method is employed. When Na_2Te from NaH and Te in DMF was used, the yields of **1** were appreciably lower[141] although the reason for these differences is not obvious.[141]

The reason for these differing yields[137] was clarified later.[144] It turned out that the preparation of Na_2Te from Te and NaH in DMF is accompanied by the formation of substantial amounts of $(Me_2NCO)_2Te_2$. Therefore, *N*-methylpyrrolidone is preferable over DMF in the preparation of Ar_2Te from aryl iodides and Na_2Te.[144] Indeed, the yield of $(C_7H_{15})_2Te$ from $C_7H_{15}Br$ and Na_2Te in *N*-methylpyrrolidone was 68% whereas in DMF it was only 43%; in addition, in the latter case $Me_2NCOTeC_7H_{15}$ was isolated in 10% yield.[144]

Diaryl tellurides **1** may be also prepared by treatment of Na_2Te (K_2Te) with aryldiazonium chlorides.[133] The synthesis of bis(2-carboxyphenyl) telluride was first performed by means of this reaction.

$$2\text{-}HOOCC_6H_4N_2^+Cl^- + K_2Te \xrightarrow[-N_2;\,-KCl]{} (2\text{-}HOOCC_6H_4)_2Te$$

A similar reaction has recently been used for the synthesis of a broad series of symmetric diaryl tellurides **1**. These compounds were prepared in 54–91% yield by the reaction of aryldiazonium borofluorides with NaHTe[171,172] or with $(EtO)_2P(O)TeNa$ in DMF.[172] The former tellurium-containing nucleophile, NaHTe, was generated by the reaction of $NaBH_4$ with powdered tellurium in DMF and the latter one by reaction of $(EtO)_2P(O)H$ with NaH and Te in ethanol.[172] When $(EtO)_2P(O)TeNa$ was used, the yields of Ar_2Te were usually lower than with NaHTe.

$$RC_6H_4N_2^{+}BF_4^{-} + NaTeH \xrightarrow[-N_2;\ -NaBF_4;\ -HBF_4]{} (RC_6H_4)_2Te$$

1

R = 4-Br (81%,[171] 91%[172]), 4-Cl (70%,[171] 89%[172]), 3-Cl (67%[172]), 4-I (94%[172]), H (54%,[171] 90%[172]), 4-Me (65%,[171] 89%[172]), 2-Me (79%[171]), 4-MeO (83%,[171] 70%[172]), 4-CH_3CO (64%[172]), 3,4-C_4H_4 (75%[171])

It is also worth mentioning that photostimulated reaction of telluride anions generated from Na and Te in liquid ammonia with aryl halides leads to a mixture of symmetric diaryl tellurides and ditellurides.[142]

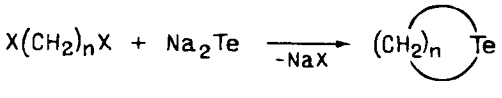
An attempt to prepare unsymmetric diaryl[141] or dialkyl tellurides[150] by treatment of Na_2Te with two different organyl halides at once gave inseparable mixture of the two symmetric tellurides and the unsymmetric telluride.

The above-mentioned bis(triphenylstannyl) telluride may be employed as synthetic equivalent of Na_2Te.[128,173] It reacts with alkyl iodides and bromides under mild conditions (stirring of reagents, dissolved in acetonitrile or in MeCN/THF, at room temperature) to form dialkyl tellurides in acceptable yields. Aryl halides and alkyl chlorides are inert toward this reagent. The passivity of alkyl chlorides in this reaction allows the selective replacement of bromine (iodine) in bromo(iodo)alkyl chlorides with Te^{2-}.

$$2RX + (Ph_3Sn)_2Te \xrightarrow[-Ph_3SnX]{CsF} R_2Te$$

R = Me_2CH, CH_2CO_2Me, CH_2CO_2Et, CH_2CO_2Pr, CH_2CO_2Bu-*t*, $(CH_2)_3CO_2Et$, $Cl(CH_2)_6$, $PhCH_2$, $PhCOCH_2$, 1,2-$(CH_2)_2C_6H_4$, $Me(CH_2)_9$

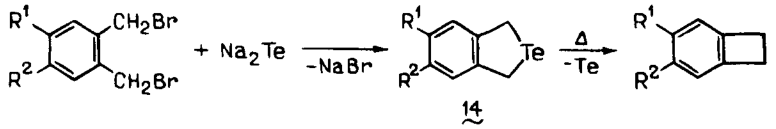
The alkylation of Na_2Te with some dihaloalkanes has been used for the preparation of tellurium-containing heterocycles. 1-Telluracyclopentane[132,140] and 1-telluracyclohexane[132] have been synthesized from α,δ- or α,ε-polymethylene dibromides (diiodides), respectively.



X = Br, I; n = 4, 5

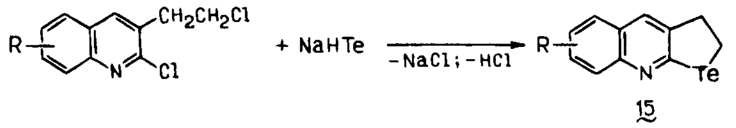
Interaction between Na_2Te and 1,2,3,4-tetrakis(iodomethyl)butane leads to 3,3-bis(tetrahydrotellurophene).[174,175] Tetrahydrotellurophenes with steroidal substituents[176,177] have been prepared from the appropriate dibromo derivatives or methanesulfonates by means of a corresponding reaction.

Sodium telluride and 1,2-bis(bromomethyl)benzene or 2,3-bis(bromomethyl)naphthalene in DMF form the corresponding [*c*]-condensed tellurophenes **14**.[178] The pyrolysis of these compounds at 500°C in a helium atmosphere takes place with extrusion of the tellurium atom and formation of benzocyclobutene derivatives.



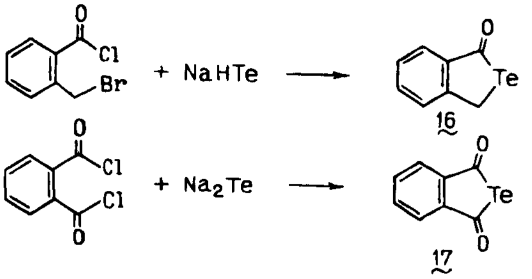
$R^1 = R^2 = H$; $R^1 + R^2 = (CH{=}CH)_2$

Sodium hydrogen telluride has been employed in the synthesis of the [*b*]-condensed tellurophenes **15**.[179]

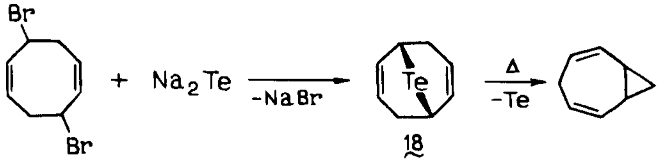


R = H, 6-Me, 4-Ph, 8-Me

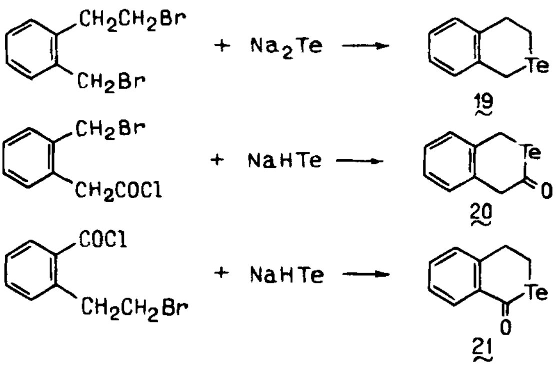
The keto derivatives **16**[180] and **17**[146] of the heterocycle **14** have been prepared in high yield according to the schemes shown below.



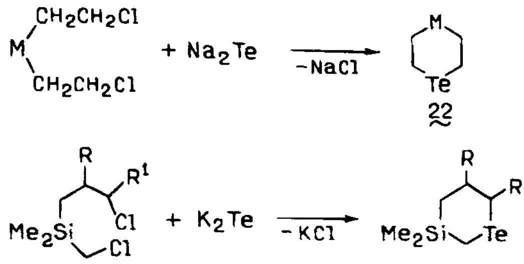
The bicyclic compound **18** which contains a tellurium bridge has been prepared from Na_2Te and 1,5-dibromocyclooctadiene in low yield. Upon heating it eliminates the tellurium atom and gives a bicyclic diene.[181]



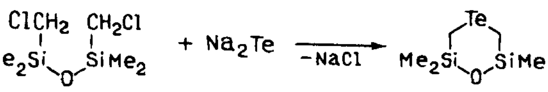
The alkylation of Na_2Te (NaHTe) by appropriately chosen dihalogen compounds has been used for the preparation of telluroisochromane **19**[131,182] and its derivatives **20**[183] and **21**.[184]



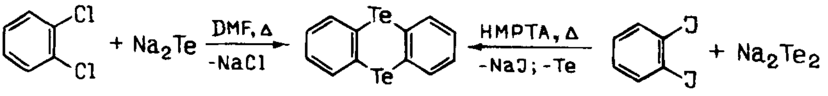
The synthesis of heterocycles containing two heteroatoms has been carried out in a similar manner. Thus, 1-oxa-4-telluracyclohexane **22** (M = O[132]) and its 1-thio analog **22** (M = S[134]) have been prepared from bis(2-chloroethyl)ether and sulfide, respectively. Six-membered heterocycles with tellurium and silicon atoms in the ring have been synthesized analogously.[153,185]



R = H: R^1 = H, Me; R = *t*-Bu; R^1 = H



Interaction between *o*-dichlorobenzene and sodium telluride leads to telluranthrene, although in very poor yield (3%[159]). With *o*-diiodobenzene and sodium ditelluride the corresponding procedure was somewhat more successful (yield 12%[186]).



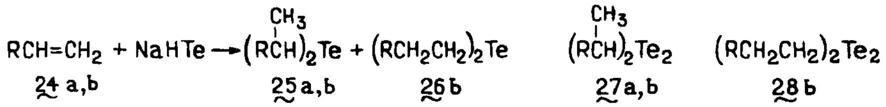
Data concerning the addition of H_2Te[187] or NaHTe[188] to C=C double bonds with the purpose to prepare diorganyl tellurides are rather scarce. Thus, addition of H_2Te to acrylonitrile in the presence of sodium methoxide leads to bis(2-cyanoethyl) telluride **23** in 22% yield. However, taking into account the possibility of the alcoholysis reaction H_2Te + MeONa

→ NaHTe + MeOH, it seems very probable that sodium hydrotelluride also participates in this nucleophilic addition. If desired **23** may be converted to tellurodipropionic acid.

$$CH_2{=}CHCN + H_2Te \xrightarrow{MeONa} \underset{\mathbf{23}}{(NCCH_2CH_2)_2Te} \xrightarrow{H_2O,H^+} (HOOCCH_2CH_2)_2Te$$

The telluride **23** has been also prepared by electrolysis of a mixture of Te and acrylonitrile in 1 N aqueous Na_2SO_4.[189] However, as described in ref. [187] an attempt to reproduce this result failed.

The addition of NaHTe to the non-activated double bond of **24a** and **24b** leads to the tellurides **25a, 25b** and **26b** contaminated with small amounts of the corresponding ditellurides **27a, 27b** and **28b.**[188]



$$\underset{\mathbf{24}\,a,b}{RCH{=}CH_2} + NaHTe \rightarrow \underset{\mathbf{25}\,a,b}{(R\overset{CH_3}{\overset{|}{C}}H)_2Te} + \underset{\mathbf{26}\,b}{(RCH_2CH_2)_2Te} \qquad \underset{\mathbf{27}\,a,b}{(R\overset{CH_3}{\overset{|}{C}}H)_2Te_2} \qquad \underset{\mathbf{28}\,b}{(RCH_2CH_2)_2Te_2}$$

a) R = $(CH_2)_8CO_2H$; b) R = $(CH_2)_4OPh$

Other non-activated alkenes either do not add sodium hydrogen telluride at all or give mixtures of the corresponding telluride and ditelluride in low yields.[188]

2.4. *From Potassium Tellurocyanate and Aryl Tellurocyanates*

The use of inorganic tellurocyanates in the synthesis of diorganyl tellurides has been rather rare. Treatment of aryldiazonium tetrafluoroborates with potassium tellurocyanate in DMSO leads to the corresponding symmetric diaryl tellurides which, according to ref.,[190] obviously are decomposition products of intermediately formed aryl tellurocyanates.

$$ArN_2^+BF_4^- + KTeCN \xrightarrow[-N_2;\,-KBF_4]{} ArTeCN \rightarrow \underset{\mathbf{1}}{Ar_2Te} + Te(CN)_2 \rightarrow Te + (CN)_2$$

Ar = 2-BrC_6H_4 (48%), 2,4,6-$Br_3C_6H_2$ (44%), 2-$NO_2C_6H_4$ (39%), 4-$NO_2C_6H_4$ (34%), 4-MeC_6H_4 (47%), 2-NCC_6H_4 (41%), 4-$MeOC_6H_4$ (47%), 2-$HO_2CC_6H_4$ (8%), 2,6-$Me_2C_6H_3$ (42%), 2-$C_{10}H_7$ (38%), 2-$C_6H_5C_6H_4$ (47%)

Only in the case of the 2-nitro- and 2,6-dimethylphenyldiazonium salts the corresponding aryl tellurocyanates were isolated in 11% and 40% yield respectively.

Phenyl tellurocyanate, synthesized either by interaction between benzenetellurolate anions and BrCN[191] or by *in situ* reaction of benzenetellurenyl chloride (generated by reduction of phenyltelluroxo chloride with $Na_2S_2O_5$) with KCN,[192] smoothly reacts with primary and secondary alcohols in the presence of Bu_3P to form the phenyl alkyl tellurides **29** in 32–78% yield.[191]

$$\mathrm{PhTeCN} + \mathrm{ROH} \xrightarrow{\mathrm{Bu_3P}} \underset{\mathbf{29}}{\mathrm{PhTeR}}$$

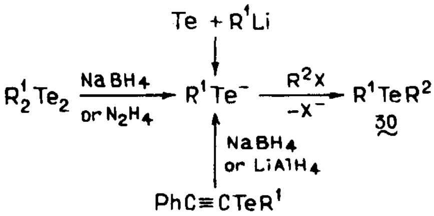
R = C_8H_{17} (41%), $PhCH_2CH_2$ (32%), $PhCH_2CH_2CH_2$ (41%), $C_{11}H_{23}$ (66%) $C_{12}H_{25}$ (62%), $C_{14}H_{29}$ (78%), $C_{12}H_{25}CHMe$ (45%), $C_{16}H_{33}$ (74%)

2.5. *From Organotellurium Derivatives*

A number of synthetically important methods for the preparation of diorganyl tellurides are based on the following organic derivatives of tellurium: tellurolate anions, tellurenyl halides, diorganyl ditellurides and δ-telluranes R_2TeX_2. Preparations of diorganyl tellurides from other organotellurium precursors are less important.

2.5.1. *From tellurolate anions.* Alkylation and arylation of tellurolate aniones are widely used for the preparation of unsymmetric dialkyl R^1TeR^2 (**30**) and aryl alkyl ArTeR (**29**) tellurides. Also the synthesis of unsymmetric diaryl tellurides Ar^1TeAr^2 is possible in this way.

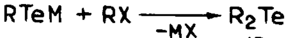
2.5.1.1. *Unsymmetric dialkyl tellurides.* The alkylation of tellurolate anions with alkyl halides is now a routine procedure. The preparation of the required tellurolate anions is usually carried out by reduction of dialkyl ditellurides with $NaBH_4$[148,150,193–203] or by interaction between tellurium and lithium[84,122,204–208] or magnesium[120] in THF. Recently two novel approaches to the generation of these anions were proposed, one based on the facile cleavage of the Te-C_{sp} bond in phenylethynyl alkyl tellurides upon the action of strong nucleophiles ($NaBH_4$, $LiAlH_4$)[209,210] and the second based on the reduction of diorganyl ditellurides with the system N_2H_4/alkali.[211,212]



R^1 = Me: R^2 = CH_2=$CHCH_2$,[120,122] $(CH_2)_3OH$,[206] $CH_2CH_2CHC(O)NHC(O)NH$,[19], $PhCH_2$,[122] $C_{12}H_{25}$,[195] 3α, 5α-cholestane;[148]
R^1 = Et: R^2 = Me;[211]
R^1 = Pr: R^2 = 2-(2,3,4,6-tetraacetyl-α-D-glucopyranosyl);[199,202]
R^1 = *i*-Pr: R^2 = $C_{12}H_{25}$,[210] $(CH_2)_3C(Et)(CO_2Et)_2$,[198] $(CH_2)_3C(CH_2CH{=}CH_2)(CO_2Et)_2$;[198]
R^1 = CH_2 = $CHCH_2$: R^2 = Me;[120]
R^1 = Bu: R^2 = Me_2NCH_2,[208] CH_2CO_2Et,[207] Me_3SiCH_2,[208] $MeOCH_2CH_2OCH_2$,[208] $PhCH_2CH_2$,[210] $PhCH_2OCH_2$,[208] Bu_3SnCH_2,[208] $(CH_2)_7CO_2Me$,[197] $(CH_2)_{11}CO_2Me$;[150]

R^1 = t-Bu: R^2 = Me,[122] $CH_2CH{=}CH_2$,[122,150] $CH_2{=}C(Me)CH_2$;[122]
R^1 = $ICH{=}CH(CH_2)_3$: R^2 = $(CH_2)_{11}CO_2Me$;[150]
R^1 = $HC{\equiv}C(CH_2)_3$: R^2 = $(CH_2)_{11}CO_2Me$;[150]
R^1 = C_6H_{13}: R^2 = $(CH_2)_4CO_2Me$,[197,203] $(CH_2)_7CO_2Me$,[197] $(CH_2)_9CO_2Me$;[197]
R^1 = $(CH_2)_3CO_2Et$: R^2 = $BrCH{=}CH(CH_2)_{11}$,[200] $(CH_2)_{11}CH{=}CHI$,[201]
$C_6H_{13}CH{=}CI(CH_2)_3$,[201] $C_8H_{17}CH{=}CI(CH_2)_3$,[201] $C_2H_5CH{=}CI(CH_2)_9$;[201]
R^1 = C_7H_{15}: R^2 = $(CH_2)_4CO_2Me$;[197]
R^1 = C_8H_{17}: R^2 = $(CH_2)_7CO_2Me$;[150,197]
R^1 = $PhCH_2CH_2$: R^2 = $C_{12}H_{25}$;[210]
R^1 = $(CH_2)_7CO_2Me$: R^2 = $(CH_2)_5CH{=}CI$,[201] $(CH_2)_7CH{=}CI$[201]
R^1 = C_9H_{19}: R^2 = CH_2CO_2Me;[203]
R^1 = $C_{10}H_{21}$: R^2 = CO_2Me;[203]
R^1 = $C_{11}H_{23}$: R^2 = $(CH_2)_2CO_2Me$,[197] $(CH_2)_5CO_2Me$;[197]
R^1 = $C_{12}H_{25}$: R^2 = i-Pr;[210]
R^1 = $4\text{-}IC_6H_4(CH_2)_9$: R^2 = $(CH_2)_4CO_2Me$;[150,196]
R^1 = $HO_2C(CH_2)_7CH{=}CH(CH_2)_6$: R^2 = Me;[193]
R^1 = $C_{18}H_{37}$: R^2 = $(CH_2)_{11}CO_2Me$[197]

The same reaction has also been employed for the synthesis of some symmetric dialkyl tellurides **13**.[84, 204,209,210]

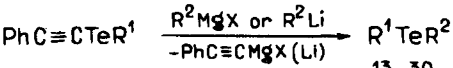


$$RTeM + RX \xrightarrow[-MX]{} R_2Te$$

13

R = Me,[204] Bu,[209,210] t-Bu,[84] $C_{12}H_{25}$[210]

The ability of the Te-C_{sp} bond in phenylethynyl alkyl tellurides to cleave under the action of the nucleophiles mentioned above was utilized in recent work[210] for the preparation of the tellurides **13** and **30**. In this case lithio- or magnesioalkanes were used as nucleophiles; the yields were 68–95%.



$$PhC{\equiv}CTeR^1 \xrightarrow[-PhC\equiv CMgX\,(Li)]{R^2MgX \text{ or } R^2Li} R^1TeR^2$$

13, **30**

R^1 = R^2 = Bu; R^2 = Me_2CH: R^2 = Bu, $C_{12}H_{25}$; R^1 = $C_{12}H_{25}$: R^2 = Bu

The demethylation of methyl alkyl tellurides by methanetellurolate anion and subsequent alkylation of the tellurolate anions thus formed constitutes a novel way to the preparation of unsymmetric dialkyl tellurides as shown in the paper.[212]

$$Me_2Te_2 \xrightarrow[KOH/H_2O]{N_2H_4\cdot H_2O/DMSO} MeTe^- \xrightarrow[-Br^-]{BuBr} MeTeBu \xrightarrow[-Me_2Te]{MeTe^-} BuTe^- \xrightarrow[-Br^-]{PrBr} PrTeBu$$

However, the yield of propyl butyl telluride was only 40% and methyl propyl telluride was isolated in comparable yield (35%) together with the desired product. Obviously, the methanetellurolate anions used in two-fold excess were also alkylated by the propyl bromide.

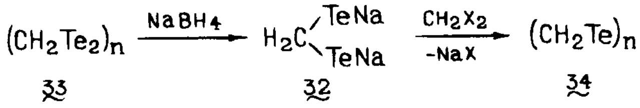
Diorganyl tellurides **31** containing two tellurium atoms per molecule have been prepared by the reaction of lithium alkane tellurolates with α,ω-dihaloalkanes at low temperature.[205,206,208]

$$\mathrm{RTeLi} + \mathrm{X(CH_2)_nX} \xrightarrow[-\mathrm{LiX}]{} \underset{\mathbf{31}}{\mathrm{RTe(CH_2)_nTeR}}$$

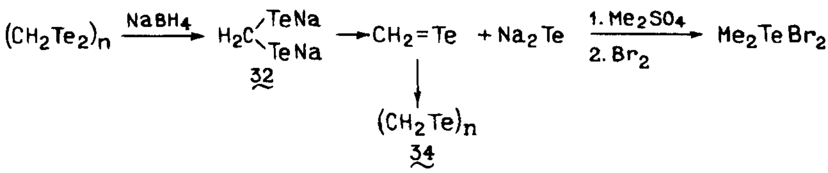
R = Me: n = 1, 3,[205,206] 5*, 6, 10;[206] R = Bu: n = 1[208]

At the same time 1,3-dihalopropanes upon reaction with MeTeLi at room temperature gave only dimethyl ditelluride. The same result was obtained in the case of 1,2-dichloroethane at low temperature, but also ethene appeared together with dimethyl ditelluride.[205,206]

According to the data presented in ref.,[156] interaction between the ditellurolate dianion **32** prepared by reduction of poly(methylene) ditelluride **33**[213] with $NaBH_4$ and dihalomethanes leads to poly(methylene) telluride **34**.



However, as shown in ref., 214 the reduction of poly(methylene) ditelluride **33** with $NaBH_4$ in ethanol and subsequent treatment of the reaction mixture with dimethyl sulfate and then with bromine leads to dimethyltellurium dibromide in 90% yield and a brown powder unsoluble in organic solvents the elemental composition of which is in agreement with the structure **34**. Probably, the ditellurolate dianion **32** is unstable and readily disproportionates to sodium telluride and telluroformaldehyde. The latter polymerizes giving rise to **34**.



It should be noted that the ditellurolate dianion **35** also undergoes disproportionation, i.e. to Na_2Te and dibenzotellurophene.[215]

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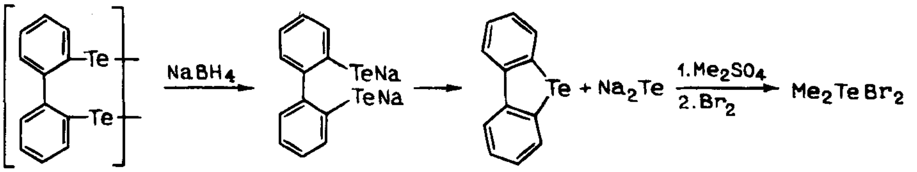
* Dimethyl telluride, 1-telluracyclohexane and 1-chloro-5-(methyl-telluro)pentane were also formed together with **31** (R = Me, n = 5)[208]



35

2.5.1.2. *Alkyl aryl tellurides.* The interaction between arenetellurolate anions and alkyl halides, dialkyl sulfates, mesylates, tosylates or oxiranes is the most general preparative method giving access to a broad range of alkyl aryl tellurides **29**. Arenetellurolate anions as well as their alkyl analogs are very readily oxidized by oxygen and therefore are used *in situ* in an inert atmosphere. Common methods for the generation of these anions are: the reduction of diaryl ditellurides with alkali metal tetrahydroborates,[118,167,195,198,216–241] lithium aluminum hydride,[242] superhydride,[243] thiourea dioxide,[244] or hydrazine hydrate,[211,245] the cleavage of the Te–Te bond in diaryl ditellurides with lithium in ether,[246] tetrahydrofuran[247,248] or a mixture of THF and DMF[249] and also by sodium in liquid NH_3,[250–253] the disproportionation of ditellurides in the presence of NaOH under phase transfer conditions[254] proceeding according to the scheme

$$2\,Ar_2Te_2 + 4\,NaOH \longrightarrow 3\,ArTeNa + ArTe(O)ONa + 2\,H_2O$$

and, finally, the insertion of tellurium atoms into C_{Ar}-Li[205–207,216,217,223,225,255–273] or C_{Ar}-Mg[274,275] bonds. When an aryllithium reagent is obtained by exchange reaction with butyllithium, the addition of tellurium to the reaction mixture leads to the corresponding arylbutyl tellurides[216,255,260,268,270,273] owing to the presence of butyl bromide formed in the exchange reaction. If it is desirable to prevent the aryl butyl telluride formation, a two-fold excess of *t*-butyllithium must be employed in the exchange reaction instead of an equimolar amount of *n*-BuLi.[264]

The generation of arenetellurolate anions from aryl iodides and Na_2Te (molar ratio 1:1) in *N*-methylpyrrolidone was first described in ref.[144] The interaction between ArTeNa prepared in such a way and RX results in the formation of alkyl aryl tellurides in good yields.[144]

$$ArTeM + RX \xrightarrow[-MX]{} \underset{\mathbf{29}}{ArTeR}$$

M = Na, Li, K; X = Cl, Br, I, OSO_2OR, OMs, OTs
Ar = 2-C_4H_3S: R = CHF_2,[226] Bu,[258] $CH_2CONHPh$;[223]
Ar = 3-C_4H_3S: R = $CH_2CH_2CO_2H$,[225] Bu;[225]
Ar = 3-$CHOCH_2CH_2OC_4H_2S$: R = Bu;[258]
Ar = 4-BrC_6H_4: R = Me,[216] C_3F_7,[242] Bu;[216,238]
Ar = 4-ClC_6H_4: R = CHF_2,[226] CH_2OMe,[275] CH_2OBu;[275]
Ar = 2-ClC_6H_4: R = CH_2OBu;[275]
Ar = 4-FC_6H_5: R = Me,[219] C_3F_7;[242]
Ar = 3-FC_6H_4: R = Me,[219] C_3H_7,[242] Bu,[244] $MeCHBr(CH_2)_2$,[244] $PhCH_2CH_2$;[244]

Ar = Ph: R = CHF_2,[226] CH_2Cl,[254] Me,[211,216,220,245,247,250,251,257] CH_2CO_2H,[207] Et,[220,235,247,274] CH_2OMe,[275] C_3F_7,[242] $CH_2{=}CHCH_2$,[211,254,257] CH_2OEt,[275] $CH_2CH_2CO_2H$,[216,218] CH_2CH_2OMe,[167,235] Pr,[247] *i*-Pr,[220,247] $CHC(O)OCH_2CH_2$,[207] $CHMeCH_2CO_2H$,[218] $CH_2CHMeCO_2H$,[218] $MeCHBrCH_2CH_2$,[244,254] CH_2CO_2Et,[207] CH_2CH_2OEt,[167,235,238,246,247,254] Me_2CHCH_2,[254] $Me_2C{=}CHCH_2$,[227] $CH_2{=}CH(CH_2)_3$,[239] $Me_2CHCH_2CH_2$,[254] CHMePr,[118] CH_2OBu,[275] $CHMeCO_2Et$,[207] $CHC(O)OCH_2CH_2CH_2CH_2$,[207] 2-*c*-C_6H_9,[227,254] *c*-C_6H_{11},[118] CMe_2CO_2Et,[207] C_6H_{13},[118] $PhCH_2$,[254] *c*-C_7H_{13},[228] $PhSeCH_2$,[254] $PhCH_2CH_2$,[118,228,244,254] $CH_2CO_2C_6H_4NO_2$-4,[207] $PhCH{=}CHCH_2$,[227,254] $PhCHMeCH_2$,[228] $C(Ph)OCH_2CH_2O$,[260] 1-adamantyl,[252] $Me(CH_2)_9$,[254,257] $C_{12}H_{25}$,[118,195,228,244] $C_{10}H_{21}CHMe$,[195] $C_{14}H_{29}$,[247] $(CH_2)_4C(Et)(CO_2Et)_2$,[198] $C_{12}H_{25}CHMe$,[228] $MeCHC(Ar')OCH_2CH_2O$ (Ar′ = 4-BrC_6H_4, Ph, 4-MeC_6H_4, 4-*i*-BuC_6H_4, 2-(5-Br-6-OMe)-naphthyl, 4-PhC_6H_4),[249] 3-β-hydroxy cholestanyl,[195] $(CH_2)_5CH{=}CHR'$ (R′ = CN, CO_2Me, NOBn);[239]
Ar = 4-MeC_6H_4: R = CHF_2,[226] Me,[216] CH_2CH_2OMe,[235] $CH_2CH_2CO_2H$,[218] Bu,[254] CH_2CH_2OEt,[235] CH_2OBu,[275] C_7F_{15};[144]
Ar = 3-MeC_6H_4: R = $CH_2CH_2CO_2H$;[218]
Ar = 2-MeC_6H_4: R = Me,[217] $CH_2CH_2CO_2H$,[218] CH_2OBu;[275]
Ar = 4-$MeOC_6H_4$: R = Me,[264] Bu,[244,254] $MeCHBr(CH_2)_2$,[244] $PhCH_2CH_2$,[244] $C_{12}H_{25}$,[244] $(CH_2)_5CH{=}CHR'$ (R′ = CO_2Me, $P(O)(OEt)_2$, SO_2Ph),[239] 1,2,3,4,6-penta-*O*-acetyl-β-D-glucopyranos-1-deoxy-1-yl, methyl-2-*O*-acetyl-4,6-*O*-benzylidene-α-D-idosopyranos-3-deoxy-3-yl, methyl-2,3-*O*-*i*-propylidene-β-D-ribofuranos-6-deoxy-6-yl, methyl-2,3,4-tri-*O*-acetyl-α-D-glucopyranos-6-deoxy-6-yl, 2,3-*O*-*i*-propylidene-6-*O*-trityl-β-D-ribofuranos-1-deoxy-1-yl,[236] 1,2:5,6-di-*O*-*i*-propylidene-α-D-glucofuranos-3-deoxy-3-yl,[241] 5′,5′-deoxy-2′,3′-*O*-*i*-propylidene-6-*N*′,*N*′-dibenzoyladenosinyl, 5′,5′-deoxy-2′,3′-*O*-*i*-propylideneuridinyl, 3′5′-*O*-butyldiphenylsilyl-5′-deoxythymidinyl;[240]
Ar = 2-HOC_6H_4: R = Me;[217]
Ar = 2-Br-6-$MeOC_6H_3$: R = $CH_2CH_2CO_2H$,[216] Bu;[216]
Ar = 3,4-$Me_2C_6H_3$, 2,5-$Me_2C_6H_3$: R = $CH_2CH_2CO_2H$;[218]
Ar = 4-$EtOC_6H_4$: R = Bu;[254]
Ar = 4-$Me_2NC_6H_4$: R = Me,[254] CH_2OEt, CH_2OBu;[275]
Ar = 2-$Me_2NC_6H_4$*: R = Me, Et, Bu[271]
Ar = 2,4,6-$Me_3C_6H_2$: R = CHF_2;[226]
Ar = 3-(2′-pyridyl)thienyl-2: R = Me;[272]
Ar = 4-Me-2-$NHCOMeC_6H_3$: R = Me;[232]
Ar = 2-$Me_3SiNHC_6H_4$: R = Bu;[273]Ar = 2-$C_{10}H_7$: R = Me,[264] $CH_2CH_2CO_2H$,[218] Bu,[244,254] $MeCHBr(CH_2)_2$,[244] C_7F_{15},[144] $PhCH_2CH_2$,[244] $C_{12}H_{25}$;[244]
Ar = 2-$C(Me)OCH_2CH_2OC_6H_4$: R = Bu;[255]
Ar = 2-$(EtO)_2CHC_6H_4$: R = Me,[217] Bu,[217,268] $CH_2CH(OEt)_2$;[256]
Ar = 2-$C({=}N)CMe_2CH_2OC_6H_4$: R = Me;[263]
Ar = 9-Br-10-anthryl: R = Me;[264]
Ar = 2,4,6-*t*-$Bu_3C_6H_2$: R = Bu;[265]

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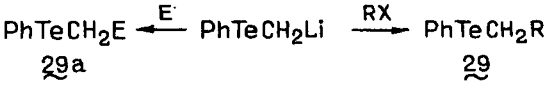
* These compounds were isolated as the corresponding diaryltellurium dihalides.

R = Me: Ar = 2-NHCOMeC_6H_4,[233] 2-NHCOPhC_6H_4,[269] 2-NHCO(4-ClC_6H_4)C_6H_4,[234] 2-NHCO(4-BrC_6H_4)C_6H_4,[234] 2-NHCO(4-MeC_6H_4)C_6H_4,[233] 2-NHCO(4-MeOC_6H_4)C_6H_4.[234]

The synthesis of some alkyl phenyl tellurides has been performed starting from phenyltelluromethyllithium, generated from bis(phenyltelluro)methane and organolithium reagents.[257,276,277] Subsequent treatment of $PhTeCH_2Li$ with various electrophiles leads to **29** and **29a**.

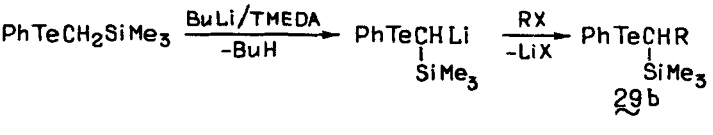


$$PhTeCH_2E \xleftarrow{E^-} PhTeCH_2Li \xrightarrow{RX} PhTeCH_2R$$

29a **29**

E = D, PhCH(OH), Ph_2COH;[257] R = C_9H_{19},[277] $C_{10}H_{21}$,[276] $C_{11}H_{23}$,[276,277] $C_{14}H_{29}$,[277] $C_{15}H_{31}$,[276] $Ph(CH_2)_2$,[276] $Ph(CH_2)_3$[276]

Compounds **29b** containing trimethylsilyl moieties have been obtained in the same manner.[278]

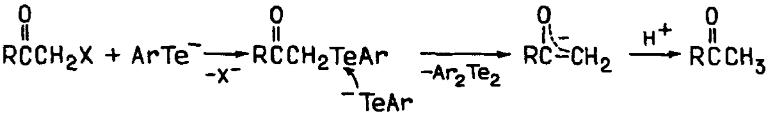


$$PhTeCH_2SiMe_3 \xrightarrow[-BuH]{BuLi/TMEDA} PhTe\underset{SiMe_3}{CH}Li \xrightarrow[-LiX]{RX} PhTe\underset{SiMe_3}{CH}R$$

29b

R = C_9H_{19}, $C_{11}H_{23}$, $C_{13}H_{27}$, $C_{15}H_{31}$

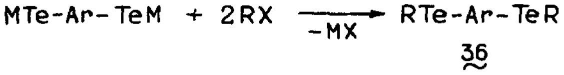
The reactions of arenetellurolate anions with activated halides (viz., α-halo ketones or α-halo esters), proceeding differently under different reaction conditions, are also of interest. At room temperature in ethanol the reduction of the above-mentioned α-halogenated substrates occurs according to the following scheme:[223]



$$R\overset{O}{\overset{\|}{C}}CH_2X + ArTe^- \xrightarrow{-X^-} R\overset{O}{\overset{\|}{C}}CH_2TeAr \xrightarrow{-Ar_2Te_2} R\overset{O^-}{C}{=}CH_2 \xrightarrow{H^+} R\overset{O}{\overset{\|}{C}}CH_3$$

However, at low temperature (−78 °C) in THF the usual substitution of bromine (but not chlorine) by phenyltelluro groups takes place and, as a result, the corresponding α-tellurocarbonyl compounds form in high yield.[207]

Arenes and hetarenes **36** with two alkyltelluro groups in the molecule have been prepared from the appropriate ditellurolate anions.

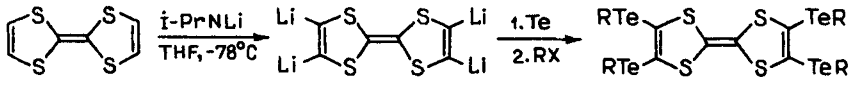


$$MTe{-}Ar{-}TeM + 2RX \xrightarrow[-MX]{} RTe{-}Ar{-}TeR$$

36

M = Li, Na; R = Me: Ar = 1,4-phenylene,[231,264] 1,2-phenylene,[279] 1,4-biphenylene,[264] 9,10-anthranylidene,[264] 3,6-(2,7-dimethoxy)naphthylene,[264] 3,6-benzothiophenylene,[264] 3,4-thiophenylene.[264]

Recently the synthesis of the compounds containing four alkyltelluro groups in the molecule was accomplished with tetrathiofulvalene as the starting material. Lithiation of this substrate with lithium diisopropylamide in THF and subsequent treatment of the tetralithio intermediate with tellurium and alkyl iodide or bromide RX (with R = Me, Et[266,267] or C_3H_7 – $C_{18}H_{37}$[267]) leads to tetrakis(alkyltelluro)tetrathiofulvalenes **37** in good yields.



37

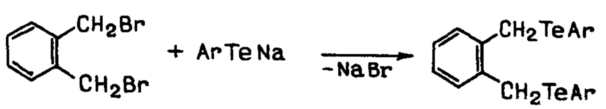
Interaction between arenetellurolate anions and α,ω-dihalo-alkanes[205,206,229,230,243,257,261] or their analogs[237] allows the synthesis of the tellurides **38–40** which are structurally related to **36** and where the aryltelluro groups are also separated by a more or less long carbon chain.

$$\mathrm{ArTeLi} + \mathrm{X(CH_2)_nX} \xrightarrow[-\mathrm{LiX}]{} \underset{\mathbf{38}}{\mathrm{ArTe(CH_2)_nTeAr}}$$

Ar = Ph: n = 1,[205,206,257] 3,[205,206] 5,[206] 6;[206]
Ar = Fc: n = 1[243]
Ar = 2-benzo[*b*]thienyl: n = 1.[261]

$$4\text{-}\mathrm{ROC_6H_4TeNa} + \mathrm{(ClCH_2CH_2)_2NR^1} \xrightarrow[-\mathrm{NaCl}]{} \underset{\mathbf{38a}}{(4\text{-}\mathrm{ROC_6H_4TeCH_2CH_2)_2NR^1}}$$

R = OMe, OEt: R¹ = H, Me.[237]



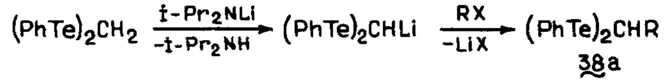
39

Ar = Ph,[230] 4-EtOC_6H_4.[229]

$$\mathrm{C(CH_2Br)_4} + \mathrm{ArTeNa} \xrightarrow[-\mathrm{NaBr}]{} \underset{\mathbf{40}}{\mathrm{C(CH_2TeAr)_4}}$$

Ar = Ph,[206] 4-EtOC_6H_4.[229]

Alkylation of bis(phenyltelluro)methyllithium results in the formation of *C*-substituted bis(phenyltelluro)methanes **38a**.[257,276,277]



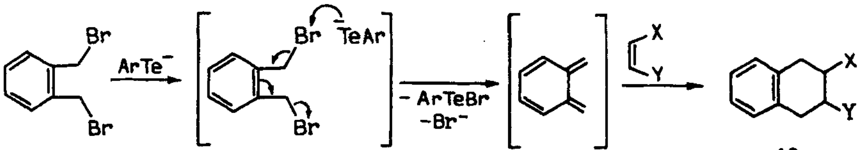
$$(PhTe)_2CH_2 \xrightarrow[-i\text{-}Pr_2NH]{i\text{-}Pr_2NLi} (PhTe)_2CHLi \xrightarrow[-LiX]{RX} (PhTe)_2CHR$$

38a

R = D, $PhCH_2$,[257] $C_{11}H_{23}$,[276,277] $C_{12}H_{25}$, $C_{14}H_{29}$, $C_{16}H_{33}$, $Ph(CH_2)_3$.[276]

The nature of the halogen-containing substrate and the temperature exert essential influence on the structure of the final products of the reaction of ArTeLi with α,ω-dihaloalkanes $X(CH_2)_nX$. When n = 2, diaryl ditellurides and ethene are the main products independent of the temperature;[205,206,224] the same result is observed at room temperature in the case of PhTeli and 1,3-dibromopropane (n = 3).[206] When n = 4, 5, mixtures of Ph_2Te and telluracyclopentane (28% yield) or telluracyclohexane (in unstated yield), respectively, together with oligomers $(Te(CH_2)_n)_m$ and partially substituted derivatives $PhTe(CH_2)_nCl$ (n = 4, 5) are formed.[206] The method used for the generation of the $ArTe^-$ anions also plays an important part. Thus, according to ref.,[221,224] 1,4-dibromobutane and $4\text{-}EtOC_6H_4TeNa$, generated by reduction of the corresponding ditelluride with $NaBH_4$ in ethanol, give rise only to 4-ethoxyphenyltelluroniacyclopentane bromide whereas PhTeLi generated from PhLi and Te leads to quite different products (*vide supra*). Obviously, in analogy with data concerning the structure and nucleophilicity of benzeneselenolate anions generated in different ways,[280] one might wish to attribute the structure $[ArTeB(OEt)_3]^-$ to the tellurolate anions generated in the former way. Such a structure causes a decrease in its nucleophilicity in comparison with "free" tellurolate anions generated from PhLi and tellurium.

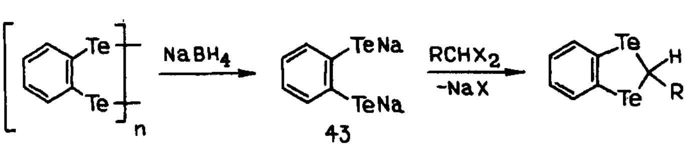
The reaction temperature is also very important in the synthesis of **39** which commonly be prepared successfully at room or lower temperature.[229,230] In boiling ethanol, *o*-quinodimethane **41** is formed (the scheme below presents one of three possible pathways of its formation) which reacts readily with various dienophiles giving rise to the Diels-Alder adducts **42** in 20–53% yield.[230]



41 42

Ar = Ph, $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $3\text{-}ClC_6H_4$; X = H, CO_2Et; Y = CN, CO_2Et, COMe

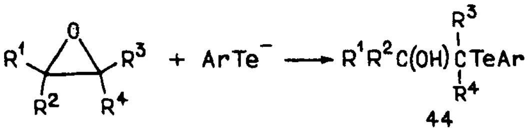
The previously unknown benzo-1,3-ditellurole and its analogs have been prepared by reaction of dibromomethane and its derivatives $RCHX_2$ with the ditellurolate anion **43**, generated by reduction of poly(*o*-phenylene) ditelluride with $NaBH_4$ in ethanol or DMF.[279,281-283]



43

R = H, OBu, Ph

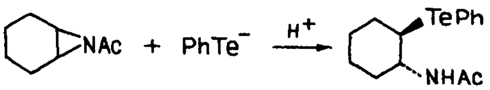
Ring opening of oxiranes occurs upon treatment with arenetellurolate anions and leads in good yields to alkyl aryl tellurides **44** containing a hydroxy group in β-position to the tellurium center.[195,222,284,285]



44

Ar = Ph: $R^1 = R^3 = H$, $R^2 = R^4 = Me$,[222,285] Pr;[195] $R^1 = R^3 = R^4 = H$, $R^2 = C_8H_{17}$;[195,284] $R^1 = Me$, $R^2 = CHCH_2CH_2CH(Me)C(O)CH_2$, $R^3 = R^4 = H$: $R^2 + R^4 = (CH_2)_5$, $(CH_2)_6$[284]

Similarly, PhTeNa opens the aziridine ring in 7-acetyl-7-azabicyclo[4.1.0]heptane forming the cycloalkyl phenyl telluride **45**. Unfortunately, this approach is only represented by a single example.[286,287]

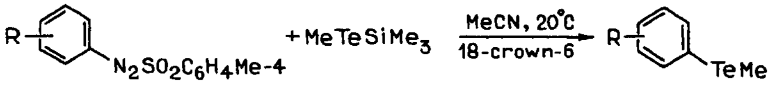


45

In the previous preparations of alkyl aryl tellurides arenetellurolate anions played the role of nucleophiles and alkyl halides, dialkyl sulfates, tosylates, mesylates and oxiranes were used as electrophiles. However, nucleophilic substitution of halogen in aryl halides by alkanetellurolate anions ("reverse" reaction) is also possible. Thus, interaction between iodobenzene and MeTeli gave phenyl methyl telluride in 35% yield,[206] and reactions of *o*-dibromo(bromoiodo)benzene with the corresponding RTeLi lead to *o*-bis[methyl(phenyl-)telluro]benzene.[288] However, it has been noted[289] that the same reaction gives rise to alkyl phenyl tellurides in very poor yields. Since the rate of dealkylation of alkyl phenyl tellurides by alkanetellurolate anions considerably exceeds the rate of aromatic nucleophilic substitution, the above mentioned observation is easily explained.

Alkyl aryl tellurides are also prepared by the reactions of appropriate substrates with (methyltelluro)trimethylsilane $MeTeSiMe_3$[290] employed as a synthetic equivalent of methanetellurolate anion as well as with diisobutylaluminium benzenetellurolate *i*-$Bu_2AlTePh$.[291,292]

The arylazo sulfones **46** are converted to **29** in modest yields (36–62%) by treatment with $MeTeSiMe_3$ generated *in situ* from lithium methanetellurolate and trimethylchlorosilane under PTC conditions.[290]

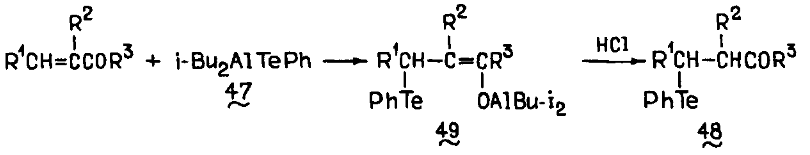


46 **29**

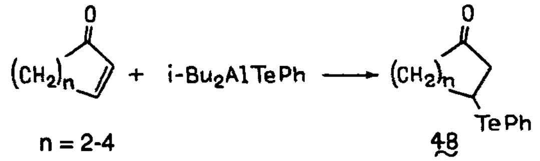
R = H, 4-Br, 4-COMe, 2-CO_2Me

The applications of diisobutylaluminium benzenetellurolate **47**, generated from diphenyl ditelluride and diisobutylaluminium hydride, are based on the addition of this reagent to α,β-unsaturated carbonyl compounds[291] or on its reactions with acetals, alkyl sulfonates or oxiranes.[292]

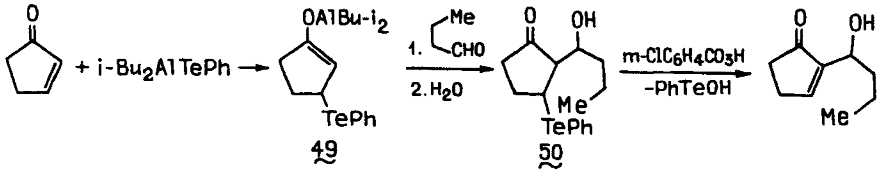
The 1,4-addition of **47** to α,β-unsaturated carbonyl compounds (ketones, aldehydes and carboxylic acid esters) smoothly proceeding at −78 °C leads to the β-phenyltelluro-carbonyl derivatives **48** in 26–87% yield.[291]



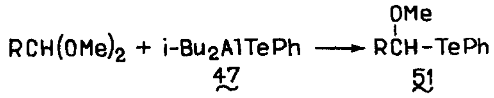
$R^1 = R^2 = R^3 = H$; $R^1 = R^2 = H$: $R^3 = Me$;
$R^1 = Me$, $R^2 = H$, $R^3 = Et$;
$R^1 = R^2 = H$, $R^3 = OBu$;
$R^1 = H$, $R^2 = Me$, $R^3 = OMe$;
$R^1 = Me$, $R^2 = H$, $R^3 = OEt$



The intermediate enolates **49** react with aldehydes yielding the β-hydroxy derivatives **50**. Taking into account that the treatment of these derivatives with *m*-chloroperbenzoic acid results in elimination of tellurium from the molecule in the shape of PhTeOH, the sequence of reactions presented below gives a novel method of hydroxyalkylation of the α-position in α,β-unsaturated carbonyl compounds.[291]



Dimethyl acetals of aldehydes upon treatment with equimolar **47** give rise to the monotelluroacetals **51**, and with excess of **47** to the ditelluroacetals **52**.[292]



$$RCH(OMe)_2 + i\text{-}Bu_2AlTePh \longrightarrow RCH(OMe)\text{-}TePh$$

R = H (42%), $Me(CH_2)_{10}$ (80%)

$$\mathrm{RCH(OMe)_2} + 2\ \underset{\mathbf{47}}{\mathrm{i\text{-}Bu_2AlTePh}} \longrightarrow \underset{\mathbf{52}}{\mathrm{RCH(TePh)_2}}$$

R = $\mathrm{Me(CH_2)_{10}}$ (50%)

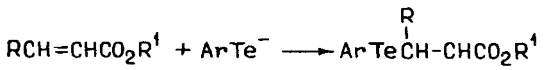
The reaction between **47** and primary alkyl methanesulfonates or *p*-toluenesulfonates also provides a synthetic route to alkyl phenyl tellurides **29** in good yields.[292]

$$\mathrm{ROMs(OTs)} + \mathrm{i\text{-}Bu_2AlTePh} \longrightarrow \underset{\mathbf{29}}{\mathrm{PhTeR}}$$

R = $\mathrm{Me(CH_2)_5}$ (72%), $\mathrm{Ph(CH_2)_3}$ (84%), $\mathrm{MeCH(CH_2)_5Me}$ (54%), *c*-$\mathrm{C_{12}H_{23}}$ (46%), 2-$\mathrm{Me_2CH}$-5-Me-*c*-$\mathrm{C_6H_9}$ (42%)

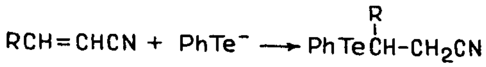
The same method can be used to prepare **29** from secondary alkyl methanesulfonates, but olefins are also form together with the desired tellurides. The reagent **47** in its reactions with oxiranes behaves just like the corresponding tellurolate anion and does not provide any advantages in comparison with the latter reagent. The special precautions required in the handling of **47**, namely, inert atmosphere, complete exclusion of air and moisture, and low temperature, suggests a preference for the use of arenetellurolate anion in reaction with oxiranes.

Besides nucleophilic substitution, nucleophilic addition of arenetellurolate anions to activated double bonds may be used to prepare alkyl aryl tellurides. In the known examples of this reaction the yields vary from 31% to 71%.[118,293]



$$\mathrm{RCH{=}CHCO_2R^1} + \mathrm{ArTe^-} \longrightarrow \mathrm{ArTe\overset{R}{\overset{|}{C}}H\text{-}CHCO_2R^1}$$

R = H: $\mathrm{R^1}$ = Na: Ar = Ph, 4-$\mathrm{MeC_6H_4}$, 4-$\mathrm{MeOC_6H_4}$, 4-$\mathrm{EtOC_6H_4}$;[293]
$\mathrm{R^1}$ = Et: Ar = Ph: R = H, Me[118]

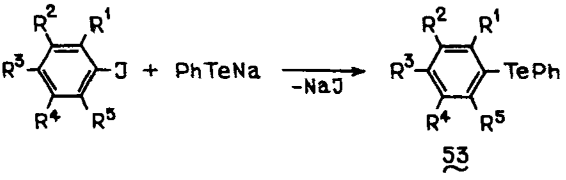


$$\mathrm{RCH{=}CHCN} + \mathrm{PhTe^-} \longrightarrow \mathrm{PhTe\overset{R}{\overset{|}{C}}H\text{-}CH_2CN}$$

R = H, Me

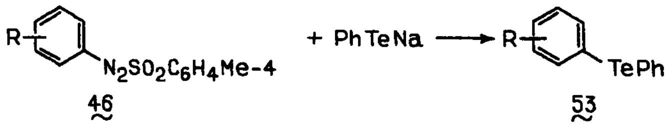
2.5.1.3. *Diaryl tellurides.* The synthesis of unsymmetric diaryl tellurides $\mathrm{Ar^1TeAr^2}$ starting from arenetellurolate anions may be performed by arylation of the latter with activated iodoarenes,[294] arylazo *p*-toluenesulfonates[290] or aryldiazonium cations.[295,296] The arenetellurolate anions used in these preparations were generated by reduction of the appropriate diaryl ditellurides with aqueous alkaline $\mathrm{NaBH_4}$,[296] solid $\mathrm{KBH_4}$[294,295] or by reaction of phenyllithium with tellurium in THF.[290]

The interaction between benzenetellurolate anions and iodonitroarenes in HMPTA at 80–90 °C in the presence of copper(I) iodide leads to the aryl phenyl tellurides **53**; the yields are modest to excellent.[294] Unactivated iodoarenes do not react under these conditions.



$R^1 = NO_2$ ($R \neq H$); $R^2 = NO_2$; $R^3 = NO_2$; $R^1 = NO_2$: $R^2 = R^4 = R^5 = Me$; $R^1 = R^2 = Me$; $R^3 = NO_2$

The use of aryldiazo sulfones **46** is more preferable in this process. The reaction of **46** with PhTeNa allows to obtain aryl phenyl tellurides **53** containing a variety of substituents in relatively poor yields.[290]



R = H, 4-I, 2-NO_2, 4-NO_2, 4-Me

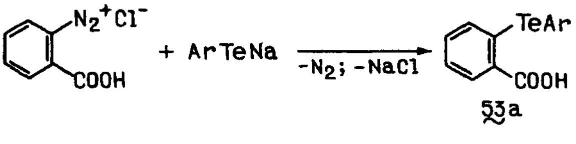
The arylation of arenetellurolate anions by aryldiazonium cations, applied for the first time in ref. 295, is a promising approach to the preparation of unsymmetric diaryl tellurides **53**. Thus, the treatment of sodium arenetellurolates with solid aryldiazonium tetrafluoroborates in ethanol gave rise to diorganyl tellurides **53**, usually isolated as the corresponding *Te,Te*-dichlorides, in 36–45% yield. The same method may also be used prepare the symmetric derivatives **1**.

$$R^1C_6H_4TeNa + R^2C_6H_4N_2^+\,BF_4^- \xrightarrow[-N_2;\,-NaBF_4]{} R^1C_6H_4TeC_6H_4R^2$$

53

$R^1 = H$: $R^2 = H$, 4-Cl, 4-Me; $R^1 = 4$-OMe: $R^2 = 4$-Me

Later[296] a series of 2-carboxyphenyl aryl tellurides **53a** was obtained by reaction of a neutral solution of 2-carboxyphenyldiazonium chloride with a solution of a sodium arenetellurolate in a mixture of ethanol and THF in lesser yields. It seems that the presence of THF in the reaction mixture ensures the reproducibility of the yields of the desired products (15–43%).



Ar = 2-C_4H_3S (15%), Ph (43%), 4-MeC_6H_4 (30%)

Whereas $(PhC{\equiv}C)_2Te$ may be considered as the synthetic equivalent of Te(II)[87] (cf. 2.2), the telluride $ArTeC{\equiv}CPh$ is obviously the synthetic equivalent of the $ArTe^-$ anion.

Indeed, interaction between aryl phenylethynyl tellurides and lithioarenes in THF at −78 °C leads to unsymmetric diaryl tellurides **53** in 44–85% yield.[87]

$$4\text{-}R^1C_6H_4TeC{\equiv}CPh + 4\text{-}R^2C_6H_4Li \xrightarrow[-PhC\equiv CLi]{} \underset{\mathbf{53}}{4\text{-}R^1C_6H_4TeC_6H_4R^2\text{-}4}$$

R^1 = OMe: R^2 = H (44%), CF_3 (77%), Me (58%); R^1 = Me_2N: R^2 = F (67%), H (85%), Me (77%), OMe (63%).

The use of organyl phenylethynyl tellurides as synthetic equivalents of RTe^- (R = alkyl) anions was first reported in ref. 210. Symmetric and unsymmetric dialkyl tellurides have been prepared by interaction between PhC≡CTeR and R^1Li (for a more detailed description see 2.5.1.1.).

The synthesis of **53** has also been performed by photo-[251,297,298] or electrochemically induced[299–301] reactions of arenetellurolate anions with aryl halides proceeding with an $S_{RN}1$ mechanism. In the former case the arenetellurolate anions were generated by cleavage of diaryl ditellurides with sodium metal in liquid ammonia, in the latter one by reduction of the same ditellurides in acetonitrile[299–301] or in DMSO[301] with ultrasonic irradiation.

The $S_{RN}1$ reactions proceed according to the following Scheme:

$$Ar^1Te^- + Ar^2X \longrightarrow (Ar^2X)^{\bullet-} + Ar^1Te^\bullet \qquad (1)$$

$$(Ar^2X)^{\bullet-} \longrightarrow Ar^{2\bullet} + X^- \qquad (2)$$

$$Ar^{2\bullet} + Ar^1Te^- \longrightarrow (Ar^1TeAr^2)^{\bullet-} \qquad (3)$$

$$(Ar^1TeAr^2)^{\bullet-} + Ar^2X \longrightarrow Ar^1TeAr^2 + (Ar^2X)^{\bullet-} \qquad (4)$$

Ar^1 = Ar^2 = Ph (90%[251,297]);
Ar^1 = Ph: Ar^2 = 4-$MeOC_6H_4$ (73%[297]), 1-$C_{10}H_7$ (51%[251,297]), 2-quinolyl (43%[298]), 9-anthryl (38%[301]), 4-NCC_6H_4 (42%[299]), 4-$PhCOC_6H_4$ (44%[300]), 3-$PhCOC_6H_4$ (48%[300]), 2-$PhCOC_6H_4$ (75%[300])

Although the unsymmetric diaryl tellurides **53** may be prepared in 38–75% yield by this method, it is of little synthetic use for synthesis because of the concomitant formation of the symmetric product. Thus, diphenyl and bis(4-methoxyphenyl) telluride were isolated together with the desired phenyl (4-methoxyphenyl) derivative (yield 73%) in 75% and 11% yield, respectively.[297]

This is caused by the fact that, in contrast to the analogous sulfur and selenium intermediates, the $(Ar^1TeAr^2)^{\bullet-}$ anion radicals are subject to three competitive conversions: dissociation to the starting species, transformation to the desired products **53** and decomposition according to eqn. (5).

$$(Ar^1TeAr^2)^{\bullet-} \longrightarrow Ar^{1\bullet} + Ar^2Te^- \qquad (5)$$

The radicals and anions formed by this degradation interact according to eqns. (1)–(4) giving rise to the symmetric products.

The data presented in refs. 298, 301 concerning the relative reactivity of phenylchalcogenide anions in $S_{NR}1$ reaction are of certain interest in the chemistry of VIa group elements. The values of relative rate constants determined in liquid ammonia are: 1.0 (PhS^-), 5.8 ($PhSe^-$), 28.0 ($PhTe^-$)[298] in their reactions with the 2-quinolyl radical and 1.0 (PhS^-), 1.4 ($PhSe^-$), 3.2 ($PhTe^-$) in their reactions with the 9-anthryl radical in DMSO.[301]

2.5.2. *From tellurenyl halides.* As distinct from sulfenyl and selenyl halides, the tellurenyl derivatives which may be obtained by controlled oxidation of diaryl ditellurides with halogens[302-306] or organyltellurium trihalides[306,307] are usually rather unstable compounds. Arenetellurenyl bromides decompose within a few hours and the iodides are somewhat more stable and may be stored in a dry atmosphere for a few weeks.[303]

In the case of alkanetellurenyl halides the chloro derivatives are more stable and alkanetellurenyl iodides decompose at room temperature within a few minutes.[306]

One of the most effective ways to stabilize these compounds is the introduction of an appropriate substituent which is able to form a coordinative bond with the tellurium center (such as CHO, COR, CH=N, N=N, NO_2, CH_2NMe_2[308,309]) in the ortho position to the TeX group. Unstabilized as well as coordinatively stabilized tellurenyl halides have been used for the preparation of diorganyl tellurides.

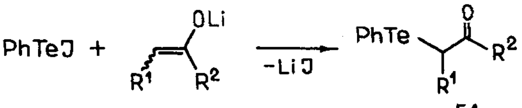
Interaction between magnesium- or lithiumorganic reagents and unstabilized tellurenyl halides generated *in situ* from Ar_2Te_2 and an equimolar amount of bromine or iodine leads to unsymmetric diorganyl tellurides in high yields.[302,306,310]

$$R^1TeX + R^2M \xrightarrow[-MX]{} \underset{\mathbf{29, 30, 53}}{R^1TeR^2}$$

X = Br, I; M = MgBr, Li; R^1 = Ph: R^2 = Bu,[310] C_6H_{11};[310] R^1 = 4-MeC_6H_4; R^2 = Bu,[310] Ph,[310] C_6H_{11};[310] R^1 = 4-$MeOC_6H_4$: R^2 = Ph;[310] R^1 = 4-$EtOC_6H_4$: R^2 = Bu,[310] Ph,[310] C_6H_{11};[310] R^1 = 2-$C_{10}H_7$: R^2 = Et,[302] Ph,[302] *c*-C_6H_{11};[302] R^1 = *n*-Alk: R^2 = *t*-Bu[306]

Benzyl tellurocyanate behaves in the same reactions like the arenetellurenyl halides. Its reaction with *o*-nitrophenyllithium produces *o*-nitrophenyl benzyl telluride in 72% yield.[311]

Later arenetellurenyl iodides were employed to prepare the α-phenyltelluro carbonyl compounds **54** as well as the α-(organyltelluro)acetic acid esters **55**.[203,313] The former have been prepared in 41–81% yield starting from PhTeI and lithium enolates at −78 °C in THF and the latter by the treatment of the same intermediate with zinc α-bromoacetates. The yields of **55** were 46–78%.



54

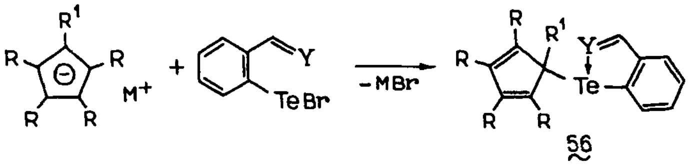
R^1 = H: R^2 = Me, Me_2N, EtO, *t*-Bu, Ph;
R^1 = Me: R^2 = EtO

$$\mathrm{RTeJ + BrZnCH_2CO_2R^1 \xrightarrow[-ZnBrJ]{} \underset{\mathbf{55}}{RTeCH_2CO_2R^1}}$$

R = Ph, 4-MeC_6H_4, 2-$C_{10}H_7$: R^1 = Me, Et;[313]
R = $Me(CH_2)_8$: R^1 = Me[203]

The reaction of *o*-halogenotellurenyl carbonyl compounds stabilized with carbonyl substituents (2-formyl,[256] 2-phenylcarbonyl[296]) with dimethylcadmium produces *o*-(methyltelluro)phenyl carbonyl derivatives in good yields.

The synthesis of aryl cyclopentadienyl tellurides **56** is worthy of special note. Attempts to prepare these compounds by condensation of metal cyclopentadienides with benzenetellurenyl bromide were unsuccessful.[314] However, the introduction in the ortho-position relative to the tellurium center of a substituent which is able to form a strong intramolecular coordination bond in the final product (for example a formyl or arenealdimino group) leads to the formation of the crystalline stable products **56**. The silver and thallium salts of the appropriate cyclopentadienes have been employed as starting materials in these preparations.[314]



56

M = Ag, Tl; R = R^1 = CO_2Me: Y = O, NPh, NC_6H_4Me-2; R = CO_2Me: R^1 = Me:
Y = NPh, NC_6H_4OMe-4

2.5.3. *From diorganyl ditellurides.* A number of preparations of unsymmetric and symmetric diorganyl tellurides is based on the relatively readily available diaryl (dialkyl) ditellurides[3,4] as starting materials.

The extrusion of one tellurium atom from a diaryl ditelluride constitutes the easiest way of their conversion to diaryl tellurides **1**. Although such an extrusion may be achieved by heating to 300 °C or higher,[3,4] a preparatively more convenient approach consists of 3–4 h boiling of Ar_2Te_2 in dry dioxane in the presence of excess active copper[68,231,315–319] or palladium on charcoal.[318] The simplicity of this process and the high purity and excellent yields of final products are unquestionable advantages of this reaction although the loss of half of the tellurium contained in the starting ditelluride is an obvious shortcoming of the method.

$$\mathrm{(RC_6H_4)_2Te_2 + Cu \xrightarrow[-CuTe]{} \underset{\mathbf{1}}{(RC_6H_4)_2Te}}$$

R = 4-Br,[315,316] 3-Br,[316] 4-Cl,[315,316] 3-Cl,[316] 4-F,[316] H,[68,315,317] 4-CF_3,[319] 4-Me,[315] 3-Me,[316] 4-H_2N,[318] 4-MeO,[315] 3-MeO,[317] 4-MeHN,[318]* 4-EtO,[315,316] 4-Me_2N,[318] 4-Me_3Si,[231] 4-NO_2,[316] 2,4,6-Me_3,[317] 3,4-C_4H_4,[316] 3-Me-4-H_2N,[318] 2-Me-4-H_2N,[318] 3-EtO-4-H_2N,[318] 3-F_3C-4-H_2N,[318] 3,5-Me_2-4-H_2N,[318] 3-MeOCO-4-H_2N,[318] 4-PhNH[318]

Upon UV irradiation the detelluration of diaryl ditellurides proceeds quantitatively at room temperature.[320] The acceleration of the reaction which occurs in the presence of tertiary phosphines can be explained by the formation of an intermadiate phosphine telluride, which subsequently easily decomposes into phosphine and Te. A possible reaction sequence is presented below.[320]

$$\begin{aligned}
&R_2Te_2 \xrightarrow{h\nu} 2\,RTe^\bullet\\
&RTe^\bullet + R'_3P \longrightarrow [R'_3PTeR]\\
&[R'_3PTeR]^\bullet \longrightarrow R'_3PTe + R^\bullet\\
&R'_3PTe \longrightarrow R'_3P + Te\\
&R_2Te_2 + R^\bullet \longrightarrow R_2Te + RTe^\bullet
\end{aligned}$$

The reaction of Ar_2Te_2 with aryldiazonium salts is probably a quite promising approach to the synthesis of unsymmetric tellurides **53** via their *Te,Te*-dihalides.[321,322] Interaction of diphenyl ditelluride with *p*-bromophenyldiazonium bromide in aqueous acetone gave a high yield of an equimolar mixture of phenyl *p*-bromophenyl telluride and the corresponding *Te,Te*-dibromide with the following stoichiometry:

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

This suggests that Ar_2Te_2 are effective one-electron reduction agents for aryldiazonium cations and the following mechanism of the above reaction has been postulated.[322]

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

However, this reaction leading to a mixture of two compounds which requires the separation or the chemical transformation into one certain derivative (by reduction of the dihalide or oxidation of the telluride) is inconvenient as a preparative method. As long as the copper(II) salts readily oxidize the tellurides to the corresponding dihalides[323] the interaction between Ar_2Te_2 and a diazonium salt in the presence of two moles of copper(II) halide produces the corresponding diaryltellurium dihalide as the sole product.[322] The good (60–90%) yields of the desired derivatives as well as the availability of the starting

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* In these cases mixtures of 4-amino substituted tellurides obtained by reduction of 2:1 complexes of aromatic amines with $TeCl_4$ have been employed in the detelluration reaction.

materials and the possibility to vary the substituents in both reaction components as well as the ease with which the dihalides can be transformed to the corresponding tellurides (cf. 2.5.6.) make this method one of the most suitable for the preparation of unsymmetric diaryl tellurides.

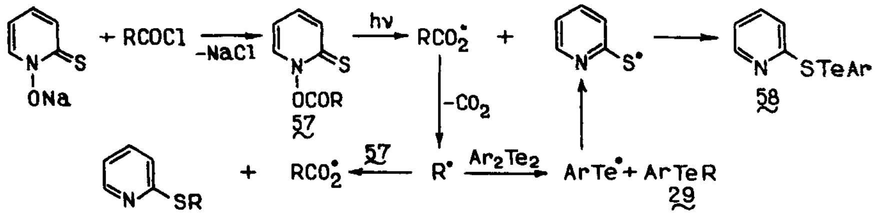
Also the alkyl aryl tellurides **29** may be obtained from aryldiazonium tetrafluoroborates and dialkyl ditellurides. Thus, the treatment of aryldiazonium tetrafluoroborates with diethyl ditelluride in the presence of 18-crown-6 leads to the aryl ethyl tellurides **29** in moderate yields (21–63%).[324]

$$RC_6H_4N_2^+\,BF_4^- + Et_2Te_2 \longrightarrow \underset{29}{RC_6H_4TeEt}$$

R = 2-F, 2-Cl, 2-Br, 2-I, 2-CN, 2-NO_2, 2-CO_2H, 2-Me, 3-Me, 4-Me, 2-MeO, 2-MeS,
2-MeSe, 2-COMe, 2-CO_2Me

However, the reaction of 2-nitrophenyldiazonium borofluoride with Et_2Te_2, according to ref. [232] under the same conditions leads to bis(2-nitrophenyl) telluride instead of the expected 2-nitrophenyl ethyl derivative.

Other approaches to the preparation of alkyl aryl tellurides **29** are based on the ready insertion of highly reactive intermediates (viz., radicals,[325–328] carbene,[257,329–331] and dehydrobenzene[332,333]) into the Te-Te bond of diaryl ditellurides. Thus, mixed anhydrides of *N*-hydroxy-2-pyridinethione and aliphatic or alicyclic carboxylic acids **57** usually generated *in situ* from an acyl chloride and the sodium salt of the thione give the desired compounds **29** in high yields upon irradiation with a tungsten lamp in the presence of Ar_2Te_2. In the case of readily decomposing ditellurides the reaction has been carried out in sun light at 35 °C. The reaction involves radical decarboxylation and subsequent S_H2 reaction of the radicals formed with the diaryl ditelluride.[325,326]



Ar = 4-$MeOC_6H_4$: R = 1-adamantyl;
Ar = 4-$PhOC_6H_4$: R = 1-adamantyl, $Me(CH_2)_{14}$, $PhCH_2CH_2$, 3α-acetoxy-23-24-norcholane-12-one, 3β-acetoxy-20-pregnane-11-one
Ar = 2-$C_{10}H_7$: R = 1-adamantyl, $Me(CH_2)_{14}$, 3α-acetoxy-23-24-norcholane-12-one

It is important for the formation of **29** that the diaryl ditelluride is completely consumed because of the easy disproportionation of the tellurosulfide **58** to ditelluride and 2,2′-dipyridyl disulfide.

A radical mechanism is also operative in the preparation of tellurides **29** by means of UV irradiation of an equimolar mixture of an alkylmercury chloride (or dialkylmercury) and Ph_2Te_2.[327,328] The ready reaction at 35 °C under irradiation and its complete inhibition in darkness or in the presence of *t*-$Bu_2NO^{\bullet}$ as well as its acceleration in the presence of azobis (isobutyronitrile) favor this mechanism. The yields of **29** are quite high (45–100%) and increase from primary to tertiary alkyl groups. The corresponding reaction with phenyl- or cyclopropylmercury(II) chloride fails because of the high energy of C-Hg bond fission.[327]

$$Ph_2Te_2 \xrightarrow{h\nu} 2\,PhTe^{\bullet}$$
$$PhTe^{\bullet} + RHgCl \longrightarrow PhTeHgCl + R^{\bullet}$$
$$R^{\bullet} + Ph_2Te_2 \longrightarrow \underset{\mathbf{29}}{PhTeR} + PhTe^{\bullet}$$

R = Me_2CH, Me_3CCH_2, $CH_2 = CHCH_2CH_2$, c-C_6H_{11}, $CH_2{=}CH(CH_2)_4$, $CH_3(CH_2)_5$, $PhCH_2$, 7-norbornyl

It has been assumed[334] that the reaction of Ph_2Te_2 with trialkylboranes in the presence of oxygen and which leads in 64–99% yield to alkyl phenyl tellurides **29** also proceeds according to radical mechanism as shown below. If an unsymmetric trialkylborane is used in this process, a mixture of the two possible alkyl phenyl tellurides is formed.

$$R_3B \xrightarrow[-R_2BO_2^{\bullet}]{O_2} R^{\bullet} \xrightarrow{Ph_2Te_2} \underset{\mathbf{29}}{PhTeR} + PhTe^{\bullet} \xrightarrow{R_2BO_2^{\bullet},\,O_2} PhTeO_2BR_2\,,\ Ph_2TeO_2$$

R = $Br(CH_2)_5$, *c*-C_6H_{11}, C_6H_{13}, $PhCHMeCH_2$, $PhCH_2OCO(CH_2)_4$, $PhCH_2OCO(CH_2)_6$, $C_{16}H_{33}$

However, the interaction between Ph_2Te_2 and a dialkylmercury in inert atmosphere proceeds probably with another mechanism.[335] Boiling an equimolar mixture of these reagents in dioxan under nitrogen leads to **29** in more than 70% yield.

$$Ph_2Te_2 + R_2Hg \xrightarrow[-Hg]{} \underset{\mathbf{29}}{PhTeR}$$

R = *i*-Pr, $PhCH_2$

Diarylmercury derivatives do not react in this manner although interaction between Ar_2Te_2 and divinylmercury gives aryl vinyl tellurides in good yields.[336]

It had been noted earlier that bis(alkyltelluro)methanes **31** and their aryl analogs **38** can be obtained by reaction of alkane[205,206,208] or arenetellurolate anions[205,206,243,257,261] with dihalomethanes. In addition, these derivatives may be successfully (60–100%) prepared by interaction between diorganyl ditellurides and diazomethane.[257,329–331]

$$R_2Te_2 + CH_2N_2 \xrightarrow[-N_2]{} \underset{\mathbf{31},\ \mathbf{38}}{RTeCH_2TeR}$$

R = Me, Et, Pr, *i*-Pr, Bu, *i*-Bu, *t*-Bu*;[330] 2-C_4H_3O,[331] 2-C_4H_3S,[331] Ph,[330,331] 4-MeC_6H_4,[331]

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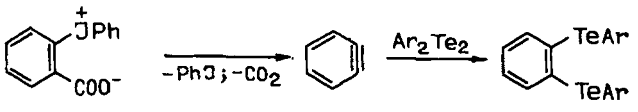
* The yields of the products and their physical constants were not reported.

$4\text{-}MeOC_6H_4$,[329,331] $4\text{-}EtOC_6H_4$,[329] $4\text{-}Me_2NC_6H_4$,[331] $1\text{-}C_{10}H_7$,[331] $2\text{-}C_{10}H_7$,[331] $4\text{-}PhOC_6H_4$[331]

Another type of tellurides containing two tellurium atoms in a molecule, namely, the 1,2-bis(aryltelluro)benzenes **59**, is available via the electrophilic attack of dehydrobenzene, generated by thermal decomposition of 2-(phenyliodonium) benzoate, on the Te-Te bond of Ar_2Te_2.[332,333]



59

Ar = $4\text{-}MeC_6H_4$, $4\text{-}MeOC_6H_4$, $4\text{-}EtOC_6H_4$

At the same time diphenyl and di(2-naphthyl) ditelluride were found to be inert toward dehydrobenzene insertion.[333] All attempts to prepare benzo-1,3-ditellurole by insertion of carbene or dehydrobenzene into the Te-Te bond of poly(*o*-phenylene) or polymethylene ditelluride, respectively, failed, probably due to the insolubility of these ditellurides.[283]

Unsymmetric diaryl **53**,[337] dialkyl **30**,[338] alkylaryl **29**[263] and a ferroceny tellurides[243] have been prepared by treatment of the appropriate ditellurides with magnesium[337] or lithium-organic[243,263,337,338] reagents.

$$R^1_2Te_2 + R^2M \longrightarrow \underset{29,30,53}{R^1TeR^2} + R^1TeM$$

R^1 = Me: R^2 = Me, Pr, Bu, *i*-Bu, *neo*-C_5H_{11},*[338] $2\text{-}Me_2NCH_2C_6H_4$,[263] $2\text{-}C(Me)(OLi)NMe_2\text{-}4\text{-}ClC_6H_3$,[263] $2\text{-}C(Me)(OLi)Me_2N\text{-}4\text{-}MeC_6H_4$,[263] $2\text{-}C(Me)(OLi)Me_2N\text{-}5\text{-}MeC_6H_3$,[263] $2\text{-}C(=N)CMe_2CH_2OC_6H_3CH_2$;[263]
R^1 = Et: R^2 = Me, Pr, Bu, *i*-Bu, *neo*-C_5H_{11};[338] $2\text{-}LiO_2CC_6H_4$,[263] $2\text{-}C(NH)CH_2CH_2NHC_6H_4$;[263]
R^1 = $4\text{-}MeOC_6H_4$: R^2 = Ph;[337]
R^1 = $4\text{-}EtOC_6H_4$: R^2 = Ph;[337]
R^1 = $4\text{-}PhOC_6H_4$: R^2 = Ph;[337]
R^1 = Fc: R^2 = Bu, $2\text{-}MeOC_6H_4$, $4\text{-}MeOC_6H_4$, Fc[243]

The formation of substantial amounts of symmetric by-products reduces the preparative significance of this method. For example, phenyl butyl, dibutyl and diphenyl telluride together with the starting diphenyl ditelluride were isolated after treatment of the latter compound with butyllithium.[339] The recovery of unreacted Ph_2Te_2 may be explained by the fact that the highly nucleophilic BuLi like other organolithium reagents[340–342] is able to attack not only Ph_2Te_2 (giving rise to PhTeBu) but also a Te-C bond of the latter compound which leads to Bu_2Te and PhLi. Interaction between the PhLi formed and

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* These compounds were characterized by ^{125}Te NMR spectra only.

Ph_2Te_2 results in Ph_2Te and PhTeLi. Oxidation of the lithium benzenetellurolate leads to diphenyl ditelluride.

$$\begin{aligned}
Ph_2Te_2 + BuLi &\longrightarrow PhTeBu + PhTeLi \\
PhTeBu + BuLi &\longrightarrow Bu_2Te + PhLi \\
Ph_2Te_2 + PhLi &\longrightarrow Ph_2Te + PhTeLi \\
\hline
2\,Ph_2Te_2 + 2\,BuLi &\longrightarrow Ph_2Te + Bu_2Te + 2\,PhTeLi
\end{aligned}$$

The fast interaction between Ph_2Te_2 and magnesium-(or lithium) organic reagents even at low temperatures and the conspicuous endpoint of reaction where the intensive red color of the ditelluride turns to pale yellow permits the use of this reaction for a rapid determination of these organometallics.[339] This method is well reproducible and gives results in excellent agreement with those obtained by other methods.

A novel approach to the preparation of alkyl phenyl tellurides **29** starting from Ph_2Te_2 was suggested recently.[343] The treatment of this ditelluride with samarium diiodide leads to samarium(III) benzenetellurolate which then reacts with alkyl halides (bromide or iodide) yielding **29** (68–82%).[343,344]

$$Ph_2Te_2 + SmI_2 \longrightarrow [PhTeSmI_2] \xrightarrow{RX} \underset{\mathbf{29}}{PhTeR}$$

R = Me, Et, Pr, *i*-Pr, Bu, $PhCH_2$

2.5.4. *From Telluronium Salts.* The synthesis of diorganyl tellurides from telluronium salts $R^1R^2R^3Te^+X^-$ (X = halide, NCY (Y = O, S, Se), OCOR, etc.) proceeding via elimination of RX[99,100,150,204,216,217,255,345–352] is of little preparative importance since telluronium salts themselves are usually only available via the desired tellurides.

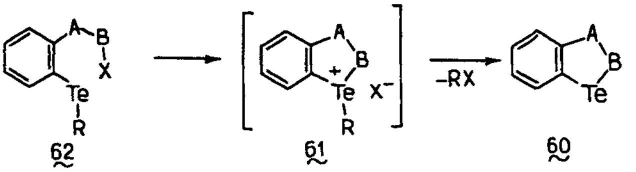
$$R^1R^2R^3Te^+X^- \xrightarrow[-R^3X]{} \underset{\mathbf{29,30}}{R^1TeR^2}$$

$R^1 = R^2 = R^3$ = Me: X = $MeCO_2$, $CHCl_2CO_2$, CCl_3CO_2, $PhCO_2$;[350] I;[204]
$R^1 = R^2$ = Me, R^3 = Ph, X = Br;[216] X = I: R^3 = 2-$CHOC_6H_4$,[217] 2-$CH(OEt)_2C_6H_4$,[217] 2-$C(Me)OCH_2CH_2OC_6H_4$;[255]
R^1 = Me, R^2 = CH_2CO_2H, X = Br: R^3 = 2-$CHOC_6H_4$,[345] 2-$MeCOC_6H_4$;[346,347]
R^1 = Me: R^2 = CH_2CO_2Et: X = Br: R^3 = 2-$CHOC_6H_4$,[346] 2-$MeCOC_6H_4$;[346,347] X = I: R^3 = 4-$MeOC_6H_4$;[352] R^2 = CH_2CN, R^3 = 2-$MeOC_6H_4$;[347] R^2 = CH_2COMe, R^3 = 2-$MeCOC_6H_4$;[347]
$R^1 = R^2$ = Bu: X = Br: R^3 = CH_2CO_2Et,[99,150] 1-menthyl acetate;[99]
$R^1 = R^2$ = C_5H_{11}: X = Br: R^3 = CH_2CO_2Et;[100]
$R^1 = R^2 = R^3$ = Ph: X = NCO, NCS, NCSe, CN, N_3;[348] OMe, OEt, OPr-*i*;[349] SC(S)OMe, SC(S)OEt, SC(S)OPr-*i*;[349] SC(S)SEt, SC(S)SPr-*i*;[349] OCOMe, $OCOCHCl_2$, $OCOCCl_3$, OCOPh;[350] $SC(S)NMe_2$, $SC(S)NEt_2$, $SC(S)NPh_2$[351]

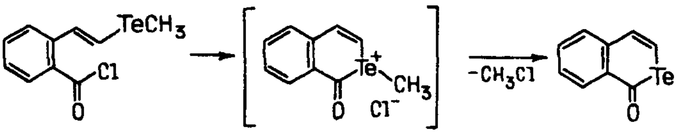
The elimination of RX is effected either merely thermally (sometimes in a solvent) or by heating of a salt with an appropriate acceptor of RX such as pyridine[216,217,255] or *N,N*-dimethylaniline[3] which are converted into *N*-alkylpyridinium and trimethylphenylammonium salts, respectively. Treatment of telluronium salts with triorganylphosphines R_3P (R = Bu, Ph)[204] leads to the same results. In these reactions neither the leaving ability of substituents nor the influence of the anion or the nature of the solvent were studied in detail, but it was noted that the most volatile alkyl halide is eliminated as a rule. Usually this method is used for the preparation of unsymmetric tellurides, especially those with alkoxycarbonyl groups[99,100,150,346,347,352] and for a long time it was the sole approach to this type of tellurides since interaction between α-tellurolate anions and α-halo carbonyl compounds at room temperature only leads to reduction (cf. 2.5.2.2.). It was reported later that low temperature (−78 °C) is required to obtain the desired products.[207]

Preparations of diorganyl tellurides by reaction of telluronium salts with magnesium-[3] or lithiumorganic reagents[85] as well as with Na_2S[353] are rather rare.

The synthesis of the tellurium-containing heterocyclic systems **60** is based on the ready elimination of alkyl halides from the cyclic telluronium salts **61**. The preparation of these heterocycles has been performed by intramolecular alkylation in *o*-substituted alkyl phenyl tellurides **62** where the halogen atom possesses enhanced electrophilicity due to the presence of electron acceptor groups in the A-B fragment of **62** followed by thermal (or even spontaneous) elimination of RX from **61**. In particular such reactions have been employed for the preparation of tellurocoumarine (A-B = CH=CHCO),[354] 2-aryl-benzotellurazoles (A-B = N=CAr),[234] benzo-1,4-tellurazin-3-one (A-B = $NHCOCH_2$)[355] and tellurisocoumarine.[356]



R = Me, Bu; X = Cl, Br



2.5.5. *From π-telluranes.* π-Telluranes, namely telluroxides and telluronium ylides, may also be useful as precursors of diorganyl tellurides. Diaryl telluroxides Ar_2TeO and alkyl aryl telluroxides ArTe(O)R (which actually exist as dihydroxides $ArTe(OH)_2R$)[3,4] have been reduced to the corresponding diorganyl tellurides **1**, **13**, **29**, **30**, and **53** in very high yields. Bis(trimethylsilyl) chalcogenides,[154] (phenylseleno)trimethylsilane,[357] formamide,[358] thiourea *S,S*-dioxide[359] and hydrazine hydrate[286,287,360–362] have been used as reducing agents.

Bis(4-methoxyphenyl) telluride **1** (Ar = 4-$MeOC_6H_4$) has also been prepared by electrochemical reduction of the corresponding diaryltelluroxide in alkaline ethanol solution.[363]

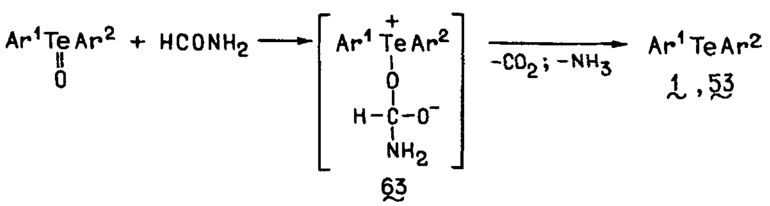
$$\mathrm{Ph_2TeO} + \mathrm{(Me_3Si)_2M} \xrightarrow[-\mathrm{(Me_3Si)_2O};\ -\mathrm{M}]{} \underset{\mathbf{1}}{\mathrm{Ph_2Te}}$$

M = S (95%), Se (89%), Te (85%)

$$\mathrm{R_2TeO} + \mathrm{PhSeSiMe_3} \xrightarrow[-\mathrm{(Me_3Si)_2O};\ -\mathrm{Ph_2Se_2}]{} \mathrm{R_2Te}$$

R = $PhCH_2CH_2$, $C_{16}H_{33}$, Ph

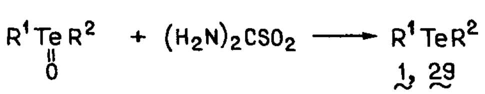
Other diorganyl chalcogenoxides, namely, sulfoxides and selenoxides, may also be reduced with bis(trimethylsilyl) chalcogenides and (phenylseleno)trimethylsilane. However, these two methods suffer from some preparative drawbacks; thus, they require advance preparation of the above-mentioned reducing agents; these preparations sometimes give modest yields and the reagents themselves possess unpleasant odors and are sensitive to moisture and air. In addition, use of these agents leads to the formation of by-products (a chalcogen and $(Me_3Si)_2O$ or Ph_2Se_2 and $(Me_3Si)_2O$, respectively) impeding the isolation of the diorganyl tellurides. Therefore, formamide is more valuable as reducing agent.[358] The reduction of diaryl telluroxides is performed by brief heating in excess formamide at 120–140 °C. The diaryl tellurides **1** and **53** form in practically quantitative yields and are usually collected at the bottom of the reaction vessel as readily crystallizing oils and may be separated from the formamide by decantation. The reaction probably proceeds via the intermediates **63** which decompose into diaryl telluride, carbon dioxide and ammonia.



$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{Ar^1TeAr^2}} + \mathrm{HCONH_2} \longrightarrow \underset{\mathbf{63}}{\left[\begin{array}{c} + \\ \mathrm{Ar^1TeAr^2} \\ | \\ \mathrm{O} \\ | \\ \mathrm{H{-}C{-}O^-} \\ | \\ \mathrm{NH_2} \end{array}\right]} \xrightarrow[-\mathrm{CO_2};\ -\mathrm{NH_3}]{} \underset{\mathbf{1},\ \mathbf{53}}{\mathrm{Ar^1TeAr^2}}$$

Ar^1 = Ar^2 = 4-$Me_2NC_6H_4$, 4-$MeOC_6H_4$, 4-MeC_6H_4, Ph;
Ar^1 = Ph: Ar^2 = 2,5-$(MeO)_2C_6H_3$, 3,4-$(MeO)_2C_6H_3$

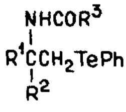
Thiourea *S,S*-dioxide in a two-phase system (aqueous alkali/petroleum ether) at room temperature has been also used for the reduction of diaryl telluroxides.[359]



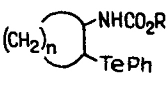
$$\underset{\substack{\| \\ \mathrm{O}}}{\mathrm{R^1TeR^2}} + \mathrm{(H_2N)_2CSO_2} \longrightarrow \underset{\mathbf{1},\ \mathbf{29}}{\mathrm{R^1TeR^2}}$$

R^1 = R^2 = 4-$MeOC_6H_4$;
R^1 = Ph, R^2 = Bu

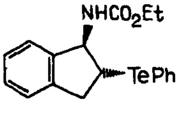
The synthesis of the alkyl phenyl tellurides **64–68** bearing an $NHCO_2R$ group in the α-position relative to PhTe has been achieved by reduction of the corresponding telluroxides with hydrazine hydrate.[286,287,360,361]



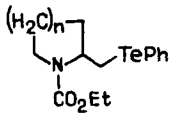
64



65



66



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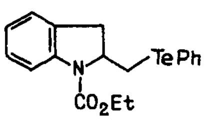


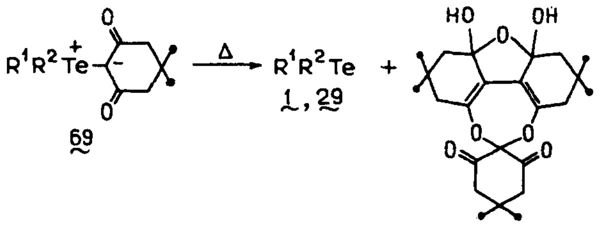
68

64, R^1 = H: R^2 = Bu: R^3 = Me,[286,361] Et;[287,360] R^2 = Ph: R^3 = Et,[360] CH_2Ph;[287] R^2 = $PhCH_2$: R^3 = Et;[287,360] R^2 = $PhOCH_2$: R^3 = Et;[287,360] R^2 = $C_{14}H_{29}$: R^3 = Et;[287,360] R^1 = Ph: R^2 = Me: R^3 = Et;[287,360]

65, n = 3: R = Me,[286,361] Et;[287,360] n = 4: R = Me,[286,361] Et;[287,360] n = 5: R = Me,[286,361] Et[287,360]

Until recently the synthesis of diorganyl tellurides starting from telluroxides was of no preparative interest since the latter compounds were prepared either by oxidation of diaryl tellurides with sodium periodate[69,317,364] or by alkaline hydrolysis of diorganyltellurium dihalides[3,4,364] which themselves may be easily reduced to the desired tellurides (cf. 2.5.6.). However, novel approaches to diaryl telluroxides (from aryltellurium oxochlorides ArTe(O)Cl and PhMgBr[365]) and to functionalized alkyl phenyl telluroxides related to **64–68** via aminotelluration of alkenes with arenetellurinyl acetates or trifluoroacetates in the presence of various nitrogen-containing substrates[286,287,360,361] (for a rewiev covering these reports and concerning other synthetic applications of this reaction see ref.[362]) have made this method important in preparative respect.

π-Telluranes of another type, namely the diorganyltelluronium ylides **69**, are able to undergo thermal decomposition giving rise to the tellurides **1** and **29**.[366]



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

However, taking into account that ylides **69** are available either from diaryl telluroxides[367] or from diorganyltellurium dihalides,[368,369] there is no point in discussing the preparative significance of this reaction.

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* The isomeric tellurides $R^1CH(TePh)CH_2NHCO_2R^3$ are formed together with the desired compounds **64**.

2.5.6. *From σ-telluranes.* One of the most general methods for the synthesis of symmetric and unsymmetric diorganyl tellurides is the reduction of the corresponding derivatives of tetracoordinated tellurium—the σ-telluranes R_2TeX_2 where X is an electronegative group (Hal, ONO_2, OCOR etc.). Since the preparation of diaryltellurium dihalides,[3,4,370,371] especially of the dichlorides, has been well elaborated, this reaction is of particular significance for the preparation of symmetric **1** and unsymmetric diaryl tellurides **53**. The following compounds have been used as reducing agents: Na_2S; $9H_2O$,[127,285,302,310,316,323,337,353,372–381] $K_2S_2O_5$ ($Na_2S_2O_5$),[65,113,125,132,382–388] Na_2SO_3,[43,52,389] $NaHSO_3$,[28–51,52,390] $Na_2S_2O_3$,[222,285,391] $Na_2S_2O_4$,[392] $LiAlH_4$,[393] $NaBH_4$,[394,395] $N_2H_4 \cdot H_2O$,[113,222,228,249,285,396–398] thiourea *S,S*-dioxide,[359,399] zinc dust in benzene[400] or in AcOH,[64,401] $SnCl_2$,[63] methyl(ethyl-) magnesium iodide,[53,55,56,58–62] lithium diethylamide,[402] and dithiols.[403] The reduction proceeds in high yields, in many cases close to quantitative. The nature of the electronegative groups at the tellurium atom has practically no influence on the reduction and not only tellurium dihalides R_2TeX_2, but also tellurium dicarboxylates $R_2Te(OCOR')_2$,[323,397,398,404] tellurium dinitrates $R_2Te(ONO_2)_2$, and other tetracoordinated tellurium derivatives[3,4,405] are readily reduced to tellurides. Depending on the nature of the reducing agent the reactions are carried out in organic solvents: C_6H_6 (or AcOH)(Zn), EtOH (N_2H_4, $NaBH_4$), dioxan ($LiAlH_4$), diethyl ether (RMgX) as well as in aqueous media ($K_2S_2O_5$, Na_2SO_3, $NaHSO_3$, $Na_2S_2O_3$, $Na_2S_2O_4$, thiourea *S,S*-dioxide) or by heating of solid tellurium dihalides in excess molten $Na_2S{\cdot}9H_2O$ at 90–100 °C. Taking into consideration that diorganyltellurium dihalides are quite easily hydrolyzed upon treatment with base[3,4,364] it is obvious that not the tellurium dihalides themselves, but the corresponding telluroxides or mixtures of these compounds undergo reduction in aqueous solutions or in molten sodium sulfide.

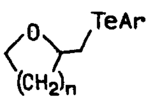
$$R^1R^2TeX_2 \xrightarrow[-2X^-]{2e^-} R^1R^2Te$$

1, **13**, **29**, **30**, **53**

$R^1 = R^2 = CH_2I$,[132] Me,[43,389] CH_2CO_2H,[382] 2-C_4H_3S,[63,391] Bu,[359] 4-BrC_6H_4,[374,388,396]
4-FC_6H_4,[377] 3-FC_6H_4,[388] 4-$O_2NC_6H_4$,[388] 2-$C_4H_3SCOCH_2$,[125,392]
Ph,[28,51,316,353,388,393,396,402,404,405] *t*-$BuCOCH_2$,[392] 4-Me-C_6H_4,[52,316,319,323,353,388,396]
3-MeC_6H_4,[55] 2-MeC_6H_4,[52] $PhCH_2$,[380] 4-$MeOC_6H_4$,[56,65,316,359,374,396,400–402]
3-$MeOC_6H_4$,[61] 2-$MeOC_6H_4$,[62] 2-Me-4-OHC_6H_3,[385] $C_5H_4Mn(CO)_3$,[381]
$C_5H_4Re(CO)$,[381] 4-$BrC_6H_4COCH_2$,[125] 4-$ClC_6H_4COCH_2$,[125] $PhCOCH_2$,[125,127,392]
2,4-$(Me)_2C_6H_3$,[53] 4-$EtOC_6H_4$,[60–64,383,396] 2-$EtOC_6H_4$,[58] 4-$Me_2NC_6H_4$,[384]
4-$MeC_6H_4COCH_2$,[125,392] 4-$MeOC_6H_4COCH_2$,[125] 1-$C_{10}H_7$,[59]
1-$C_{10}H_7COCH_2$,[125] 2-$C_{10}H_7COCH_2$,[125] 2-benzo[*b*]furanyl-$COCH_2$,[125] $C_{12}H_{25}$,[359]
9-anthryl-$COCH_2$,[125] $C_{16}H_{33}$;[379]
R^1 = 4-BrC_6H_4: R^2 = 4-$Me_2NC_6H_4$;[316]
R^1 = 4-FC_6H_4: R^2 = 4-ClC_6H_4, 4-BrC_6H_4, 4-$Me_2NC_6H_4$;[377]
R^1 = Ph: R^2 = MeCHCH(OMe)Me,[222,285] $Me_2C(OMe)CH_2$,[285] 4-BrC_6H_4,[316] 4-FC_6H_4,[377]
2-$MeOC_5H_8$-*c*,[285] 2-HOC_6H_{10}-*c*,[228,285] C_6H_{11}-*c*,[310] 4-MeC_6H_4,[310]
4-$MeOC_6H_4$,[316,372] 2-$MeOC_6H_{10}$-*c*-[222,228,285] PrC(Me)(OMe)CH_2,[285] 4-$EtOC_6H_4$,[310]
4-$Me_2NC_6H_4$,[316,376] 2-$MeOC_7H_{12}$-*c*,[228,285] 2-$EtOC_6H_{10}$-*c*[222,285] 2-Me_2N-5-MeC_6H_3,[387]
2-$MeOC_8H_{14}$-*c*,[285] 2-*i*-$PrOC_6H_{10}$-*c*,[222,285] PhCH(OMe)CH_2,[222,228,285]
PrCH(OMe)CHPr,[285] C_6H_{13}CH(OMe)CH_2,[285] 1-$C_{10}H_7$,[372] 2-$C_{10}H_7$,[302,372]

2-MeO-1,2,3,4-tetrahydronaphthyl-3,[228] PhC(OMe)(Me)CH$_2$,[228,285]
C$_8$H$_{17}$CH(OMe)CH$_2$,[222,285] 4-PhOC$_6$H$_4$,[337,372] MeCHC(Ar′)OCH$_2$CH$_2$O [Ar′ = 4-BrC$_6$H$_4$, Ph, 4-MeC$_6$H$_4$, 4-*i*-BuC$_6$H$_4$, 4-PhC$_6$H$_4$, 2-(5-Br-MeOC$_{10}$H$_4$)],[249]
CH=CHOC(O)CPh$_2$CH$_2$,[390]
R^1 = 4-MeC$_6$H$_4$: R^2 = 4-FC$_6$H$_4$,[377] C$_6$H$_{11}$-*c*,[310] 2-MeOC$_6$H$_{10}$-*c*;[285]
R^1 = 4-MeOC$_6$H$_4$: R^2 = Me,[386] Et,[373] 4-FC$_6$H$_4$,[377] PhCH$_2$,[373] 2-MeOC$_6$H$_{10}$-*c*,[385] 4-Me$_2$NC$_6$H$_4$,[316] 4-EtOC$_6$H$_4$,[64] 2-Me$_2$N-5-MeC$_6$H$_3$,[387] 1-C$_{10}$H$_7$,[372] CH$_2$CHOC(O)CPh$_2$CH$_2$;[390]
R^1 = 4-EtOC$_6$H$_4$: R^2 = C$_6$H$_{11}$-*c*,[310] 2-Me$_2$N-5-MeC$_6$H$_3$,[387] 1-C$_{10}$H$_7$,[337] CH$_2$CHOC(O)CPh$_2$CH$_2$;[390]
R^1 = 4-Me$_2$NC$_6$H$_4$: R^2 = 4-MeC$_6$H$_4$,[376] 4-MeOC$_6$H$_4$,[375,376] 4-EtOC$_6$H$_4$,[375,376] 4-PhOC$_6$H$_4$;[375,376]
R^1 = 1-C$_{10}$H$_7$: R^2 = 2-C$_{10}$H$_7$,[372] 4-PhOC$_6$H$_4$,[372] CH$_2$CHOC(O)CPh$_2$CH$_2$;[390]
R^1 = 2-C$_{10}$H$_7$: R^2 = C$_6$H$_{11}$-*c*,[373] PhCH$_2$,[373] 4-PhOC$_6$H$_4$;[372]
R^1 = 4-PhOC$_6$H$_4$: R^2 = CH$_2$CHOC(O)CPh$_2$CH$_2$[390]

The diorganyl tellurides **70** and **71** containing tetrahydrofuran (n = 2) and tetrahydropyran (n = 3) rings as well as lactone rings have been synthesized in high yields by reduction of the appropriate cyclic σ-telluranes obtained in turn by cyclofunctionalization of hydroxyalkenes[113,395,397–399] and unsaturated carboxylic acids,[390,394,395] by treatment with arenetellurenyl acetates,[397,399] aryltellurium trichlorides,[390,394,395,399] or with the TeO$_2$/LiCl system in AcOH.[113]



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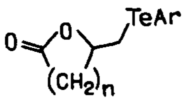
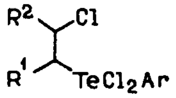


71

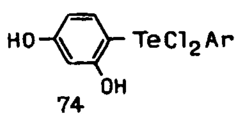
At the same time reduction of the tellurium dihalides **72**,[378,390,406] **73**,[375] and **74**[375] results in decomposition with formation of either tellurium metal[390] or diaryl ditellurides.[375,378,406]



72

RCOCH$_2$TeX$_2$Ar

73

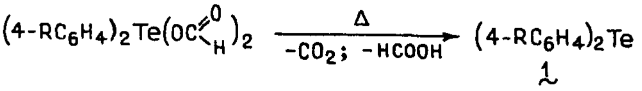


74

72 R^1 = H, R^2 = Me: Ar = 2-C$_{10}$H$_7$;[378] R^1 = R^2 = Me: Ar = 2-C$_{10}$H$_7$;[378,406] R^1 + R^2 = (CH$_2$)$_4$: Ar = Ph, 4-EtOC$_6$H$_4$, 1-C$_{10}$H$_7$, 2-C$_{10}$H$_7$, 4-PhOC$_6$H$_4$;[390] R^1 = H, D: R^2 = C$_8$H$_{17}$, Ar = 2-C$_{10}$H$_7$;[406]
73 R = Me, Ph: Ar = 4-MeOC$_6$H$_4$, 4-EtOC$_6$H$_4$, 4-PhOC$_6$H$_4$;[375]
74 R = 4-MeOC$_6$H$_4$, 4-EtOC$_6$H$_4$, 4-PhOC$_6$H$_4$[375]

Nevertheless, by proper choice of the reducing agent and the reaction conditions it should be possible to transform the above mentioned dihalides to the corresponding tellurides. This statement is based on the fact that though early attempts to reduce acetonyl- and phenacyltellurium dihalides **73**[375] and their analogs[407] with Na$_2$S or Na$_2$S$_2$O$_5$ were unsuccessful, the reduction of diphenacyltellurium dichlorides succeeded upon treatment with $Na_2S_2O_5$[125] or $Na_2S_2O_4$[392] in a two-phase system.

Thermal decomposition of diaryltellurium diformates is a specific way to diaryl tellurides **1** in 95–100% yield.[408,409]



$$(4\text{-}RC_6H_4)_2Te(OC(=O)H)_2 \xrightarrow[-CO_2;\ -HCOOH]{\Delta} \underset{\mathbf{1}}{(4\text{-}RC_6H_4)_2Te}$$

R = H, Me, OMe, NMe_2

Exchange reactions of diaryl tellurides with diaryltellurium dihalides lead to novel diaryl tellurides and tellurium dihalides.[410–412]

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

The rate of this process depends on the solvent as well as on the substituents in the aryl groups and at the tellurium atom; it decreases in the order PhCN > $PhNO_2$ > $o\text{-}Cl_2C_6H_4$ > PhMe[412], Br ≫ Cl > F.[411–412] The exchange reaction is also very sensitive to catalytic agents and to the method of purification of the solvent. Since this reaction results in an equilibrium it is of limited preparative significance.

2.5.7. *From tetraorganyl telluranes.* Another possible approach to the preparation of diorganyl tellurides is thermal decomposition of tetraorganyl telluranes R_4Te **75**. However, like other reactions described above such as the thermolysis of telluronium ylides, diaryltellurium diformates, etc. this is only of little preparative use because the tellurium-containing substrates employed in the synthesis of **75** (interaction between lithiumorganic reagents RLi and $TeCl_4$,[29,31,32,34,90,413–416] R_2TeCl_2,[31–33,90,413] R_3TeCl,[413] or between $(CF_3)_2TeCl_2$ and $(CF_3)_2Cd$[417]) can be directly converted to diorganyl tellurides (cf. 2.2., 2.5.6., 2.5.4.). However, **75** are of interest as examples of the increased stability of tetracoordinated tellurium derivatives in comparison with their sulfur and selenium analogs. Indeed, whereas Ar_4S and Ar_4Se exist in solution only at very low temperature (−78 °C and below) and decompose upon heating,[413] tetraaryltelluranes Ar_4Te are stable crystalline compounds at room temperature.[413–415] Interestingly tetraalkyltelluranes R_4Te (R = Me,[84,416] CF_3,[417] Bu,[84] Me_3SiCH_2[84]), postulated earlier only as intermediates in some reactions,[85] have been isolated recently as individual compounds.

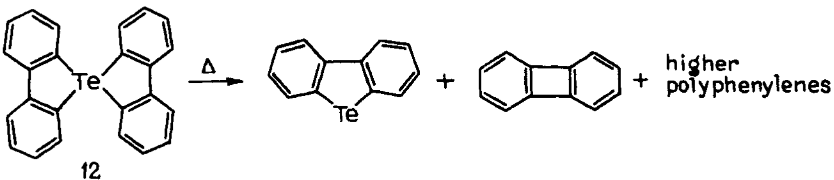
Tetraaryltelluranes **75** smoothly decompose upon heating to diaryl tellurides and biaryls together with small amounts of the corresponding hydrocarbons.

$$Ar_4Te \xrightarrow{\Delta} \underset{\mathbf{1}}{Ar_2Te} + Ar\text{-}Ar$$

Ar = C_6F_5,[29] Ph,[413–415] $4\text{-}MeC_6H_4$,[414,415] C_6D_5[414,415]

The formation of diaryl tellurides and diaryls upon the preparation of the former compounds starting from tellurium tetrahalides and Grignard reagents as well as the necessity of employing a 5–6 fold excess of the latter may be convincingly explained by the above reaction (cf. 2.2).

The tellurospirane **12** upon heating gives rise to dibenzotellurophene and diphenylene.[31–33,90]



12

The decomposition of tetraalkyltelluranes, especially of $(CF_3)_4Te$,[417] proceeds in a more complicated manner and leads to a mixture of side reaction products besides the expected dialkyl tellurides and the corresponding hydrocarbons.

Thermolysis of a mixture of two different tetraaryltelluranes gives besides symmetric biaryls and diaryl tellurides, rise to substantial amounts of their unsymmetric analogs.[414,415]

$$\underset{\mathbf{75}}{Ar^1_4Te} + \underset{\mathbf{75}}{Ar^2_4Te} \xrightarrow{\Delta} \underset{\mathbf{1}}{Ar^1_2Te} + \underset{\mathbf{1}}{Ar^2_2Te} + \underset{\mathbf{53}}{Ar^1TeAr^2} + Ar^1\text{-}Ar^1 + Ar^2\text{-}Ar^2 + Ar^1\text{-}Ar^2$$

$Ar^1 = Ph$, $Ar^2 = 4\text{-}MeC_6H_4$;
$Ar^1 = Ph$, $Ar^2 = C_6D_5$

This reaction causes the formation of unsymmetric diaryl tellurides upon interaction between phenyl- and 2-methyl-phenylmagnesium bromide and di(2-methylphenyl)-, diphenyl-[418] and di(4-methylphenyl)tellurium dibromide,[419] respectively.

2.6. *Other Methods of Synthesis*

In this section reactions leading to diorganyl tellurides not covered in the preceding sections and only represented by isolated examples will be reviewed.

Bis(pentafluoroethyl) telluride, together with the corresponding ditelluride, has been obtained by interaction between tetrafluoroethene and the cation **76**.[420,421]

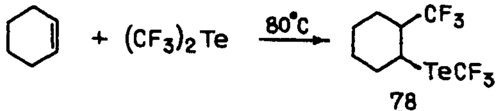
$$\underset{\mathbf{76}}{Te_4(AsF_6)_2} + CF_2{=}CF_2 \longrightarrow (C_2F_5)_2Te + (C_2F_5)_2Te_2$$

Besides these products, $(C_4F_9)_2Te$, $C_2F_5TeC_4F_9$, and $C_2F_5TeTeC_4F_9$ were formed in small amounts. The existence of the latter compound has been proven only by means of mass spectroscopy and this compound remained for a long time the sole representative of unsymmetric diorganyl ditellurides.

Alkyl **77**[422] and fluoroalkyl tellurides **78**[423] have been obtained by either light irradiation (λ = 310 nm) of mixtures of dimethyl telluride and perfluoroalkyl iodides or thermally promoted addition of bis(trifluoromethyl) telluride to the double bond of cyclohexene.

$$Me_2Te + R_FI \longrightarrow \underset{77}{MeTeR_F} + \underset{79}{(R_F)_2Te}$$

$R_F = CF_3, C_2F_5$



78

However, this mixture of **77** and **79** was not separated. It must be noted that the trifluoromethylating ability of bis(trifluoromethyl) telluride exceeds those of $(CF_3)_2Hg$ and CF_3I in thermal as well as in photochemical reactions.[423]

It has been shown recently[424] that unsymmetric dialkyl tellurides containing a trifluoromethyl group can be prepared by ligand exchange reactions of symmetric dialkyl tellurides. Thus, prolonged stirring of a mixture of $(CF_3)_2$ Te and R_2Te (molar ratio 1:1.1-1.5) at ambient temperature leads to **77** in 72–82% yield.

$$R_2Te + (CF_3)_2Te \longrightarrow \underset{77}{RTeCF_3}$$

R = *t*-Bu, $PhCH_2$

Alkyl and allyl ligand exchange was observed in solutions of two symmetrical tellurides, but the relatively small equilibrium constants impact these reactions no preparative importance.[425]

A novel method for the synthesis of unsymmetric tellurides **30** based on bis(*N,N*-dimethylcarbamoyl) ditelluride $(Me_2NCO)_2Te_2$ as a synthon should be mentioned.[426] This synthon can be prepared in high yield by interaction of DMF with Na and Te under an argon atmosphere. The reaction sequence and the yields of each reaction step are presented below.

$$(Me_2NCO)_2Te_2 \xrightarrow[2.\,RX]{1.\,NaBH_4} RTeCONMe_2 \xrightarrow[2.\,R^1X]{1.\,LiAlH_4} \underset{30}{RTeR^1}$$

R = C_8H_{17}, 63%	R^1 = Me, 97%
R = *c*-C_6H_{11}, 28%	R^1 = Me, 84%
R = C_6H_{13}, 92%	R^1 = $PhCH_2$, 93%

3. REACTIONS OF DIORGANYL TELLURIDES

Diorganyl tellurides enter into various chemical transformations which fall into the following three main types.

1) Reactions which increase the coordination number of the tellurium atom and retain the Te-C bonds already present in the molecule. 2) Reactions accompanied by rupture of

one or both Te-C bonds. Accordingly the number of Te-C bonds decreases or the tellurium atom is extruded. Some of these reactions are of preparative interest. 3) Reactions leading only to chemical transformations of functional groups present in the diorganyl telluride and not affecting Te-C bonds nor the Te atom.

Some reactions of diorganyl tellurides are combinations of the main types mentioned above.

3.1. *Reactions Accompanied by an Increase of the Coordination Number of Tellurium*

3.1.1. *Oxidative addition of halogens.* One of the characteristic features of diorganyl tellurides is their capacity for oxidative addition of halogens with formation of tetracoordinated tellurium derivatives (σ-telluranes R_2TeX_2). Diorganyl tellurides under mild conditions (ambient or low temperature) immediately add chlorine,[25–28,53–56,58,60–64,67,68,78,81,113,216,217,219,231,235,255,279,295,306,315,330,398,418,419,427–429] bromine,[22,23,25,51–65,68,69,80,82,91,189,214–217,219,228,231,247,249,251,270,272,273,276,279,297,302,306,310,317,330,366,372–374,398,413,418,419,427,429–436] iodine,[53–56,58–65,80,82,99,100,114,219,247,273,276,306,330,372–374,390,419,432,433] and fluorine, diluted with an inert gas.[94,437,438]

$$R^1R^2Te + X_2 \longrightarrow R^1R^2TeX_2$$

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

Bis(trifluoromethyl) telluride $(CF_3)_2Te$ represents an exceptional case where a telluride does not enter any of the above addition reactions.[427] Contrary to the corresponding dichloride and dibromide, bis(trifluoromethyl)tellurium diiodide cannot be obtained by oxidation of the telluride with iodine. This fact confirms to a certain degree our earlier assumption (cf. 2.1.) about the reason for the formation of bis(perfluoroaryl) tellurides instead of the corresponding diiodides (expected by analogy with the well known reaction of tellurium with alkyl iodides) in the interaction between monoiodoperfluoroarenes and tellurium metal.

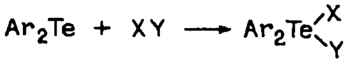
Sulfuryl chloride[26,65,76,79,80,82,167,195,219,225,234,271,276,302,310,337,372,373,432,433,439–441] or thionyl chloride[234,331,372,373,379,429] are good substitutes for gaseous chlorine in the preparation of diorganyltellurium dichlorides. Metal salts such as $FeCl_3$,[323] $HgCl_2$,[323] and $CuCl_2$[321–323] are also convenient oxidants for tellurides which avoid the handling of the above-mentioned toxic reagents and give access to diorganyltellurium dichlorides under quite mild conditions and in high yields. In a fashion similar to copper(II) chloride, $CuBr_2$ has been employed in the synthesis of tellurium dibromides.[322] However, whereas diaryl tellurides when treated with $CuCl_2$ gave diaryltellurium dichlorides only, the reaction of diethyl telluride with the same reagent proceeds in a more complicated manner.[442]

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

In addition, diorganyltellurium difluorides have been prepared by treatment of tellurides with SF_4,[443] XeF_2,[428,438,444] ClF,[428] and Ph_2SF_2[437] (in conformity with the purpose of this review we do not consider the preparation of difluorides and other dihalides by exchange reactions of σ-telluranes). The oxidation of diaryl tellurides with tris(*p*-tolyl)bismuth difluoride also leads to diaryltellurium difluorides.[80–82]

The structure of the products obtained by oxidation of tellurides is mainly determined by the nature of the fluorinating agent and the reaction conditions. Thus, treatment of $(C_2F_5)_2Te$ with xenon difluoride gave $(C_2F_5)_2TeF_2$,[428] whereas a mixture of *trans*-$C_2F_5TeClF_4$ and *trans*-$(C_2F_5)_2TeF_4$ was obtained by reaction of the same telluride with ClF at low temperature.[428] Interaction between Ph_2Te and XeF_2 gives rises to Ph_2TeF_2 and Ph_2TeF_4, (with XeF_2 in excess).[444]

Diorganyl tellurides are also capable of oxidative addition reactions with pseudohalides such as thiocyanogen $(SCN)_2$,[68,445–449] interhalides (ICl, IBr),[449] or cyanogen halides (BrCN, ICN)[449] leading to the corresponding σ-telluranes in good yields.



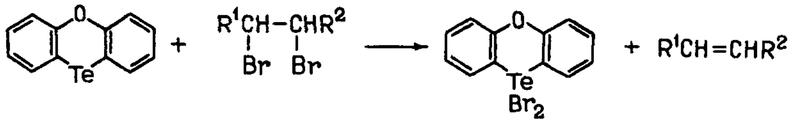
$$Ar_2Te + XY \longrightarrow Ar_2Te\begin{smallmatrix}X\\Y\end{smallmatrix}$$

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

The considerable ability of tellurides to add halogens allows their use as dehalogenating agents in the synthesis of alkenes from the appropriate organic dihalides. Vicinal[450–452] and geminal[453] dibromides have been converted to the corresponding alkenes in quite high yields by treatment with diaryl tellurides[450,452] or with their cyclic analog phenoxatellurine.[451,453]

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

$R^1 = R^2$ = Ph (94%,[450] 100%[452]);*
$R^1 + R^2$ = cholesterol (93%[450]);
R^1 = Ph: R^2 = CO_2H (100%[450]), CO_2Et (57%[452]), COPh(61%[452]), 2-pyridyl (100%[452]);
$Ar^1 = Ar^2$ = Ph,[450] 4-$MeOC_6H_4$;[452]
Ar^1 = 4-$MeOC_6H_4$, Ar^2 = 1-$C_{10}H_7$, 2-$C_{10}H_7$[452]



$R^1 + R^2$ = $(CH_2)_3$ (83%), $(CH_2)_4$ (62%), 1,8-naphthylidene (23%),
R^1 = Ph: R^2 = H (77%), CO_2H (93%), CO_2Et (89%);
R^1 = Me, R^2 = CO_2H (75%)[451]

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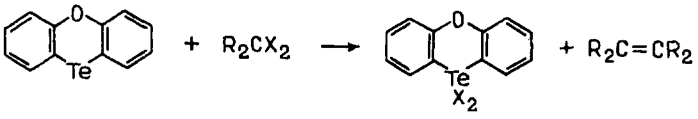
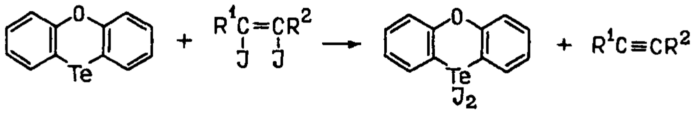
* The yield of alkene is shown in parentheses.



R = Ph (73%), CO_2Et (52%);
R + R = $C_{12}H_8$ (97%), X = Cl, Br[453]

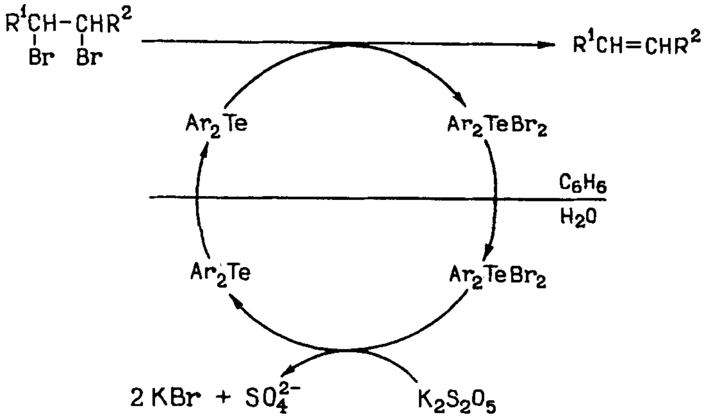
The dehalogenating ability of phenoxatellurine obviously exceeds that of diaryl tellurides since not only 1,2-dibromoalkanes, but also 1,2-diiodoalkenes can be dehalogenated with the former reagent to yield acetylenes in more than 80% yield.[451]



R^1 = Ph: R^2 = H (80%), CO_2H (87%)

However, dehalogenation reactions with phenoxatellurine are not of sufficiently general applicability. Thus, 1,2-dichlorocyclohexane,[451] benzylidene dichloride and dibromide[453] as well as 1,2-dibromo-1,2-diphenylethane[451] were unaffected by this reagent although in the latter case the use of diaryl tellurides led to almost quantitative transformation into stilbene.

The possibility to use catalytic amounts of diaryl tellurides[452] (5 mol % of the quantity of halogenated substrate in the case of bis(4-methoxyphenyl) telluride) is of special interest in preparative respect. Such processes have been carried out in two-phase systems (benzene-water) and the tellurium dibromide formed was regenerated to telluride with potassium metabisulfite which itself was unable to reduce vicinal dibromides. The following scheme illustrates this procedure.



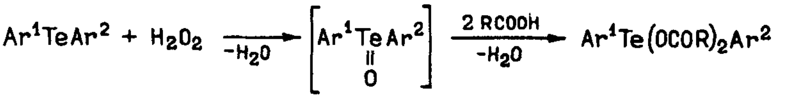
3.1.2. *Reactions of tellurides with other oxidizing agents.* Whereas the reactions of diorganyl tellurides discussed in Section 3.1.1. as a rule lead to σ-telluranes R_2TeX_2, interaction between tellurides and other oxidizing agents give rises to σ-telluranes, telluronium salts, telluroxides or to products of a more complex structure.

The oxidation of diorganyl tellurides with lead tetraacetate at room temperature leads to diorganyl tellurium diacetates in excellent yields.[379,404,454]

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

R = Alk, Ar

Interaction between diaryl tellurides, carboxylic acids and hydrogen peroxide in $CHCl_3$ provides a convenient synthetic route to diaryltellurium dicarboxylates containing various acyloxy groups.[455] Probably the reaction proceeds via intermediate formation of diaryl telluroxides. It is known[456,457] that interaction between telluroxides and carboxylic acids gives rise to σ-telluranes $Ar_2Te(OCOR)_2$

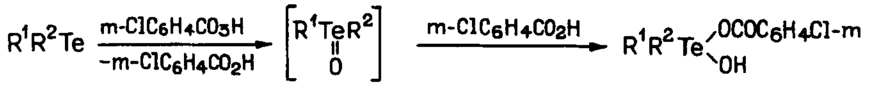


$$Ar^1TeAr^2 + H_2O_2 \xrightarrow[-H_2O]{} \left[Ar^1\overset{}{\underset{\underset{O}{\|}}{Te}}Ar^2 \right] \xrightarrow[-H_2O]{2\,RCOOH} Ar^1Te(OCOR)_2Ar^2$$

Undoubtedly telluroxides are also intermediates in the reaction of tellurides with benzoyl peroxide leading to diorganyltellurium dibenzoates.[99,100] The preparation of diaryltellurium dicarboxylates starting from diaryl telluroxides and carboxylic acid anhydrides[456–458] confirms this assumption.

$$R_2Te + (PhCOO)_2 \xrightarrow[-(PhCO)_2O]{} \left[R_2Te{=}O\right] \xrightarrow{(PhCO)_2O} R_2Te(OCOPh)_2$$

However, the reaction of tellurides with an equivalent amount of *m*-chloroperbenzoic acid gave the σ-telluranes **80**.[459] In this case the initially formed telluroxide reacts with one equivalent of carboxylic acid, formed in the oxidation of the telluride, to the σ-telluranes **80**.

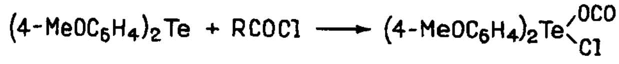


$$R^1R^2Te \xrightarrow[-m\text{-}ClC_6H_4CO_2H]{m\text{-}ClC_6H_4CO_3H} \left[R^1\underset{\underset{O}{\|}}{Te}R^2 \right] \xrightarrow{m\text{-}ClC_6H_4CO_2H} R^1R^2Te\begin{matrix} OCOC_6H_4Cl\text{-}m \\ OH \end{matrix}$$

80

Thus, the last three reactions proceed via intermediate formation of telluroxides, which then react with added (or reaction generated) carboxylic acids or their anhydrides. The formation of bis(4-methylphenyl)tellurium dibenzoate or a mixture of this benzoate with the corresponding dichloride upon prolonged boiling of bis(4-methylphenyl) telluride with benzoic acid or benzoyl chloride, respectively,[323] may be explained by this mechanism. The latter result is obviously caused by the hydrolysis of benzoyl chloride and the following reactions of both liberated acids with the diaryl telluroxide formed by the action of atmospheric oxygen. At the same time, 5 h boiling of bis(4-methoxyphenyl) telluride with

3,5-dinitrobenzoyl chloride (but not with benzoyl or acetyl chloride) in CH_2Cl_2 or C_6H_6 results in an oxidative addition reaction with formation of the σ-tellurane **81**.[460]



$$(4\text{-}MeOC_6H_4)_2Te + RCOCl \longrightarrow (4\text{-}MeOC_6H_4)_2Te\begin{smallmatrix}OCOR\\ Cl\end{smallmatrix}$$

81

R = $3,5\text{-}(NO_2)_2C_6H_3$

This "telluroxide" mechanism also explains the result of the interaction between tellurides and dilute nitric acid leading to diorganyltellurium dinitrates[3] (or, according to ref.,[99] to diorganyltellurium hydroxynitrates $R_2Te(OH)(ONO_2)$).

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

Dinitrates are also obtainable by oxidation of tellurides with $ClONO_2$ as has been demonstrated in the case of bis(trifluoromethyl) telluride.[427]

In contrast to the reaction presented above where telluroxides are intermediates, the oxidation of diaryl tellurides with sodium periodate leads to telluroxides as final products in good yields.[69,317]

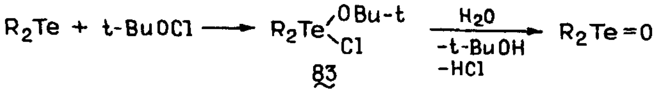
$$Ar_2Te + NaIO_4 \xrightarrow[-NaIO_3]{} Ar_2Te{=}O$$

Another type of three-coordinated tellurium derivatives, telluronium salts **82** containing Te-N bonds, is obtainable by oxidation of diorganyl tellurides with *N*-halosuccinimides,[112,461] their benzo analogs,[461] *N*-bromoamides, and *N*-chlorobenzotriazole.[461] Subsequent treatment of the salts **82** with aqueous solutions of NaOH, Na_2CO_3, or $NaHCO_3$ is a convenient route to telluroxides Ar_2TeO (or to dihydroxytelluranes $R_2Te(OH)_2$ where R is alkyl) in high yields.[112]

$$R_2Te + R^1\text{-}NX \longrightarrow \underset{\mathbf{82}}{[R_2\overset{+}{T}e\text{-}NR^1]X^-} \xrightarrow[-R^1NH,\ -X^-]{H_2O} R_2Te{=}O$$

X = Cl, Br; R^1 = $COCH_2CH_2CO$, NCOPh, *o*-COC_6H_4CO, *o*-NC_6H_4H-*o*

When *t*-butyl hypochlorite is used as oxidant, the intermediates, the diorganyl(*t*-butoxychloro)telluranes **83** possess most likely a σ-tellurane structure.[112] Hydrolysis of these compounds under basic conditions also leads to diorganyl telluroxides.



$$R_2Te + t\text{-}BuOCl \longrightarrow \underset{\mathbf{83}}{R_2Te\begin{smallmatrix}OBu\text{-}t\\ Cl\end{smallmatrix}} \xrightarrow[-t\text{-}BuOH,\ -HCl]{H_2O} R_2Te{=}O$$

Diorganyl tellurides, especially dialkyl derivatives, are oxidized by oxygen either neat or in solution with the formation of products which are as a rule of a complicated composition. Thus, it follows from refs.[99,100] that the initially formed dialkyl telluroxides existing in the σ-tellurane form $R_2Te(OH)_2$ are subject further oxidation accompanied by Te-C bond rupture and formation of the tellurinic acid RTe(O)OH (R = Bu[99]). Depending of the nature of the dialkyl telluride and of the oxidant (oxygen, neutral or alkaline solutions of H_2O_2) the final products are complexes with compositions such as $(R_2TeO)_n\cdot(RTe(O)OH)_m$.[99,100] However, the suggested structures and compositions of these compounds have only been on based on elemental analyses and thus require additional confirmation. Bis(trifluoromethyl) telluride upon oxidation with oxygen gives the oxide $(CF_3)_2TeO$[427] contrary to dialkyl[3,4,112] and aryl alkyl[317] analogs which give rise to dihydroxides $R_2Te(OH)_2$.

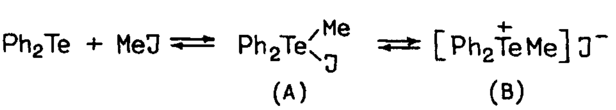
3.1.3. *Formation of telluronium salts.* Reactions accompanied by an increase of the coordination number of tellurium to 3, some of which (the formation of telluroxides) have already been considered in Section 3.1.2., are also typical of diorganyl tellurides. The latter compounds readily form telluronium salts when treated with alkyl halides with or without activation by neighboring electronegative groups.[3,4]

$$R^1R^2Te + R^3X \longrightarrow R^1R^2R^3Te^+X^-$$

Alkyl halides (bromides and iodides) RX where R = methyl,[43,52–56,58–62,85,99,100,107,204,217,255,263,386,387,391,418,419,462–466] ethyl,[43,189,467,468] propyl,[43] butyl,[216] benzyl,[51,101,469] or allyl[470–472] have been used as alkylating agents. Further, bromoacetic acid[99,345–347,355,473,474] and esters of bromoacetic,[99–101,150,273,346,347,352,473–478] α-bromopropionic,[479] and α-bromoisobutyric acid,[479] *N*-substituted amides of bromoacetic acid,[480] bromo-[3,4] and dibromomalonic esters,[481] α-bromoacetophenones,[99–101,466,476–478] bromoacetone,[347] and chloro(bromo)acetonitriles[347,476,477] have also been employed as activated halogen-containing substrates. The nucleophilicity of the tellurium atom of diorganyl tellurides being higher than that of the chalcogen center of other chalcogenides[482] makes it possible that not only dialkyl[43,85,99–101,107,150,189,204,464,465,467–472,475–478,480,481] and aryl alkyl,[216,217,255,263,273,345–347,352,355,386], but also diaryl tellurides[51–56,58–62,387,391,418,419,462,463,466,473,474,479] form telluronium salts on treatment with activated or nonactivated alkyl halides. Moreover, also iodobenzene can act as halogen-containing substrate towards dialkyl tellurides. Thus, dimethylphenyltelluronium iodide has been obtained in 50% yield by treatment of iodobenzene with Me_2Te.[43]

In contrast to diaryl tellurides, diphenyl sulfide[483] or selenide[484] can be transformed to onium salts by treatment with alkyl halides only in the presence of silver(I) cations. Such a difference in reactivity is also observed in the case of chalcogen-containing heterocycles. Thus, although benzo[*b*]tellurophene has been readily alkylated with methyl bromide,[345] the related sulfur and selenium salts could only be obtained in the presence of $AgBF_4$ or $AgClO_4$.[485]

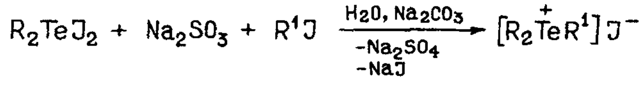
According to McWhinnie's data[466] interaction between methyl iodide and Ph_2Te leads to an equilibrium mixture of covalent (**A**) and ionic (**B**) forms of telluronium salts, the latter being formed from the former.



$$Ph_2Te + MeJ \rightleftharpoons \underset{(A)}{Ph_2Te\genfrac{}{}{0pt}{}{Me}{J}} \rightleftharpoons \underset{(B)}{[Ph_2\overset{+}{Te}Me]J^-}$$

This equilibrium is determined by the solvating ability of the solvent and can be shifted in either direction. The addition of CH_3I proceeds in accordance with a radical mechanism as has been shown in experiments in the presence of phenyl *t*-butyl nitrone.[466]

Since handling of lower dialkyl tellurides owing to their extremely unpleasant odor and their sensitivity towards air presents certain difficulties in the preparation of telluronium salts, use of the former reagents *in situ* provides a more convenient preparative way to the latter compounds. This can be achieved by reduction of the corresponding tellurium diiodides with an aqueous solution of Na_2SO_3 in the presence of alkyl halides.[43]

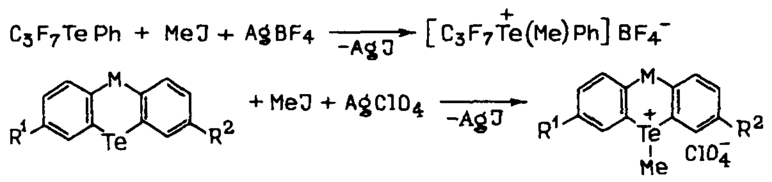


$$R_2TeI_2 + Na_2SO_3 + R^1I \xrightarrow[-Na_2SO_4 \atop -NaI]{H_2O,\ Na_2CO_3} [R_2\overset{+}{Te}R^1]I^-$$

Treatment of an ethereal solution of an lithium arenetellurolate with excess alkyl halide is an alternative to the above-mentioned method.[216,217,255]

$$ArTeLi \xrightarrow[-LiX]{RX} ArTeR \xrightarrow{RX} [Ar\overset{+}{Te}R_2]X^-$$

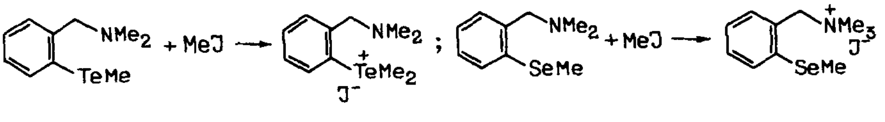
Tellurides containing strong electron acceptor groups[486] as well as some tellurium-containing heterocycles (telluroxanthene,[487] phenotellurazines[72]) can be forced to react with alkyl halides by addition of equimolar amounts of silver perchlorate[72,487] or tetrafluoroborate.[486]



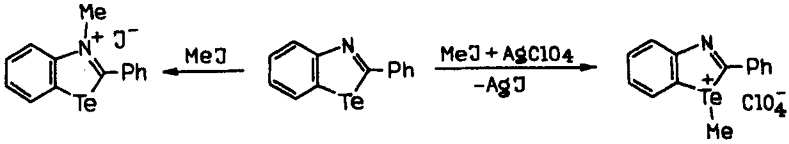
$$C_3F_7TePh + MeI + AgBF_4 \xrightarrow[-AgI]{} [C_3F_7\overset{+}{Te}(Me)Ph]BF_4^-$$

M = CH_2, R^1 = R^2 = H;
M = NEt, R^1 = R^2 = Me;
M = NMe, R^1 = R^2 = H

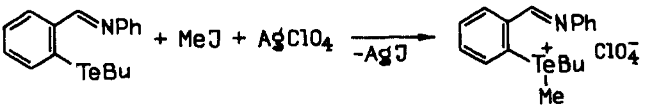
Also alkylations of compounds with two nucleophilic centers, nitrogen and tellurium atoms, are of interest. Interaction between 2-methyltelluro-*N,N*-dimethylbenzylamine and CH_3I leads to telluronium salts whereas in the case of the selenium analog the alkylation takes place at the nitrogen atom.[263]



In the case of 2-phenylbenzotellurazole, alkylation of both heteroatoms has been performed. Heating of this heterocycle with excess CH_3I gives a high yield of the corresponding immonium salt whereas reaction in the presence of $AgClO_4$ leads to the corresponding telluronium salt.[488,489] The latter is the first representative of a benzo azole alkylated on a heteroatom of the VIA group.

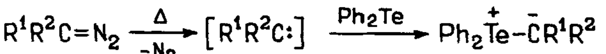


Interaction between 2-butyltellurobenzalaniline and CH_3I in the presence of silver(I) cations also results in the alkylation of the tellurium center.[490,491]



3.1.4. *Transformation to π-telluranes.* It was already noted above (cf. Sect. 3.1.2.) that diorganyl tellurides upon treatment with a number of oxidizing agents are converted to tricoordinated tellurium derivatives such as diorganyl telluroxides (or their hydrates in the case of the dialkyl compounds). Some reactions leading to the conversion of tellurides to telluronium ylides and tellurimides have been reported.[364]

Carbenes generated by thermal[492-495] decomposition of diazo compounds are capable of addition to diorganyl tellurides giving rise to telluronium ylides **84** in modest yields.

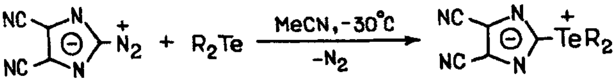


$$R^1R^2C{=}N_2 \xrightarrow[-N_2]{\Delta} [R^1R^2C\!:] \xrightarrow{Ph_2Te} Ph_2\overset{+}{Te}{-}\overset{-}{C}R^1R^2$$

84

$R^1 + R^2$ = PhC=C(Ph)−C(Ph)=CPh,[492-494] $COCH_2CMe_2CH_2CO$[495]

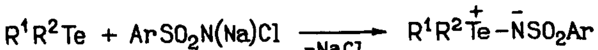
Diorganyltelluronium-4,5-dicyanoimidazol-2-ylidenes **85** have been obtained in the same manner.[496]



85

R = Me (49%), Me_3SiCH_2 (42%), Ph (47%)

Diorganyl tellurides (in analogy with other diorganyl chalcogenides) can be converted to tellurimides **86** by treatment with sodium salts of *N*-chloroarenesulfonamides.[32,33,497]



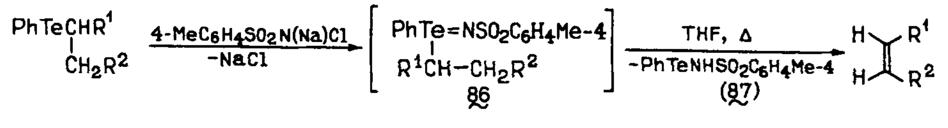
$$R^1R^2Te + ArSO_2N(Na)Cl \xrightarrow[-NaCl]{} R^1R^2\overset{+}{Te}{-}\overset{-}{N}SO_2Ar$$

86

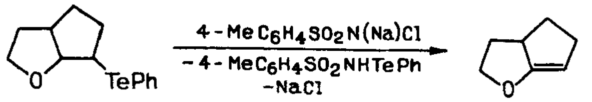
Ar = Ph: $R^1 = R^2$ = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$;[497]

Ar = 4-MeC$_6$H$_4$: R^1 = Me: R^2 = Ph, 4-MeC$_6$H$_4$, 4-MeOC$_6$H$_4$;[497] $R^1 = R^2$ = Ph, 4-MeOC$_6$H$_4$, 4-Me$_2$NC$_6$H$_4$;[497] $R^1 + R^2$ = o-C$_6$H$_4$-C$_6$H$_4$-o[32,33]

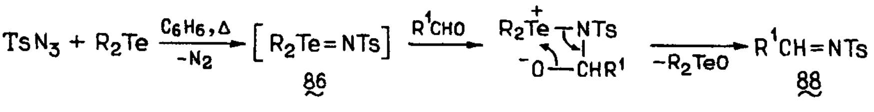
Tellurimides **86** prepared from phenyl alkyl tellurides readily eliminate a PhTeNHSO$_2$Ar molecule **87** upon heating and give alkenes. This property of **86** allows their use in the synthesis of alkenes which are formed in high yields upon treatment of appropriate phenyl alkyl tellurides with chloramine-T in boiling THF.[277,278,398] The alkylvinylsilanes obtained in this manner are formed solely in the E-form.[278]



R^1 = H: R^2 = C_9H_{17} (66%), $C_{10}H_{21}$ (78%), $C_{12}H_{25}$ (89%), $C_{13}H_{27}$ (75%);[277]
R^1 = SiMe$_3$: R^2 = C_9H_{19} (72%), $C_{11}H_{23}$ (71%), $C_{10}H_{27}$ (54%), $C_{15}H_{31}$ (59%)[278]



The acceleration of the interaction between tosyl azide and aromatic aldehyde observed in the preparation of the N-tosylimines **88** may be considered to be due to the intermediate formation of the tellurimides **86**.[498]



3.1.5. *Complexation reactions.* One of the characteristic properties of diorganyl tellurides is their ability to act as ligands in complexation reactions. In accordance with HSAB theory[499] diorganyl tellurides are "soft" bases capable of forming complexes with soft Lewis acids. Such complexes have been prepared by reaction of tellurides with transition and non-transition metal salts MX$_n$ or K$_2$(Na)MX$_4$ (M = Pd, Pt), metal carbonyls and metal carbonyl halides as well as with cyclopentadienyl derivatives of metals. Ligand exchange reactions have also been employed for the preparation of complexes. We do not intend a detailed discussion of the preparation, structure, and properties of complexes containing diorganyl tellurides as ligands since a review[7] has been devoted to this subject.

Complexes derived from mercury(II) halides $R_2Te\cdot HgX_2$ (X = Cl, Br, I)[53,55,56,58-62,74,100,101,229,237,268,391,418,419,500-509] present the most numerous class of such derivatives. Due to their poor solubility in the usual organic solvents and their propensity to decomposition into their components upon treatment with alkali these complexes can be conveniently used for the identification and isolation of tellurides from reaction mixtures.

A large number of reports have been devoted to another type of complexes derived from Pd(II)[21,110,111,114,229,237,387,505,507,510-528] and Pt(II)[98,103,114,229,237,387,507,513-515,519-523,525-527,529-539] halides. They obey $2R_2Te\cdot MX_2$ (where M = Pd, Pt; X = Cl, Br, I) stoichiometry. Diorganyl tellurides of various types also form complexes with Cu(I) halides[21,442,507,540,541] with compositions varying from $R_2Te{\cdot}CuX$ to $3R_2Te{\cdot}CuX$, as well as with silver(I) halides $R_2Te{\cdot}AgX$.[19–21,542,543] Of complexes with other metal halides the following types can be mentioned: $R_2Te{\cdot}AuX$,[543,544] $R_2Te{\cdot}MX_5$ (M = Nb, Ta; X = Cl, Br),[545,546] $(R_2Te)_3{\cdot}RhCl_3$,[525,547,548] and, finally, a complex of pentaaminoruthenium(II) of the structure $[(NH_3)_5Ru{\cdot}Te(CH_3)_2]{\cdot}(PF_6)_2$.[549]

Diorganyl tellurides also form complexes with carbonyls of Mn,[550] Fe,[550] Co,[550] Cr,[551] carbonyl halides of Mn,[550,552–554] Rh,[555–557] Re,[558,559] Ir,[560] Ru,[561] with iron carbonylnitrosyl,[550] nickel cyclopentadienyl,[562] and cyclopentadienyl carbonyls of Fe,[563,564] Co,[565] and Mo.[566]

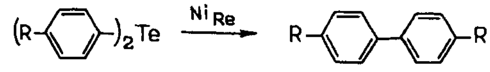
Crystalline complexes of 1:1 stoichiometry have prepared by reaction of diorganyl chalcogenides, including tellurides, with boron halides.[567]

Charge-transfer complexes of acyclic diorganyl tellurides with organic acceptors such as trinitrobenzene[568] or tetracyanoethylene[569] have not been studied in depth while the formation of phenoxachalcogenine complexes, not only with the above-mentioned, but also with other organic acceptors, has been the subject of quite detailed investigations.[570,571]

3.2. *Reactions Accompanied by Te-C Bond Cleavage*

All types of tellurides under review here, i.e. dialkyl, aryl alkyl and diaryl compounds, are subject to reactions proceeding with rupture of one or both Te-C bonds. Such reactions are the basis of the application of organotellurium compounds in preparative organic chemistry.[6,8–14,362] Rupture of a Te-C bond usually takes place upon treatment with Raney nickel, palladium and its derivatives, metal carbonyls, element IVA group hydrides, with some electrophilic and nucleophilic reagents as well as upon thermolysis or photolysis.

The synthesis of symmetric biaryls starting from diaryl tellurides is of considerable interest in preparative organic chemistry.[396] It is carried out by prolonged boiling of the precursors in bis(2-methoxyethyl) ether in the presence of 20-fold molar excess of freshly prepared Raney nickel and gives the desired biaryls in 72–90% yield.

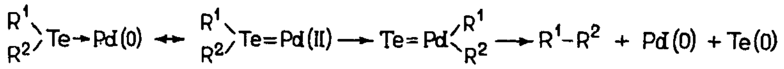


53

R = EtO, MeO, Me, H, Br

However, according to ref,[572] diphenyl telluride upon treatment with Raney nickel is reduced to benzene. Obviously, the tellurium is converted to nickel telluride since subsequent treatment of the reaction mixture with mineral acid leads to the evolution of H_2Te.

The conversion of tellurides R^1TeR^2 to the corresponding hydrocarbons R^1-R^2 by action of Pd(O) generated *in situ* from $Pd(OAc)_2$ and Et_3N[573] seems to possess large synthetic potential. No symmetric derivatives R^1-R^1 or R^2-R^2 are found in the reaction mixture. A possible mechanism of the reaction is presented below.[573]



$$\begin{matrix}R^1\\R^2\end{matrix}\!\!>\!Te\rightarrow Pd(0) \longleftrightarrow \begin{matrix}R^1\\R^2\end{matrix}\!\!>\!Te{=}Pd(II) \longrightarrow Te{=}Pd\!<\!\!\begin{matrix}R^1\\R^2\end{matrix} \longrightarrow R^1\text{-}R^2 + Pd(0) + Te(0)$$

R^1 = 4-$MeOC_6H_4$: R^2 = 4-$MeOC_6H_4$ (100%); 1-Ad (89%), $C_{15}H_{31}$ (76%);

$R^1 = R^2 = PhCH_2CH_2$ (85%); $R^1 = PhCH_2CH_2$, $R^2 = CH_2Ph$ (81%)

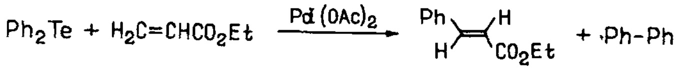
Palladium(II) salts promote the insertion of carbon monoxide into the Te-C bonds of tellurides leading finally to methyl esters of carboxylic acids in high yields.[524,574,575] Such processes are most conveniently carried out by treatment of a diorganyl telluride solution in $MeOH/Et_3N$ at ambient temperature with carbon monoxide in the presence of a stoichiometric amount of a Pd(II) salt.[524] The reactions may be also performed with catalytic amounts of $PdCl_2$ provided that oxidizing agents (most effective is copper(II) chloride) are present in the reaction mixture.[524] The authors of refs.[524,575] consider the formation of monomeric $(R_2Te)_2PdCl_2$ or dimeric $[R_2Te\cdot PdCl_2]_2$ complexes as the initial stage of the reaction. Subsequent migration of alkyl or aryl groups from tellurium to palladium, insertion of CO into a Pd-C bond and hydrolysis of the acylpalladium intermediates lead to the final products.

$$R^1R^2Te + CO \xrightarrow[r.t.]{PdCl_2,\ MeOH/Et_3N} R^1CO_2Me + R^2CO_2Me$$

$R^1 = R^2 = Ph$; $R^1 = Ph$, $R^2 = C_{12}H_{25}$

Substituted cinnamic acids have been synthesized by means of the above reactions.[524,574,575] Similarly, carbonylation of the addition products of tellurolate anions to propargyl alcohols gave butenolides.[524] When salts of other transition metals capable of forming complexes with diorganyl tellurides, such as Rh(III), Ru(III), Ir(III) were used, the carbonylation either resulted in very poor yields ($RhCl_3\cdot 3H_2O$) or failed. The reactivity of diorganyl chalcogenides towards carbonylation under the above conditions increases distinctly in the order S << Se < Te.[524,575] Thus, Ph_2S does not react, Ph_2Se gives methyl benzoate in 14% yield, whereas Ph_2Te gives rise to the latter ester in 96% yield.[524,575]

The arylation of alkenes by diorganyl tellurides proceeds similarly via arylpalladium intermediates formed by aryl migration from Te to Pd.[576] Interaction between Ph_2Te and ethyl acrylate in the presence of $Pd(OAc)_2$ leads to ethyl *trans*-cinnamate in 90% yield.[576] Biphenyl is the by-product of the reaction.

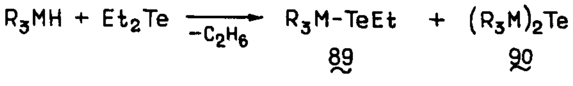


Thus, such reactions with participation of Pd(II) salts proceed via Te-C bond rupture upon interaction between an initial complex and various substrates. However, in some cases this rupture proceeds directly when the diorganyl telluride reacts with potentially complexable agents. Thus, the interaction between Ph_2Te and $Co_2(CO)_8$ or $Ni(CO)_4$ is accompanied by rupture of both Te-C bonds leading to $Co_2Te(CO)_5$ or Te and Ni, respectively.[550] In the case of $[Mn(CO)_5]_2$ only one Te-C bond is broken and a binuclear complex with bridging phenyltelluro groups is formed.[550]

$$[Mn(CO)_5]_2 + 2\ Ph_2Te \xrightarrow{130^\circ C} [Mn(CO)_4TePh]_2 + Ph\text{-}Ph + 2CO$$

For other examples of such Te-C bond cleavage cf. refs.[548,577]

Group IVA element triorganylhydrides R_3MH (M = Si, Ge, Sn; R = Et, Bu, Ph)[113,195,394,395,398,578,579] can also cleave one or both Te-C bonds in tellurides under more or less mild conditions. The structure of the final reaction products (i.e. the number of bonds cleaved) is determined in the first instance by the nature of the hydride. Thus, Et_3SiH and Et_2Te gave comparable yields of the products **89** and **90** at 200 °C and Et_3GeH did so at 140 °C whereas in the case of Et_3SnH the sole product, even at 20 °C, was bis(triethylstannyl) telluride **90** (M = Sn).[578,579]



$$R_3MH + Et_2Te \xrightarrow[-C_2H_6]{} \underset{\mathbf{89}}{R_3M\text{-}TeEt} + \underset{\mathbf{90}}{(R_3M)_2Te}$$

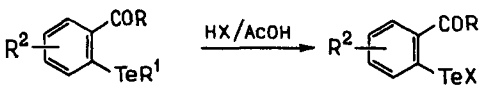
M = Si, Ge

The mild conditions of the reactions with triorganyltin hydrides as well as the high yields allow diorganyl tellurides to be employed in the preparation of hydrocarbons.[113,195,394,395,398] This method was first used in ref.[195] Later these reactions were extended to tellurides obtained by reduction of the products of the interaction between unsaturated carboxylic acids and alcohols and aryltellurium trichlorides,[394,395] aryltellurinyl acetate,[398] or $TeO_2/LiCl$ in AcOH.[113] Usually Ph_3SnH[113,195] or Bu_3SnH[394,395,398] are used for these preparations.

The reduction of tellurides and selenides with tin hydrides probably proceeds according to an S_H2 mechanism;[195,580] the reaction rate being faster with selenides than with tellurides.[580]

$$\begin{aligned}
&R_3SnH \longrightarrow R_3Sn^{\bullet} + H^{\bullet}\\
&R_3Sn^{\bullet} + R^1TeR^1 \longrightarrow R_3SnTeR^1 + R^{1\bullet}\\
&R^{1\bullet} + R_3SnH \longrightarrow R^1H + R_3Sn^{\bullet}
\end{aligned}$$

Protodetelluration and halogenolysis of some diorganyl tellurides are also accompanied by the rupture of one or, more rarely, both Te-C bonds. Such cleavages are most typical for aryl alkyl tellurides containing in the ortho position functional groups capable of coordination with the tellurium atom and thus lead to the rupture of the weak $Te\text{-}C_{aliph.}$ bond. For example, *o*-halotellurenylphenylcarbonyl compounds have been prepared in good yield by treatment of *o*-carbonyl containing aryl alkyl tellurides with hydrogen halides (mostly HBr) in acetic acid.[256,260,263,581]

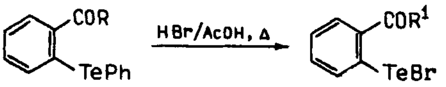


X = Cl, Br, I: R = R^2 = H: R^1 = CH_2CO_2Et, $CH_2CH(OEt)_2$;[256]
X = Br: R = R^1 = Me: R^2 = H, 4-Cl, 4-Me, 5-Me;[283] R^1 = Bu: R^2 = H: R = Me,[581] Ph[260]

In the case of *para*-isomers, not tellurenyl halides, but ditellurides are the final products under these conditions.[256]

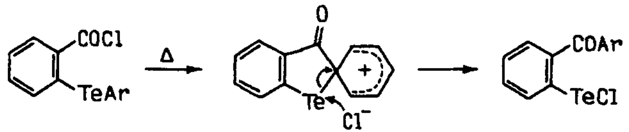
$$4\text{-}MeCOC_6H_4TeCH_2CH(OEt)_2 \xrightarrow{HX/AcOH} (4\text{-}MeCOC_6H_4)_2Te_2$$

It must be noted that Te-$C_{arom.}$ bonds, similarly to Te-$C_{aliph.}$ bonds, can also be cleaved by the HBr/AcOH reagent.[296]



R, R' = Cl, OH; OMe, OMe; OEt, OEt

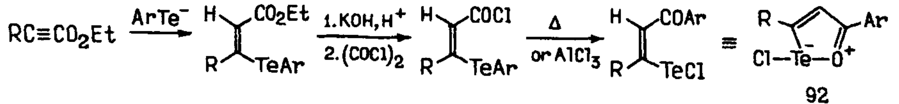
The thermal rearrangement of 2-chloroformylphenyl aryl tellurides to 2-aroylbenzenetellurenyl chlorides **91**,[296,582] the possible mechanism of which is given below, provides an interesting example of Te-$C_{arom.}$ bond rupture.



91

Ar = Ph, 4-MeC_6H_4, 2-C_4H_3S, 2,4,6-$Me_3C_6H_2$

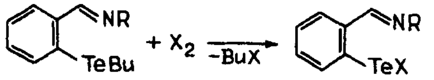
β-Aryltelluropropenoyl chlorides with *p*-substituted aryl groups (prepared by nucleophilic addition of arenetellurolate anions on esters of acetylenecarboxylic acids, followed by hydrolysis and conversion of the corresponding acids to acid chlorides, are subject to analogous thermal or $AlCl_3$ promoted rearrangements.[583-586] Based on X-ray investigations, Detty[583] attributed the structure of 1,2-oxatellurolium chlorides **92** to these products.



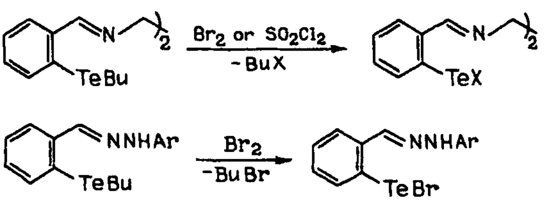
92

Oxygen or sulfur analogs of 2-chloroformylphenyl aryl tellurides or β-aryltelluropropenoyl chlorides under similar conditions (heating in the presence of $AlCl_3$) are subject to cyclization to the corresponding xanthones or benzopyrones.

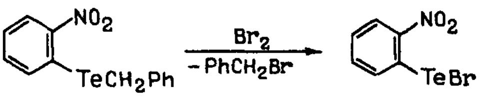
The driving force of these protodetelluration and rearrangement reactions of *o*-alkyltellurophenylcarbonyl compounds is the stabilization of the final products, *o*-halotellurenylcarbonyl compounds, by intramolecular coordination O → Te.[308,309] The facile cleavage of Te-$C_{aliph.}$ bonds which takes place upon halogenolysis of *o*-butyltellurobenzalanilines,[491,587-589] 1,6-bis(2-butyltellurophenyl)-2,5-diazahexa-1,5-diene,[429] *o*-butyltellurobenzaldehyde arylhydrazones[434] or 2-nitrophenyl benzyl telluride[311] under mild conditions is obviously caused in the same way.



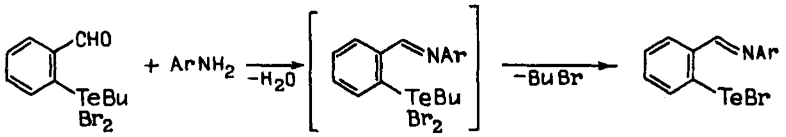
R = Ph: X = Cl; R = 4-$MeOC_6H_4$, 4-MeC_6H_4: X = Cl, Br, I; R = 2,3,4,5,6-F_5C_6: X = Cl, Br, I



Ar = 4-MeC_6H_4



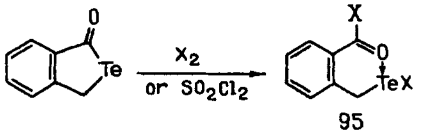
It is safe to assume that σ-telluranes like **93**, formed by addition of halogen to a tellurium atom, are intermediates of these reactions and then eliminate butyl halide. Indeed, interaction between 2-(butyldibromotelluro)benzaldehyde, prepared independently, and anilines at room temperature leads directly to tellurenyl bromides **94** instead of the expected σ-telluranes **93**.[589]



93 94

Ar = 2,4,6-$Me_3C_6H_2$, 4-IC_6H_4, 4-MeC_6H_4, 4-$MeOC_6H_4$

The Te-C_{aliph}. bond rupture taking place at low temperatures upon halogenolysis of tellurophtalide results in the formation of **95** which were the first representative of stable alkanetellurenyl halides.[180] The stability of these derivatives is also caused by the presence of intramolecular coordinative O → Te bonds.



95

X = Cl, Br, I

Halogenolysis of organyl benzyl tellurides with Br_2, I_2, SO_2Cl_2, and $SOCl_2$ proceeds quite specifically and is accompanied by both Te-C_{aliph}. bond rupture and an increase of the coordination number of the tellurium atom.[109,373]

$$RTeCH_2Ph + X_2 \longrightarrow RTeX_3 + PhCH_2X$$

R = 4-$MeOC_6H_4$, 2-$C_{10}H_7$

$$(PhCH_2)_2Te + Br_2 \longrightarrow TeBr_4 + PhCH_2Br$$

2-Thienyl alkyl tellurides behave similarly and are subject under mild conditions to bromodetelluration giving rise to 2-bromothiophene and alkyltellurium tribromides.[258]

Te-C bond cleavage also takes place by attack of ClF (in excess) on $(C_2F_5)_2Te$ and results in the formation of substantial amounts of $C_2F_5TeF_4Cl$ and TeF_5Cl together with $(C_2F_5)_2TeF_4$.[428]

A number of other oxidizing reagents which cause Te-C bond rupture is known. Thus, according to refs.,[99,100] oxidation of dialkyl tellurides with O_2 or H_2O_2 results in tellurenic acid formation, although these data are out of date and, probably, require additional study.

$$R_2Te + O_2 \xrightarrow{H_2O} RTe(O)OH$$

Oxidation of organyl benzyl tellurides with atmospheric oxygen gave the corresponding benzaldehydes.[109,123,373]

The transformation of phenyl alkyl tellurides to alkenes is of unquestionable interest in preparative organic chemistry.[222,227,228,249,284,285,291,459,590–594] However, these processes proceed via elimination of PhTeOH ("telluroxide" elimination) from phenyl alkyl telluroxides or their hydrates, obtainable by oxidation of the corresponding tellurides with *m*-chloroperbenzoic acid,[228,249,291,459,592,593] *t*-butyl hydroperoxide,[227,590–592] H_2O_2,[227,593] $NaIO_4$,[227,593,594], or by hydrolysis of phenylalkyltellurium dibromides[222,284,591] and thus are not considered in detail in the present survey (cf. the reviews[6,8–14]).

There are a number of cases where the rupture of one or both Te-C bonds has been achieved by the action of nucleophilic reagents. Thus, both Te-C bonds in Ph_2Te are cleaved by potassium amide in liquid ammonia in accordance with the scheme given below.[595] For comparison, Ph_2Se under the same conditions is transformed to selenanthrene.

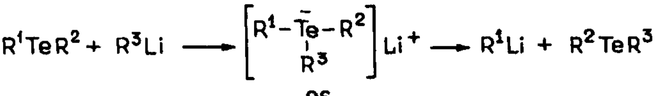
$$Ph_2Te + KNH_2 \xrightarrow{NH_3\,(liq.)} PhH + K_2Te(NH)_3 + K_2Te_3$$

Perfluoroalkanes have been obtained by Te-C bond cleavage ,in bis(perfluoroalkyl) tellurides taking place upon treatment of the latter with aqueous alkali at room temperature.[422]

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

$R_F = CF_3, C_2F_5$

Recently a number of reports devoted to Te-C bond rupture on the action of lithium- or magnesiumorganic reagents was published. The first reaction of this type, with bis(phenyltelluro)methane, was observed by Seebach.[257] Treatment of this telluride with lithiumalkyls leads to the formation of phenyl alkyl tellurides and (phenyltelluro)methyllithium in high yields. The formation of the latter product has been confirmed by subsequent reactions with various electrophiles (cf. Sect. 2.5.1.2.).[257,276,277] Lithiation of bis(phenyltelluro)methane to bis(phenyltelluro)methyllithium has been performed with lithium diisopropylamide.[257,276,277] Later it was shown that lithium- as well as magnesiumorganic reagents are capable of cleaving Te-C bonds in dialkyl,[208,340,342] aryl alkyl, [339,340,342] and even diaryl tellurides.[340,341,596,597] The reactions of butyllithium with organyl vinyl and divinyl tellurides are accompanied by Te-C_{sp^2} bond rupture leading to vinyllithium compounds.[342,598,599] It has been shown in ref.[598] that the generation of the latter compounds proceeds without change of the initial geometry of the double bond. By means of NMR spectroscopy it was demonstrated that these reactions of organolithium reagents with diorganyl tellurides proceed via intermediate formation of ate complexes **96** involving a tricoordinated tellurium atom. These complexes decompose to the thermodynamically more stable alkyllithium derivatives (R^1Li in the Scheme below) and diorganyl tellurides.



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

96

$R^1 = R^2$ = alkyl, alkenyl, aryl;
R^1 = alkyl, R^2 = aryl;
R^3 = alkyl, aryl

Taking into account that tellurides are easily prepared by reaction of alkyl halides with lithium tellurolates (cf. Sect. 2.5.1.1.), the preparation of lithiumorganic reagents of various types may be performed starting from the appropriate organyl halides without isolation of the intermediate tellurides according to the following Scheme.[208,340]

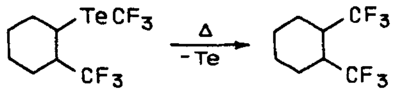
$$R^1X + R^2TeLi \xrightarrow[-LiX]{} [R^1TeR^2] \xrightarrow[-R^2TeR^3]{R^3Li} R^1Li$$

Treatment of diaryl or aryl alkyl tellurides with Grignard reagents in the presence of nickel or cobalt complexes such as $NiCl_2 \cdot (PPh_3)_2$, $NiCl_2[Ph_2P(CH_2)_2PPh_2]$ and $CoCl_2$-$(PPh_3)_2$ also leads to Te-C bond rupture, but gives a mixture of products derived from homo- and cross-coupling of radicals.[600,601]

$$Ar_2Te + RMgX \xrightarrow{Ni^{2+}(Co^{2+})} Ar-R + Ar-Ar + R-R$$

Ar = 4-$MeOC_6H_4$, Ph; R = Ph, 4-$MeOC_6H_4$, C_6H_{13}

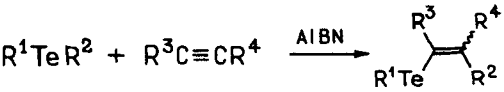
Pyrolysis and photolysis of diorganyl tellurides are also accompanied by Te-C bond cleavage. Earlier we discussed a few examples of such reactions which present novel approaches to the synthesis of cyclic hydrocarbons and 1,5-dienes, namely the pyrolysis of 1,3-dihydrobenzo[*c*]tellurophene and 1,3-dihydronaphtho[2,3-*c*]tellurophene leading to annelated cyclobutenes;[178] the thermal decomposition of 9-tellurabicyclo[3.3.1.]nona-2,6-diene to bicyclo[5.1.0.]octa-2,5-diene[181] and that of diallyl tellurides[120,125] and of dibenzyl telluride[129,130] giving rise to 1,5-dienes and dibenzyl, respectively (cf. Sect. 2.3). The extrusion of the tellurium atom from **78** (for the synthesis of **78** cf. Sect. 2.6.), leading to 1,2-bis(trifluoromethyl)cyclohexene, may be ascribed to the same type of reactions.[423]



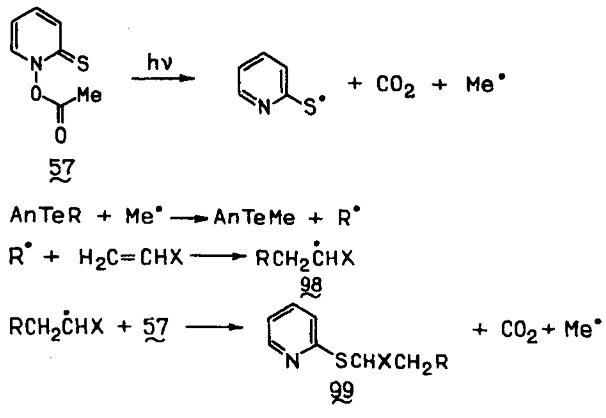
78

The high temperature pyrolysis of dimethyl telluride is regarded to follow radical mechanism.[3,4] The pyrolytic decomposition of other symmetric and unsymmetric diorganyl tellurides also proceeds mainly via homolytic fission of Te-C bonds.[122] However, compounds containing an active β-hydrogen atom such as *i*-Pr_2Te, *t*-Bu_2Te or RTeBu-*t* (R = Me, allyl) may also decompose with elimination of these atoms leading to alkanetellurols and dialkyl ditellurides.[122]

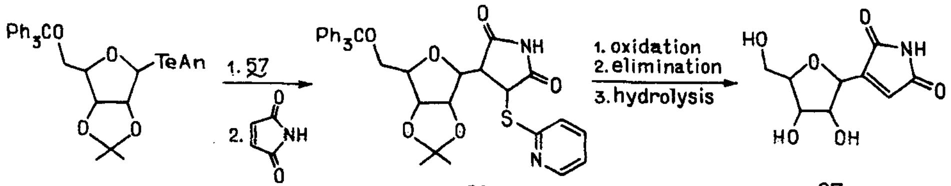
The addition of diorganyl tellurides R^1TeR^2 to alkynes,[602,603] giving rise to alkenyl tellurides in high yields, also proceeds via homolysis of Te-C bonds promoted by catalytic amounts of 2,2′-azobisisobutyronitrile.[602,603] Only the Te-C_{sp^3} bonds are affected by the rupture process and, in addition, the cleavage of C_{tert}-Te and $PhCH_2$-Te was more favored than that of C_{prim}-Te and Bu-Te bonds, respectively.[603] The alkenyl tellurides formed have been isolated as mixtures of Z- and E-isomers.



Facile cleavage of Te-C bonds by radicals was recently used by Barton for the synthesis of the antibiotic showdomycin **97**.[236] The tellurides AnTeR where R is a carbohydrate group when treated with methyl radicals generated by photolysis of the mixed anhydride of *N*-hydroxy-2-pyridinethione and acetic acid **57** are subject to C_R-Te bond rupture which gives rise to carbohydrate radicals $R^{\bullet}$ (methyl anisyl telluride is another product). Addition of the carbohydrate radicals formed to alkenes leads to the relatively electrophilic radicals **98** which then react with **57** to yield **99** together with methyl radicals.



A brief presentation of the synthesis of **97** is given below.[236]



99a

97

Impulse photolysis of bis(4-methoxyphenyl) telluride in neutral or acidic methanol solution is also accompanied by Te-C bond rupture and leads to ArTe• radicals identified by their absorption at 508 nm.[604] It has been suggested that the decomposition of methanol to methoxyl and hydrogen radicals is the first step of the process while ArTe• radicals first appear in subsequent stages.

$$\mathrm{MeOH} \xrightarrow{h\nu} \mathrm{MeO^\bullet} + \mathrm{H^\bullet}$$
$$\mathrm{H^\bullet} + \mathrm{CH_3OH} \longrightarrow \mathrm{H_2} + {}^\bullet\mathrm{CH_2OH}$$
$$\mathrm{H^\bullet} + \mathrm{Ar_2Te} \longrightarrow \mathrm{ArH} + \mathrm{ArTe^\bullet}$$

The photolysis of dibenzyl telluride in $CDCl_3$ in an inert atmosphere proceeds very slowly.[109] However, in the presence of atmospheric oxygen the process is complete after 5 h and gives a mixture of detelluration products among which dibenzyl, benzaldehyde, benzyl alcohol and toluene could be identified.

Heating of diaryl tellurides with elemental chalcogens at high temperatures leads to replacement of the Te atom by sulfur or selenium.[29,605,606]

$$\mathrm{Ar_2Te} + \mathrm{M} \xrightarrow[-\mathrm{Te}]{\Delta} \mathrm{Ar_2M}$$

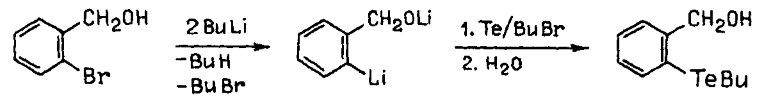
M = S: Ar = C_6F_5,[29,606] Ph;[605]
M = Se: Ar = C_6F_5[29,606]

Similar replacement reactions have been studied in much more detail in the case of tellurium-containing heterocycles such as perfluorodibenzotellurophene,[606] phenoxatellurines, phenotellurazines, and benzotellurazoles.[570,571] The replacement of tellurium by a sulfur atom in diallyl telluride proceeds under milder conditions[124] by the action of the H_2S/DMSO system on this substrate at room temperature and leads to a mixture of diallyl sulfide and disulfide in 33% and 17% yield, respectively.

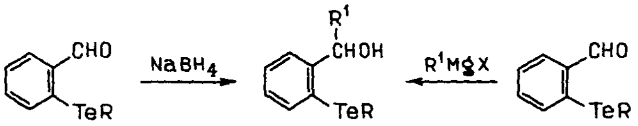
3.3. *Transformations of Functional Groups*

Chemical reactions which transform a functional groups in an organotellurium compound in general and in diorganyl tellurides in particular have been investigated quite insufficiently. Such reactions have been described mainly for diorganyl tellurides with CH_2OH, CHO, COR, COOH (and its derivatives) or NH_2 groups. Although these transformations of functional groups follow as a rule the usual reaction schemes, nevertheless some anomalies, caused by the specific reactivity of tellurium organic compounds, have been observed.[482]

Alcohols. The preparation of tellurium containing alcohols is possible either by introduction of appropriate groups into compounds already involving a hydroxy function,[270,607]



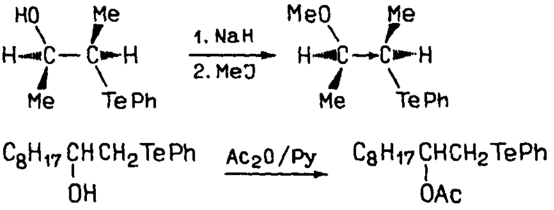
or by interaction between tellurium-containing aldehydes and ketones and sodium tetrahydroborate[67,68,217,607] or Grignard reagents.[217,607]



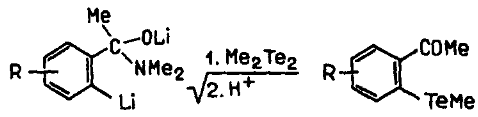
R^1 = H: R = Me,[217] Bu[607], 2-HOCC$_6$H$_4$[67,68,607];
R = Me: R^1 = Me;[217]
R = Bu: R^1 = Me, Ph, 4-MeC$_6$H$_4$[607]

Tellurium-containing alcohols have also been prepared by oxirane ring opening with arenetellurolate anions[195,222,284,285] (cf. Sect. 2.5.1.2.).

Transformations of these alcohols into their ethers[222] and esters,[195] proceeding under the usual conditions, have been described.

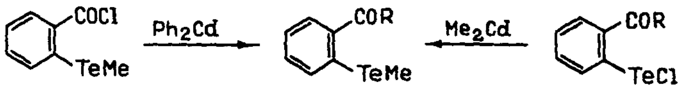


Aldehydes and ketones. o-(Alkyltelluro)benzaldehydes (methyl,[217,345] butyl[217,268,491,587,588]) and bis(2-formylphenyl) telluride,[67,68,440,441,491] *o*-(alkyltelluro)acetophenones (methyl,[255] butyl[255,436,581]) and *o*-(butyltelluro)benzophenone[260] have been prepared by interaction between the appropriate *o*-lithiophenyldiethyl acetals or −1′,3′-ethylene ketals and TeI$_2$ or elemental tellurium, followed by treatment of the lithium tellurolates formed with alkyl halides and hydrolysis of the acetal (ketal) group. *o*-(Methyltelluro)acetophenones substituted in the aryl group have also been obtained in poor yield by cleavage of the Te-Te bond in dimethyl ditelluride with the lithium intermediate **100**,[263] and 2-(methyltelluro)-benzophenone by interaction between 2-(methyltelluro)benzoyl chloride and diphenyl cadmium or by reaction of 2-(chlorotellurenyl)benzophenone with dimethylcadmium.[298]



100

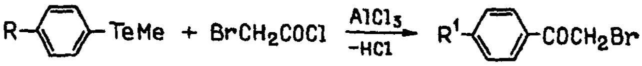
R = 4-Cl, 4-Me, 5-Me



R = H, Ph

2-(Methyltelluro)benzaldehyde has been prepared in a similar manner starting from 2-(bromotellurenyl)benzaldehyde and $(CH_3)_2Cd$.[256]

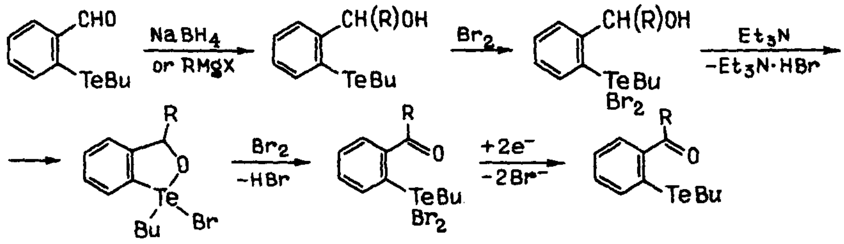
The usual approach to the preparation of ketones, the Friedel-Crafts reaction, has only been successfully employed in the synthesis of *p*-tellurated ω-bromoacetophenones.[75]



R = H, Ph; R^1 = MeTe, $4\text{-}MeTeC_6H_4$

However, according to ref.,[255] interaction between telluroanisole and acetyl chloride in the presence of $AlCl_3$ only leads to the corresponding *Te*,*Te*-dichloro derivative.

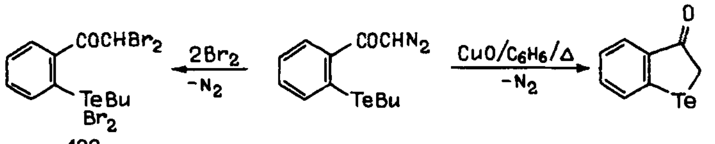
An attempt to prepare *o*-(methyltelluro)acetophenone by oxidation of 1-[*o*-(methyltelluro)phenyl]ethanol with DMSO in acetic anhydride failed; only decomposition leading to TeO_2 was observed under these conditions.[255] A novel approach to the transformation of primary alcohols to aldehydes and of secondary ones to ketones via intermediate formation of 2,1-benzoxatelluroles,[101] proposed in ref.,[270,607] may be of interest. Treatment of 2-(butyldihalogenotelluro)benzyl alcohols with Et_3N leads to 1-butyl-1-halo-2,1-benzoxatelluroles in excellent yields. The latter compounds interact with an equimolar amount of bromine in boiling CCl_4 or $CHCl_3$ with elimination of HBr and yield the desired *o*-(butyldibromotelluro)benzaldehyde or the corresponding *o*-tellurated ketones. Taking into account that secondary alcohols are easily obtainable by reaction of Grignard reagents with *o*-(butyltelluro)benzaldehyde, this approach can also be considered as a novel access from tellurated aldehydes to ketones.



101

R = H, Ph

Tellurium-containing aldehydes and ketones are amenable to the usual carbonyl reactions. Thus, they are reduced with $NaBH_4$ to alcohols,[67,68,217,607] react with Grignard reagents to give secondary alcohols,[217,607] readily form Schiff bases (*o*-(butyltelluro)benzaldehyde,[268,429,491,587,588] bis(2-formylphenyl) telluride[440,441,491]), azines and phenylhydrazones (*o*-(alkyltelluro)benzaldehydes[217,429,434]) as well as oximes (*o*-(methyltelluro)benzaldehyde[217]) which in turn are converted to the corresponding nitriles by treatment with $KHSO_4$.[217] On the other hand, according to ref.,[392] diphenacyl telluride when treated with hydrazine decomposes to elemental tellurium. 2-(Methyltelluro)benzaldehyde has also been used in Wittig reactions[346] and in condensation reactions with malonic acid.[354] 2-(Methyltelluro)acetophenone gives the corresponding chalcone with benzaldehyde.[255] 2-(Butyltelluro)acetophenone by means of a standard procedure (formylation with $HCOOCH_3/Na$, followed by treatment with tosyl azide) has been converted to the corresponding ω-diazoacetophenone[436] which can be subjected to further standard transformations. Thus, boiling of this derivative with CuO in benzene leads to benzo[*b*]tellurophen-3-one in 40% yield and treatment with bromine to the dibromo ketone **102**. The latter reaction is accompanied by oxidation of Te(II) to Te(IV).



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The oxidation of the formyl group of 2-(alkyltelluro)benzaldehydes to a carboxyl group is accompanied by partial rupture of the Te-$C_{aliph.}$ bond and formation of bis(2-carboxyphenyl) ditelluride together with the desired 2-(alkyltelluro)benzoic acids.[217]

Carboxylic acids and their derivatives. The synthesis of carboxyl derivatives of diorganyl tellurides has mainly been achieved by introduction of the tellurium-containing moiety into compounds with a preformed CO_2H (CO_2R) function. o-Carboxyphenyl aryl tellurides have been prepared by interaction between *o*-carboxyphenyldiazonium cations and arenetellurolate anions[296] (cf. Sect. 2.5.1.3.); (aryltelluro)acetic and β-(aryltelluro)propionic acids have been obtained by reaction of arenetellurolate anions with haloacetic (propionic) acids[207,216,218,225] or by addition of the same anions to the C=C double bond of acrylic acid[293] as well as by thermolysis of appropriate telluronium salts.[345] Preparations of *o*-(alkyltelluro)benzoic acids by oxidation of *o*-(alkyltelluro)benzaldehydes are few and moreover complicated by $C_{aliph.}$-Te bond cleavage.[217] Preparations of tellurobis(propionic) acid by acid hydrolysis of bis(2-cyanoethyl) telluride,[187,189] of 2-(ethyltelluro)benzoic acid by Te-Te bond fission in diethyl ditelluride with lithium 2-lithiobenzoate[263] and of a carboxylic acid derivative, 2-(methyltelluro)benzamide, by alkylation of a lithium derivative of the type **100**[269] have been reported as isolated axamples. Some tellurium-containing carboxylic acids have been obtained by alkaline hydrolysis of the corresponding esters.[196,200,201]

Carboxylic acids with tellurium-containing substituents can be converted to the corresponding acyl chlorides by treatment with dichloromethyl alkyl ethers in the presence of anhydrous $ZnCl_2$[217,218,296,354,356,582,585] or with oxalyl chloride.[583,584,586] Use of reagents such as PCl_5 or $SOCl_2$ results only in the oxidation of Te(II) to Te(IV).

These acyl chlorides under standard conditions furnish esters[217,296] and react with R_2Cd[296] (see the preceding section) (for rearrangements of 2-chlorocarbonylaryl tellurides and β-(aryltelluro)propenoyl chlorides, cf. Sect. 3.2.). Preparative methods which are successful in the synthesis of sulfur and selenium heterocycles are often useless in the case of the tellurium analogs as a consequence of the low energy of the Te-$C_{aliph.}$ bonds. Thus, attempts to prepare tellurochromanone by pyrolysis of β-(2-carboxyphenyltelluro)propionic acid or by Dieckmann cyclisation of the corresponding diester led only to bis(2-carboxyphenyl) ditelluride.[218] Heating of β-phenyltelluropropionic acid in polyphosphoric acid or its esters resulted in complete decomposition with elimination of elemental tellurium[218] whereas the selenium analog under the same conditions gave selenochromanone. However, it must be noted that the interaction between diethyl (organyltelluro)(alkyl)malonates and urea or thiourea in the presence of *t*-BuOK proceeds as usual and gives rise to (organyltelluro)alkylbarbiturates in yields ranging from low to good.[198]

Amines and their derivatives. The number of known diorganyl tellurides containing amino groups is very limited. 2-(Butyltelluro)aniline has been obtained by alkylation of lithium 2-[*N*-lithio(trimethylsilyl)aminobenzene] tellurolate, followed by removal of the trimethylsilyl group[273,355] and 2-(ethyltelluro)aniline by reduction of 2-(ethyltelluro)nitrobenzene with zinc dust in aqueous HCl.[608] Tellurium-containing amines form hydrochlorides[273,355] and are subject to acylation by acyl chlorides.[273,355,608] In addition, *N*-acyl derivatives of *o*-(alkyltelluro)anilines have been obtained by alkylation of sodium *o*-(*N*-acylamino)benzenetellurolates with dimethyl sulfate.[232-234] Treatment of *N*-acyl derivatives of *o*-(methyltelluro)-anilines with thionyl chloride leads to the transformation of the NHCOR group to N=C(Cl)R as well as to the oxidation of Te(II) to Te(IV).[234]

R = Ph, 4-ClC_6H_4, 4-BrC_6H_4

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