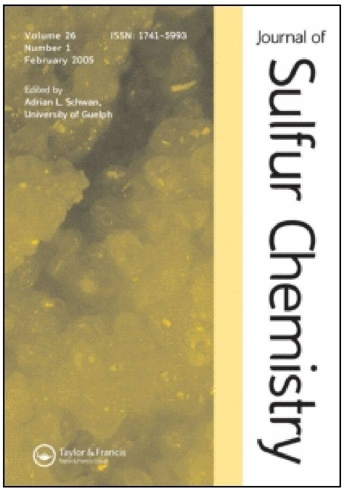

Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

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To cite this Article Sadekov, Igor D. and Minkin, Vladimir I.(1997) 'Synthesis and Reactions of Diorganyl Ditellurides', Journal of Sulfur Chemistry, 19: 2, 285 — 340
To link to this Article: DOI: 10.1080/01961779708047909
URL: http://dx.doi.org/10.1080/01961779708047909

Sulfur Reports, Vol. 19, pp. 285-348
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Amsterdam B.V. Published in The Netherlands
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SYNTHESIS AND REACTIONS OF DIORGANYL DITELLURIDES

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(Received 15 December 1995)

Syntheses and reactions of diorganyl ditellurides are systematically reviewed with 365 references.

Keywords: Dialkyl ditellurides; diaryl ditellurides; divinyl ditellurides

CONTENTS

I. INTRODUCTION

Diorganyl ditellurides are widely usable synthons for the preparation of various diorganyl tellurides R_2Te and organyltellurium trihalides $RTeHal_3$. Some of these compounds are also important ligands in coordination chemistry.[1] Cyclic *peri*-bridged ditellurides play a role as the donor components of organic charge-transfer complexes and ion-radical salts possessing high conductivity.[2] The chemistry of diorganyl ditellurides has been relatively scarcely reviewed. There are brief chapters in a few monographs,[3-6] the last of which appeared a decade ago. Since then a considerable number of publications concerned with various aspects of the chemistry of acyclic and especially cyclic ditellurides have appeared, and a trend to increasing application of ditellurides and their derivatives in preparative organic chemistry has made itself felt. The present review is an attempt to summarize in a systematic manner and update the data available on the synthesis and reactivity of diorganyl ditellurides.

It is worth noting that, in contrast to diorganyl disulfides and diselenides, unsymmetrical diorganyl ditellurides R^1TeTeR^2 are very uncommon. The only examples are the observation of pentafluoroethyl nonafluorobutyl ditelluride $C_2F_5TeTeC_4F_9$[7,8] which was characterized by its mass spectrum only and a recent report[9] on the preparation of unsymmetric diaryl ditellurides in more than 90% yield by coupling of sodium arenetellurolates ArTeNa with arenetellurenyl iodides in tetrahydrofuran. All attempts to prepare such ditellurides by either UV irradiation of benzene solutions of two symmetric ditellurides $R^1_2Te_2$ and $R^2_2Te_2$ or by reduction of a mixture of two different aryltellurium trichlorides Ar^1TeCl_3 and Ar^2TeCl_3 failed.[10-12]

The situation with the corresponding olygotellurides is similar. Important for the stability of tritellurides in the crystalline state and in solution are bulky organic groups preventing the attack of reagents at the tritelluride chain or intramolecular coordination between imine nitrogen and tellurium atoms. These are the factors which are responsible for the kinetic and thermodynamic stability of bis[tris(trimethylsilyl)methyl] tritelluride $[(Me_3Si)_3C]_2Te_3$[13,14] as well as of bis[2-(2-pyridyl)phenyl] tritelluride[15,16] and bis[2-(2-quinolyl)phenyl] tritelluride.[16] The length of the intramolecular coordination N→Te bond in the pyridyl-containing tritelluride is 2.554 Å,[15] the sum of the van der Waals radii of Te and N atoms being 3.70 Å.[17]

2. SYNTHESIS OF DIORGANYL DITELLURIDES

General methods for the preparation of symmetric diorganyl ditellurides of various types such as dialkyl, diaryl, divinyl and dialkynyl ditellurides include: (1) oxidation of the corresponding metal tellurolates RTeM (M = Li, MgHal); (2) nucleophilic substitution of a halogen atom in an organic halide by the ditelluride anion Te_2^{2-} and (3) reduction of the corresponding organyltellurium trihalides, usually the trichlorides $RTeCl_3$. The synthetic potential of these methods for the synthesis of diorganyl ditellurides is rather unequal. Whereas the second approach is applied in the preparation of aliphatic ditellurides, the first and the third one are usually employed in the synthesis of diaryl ditellurides. It should be noted that the common method for the preparation of organic disulfides and diselenides consisting of the oxidation of the corresponding thiols and selenols RMH (M = S, Se) cannot be realized in the case of the tellurium analogs. Only a few thermally unstable alkanetellurols have been described which are readily oxidized in air[3,4,18-21] and even by dilute H_2SO_4.[21] A kinetic stabilization of tellurols is achieved when the organyl moiety is a bulky group like tris(trimethylsilyl)silyl in $(Me_3Si)_3SiTeH$[22] or 2,4,6-trialkylphenyl in 2,4,6-$R_3C_6H_2TeH$ (R = Me, *i*-Pr, *t*-Bu).[23] These compounds have been prepared by protonation of the corresponding relatively stable lithium tellurolates.

2.1. Oxidation of Tellurolates

A common method for the preparation of organic ditellurides **1** is oxidation of lithium arenetellurolates **2**.[24-38] The compounds **2** are prepared by treatment of an aryllithium with tellurium powder in ether or THF. Usually, atmospheric oxygen and aqueous potassium ferricyanide[31] serve as mild oxidant. It is worth noting that oxidation of sodium phenylethynetellurolate with air oxygen or iodine leads to bis(2-phenylethynyl) telluride. The reaction occurs most probably by elimination of tellurium from the ditelluride initially formed.[39]

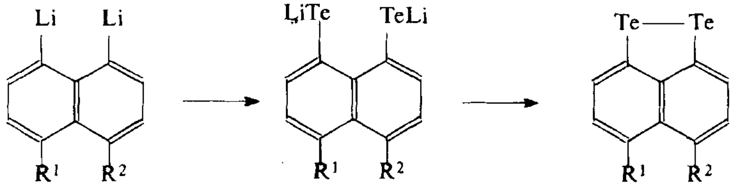
The high nucleophilicity of the tellurolate anions **2** imposes certain restraints on the method of preparation for the starting aryllithium reagent. These compounds are known to be generated by either interaction of bromo(iodo)arenes with lithium or of aryl halides with *t*-butyllithium. When *n*-butyllithium is used instead of *t*-BuLi, the *n*-butyl bromide formed reacts with **2** giving rise to aryl butyl tellurides **3**.[25,28,29]

$$\underset{}{\mathrm{ArLi + Te}} \longrightarrow \underset{\mathbf{2}}{\mathrm{ArTeLi}} \xrightarrow[2.\ O_2]{1.\ H_2O/H^+} \underset{\mathbf{1}}{\mathrm{Ar_2Te_2}}$$

Ar = Ph,[24-27,31] 2-MeC_6H_4,[25,27] 3-MeC_6H_4,[27,31] 4-MeC_6H_4,[25,27,31] 2-$MeOC_6H_4$,[27] 4-$MeOC_6H_4$,[31] 4-$CF_3C_6H_4$,[31] 4-FC_6H_4,[31] 4-ClC_6H_4,[31] 4-BrC_6H_4,[31] 2-OHC_6H_4,[28] 2-C(Me)$OCH_2CH_2OC_6H_4$,[29] 4-$Me_2NC_6H_4$,[31] 2-$PhCH_2C_6H_4$,[32,33] 2,4,6-$Me_3C_6H_2$,[30] 1-$C_{10}H_7$,[25,27,31] 2-$C_{10}H_7$,[27] 4-PhC_6H_4,[31] ferrocenyl,[34] $C_5H_4Mn(CO)_3$,[35] $C_5H_4Re(CO)_3$,[35] 2-furyl,[37] 2-[(*N*-tosyl)pyrryl],[37] 2-thienyl,[36,37] 2-[(*N*-tosyl)indolyl],[37] 2-pyridyl,[37] 2-[(3-thienyl)pyridyl][38]

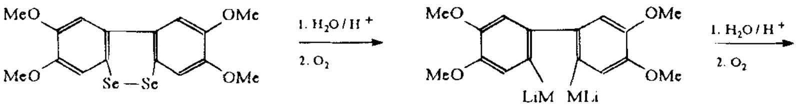
$$\mathrm{ArX} \xrightarrow[-\,n\text{-BuX}]{n\text{-BuLi}} \mathrm{ArLi} \longrightarrow \underset{\mathbf{2}}{\mathrm{ArTeLi}} \xrightarrow[-\,\mathrm{LiX}]{n\text{-BuX}} \underset{\mathbf{3}}{\mathrm{ArTeBu}}$$

Oxidation of dilithium *peri*-ditellurolates **4** has been used for the preparation of cyclic 1,2-ditelluroles **5** ($R^1 = R^2 = H$[40-42]) and **6** ($R^1 + R^2 = (CH_2)_2$[43,44]). The yields of the latter compounds are rather low (4–12%).

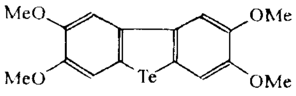


4 **5, 6**

Oxidation of dilithium ditellurolates **7** (M = Te[45]) and **8**[46] does not lead to cyclic ditellurides as might expected by analogy with the above reaction. Dibenzotellurophene **9** and telluroxanthene **10**, respectively, proved to be the main products.



11 **7**



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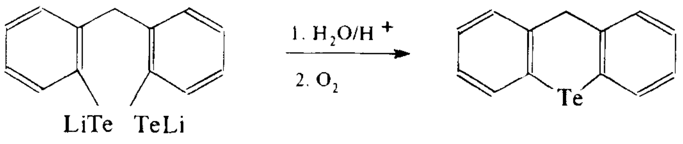
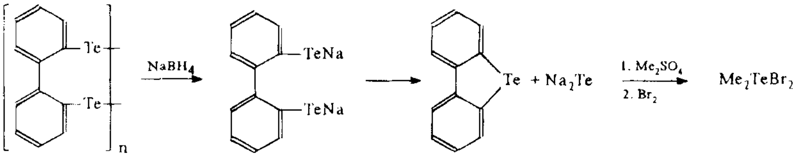


8

10

The selenium analog of **7** affords upon oxidation the six-membered cyclic diselenide **11** in 13% yield.[45] Under the same conditions the lithium ditellurolate **7** (M = Te) undergoes disproportionation to the dibenzotellurophene **9** and lithium telluride. The oxidation of the sodium ditellurolate **7a**, generated by reduction of the oligoditelluride **12**,[47] takes a similar course leading to dibenzotellurophene **9a** and sodium telluride. Indeed, treatment of the reaction mixture with dimethyl sulfate and subsequent bromination and separation of the products gave dimethyltellurium dibromide together with **9a**.



12 **7a** **9a**

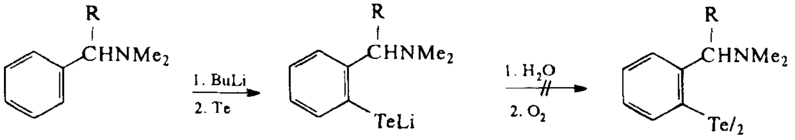
A novel synthesis of sodium arenetellurolates **2** by coupling of aryl iodides with sodium telluride (in a molar ratio 0.5–0.6:1) in *N*-methyl-2-pyrrolidone has good potential for the preparation of diaryl ditellurides. The ditellurides are readily obtained from **2** in 51–71% yield by oxidation with air oxygen. The sodium telluride solution is prepared by reaction of tellurium with sodium hydride in the same solvent.[48]

$$\mathrm{ArI + Na_2Te \xrightarrow[-NaI]{} \underset{\mathbf{2}}{ArTeNa} \xrightarrow[2.\ O_2]{1.\ H_2O/H^+} \underset{\mathbf{1}}{Ar_2Te_2}}$$

Ar = Ph, 4-MeC_6H_4, 4-$MeOC_6H_4$, 2,4,6-$Me_3C_6H_2$, 1-$C_{10}H_7$, 2-Me-1-$C_{10}H_6$

It should be noted that such a method was first applied in Ref.[49] The photoinitiated reaction of Na_2Te (generated from Na and Te in liquid ammonia) with 1-iodoadamantane and subsequent oxidation of the intermediate tellurolate with air oxygen gave rise to di(1-adamantyl) ditelluride in 47% yield.

Lithium arenetellurolates bearing dimethylaminomethyl groups in an *o*-position behave in a special manner upon oxidation.[50,51] Under the customary conditions not the expected diaryl ditellurides, but "oxygenated" derivatives are formed which probably have the structure of tellurenic acid anhydrides.



R = H, Me

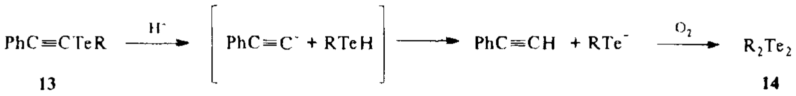
Oxidation of lithium alkanetellurolates (generated from alkyllithiums and tellurium powder) has been used for the synthesis of dialkyl ditellurides only occasionally. Dibutyl and di(*t*-butyl) ditelluride have been synthesized in this way.[52] The reaction occurs smoothly only when THF is used as a solvent.

$$\mathrm{RLi + Te \longrightarrow RTeLi \xrightarrow{O_2} R_2Te_2}$$

R = Bu, *t*-Bu

However, according to Ref.,[53] the interaction between *t*-BuLi and Te, followed by oxidation, leads not to di(*t*-butyl) ditelluride, but to the ditelluride $(Me_3CCH_2)_2Te_2$. The formation of the latter compound is due to the fact that *t*-BuLi can react with THF affording Me_3CCH_2Li. The reaction of this lithium intermediate with Te and subsequent oxidation give rise to the observed product.

Alkanetellurolate anions have also been generated by a specific method based on the facile cleavage of the C_{sp}-Te bonds in phenylethynyl tellurides **13** under the action of certain reducing agents. [54,55] Treatment of **13** with $NaBH_4$ in ethanol (or with $LiAlH_4$ in THF) or with the system N_2H_4/NaOH gives rise to alkanetellurolate anions which form dialkyl ditellurides **14** in high yields (70–96%) upon oxidation with air oxygen.



$$\underset{\mathbf{13}}{PhC{\equiv}CTeR} \xrightarrow{H^-} \left[PhC{\equiv}C^- + RTeH \right] \longrightarrow PhC{\equiv}CH + RTe^- \xrightarrow{O_2} \underset{\mathbf{14}}{R_2Te_2}$$

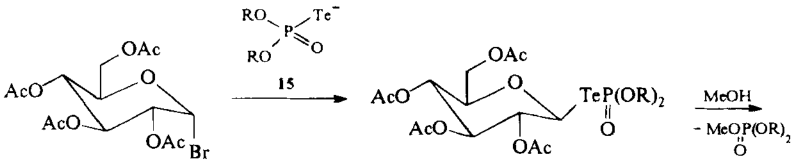
R = Et, *i*-Pr, *t*-Bu, $Me(CH_2)_2$ CHMe, $PhCH_2CH_2$, $C_{12}H_{25}$

The above reactions provide a very convenient access to dialkyl ditellurides. The starting phenylethynyl tellurides **13** can easily be obtained in almost quantitative yield by coupling of lithium 2-phenylethynetellurolate with alkyl halides.

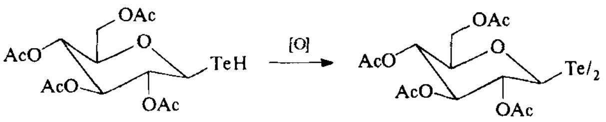
The synthetic potential of another approach to ditellurides containing C_{sp^3}-Te bonds[56,57] has been less studied. In this method *O,O*-dialkylphosphotellurolates **15** (generated by reaction of 2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorine with Te in an inert atmosphere) are used *in situ* for the formation of C-Te bonds. Reaction between **15** and 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide leads to **16** which upon treatment with methanol in the presence of air yields the ditelluride **17**.[56,57] Obviously, the tellurol **18** serves as the intermediate of the reaction.

Magnesiumorganic reagents have been successfully used for the synthesis of diaryl and divinyl ditellurides. For the first time such a reaction was used by Petragnani [24] for the synthesis of diphenyl ditelluride. Later a number of aromatic ditellurides **1** has been prepared in 15–80% yield by reaction of Grignard reagents with elemental tellurium in THF, followed by oxidation of the intermediate products with air oxygen without preliminary hydrolysis.[58-60]

However, this method of the preparation of diaryl ditellurides yield in preparative value to the method based on using of lithioarenes. Indeed, aro-



16



18

17

$$\mathrm{ArMgBr + Te} \xrightarrow{\mathrm{THF}} \mathrm{ArTeMgBr} \xrightarrow{\mathrm{O_2}} \mathrm{Ar_2Te_2}$$

1

Ar = 3-FC_6H_4,[58] 4-FC_6H_4,[58] 4-BrC_6H_4,[58] 2-ClC_6H_4,[58] 2-MeC_6H_4,[58,60] Ph,[58,59] 4-MeC_6H_4,[58,59] 4-$MeOC_6H_4$,[60] 4-$OCH_2CH_2OC(Me)C_6H_4$,[60] 1-$C_{10}H_7$[60]

matic Grignard reagents containing such radicals as 2-fluoreMnyl, 2-naphthyl, 2,5-diphenylphenyl, 3-methylphenyl, 2-fluorophenyl, 4-methoxyphenyl, as well as alipathic magnesiumorganic reagents (BuMgCl, $C_5H_{11}MgBr$, $C_8H_{17}MgBr$) do not react with tellurium. Furthermore, only THF may be used as the reaction media, because no insertion of Te into the C-Mg bond was observed in diethyl or dibutyl ether.

A reaction analogous to those considered above also allowed the synthesis of divinyl ditellurides **19**[54,61] (yields 58–68%).

$$\mathrm{RCH{=}CH(R^1)MgX + Te \longrightarrow RCH{=}CH(R^1)TeMgBr \xrightarrow{O_2} [RCH{=}CH(R^1)]_2Te_2}$$

19

R^1 = H:R = Ph, Me, H; R = H, R^1 = Me

2.2 From Organyl Halides and Sodium Ditelluride

A principal method for the preparation of aliphatic ditellurides R_2Te_2 **14** is the reaction of organyl halides with sodium ditelluride. The latter reagent is obtained starting from elemental tellurium and the following reducing systems: (1) rongalite in water-alkali solution;[62,63] (2) sodium in liquid ammonia,[20,49,64-70] DMF,[71,72] HMPTA, *N*-methylpyrrolidone[71] or in THF in the presence of a catalytic amount of naphthalene;[73] (3) sodium hydride in DMF;[74,75] (4) sodium borohydride in ethanol[76-78] or in DMF;[79] (5) lithium triethylborohydride;[53] (6) hydrazine hydrate[59,80] or phenylhydrazine[81] in the presence of NaOH; (7) thiourea *S*,*S*-dioxide.[82] When sodium ditelluride generated by electrochemical reduction of tellurium is used, excellent yields of dialkyl ditellurides are achieved.[83-85] Usually alkyl bromides or iodides are employed as the alkylating agents.

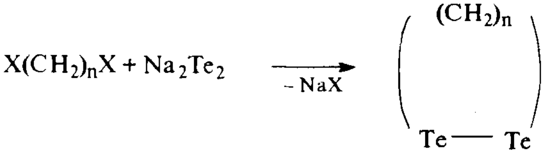
$$RX + Na_2Te_2 \xrightarrow[-NaX]{} R_2Te_2$$

14

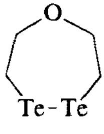
R = Me,[20,53,64,66,67,69,78,83,84] Et,[66,68,73,81,83] Pr,[73,81,83] *i*-Pr, [53,81,83] $MeOCH_2CH_2$,[73] Bu,[62,73,81,83] *i*-Bu,[83] C_5H_{11},[81,83] $Me_2CHCH_2CH_2$,[82] C_6H_{13},[79,83] *c*-C_6H_{11},[83] CH_2SiMe_2Pr[83] $EtO_2C(CH_2)_3$,[74] C_7H_{15},[83] $Me(CH_2)_4CHMe$,[82] $PhCH_2$,[65,66,83,84] $MeO_2C(CH_2)_5$,[74] C_8H_{17},[82,83] C_9H_{19},[79,83] CH_2SiMe_2Ph,[83] $MeO_2C(CH_2)_7$,[74] $C_{10}H_{21}$,[79,83] $C_{11}H_{23}$,[82] $MeO_2C(CH_2)_9$,[74] $C_{12}H_{25}$,[63,83] $\underline{CH_2(CH_2)_3CHO}(CH_2)_6$,[82] $CH_2(CH_2)_5CH{=}CH(CH_2)_7CO_2H$[77]

It should be pointed out that according to a report,[83] application of the method with electrochemical generation of sodium ditelluride allows one to prepare an unsymmetric ditelluride, namely a cyclohexylmethyl derivative in more than 60% yield.

The synthesis of the cyclic ditellurides **20**[72,83] and **20a**[83] has been accomplished by coupling of sodium ditelluride with the corresponding dihaloalkanes.



20



20a

n = 3 (20%[83]), 4 (11%[72]), 5 (26%[83]), 6 (30%[83])

However, attempts to prepare cyclic ditellurides starting from sodium ditelluride and α,α-dichloro-*o*-xylene or phthaloyl chloride failed.[72] The only products of these reactions were described earlier[86,87] as the cyclic tellurides, 3,4-benzo-1-telluracyclopentane and 3,4-benzo-1-telluracyclopentane-2,5-dione (tellurophthalic anhydride), respectively.

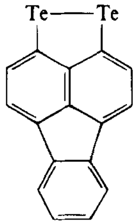
Reactions of sodium ditelluride with appropriate aryl halides have rarely been applied in the synthesis of aromatic ditellurides **1**. In this case, sodium ditelluride was generated either from the elements in DMF,[71,88-91] HMPTA [44,71,92,93] and *N*-methylpyrrolidone,[71] or by reduction of tellurium with sodium hydride in DMF.[75] Interaction between thus obtained of sodium ditelluride with aryl halides leads to diaryl ditellurides in relatively low yields (1–40%).

$$\mathrm{ArX + Na_2Te_2 \xrightarrow[-NaX]{} Ar_2Te_2}$$

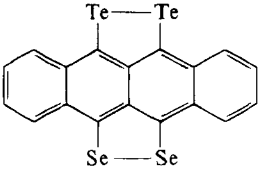
1

X = Cl, Br, I; Ar = Ph, 1-$C_{10}H_7$, 2-$C_{10}H_7$, 9-anthryl,[71] 2-(3-chloropyridyl)[75]

Under similar conditions various *peri*-dihalides may be converted to the corresponding *peri*-bridged cyclic ditellurides **6**,[44] **21**[89,90] and **22**[88] in poor yields (5–22%).



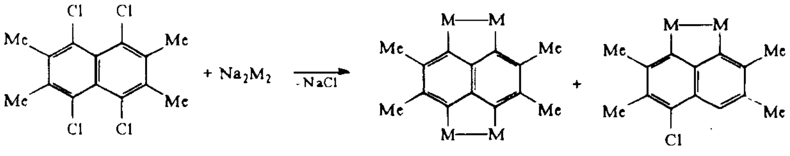
21



22

The reactions of sodium ditelluride with *peri*-aromatic tetrahalides are somewhat complicated.[91,92] Owing to the increase in reductive properties of sodium dichalcogenides Na_2M_2 (M = S, Se, Te) in the order S ≤ Se ≤ Te the products of the partial reduction of the tetrachloride **23**, the heterocycles

25 were formed in appreciable amount along with the expected heterocycles **24**. The yield of tetrachalcogenonaphthalenes **24** decreases and that of dichalcogenonaphthalenes **25** increases when going from sulfur to tellurium.



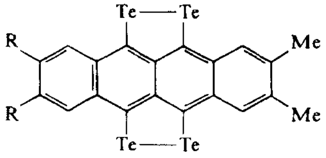
23

24

M = S 19 %
M = Se 11.6 %
M = Te 6 %

25

M = S 21.7 %
M = Se 25.9 %
M = Te 30.8 %



26

R = H, Me

In a similar way the reaction between sodium ditelluride and dimethyl- and tetramethyltetrachloroanthracene in DMF leads to both the tetratellurides **26** and the reduction products of the starting polychloroanthracenes.[91]

Recently a novel approach to the preparation of aromatic ditellurides **1** based on the reaction of aryl halides with sodium hydrotelluride NaTeH in DMF was developed.[94] The latter reagent was generated by reduction of Te with $NaBH_4$. As compared with the method in which sodium ditelluride is used as the tellurium-containing nucleophile, this approach possesses an obvious advantage, affording in most cases high yields of ditellurides **1** (60–94%). As is the case with other nucleophilic substitution reactions, electronacceptor substituents in the aromatic rings increase whereas electronodonor ones decrease the reactivity of aryl halides.

$$\mathrm{ArX + NaTeH \xrightarrow{DMFA/80\text{-}90^\circ C} Ar_2Te_2}$$

1

X = Cl, Br, I; Ar = Ph, 4-ClC_6H_4, 4-BrC_6H_4, 4-$PhCOC_6H_4$, 4-$MeCOC_6H_4$, 3-$MeCOC_6H_4$, 4-$OHCC_6H_4$, 2-pyridyl

However, *p*-carboxy- and *p*-carbethoxyphenyl bromide gave only trace amounts of ditellurides, and *p*-iodoaniline did not react at all.[94] In the case of *m*- or *o*- (but not *p*-) bromo(chloro)benzaldehydes and *p*-nitroiodobenzene as substrates a competing reduction of functional groups takes place. The latter process leads to bis(3-hydroxy)phenyl, bis(2-hydroxyphenyl) and bis(4-aminophenyl) ditelluride in 86%, 93% and 60% yield, respectively. It was suggested[94] that in the case of *p*-nitroiodobenzene, the substitution of I by HTe represented the first stage of a process yielding $ArTe^-$ which then reduced the nitro group.

2.3 Reduction of Monoorganyltellurium Halides and Reductive Dealkylation of Alkylaryltellurium Dihalides

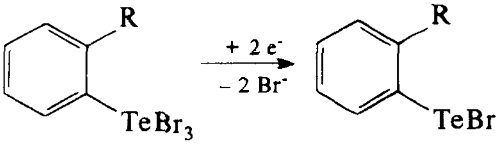
Of the two types of monoorganyltellurium halides known in tellurium-organic chemistry, RTeHal and $RTeHal_3$, the former group of compounds is only occasionally used for the synthesis of diorganyl ditellurides. At the same time, aryltellurium trihalides and, especially, aryltellurium trichlorides $ArTeCl_3$, **27**[3,4] serve as convenient synthons for the synthesis of diaryl ditellurides **1**. The synthesis of the latter compounds is performed by treatment of **27** with various reducing agents, in particular $Na_2S{\cdot}9H_2O$,[95-101] $K_2S_2O_5$ ($Na_2S_2O_5$),[103-114] Na_2SO_3,[114] $NaHSO_3$,[115,116] hydrazine hydrate,[117-119] zinc dust in ethanol,[104,120,121] thiourea *S*,*S*-dioxide[122] and others. Treatment of phenyltellurium trichloride with 4-methylphenylsulfonylhydrazide also gives rise to diphenyl ditelluride.[123] The corresponding reaction with phenylselenium trichloride leads to phenylselenosulfonates $PhSeSO_2R$.[123]

The majority of these reducing agents is used in aqueous solution, while the reduction with sodium sulfide nonahydrate is carried out in the molten reagent. From this it is inferred that not only aryltellurium trihalides, but also the products of their hydrolysis, arenetellurenic acids ArTe(O)OH are subject to reduction reactions. It should be noted that attempts at controlled

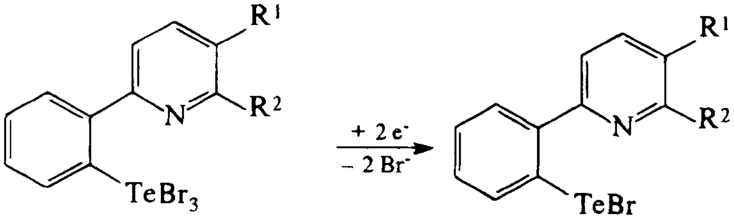
$$\underset{\mathbf{27}}{ArTeCl_3} \xrightarrow[-6\ Cl^-]{+6\ e^-} \underset{\mathbf{1}}{Ar_2Te_2}$$

Ar = 2-thienyl,[119] C_6F_5,[120,121] 4-ClC_6H_4,[98] 4-BrC_6H_4,[98,117] 3-FC_6H_4,[98] 4-$Me_3SiC_6H_4$,[113] 2-$O_2NC_6H_4$,[116] Ph,[107-109,117,122,123] 2-MeC_6H_4,[122] 4-MeC_6H_4,[107,108,110,117] 4-$MeOC_6H_4$,[95,98-100,104,105,108,110,112,117,118,122] 4-$MeSC_6H_4$,[98] 4-$EtOC_6H_4$,[95,98,99,100,102,105,108,110,112,114,115,117] 2-Me-4-$MeOC_6H_3$,[104] 3-Me-4-$MeOC_6H_3$,[104,117] 3-HO-4-$MeOC_6H_3$,[102] 2,4-$(MeO)_2C_6H_3$,[102] 3,4-$(MeO)_2C_6H_3$,[98] 4-$AcOC_6H_4$,[98] 4-$PrOC_6H_4$,[98] 4-$BuOC_6H_4$,[98] 4-$MeCONHC_6H_4$,[105,106] 2-MeCONH-5-MeC_6H_3,[101] 2-MeCONH-5-*t*-BuC_6H_3,[101] 2-MeCONH-5-ClC_6H_3,[101] 1-$C_{10}H_7$,[97] 2-$C_{10}H_7$,[96] 2-PhC_6H_4,[111] 4-$PhOC_6H_4$,[95,98,100,103,108] 4-$PhSC_6H_4$,[97] 2-$PhSC_6H_4$[97]

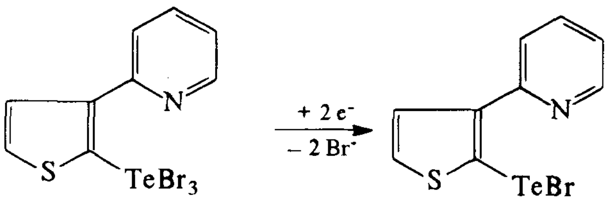
reduction of $ArTeCl_3$ to arenetellurenyl chlorides ArTeCl failed. However, if an aryltellurium trichloride contains an *o*-substituent which can stabilize the arenetellurenyl halide formed through intramolecular Te←N(O) coordination such a process becomes possible.[15,16,38,50,51,116]



R = NO_2,[116] CH_2NMe_2,[50] $CHMeNMe_2$[51]



$R^1 = R^2 = H$,[15] $R^1 + R^2 = (CH)_4$[16]



Arylsilicon hydrides when used as reducing agents behave peculiarly in this reaction.[124] At room temperature and in the molar ratio $ArTeCl_3:Ph_nSiH_{4-n}$ = 4:3 diaryl ditellurides **1** are formed in 70–95% yield. When the reduction is carried out in boiling benzene in the molar ratio 2:1, diaryltellurium dichlorides **28** (80–95%) and elemental tellurium were found as products.

$$Ar_2Te_2 \xleftarrow[\text{r. t.}]{Ph_nSiH_{4-n}} ArTeCl_3 \xrightarrow[80\text{-}90^\circ C]{Ph_nSiH_{4-n}} Ar_2Te_2Cl_2 + Te$$

1 **28**

Ar = Ph, $4\text{-}MeOC_6H_4$, $4\text{-}EtOC_6H_4$; n = 1, 2

Analogous results were obtained with the hydrides $(C_6H_{13})_3SiH$ and Ph_2MeSiH.[124]

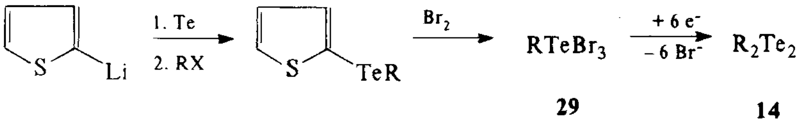
Reduction of organyltellurium trihalides is of less important for the synthesis of dialkyl ditellurides **14**. It has been mainly used for the preparation of functionalized ditellurides **14**.[104,125-129] These compounds were usually prepared by coupling organic substrates containing multiple bonds with tellurium tetrachloride.[126-129] Subsequent reduction of the intermediate trichlorides can be performed with the usual reagents, such as $K(Na)_2S_2O_5$, $Na_2S_2O_3$ and $Na_2S\cdot 9H_2O$.

$$RTeCl_3 \xrightarrow[-6\,Cl^-]{+6\,e^-} RTeTeR$$

14

R = CH_2CO_2H,[125] $CH(Me)CO_2H$,[104] $CH_2CHOCH_2CH_2CH_2$,[127] $PhC(Cl){=}C(Ph)$,[129] $CH_2C(Me)(OCOPh)CH_2Cl$,[126] $CH_2CH(OCOPh)CH(Me)Cl$,[126] $CH_2CH(OCOPh)CMe_2Cl$,[126] $CH_2CH(NHPh)CH_2OCOPh$;[126] $CH_2CH(OCOR^1)CH_2Cl$[126]: [R^1 = Me, MeCH=CH, PhCH=CH, Ph]; $R^1CH(OR^2)CH_2$[127]: [R^2 = Me: R^1 = Bu, *s*-Bu, *i*-Bu, Ph, C_6H_{13}, $PhCH_2$, HOC_9H_{18}, $C_{10}H_{21}$, $C_{14}H_{29}$; R^1 = Et: R^2 = $PhCH_2$, $C_{10}H_{21}$; R^2 = *i*-Pr, R^1 = $C_{10}H_{21}$]; $MeO_2CCH_2CH_2CH(OMe)CH_2$,[127] $CHCH(OMe)CH_2CH_2CH_2CH_2$;[127] $R^1CH(OAc)CHR^2$[128]: [R^2 = H: R^1 = Pr, Bu, Ph, OAc; R^1 = R^2 = Me]; $CHCH(OAc)CH_2CH_2CH_2$,[128] $CHCH(OAc)CH_2CH_2CH_2CH_2$,[128] $(AcO)_2CHCH_2$[128]

An example of the application of this reduction for the preparation of simple dialkyl ditellurides **14** is the preparation of these compounds from the corresponding alkyltellurium tribromides **29**[130] as shown in the Scheme below. Unfortunately, the synthetic potential of this preparation remained practically unexplored.



It should be noted that many organyltellurium trichlorides containing C_{sp^3}-Te bonds eliminate elemental tellurium under the reduction conditions.[126,131-133] These tellurium trichlorides **30** are usually obtained by electrophilic addition of $TeCl_4$ to the corresponding alkenes. Reduction of 4-hydroxyphenyltellurium trichloride also results in the elimination of tellurium[105] while under the conditions of phase-transfer catalysis this reaction leads to the corresponding ditellurides.

$R^1CH(Cl)-CH(R^2)TeCl_3 \longrightarrow R^1CH=CHR^2$

30

$R^1 = C_8H_{17}$; $R^2 = H$,[132,133] D;[132,133] $R^2 = H$, $R^1 = C_6H_5CH_2OCH_2$,[126] 4-$ClC_6H_4OCH_2$;[126] $R^1 = R^2 = Me$,[132,133] $R^1 + R^2 = (CH_2)_3$,[133] $(CH_2)_4$,[131,133] $(CH_2)_6$[133]

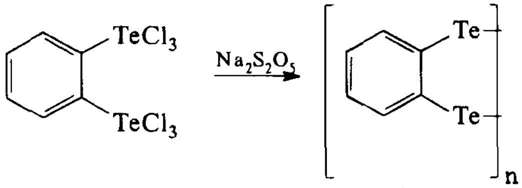
The addition of $TeCl_4$ to simple alkenes and subsequent reduction of the so formed 2-chloroalkyltellurium trichlorides **30** with aqueous sodium sulfide gives rise to elemental tellurium and alkenes. Their configuration is opposite to that of the starting alkene.[132,133] For instance, (*E*)-2-butene upon such treatment converts to a mixture of (*Z*)- and (*E*)-isomers in the ratio 97:3.

Reduction of bis(tellurium trichlorides) has been for the preparation of the polymeric ditellurides **31**,[125,134,135] **32**,[136,137] **33**[113] and **12**.[47]

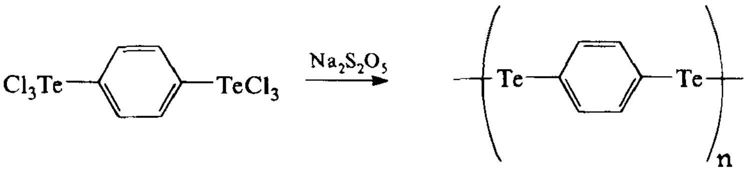
Although reduction of organyltellurenyl halides RTeHal leads to the corresponding ditellurides in high yields[15,16,138,139] the preparative value of this reaction is rather small. The only exception is the reduction of 2-(chlorotellurenyl) azobenzene to the corresponding ditelluride.[140]

$$Cl_3TeCH_2TeCl_3 \xrightarrow{K_2S_2O_5} (\text{-}CH_2Te\text{-}Te\text{-})_n$$

31

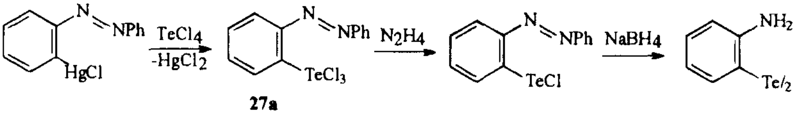


32



33

2-(Trichlorotelluro) azobenzene **27a** may be reduced directly to bis-(2-aminophenyl) ditelluride, but in this case excess sodium borohydride is required.[141]



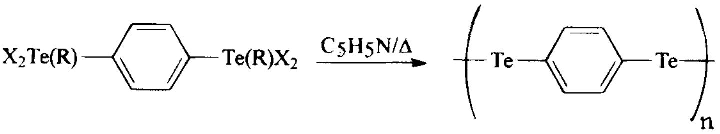
27a

σ-Telluranes of the Ar(R)TeHal$_2$ type may be used for the preparation of diaryl ditellurides **1**.[25,28,29,113,142] Refluxing of the latter compounds in pyridine solution leads to diaryl ditellurides **1** in moderate yields. The reaction proceeds probably *via* intermediate formation of the arenetellurenyl halides **34** which eliminate a halogen molecule giving rise to ditelluride **1**.[25]

$$ArTe(R)X_2 \xrightarrow[-C_5H_5N^+\,RX^-]{C_5H_5N/\Delta} \left[ArTeX\right] \xrightarrow[-X_2]{} Ar_2Te_2$$

34 **1**

R = Bu, Me; X = Cl, Br; Ar = 2-thienyl, 4-MeC$_6$H$_4$, 4-BrC$_6$H$_4$, 2-OHCC$_6$H$_4$, 2-MeCOC$_6$H$_4$



33

R = Me, Et; X = Cl, Br

The synthetic potential of this reaction is rather limited considering that the initial alkyl aryl tellurides must be obtained by alkylation of the corresponding arenetellurolate anions, which can be directly oxidized to the required diaryl ditellurides (see Sect. 2.1).

2.4 Other Methods

The reactions considered in this section are of limited usefulness. Some of these allow one to prepare only dialkyl derivatives while others lead to aromatic ditellurides. Another group of reactions leading to diorganyl ditellurides *via* fission of C_{sp^3}-Te bonds in alkyl aryl tellurides or the respective σ-telluranes is also discussed in this Section.

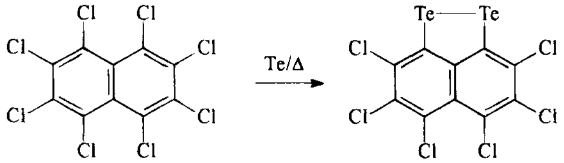
A few diorganyl ditellurides have been obtained by interaction between a tellurium mirror and free radicals generated by various methods.[143-147] This reaction is often used for the preparation of bis(trifluoromethyl) ditelluride[148-150] in moderate yields and the corresponding symmetrical tellurides are encountered as by-products.

$$R^{\bullet} + Te \longrightarrow R_2Te_2$$

R = Me, CF_3, Ph

The synthesis of 3,4,5,6,7,8-hexachloro-1,2-ditelluranaphthalene starting from Te and octachloronaphthalene[152] is probably the only example of the high-temperature synthesis of a ditelluride.

A general method for the preparation of various organic diselenides is the basic hydrolysis of alkyl and aryl selenocyanates.[153] Among the ditellurides, only dibenzyl ditelluride has been obtained in such a similar manner.[154] The reaction of benzyl tellurocyanate with sodium hydroxide in methanol leads to this ditelluride in low yield (29%). A more preferable



way to this compound is the use of hypophosphorous acid which increases the yield up to quantitative.

$$(PhCH_2)_2Te \xleftarrow{H_3PO_2} PhCH_2TeCN \xrightarrow{NaOH} (PhCH_2)_2Te_2$$

A number of aliphatic ditellurides **14** has been obtained in moderate yields (34–56%) upon treatment of aliphatic aldehydes with hydrogen telluride in acidic media.[155] Hydrogen telluride was generated *in situ* by hydrolysis of aluminum telluride. The corresponding primary alcohols were isolated as by-products.

$$RCHO \xrightarrow[THF]{Al_2Te_3/H_2O,\ H^+} (RCH_2)_2Te_2 + RCH_2OH$$

$R = Me_3C$, $c\text{-}C_6H_{11}$, C_7H_{15}, $PhCH_2$, $PhCH_2CH_2$

Under the same conditions aromatic aldehydes are reduced to benzyl alcohols. The reaction with ketones gives rise to the corresponding ditellurides in low yields. Thus, dicyclohexyl ditelluride has been obtained from cyclohexanone in only 11% yield.[155] Apparently, an earlier report[156] about the preparation of telluroketones by treatment of ketones with a mixture of HCl and H_2Te (similar to the preparation of thio- and selenoketones) is erroneous.

A particular approach to the synthesis of bis(pentafluoroethyl) ditelluride (**14**, $R = C_2F_5$) has been proposed.[7,8] It involves the reaction of tetrafluoroethene and cyclic dications $[Te_n(AsF_6)_2]^{2+}$ ($n = 4, 6$). The by-products of this reaction are the corresponding symmetrical tellurides and a number of additional poorly identified compounds the amounts of which vary depending on the reaction conditions.

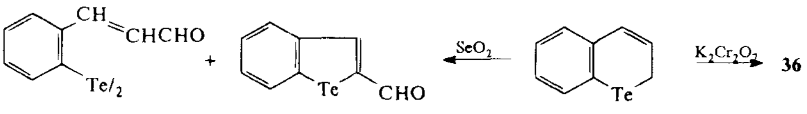
$$CF_2{=}CF_2 + Te_n(AsF_6)_2 \longrightarrow \underset{\textbf{14}}{(C_2F_5)_2Te_2} + (C_2F_5)_2Te$$

The formation of dialkyl ditellurides and dialkyl tellurides also takes place in the reaction of sterically hindered alkenes with NaTeH.[157]

It has been reported[53] that the reaction of *t*-BuMgCl with $TeCl_4$ in THF leads to a mixture of $(t\text{-}Bu)_2Te_2$ and $(t\text{-}Bu)_2Te$. While the formation of the latter compound may be explained (by analogy with the behavior of other tetraalkyltelluranes[3,4,158]) by thermal decay of tetra(*t*-butyl)tellurane, the mechanism of formation of the former is unclear.

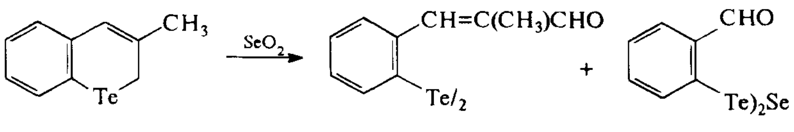
It has already been noted (see Sect. 2.2) that one of the methods for the preparation of sodium ditelluride consists in coupling the elements in dimethylformamide.[48,71,72,88-91] A detailed study of this process[159] revealed that freshly formed Na_2Te_2 reacts with the solvent leading to bis(dimethylaminocarbonyl) ditelluride the structure of which has been proven by X-ray analysis.

Some functionalized aromatic ditellurides have been obtained by reaction of tellurium-containing heterocycles with oxidants causing cleavage of the C_{sp^3}-Te bonds. Thus, oxidation of 2*H*-tellurochromenes with thallium triacetate leads to bis[2-(3-oxopropenyl)phenyl] ditelluride **35**[142] as one of the products. The same compound together with 2-formylbenzo[*b*]tellurophene **36** is formed when selenium dioxide is used as the oxidizing agent (molar ratio SeO_2/substrate = 1:1). When SeO_2 is taken in excess the only product of the reaction is the heterocycle **36**.[142] The same aldehyde is produced by oxidation of tellurochromene with $K_2Cr_2O_7$.[160]



35 **36**

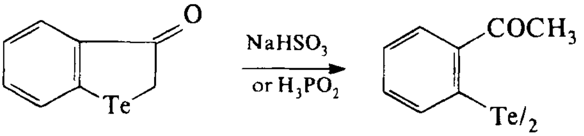
Oxidation of 3-methyltellurochromene with SeO_2 gives rise to the ditelluride **37** in more that 60% yield. The product of the insertion of selenium into the Te-Te bond, **38**, together with the ditelluride **37**, was isolated when a reduced amount of SeO_2 was used.



37 **38**

It should be noted that oxidation of tellurochromenes bearing methyl groups in 2,4,7,8-positions leads only to 2-acetylbenzo[*b*]tellurophene (in the case of 2-methyltellurochromene) or to the corresponding 2-formylbenzo[*b*]tellurophenes.[142]

Bis(2-acetylphenyl) ditelluride **1** (Ar = 2-$MeCOC_6H_4$) was formed in high yield upon treatment of telluroindoxyl with sodium bisulfite[161] or hypophosphorous acid.[162]



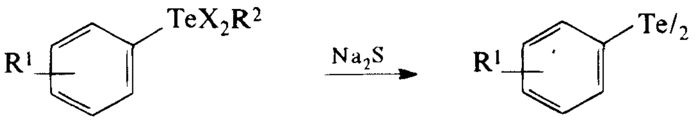
1

Cleavage of the $C_{aliph.}$-Te bond is also observed when the diethyl acetal of (4-acetylphenyltelluro)acetaldehyde is heated with mineral acids. The reaction leads to the corresponding ditelluride.[163]

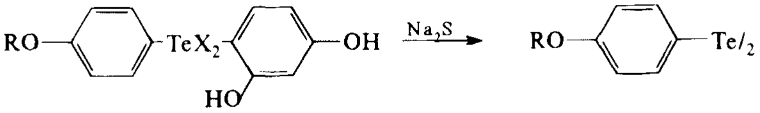
$$4\text{-}MeCOC_6H_4TeCH_2CH(OEt)_2 \xrightarrow{H^+} (4\text{-}MeCOC_6H_4)_2Te_2$$

Reduction of some alkylaryl, cycloalkylaryl[131,164,165] and diaryltellurium dihalides **39**[164] with sodium sulfide leads to the formation of aromatic ditellurides **1** owing to the cleavage of C_{sp^3}-Te and $C_{arom.}$-Te bonds. With phase-transfer catalysis the above mentioned arylphenacyltellurium dihalides when treated with $Na_2S_2O_5$ may be reduced to the corresponding aryl phenacyl tellurides.

Interaction between tellurolate anions and dihaloalkanes **40** (X = Cl, Br) leads either to the usual nucleophilic substitution of halide with an organyl-



X = Cl: R^2 = 2-Cl-*c*-C_6H_{10}: R^1 = H, 4-EtO, 4-PhO, 2,3-C_4H_4, 3,4-C_4H_4,[131] R^2 = $CH_2CH(Cl)Me$, R^1 = 3,4-C_4H_4;[165] X = Cl, Br: R^2 = $PhCOCH_2$: R^1 = 4-MeO, 4-EtO, 4-PhO[164]



39

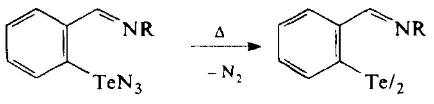
X = Cl, Br: R = Me, Et, Ph

telluro group, i.e. the products **41**[26,166-168] or the diorganyl ditellurides **1** or **14**, accompanied by the corresponding alkenes.[166-169] The direction of the reaction depends on the length of the carbon chain of the dihaloalkane and the temperature at which the reaction is carried out. At low temperature dihalomethanes (n = 1)[26,166-168] and dihalopropanes (n = 3)[166-168] give only **41** in high yields. At the same time the reaction of tellurolate anions with 1,2-dihaloethanes (n = 2),[166-169] regardless of the temperature, leads to the ditellurides **1** or **14**.

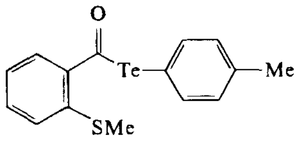
$$\underset{\textbf{41}}{RTe(CH_2)_nTeR} \xleftarrow{RTe^-} \underset{\textbf{40}}{X(CH_2)_nX} \xrightarrow{RTe^-} \underset{\textbf{1, 14}}{R_2Te_2 + C_nH_{2n}}$$

n = 1: R = Me, Ph, 2-benzo[*b*]thienyl
n = 3: R = Me, Ph

Formation of diaryl ditellurides **1** was also observed upon thermolysis of tellurenyl azides **42**[170] and UV irradiation of telluroesters **43**.[171,172] The former compounds, which are quite stable at room temperature, eliminate nitrogen upon heating, affording diaryl ditellurides in excellent yields. Unlike their thio and seleno analogs (which upon UV irradiation give the corresponding thio(seleno)xanthones) the telluroesters **43** under the same conditions form mixtures of diverse products which include diaryl ditellurides formed cleavage of Te-C=O bonds.



42



43

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

3. REACTIONS OF DIORGANYL DITELLURIDES

Due to the high and multifaceted reactivity of the ditelluride group diorganyl ditellurides serve as useful synthons in organotellurium chemistry.

3.1. Reduction

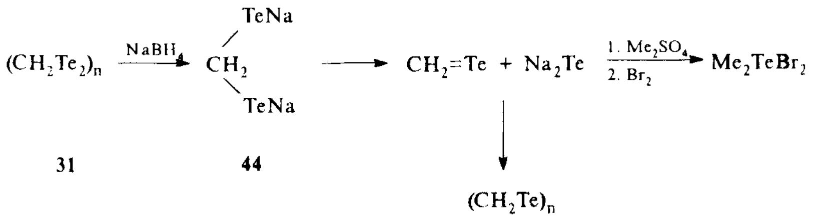
Various ditellurides may be converted to tellurolates under mild conditions when treated with strong reducing agents.

$$\underset{\mathbf{1,\ 14}}{R_2Te_2} \xrightarrow{+\,2\,e^-} RTe^-$$

Sodium borohydride in alkaline aqueous solution or in the solid state is most often used for this purpose.[25,27,28,36,56,57,69,76,77,79,101,141,172-206] The reductions are usually carried out in ethanol or its mixture with benzene, other solvents being also applicable. Reagents such as $LiAlH_4$,[54,61] $LiBEt_3H$ [34,207,208] or KBu_3HB[209] have also been successfully utilized for the reduction of ditellurides. Solutions or suspensions of highly nucleophilic tellurolate anions are formed upon reduction of organic ditellurides with lithium in liquid ammonia,[61] ether[210] or THF;[211] with sodium metal in liquid ammonia,[18,19,21,212-214] THF[215,216] (THF is also used as solvent when ditellurides are reduced with sodium amalgam), mixtures of

THF/DMF,[217] HMPTA[182] with electrochemical reduction.[218-220] The use of hydrazine hydrate[221-224] and thiourea *S,S*-dioxide[225] as reducing agents is less convenient because it requires strongly alkaline conditions. Under these conditions it is unlikely that the tellurolate anions are partly formed by the disproportionation of ditellurides under the action of alkali[226] (see also Sect. 3.4).

It is worth noting that in spite of their practical insolubility polyditellurides, namely, poly(*o*-phenylene), [136,137] poly(*p*-phenylene),[113] poly(*o*-biphenylene)[47] and poly(methylene) ditelluride,[227,228] when treated with $NaBH_4$, are smoothly reduced in ethanol to the corresponding ditellurolate anions. The methaneditellurolate anion **44** behaves in a different way than its selenium analog. Similarly to the disodium salt of 2,2-ditellurolobiphenyl,[113] this anion disproportionates in solution to sodium telluride and telluroformaldehyde. Further polymerization of the latter gives rise to poly(methylene) telluride **45**.[228]



31 **44** **45**

In view of this observation, a reaction scheme for the formation of the polymer **45** upon reduction of the polyditelluride **31** with $NaBH_4$, followed by alkylation of **44** with dibromo(diiodo)methane, which was suggested earlier[227] seems to be erroneous. Poly(methylene) telluride **45** is formed not by alkylation, but rather by disproportionation of the dianion **44**.[228]

The above described lithium and sodium tellurolates are readily oxidized by air oxygen and therefore can be used only *in situ*. These compounds were employed most often for the preparation of unsymmetrical diorganyl tellurides of various types,[3,4,158] organyl telluroesters,[3,4] compounds containing Te-element bonds[3,4] and metal complexes.[1]

The formation of tellurolates was also observed in the reaction of ditellurides with other reductants. Thus, mercury tellurolates **46** have been obtained in high yields upon shaking of a solution of the ditelluride with mercury metal.[7,8,229-231] The thermal decomposition of **46** is a convenient approach to the preparation of mercury telluride.

$$R_2Te_2 + Hg \longrightarrow \underset{\textbf{46}}{(RTe)_2Hg} \xrightarrow{\Delta} R_2Te_2 + HgTe$$

$R = C_2F_5$, Ph, 4-$EtOC_6H_4$

Interaction between ytterbium and diphenyl ditelluride in liquid ammonia leads to ytterbium derivatives of similar structure[232] which are isolated as complexes with pyridine, i.e. $(C_5H_5N)_4Yb(TePh)_2$.

It is of interest that the reaction of diphenyl ditelluride with dialkylmercury compounds gives phenyl alkyl tellurides in high yields.[229] Diarylmercury compounds do not react in such a way, and interaction of divinylmercury with diaryl ditellurides gives rise to aryl vinyl tellurides.[233]

$$Ph_2Te_2 + R_2Hg \xrightarrow{\Delta} PhTeR + Hg$$

Samarium arenetellurolates **47** have been prepared by reduction of diaryl ditellurides with samarium diiodide.[234,235] The derivatives **47** smoothly react with alkyl halides and acyl chlorides, thus allowing the preparation of alkyl aryl tellurides and aryl telluroesters in more than 70% yield.

$$Ar_2Te_2 + SmI_2 \longrightarrow \underset{\textbf{47}}{ArTeSmI_2} \xrightarrow{RX} ArTeR$$

R = Alk, COR

Diisobutylaluminium benzenetellurolate **27**, generated by treatment of diphenyl ditelluride with diisobutylaluminum hydride possesses very high nucleophilicity.[7,23,236] By its coupling with acetals, alkylsulfonates or oxiranes alkyl phenyl tellurides were obtained in high yields.[237] Reaction with α,β-unsaturated carbonyl compounds affords β-phenyl tellurocarbonyl derivatives.[236]

$$Ph_2Te_2 + (i\text{-Bu})_2AlH \xrightarrow[-H_2]{} PhTeAl(i\text{-Bu})_2$$

48

3.2 Oxidation

A propensity towards oxidative addition of halogens is a characteristic property of diorganyl ditellurides. Depending on the molar ratio of the reagents either tellurenyl halides RTeHal **34**[12,77,238-245] or organyltellurium trihalides $RTeHal_3$ **49**[3,4] may be prepared. Obviously the reactions proceed in a stepwise manner.[246] Thus, diaryl ditellurides when treated with iodine initially form arenetellurenyl iodides **34** which then convert to the charge-transfer complexes **50** and eventually give the triiodides **49**.

$$\underset{\mathbf{1}}{Ar_2Te_2} + I_2 \longrightarrow \underset{\mathbf{34}}{ArTeI} \xrightarrow{I_2} \underset{\mathbf{50}}{ArTeI \cdot I_2} \longrightarrow \underset{\mathbf{49}}{ArTeI_3}$$

Tellurenyl halides, in contrast to their sulfur and selenium analogs, are thermally and kinetically unstable and subject to rapid decomposition in the solid state and in solution. The lower the electronegativity of the halogen atom attached to tellurium the higher is the thermal stability of the tellurenyl halide.[238] On the contrary, in the case of alkanetellurenyl halides the most stable compounds are the chlorides while the iodides decompose at room temperature in few minutes.[242]

The thermal stability of tellurenyl halides is greatly enhanced by complexation with neutral ligands in type **51** compounds[3,4] or by intramolecular O(N)→Te coordination.[247-249] The complexes **50** are usually prepared by treatment of the mixture of a diaryl ditelluride and a ligand with a halogen[250-253] or thiocyanogen.[250,254]

$$\underset{\mathbf{1}}{Ar_2Te_2} + X_2 + L \longrightarrow \underset{\mathbf{51}}{ArTeX{\cdot}L}$$

X = Cl, Br, I, SCN; L = thioureas, selenoureas, $Ph_3P{=}Se$, $Ph_3As{=}O$, trimorpholinylphosphine selenide, β-picoline

Arenetellurenyl halides can also be prepared by coupling of diaryl ditellurides with aryltellurium trihalides.[255]

$$\underset{\mathbf{1}}{Ar_2Te_2} + \underset{\mathbf{49}}{ArTeX_3} \longrightarrow \underset{\mathbf{34}}{ArTeX}$$

$X = Cl, Br, I$

Diorganyl ditellurides are oxidized by chlorine,[28,29,32,33,38,67,68] bromine,[28, 33,38,50,51,96,97,99,100,108,110,112,256-258] iodine[96,97,99,108,110-112,257] and fluorine (in inert gas[259]) at ambient or low temperature to form organyltellurium trihalides $RTeHal_3$ **49**.

$$\underset{\mathbf{1,\ 14}}{R_2Te_2} + 3\,X_2 \longrightarrow \underset{\mathbf{49}}{2\,RTeX_3}$$

$X = Cl, Br, I, F$

Dibenzyl ditelluride when treated with halogens behaves anomalously. The reaction with bromine in CCl_4 leads to cleavage of both C-Te bonds with formation of benzyl bromide and tellurium tetrabromide. When an equivalent amount of bromide is used, elimination of one tellurium atom occurs and dibenzyltellurium dibromide is formed.[260]

$$C_6H_5CH_2Br + TeBr_4 \xleftarrow{2\,Br_2} (C_6H_5CH_2)_2Te_2 \xrightarrow{Br_2} (C_6H_5CH_2)_2TeBr_2 + Te$$

Sulfuryl chloride can be used instead of chlorine for the preparation of trichlorides.[24,50] Xenon difluoride[259,261,262] and chloride fluoride[261,263] as oxidizing agents have been employed for the synthesis of organyltellurium trifluorides and derivatives of hexacoordinate tellurium **52**.

By contrast, elimination of a tellurium atom and formation of diorganyltellurium difluorides instead of aryltellurium trifluorides is observed upon oxidation of diaryl ditellurides with SF_4.[264] The yields of the difluorides exceed 70%.

$$C_2F_5TeF_3 \xleftarrow[-Xe]{XeF_2} (C_2F_5)_2Te_2 \xrightarrow{ClF} C_2F_5TeClF_4$$

49 **14** **52a**

$$Ph_2Te_2 \xrightarrow[-Xe]{XeF_2} PhTeF_5 \xleftarrow[-Xe]{XeF_2} PhTeF_3$$

1 **52**

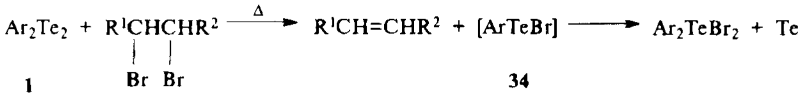
$$Ar_2Te_2 + SF_4 \longrightarrow Ar_2TeF_2 \longleftarrow Ar_2Te + SF_4$$

Elimination of one tellurium atom takes place also upon interaction between diaryl ditellurides and $TeHal_4$.[265]

$$Ar_2Te_2 + TeX_4 \longrightarrow Ar_2TeX_2 + Te$$

X = Cl, Br, I

The high halogenophilicity of diaryl ditellurides allows their employment for the dehalogenation of vicinal dibromides.[265] Reflux of an equimolar mixture of **1** and organic dihalides in toluene or acetic acid leads to the (*E*)-isomers of the corresponding alkenes in good yields. The reaction proceeds probably *via* intermediate formation of an arenetellurenyl bromide **34** with subsequent disproportionation to a diaryltellurium dibromide and elemental tellurium.



$$\underset{\mathbf{1}}{Ar_2Te_2} + R^1\underset{Br}{CH}\underset{Br}{CH}R^2 \xrightarrow{\Delta} R^1CH{=}CHR^2 + \underset{\mathbf{34}}{[ArTeBr]} \longrightarrow Ar_2TeBr_2 + Te$$

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

Dialkyl ditellurides and dialkyl disulfides enter into slow exchange reactions, the equilibrium being shifted to the left side.[266] Thus, in the case of Me_2Te_2 and Me_2S_2 the equilibrium constant is 0.047.

$$R_2Te_2 + R'_2S_2 \rightleftharpoons 2\,RTeSR'$$

Some disulfides, namely bis(thiocarbamoyl) and bis(2-benzothiazolyl) disulfide, react with diaryl ditellurides like the halogens.[267]

$$Ar_2Te_2 + R_2S_2 \longrightarrow ArTe(SR)_3$$

$Ar = Ph, 4\text{-}MeOC_6H_4;\ R = R'_2NC(S)S\ (R' = Me, Et);$ 2-benzothiazolyl

Oxidation of diaryl ditellurides with lead tetraacetate leads to aryltellurium triacetates **49** (X = OCOMe).[268-270] The existence of these derivatives in solution has been proven by ^1H NMR spectroscopy. Attempts to isolate these compounds failed owing to their tendency to hydrolysis.

The compounds **38** containing a Te-Se-Te fragment were mentioned above (see Sect. 2.4.). Other compounds **38**, namely bis(aryltelluro) selenides, have been prepared by oxidation of diaryl ditellurides with powdered selenium dioxide (molar ratio 1:0.9).[271] When the reagents were taken in equimolar amounts arenetellurenyl arenetellurinyl selenides **53** were formed.

$$\underset{\mathbf{53}}{ArTeSeTe(O)Ar} \xleftarrow{SeO_2} Ar_2Te_2 \xrightarrow{SeO_2} \underset{\mathbf{38}}{(ArTe)_2Se}$$

Among the reactions leading to **38** and their sulfur analogs are also insertion of chalcogens into the Te-Te bond of diorganyl ditellurides upon ultrasonic irradiation[272] and oxidation of organylchalcogenochalcogenolate anions.[273] These anions are generated by addition of sulfur or selenium to lithium organyltellurolates in solution.

$$R_2Te_2 + M \longrightarrow \underset{\mathbf{38}}{(RTe)_2M} \xleftarrow[2.\ O_2]{1.\ H_2O} RTeMLi \xleftarrow{M} RTeLi$$

M = S, Se

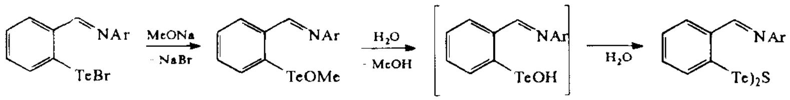
White phosphorus reacts with diaryl ditellurides in much the same way as the chalcogens. The relatively unstable tris(*p*-anisyltelluro)phosphine **54**

(Ar = 4-MeOC$_6$H$_4$) has been prepared in 37% yield by interaction of the reagents in acetone under N$_2$.[274]

$$(4\text{-}MeOC_6H_4)_2Te_2 + P_4 \longrightarrow (4\text{-}MeOC_6H_4Te)_3P$$

54

There exists scant information concerning the oxidation of diorganyl ditellurides by oxygen or compounds containing active oxygen. Thus, the disappearance of characteristic intense red color of ditellurides observed upon UV irradiation of their alcohol solutions has been explained[275] by formation of arenetellurenic acid anhydrides ArTe$_2$O **55**. However, no chemical or spectral evidence for their evidence for their structure has been given. Compounds **55a** are the first representatives of areneltellurenic acid anhydrides isolable as such and whose stability is due to intramolecular N →Te coordination.[170] The structure of **55a** has been proven by chemical as well as spectral (^{1}H NMR and mass spectroscopy) methods. The synthesis of **55a** is shown in the scheme below.



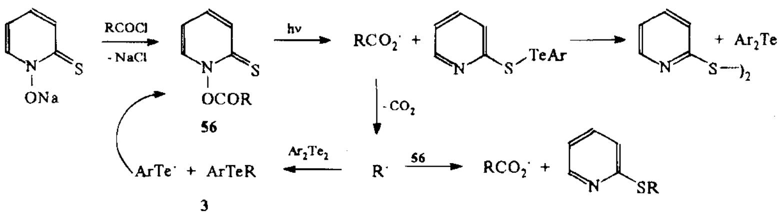
55a

It has been suggested[276-278] that the oxidation of arylalkenes with air oxygen, organic hydroperoxides or peroxy acids in methanol or acetic acid leading to vicinal dimethoxy and diacetoxy derivatives, respectively, proceeds *via* intermediate formation of arenetellurinic acid anhydrides [ArTe(O)]$_2$O.

It has been stated that the same compounds are formed during oxidation of diaryl ditellurides in solution by oxygen.[279] However, no attempts at their preparative isolation yet have been undertaken.

3.3. Reactions with Radicals and Carbenes

Under the action of highly reactive intermediates, such as free radicals, carbenes, or dehydrobenzene the Te-Te bond of diorganyl ditellurides may be easily broken. These reactions provide convenient, at times exclusive methods for the synthesis of certain diorganyl tellurides. Various alkyl aryl tellurides ArTeR **3** have been obtained by decarboxylation of mixed anhydrides of *N*-hydroxy-2-pyridinethione and aliphatic or alicyclic carboxylic acids **56** followed by the reaction of the radicals formed with the diaryl ditellurides.[280,281] The anhydrides **56** are usually generated *in situ* from the corresponding acyl chlorides and the sodium salt of the thione. Their reactions with diaryl ditellurides under UV irradiation give rise to the tellurides **3** in good yields.



A free-radical mechanism governs also the reaction of diphenyl ditelluride with an alkylmercury chloride or a dialkylmercury initiated by UV irradiation.[282,283] The reaction is completely inhibited in the dark or in the presence of radical trapping compounds, namely, azobis(isobutyronitrile). The yields of alkyl aryl tellurides are rather high (45–100%) and increase when from primary to tertiary alkyl groups. However, diphenyl ditelluride does not react with phenyl- or cyclopropylmercury chloride, probably due to the strength of the C-Hg bond in these compounds.

$$Ph_2Te_2 \xrightarrow{h\nu} PhTe^{\cdot}$$

$$PhTe^{\cdot} + RHgCl \longrightarrow RTeHgCl + R^{\cdot}$$

$$Ph_2Te_2 + R^{\cdot} \longrightarrow \underset{\mathbf{3}}{PhTeR} + PhTe^{\cdot}$$

It has been suggested that the interaction between diphenyl ditelluride and trialkylboranes in the presence of oxygen also proceeds by a radical mechanism giving rise to alkyl tellurides **3** in 64–99% yield.[284] A mixture of two phenyl alkyl tellurides was obtained when unsymmetrical trialkylboranes were used in this reaction.

$$R_3B \xrightarrow[-\,R_2BO_2^{\cdot}]{O_2} R^{\cdot} \xrightarrow{Ph_2Te_2} \underset{\mathbf{3}}{PhTeR} + PhTe^{\cdot} \xrightarrow{R_2BO_2^{\cdot}\,,\,O_2} PhTeO_2BR_2 + PhTeO_2^{\cdot}$$

Unlike diaryl disulfides, diaryl ditellurides react with diazonium salts in the absence of a catalyst. Thus, the interaction between Ph_2Te_2 and *p*-bromophenyldiazonium bromide in aqueous acetone affords an equimolar mixture of phenyl *p*-bromophenyl telluride and the corresponding tellurium dibromide.[285]

$$\underset{\mathbf{1}}{Ph_2Te_2} + ArN_2Br \xrightarrow[-\,N_2]{} PhTeAr + PhTeBr_2Ar$$

It has been proposed that diaryl ditellurides should display a pronounced propensity towards one-electron reduction reactions, e.g. reactions with aryldiazonium cations according to the following scheme

$$\begin{aligned} Ar_2Te_2 + Ar^1N_2X &\longrightarrow ArTe^{\cdot} + Ar^{1\cdot} + ArTeX + N_2 \\ ArTe^{\cdot} + Ar^{1\cdot} &\longrightarrow ArTeAr^1 \\ ArTeX + Ar^1N_2X &\longrightarrow ArTeX_2Ar^1 + N_2 \end{aligned}$$

In the oxidation of diaryl tellurides with Cu(II) salts diaryltellurium dihalides had been isolated as single products of reactions between diaryl ditellurides and aryldiazonium halides in the presence of copper(II) halides.[285,286] The high yields of the final products, the availability of the starting materials and the possibility of their structural variation allow one to consider this reaction as the most convenient method for the preparation of unsymmetrical diaryltellurium dihalides. It should be noted that an arylation of diaryl disulfides with aryldiazonium chlorides can only be carried out in the presence of $CuCl_2$ which promotes the formation of free radicals.[287,288]

Arylation of dialkyl ditellurides has been achieved by treatment with aryldiazonium tetrafluoroborates and potassium acetate in the presence of 18-crown-6.[289] The corresponding alkyl aryl tellurides **3** have been isolated in 21–63% yield.

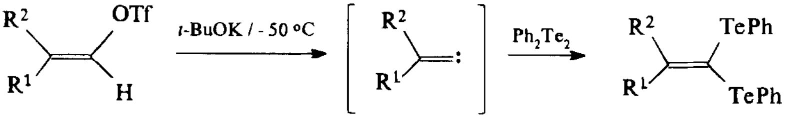
$$Et_2Te_2 + ArN_2BF_4 \xrightarrow[\text{18-crown-6}]{\text{KOAc}} \underset{\mathbf{3}}{ArTeEt}$$

On the other hand, reaction of 2-nitrophenyldiazonium tetrafluoroborate with diethyl ditelluride leads to di(2-nitrophenyl) telluride[101] instead of the expected ethyl 2-nitrophenyl telluride.

The carbene generated by thermal decomposition of diazomethane readily insert into the Te-Te bond of diaryl[26,290,291] or dialkyl ditellurides[292] giving rise to di(organyltelluro)methanes **41** in 60–100% yield.

$$\underset{\mathbf{1,\ 14}}{R_2Te_2 + CH_2N_2} \xrightarrow[-N_2]{} \underset{\mathbf{41}}{(RTe)_2CH_2}$$

The unsaturated carbenes behave similarly. Thus, carbenes **57** insert into the Te-Te bond of diphenyl ditelluride[293] to give low stable tellurides **58** in 26–30% yields.

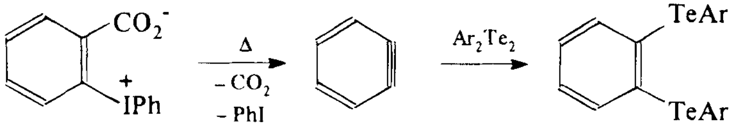


57 **58**

$R^1 = R^2 = Me$; $R^1 + R^2 = (CH_2)_5$

However, the reaction of diaryl ditellurides with dichlorocarbene generated from phenyl(trichloromethyl)mercury leads to products of unidentified structure.[290]

Tellurides containing two tellurium atoms in the molecule, namely 1,2-bis(aryltelluro)benzenes **59**, have been prepared by coupling diaryl ditellurides containing electron donor substituents and dehydrobenzene generated by thermal decomposition of 2-phenyliodoniobenzenecarboxylate.[294,295] Diphenyl and di(1-naphthyl) ditelluride do not react with dehydrobenzene.



59

3.4. Reactions with Nucleophiles

Reactions of diorganyl ditellurides with nucleophiles have been scantily studied. Under action of alkali diaryl ditellurides disproportionate to sodium tellurolates and sodium salts of arenetellurenic acids.[226] Treatment of this reaction mixture with alkyl halides leads to alkyl aryl tellurides **3** in more than 50% yield.

Nucleophilic addition of cyanide anion to a tellurium atom in diaryl ditellurides leads to aryl tellurocyanates **60** and tellurolate anions **2**.[296] The latter are readily oxidized to the initial ditellurides. The equilibrium in this reaction is shifted to the left side, so that the corresponding aryl tellurocyanates **60** have been isolated in no more than 20% yield.

$$\underset{\mathbf{1}}{Ar_2Te_2} + CN^- \rightleftharpoons \underset{\mathbf{60}}{ArTeCN} + \underset{\mathbf{2}}{ArTe^-} \xrightarrow{O_2} \mathbf{1}$$

Attempts to increase the yields of **60** by varying the reaction conditions such as the concentration of cyanide anion, the temperature, etc. were unsuccessful.

Reactions of diorganyl ditellurides with organolithium reagents are well studied; they are often used for the preparation of diorganyl tellurides. Rupture of the Te-Te bond of the starting ditellurides under the action of lithiumorganic reagents leads to diorganyl tellurides.[34,297-299]

$$R_2Te_2 + R^1Li \longrightarrow RTeR^1 + RTeLi$$

1, 14

R = Ar, Fc, Alk; R^1 = Ar, Alk

The yields of the diorganyl tellurides in this reaction are low because of the high nucleophilicity of the organolithium reagents which cleave not only Te-Te, but also Te-C_{sp^3},[300-302] Te-C_{sp^2}[300,302,303] and Te-C_{Ar} bonds.[300,304-306]

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

1, 14

The concentration of lithium- and magnesiumorganic reagents can be determined by a method[299] based on the reaction of these reagents with diorganyl ditellurides. The latter compounds which are intensively colored both in the solid state and in solution rapidly react with the organometal even at low temperature and sharply change their colour to pale yellow when the reaction is completed.

In the case of diaryl ditellurides and arylmagnesium halides the main direction of the process is cleavage of the Te-Te bond. It allows one to prepare diaryl tellurides in moderate yields.[297]

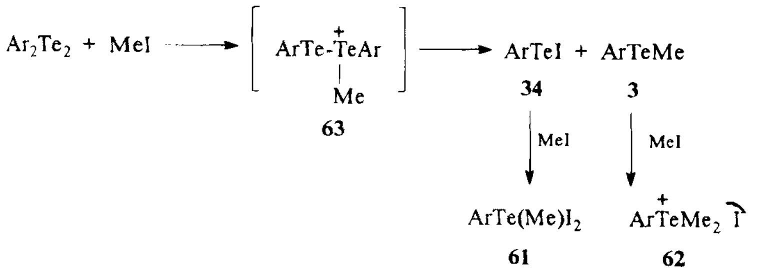
$$Ar_2Te_2 + Ar^1MgX \longrightarrow ArTeAr^1 + ArTeMgX$$

1

Ar^1 = Ph: Ar = 4-$MeOC_6H_4$, 4-$PhOC_6H_4$; Ar = 4-$EtOC_6H_4$, Ar^1 = 1-$C_{10}H_7$

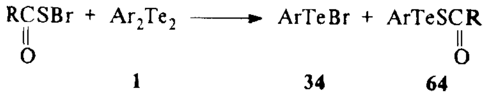
3.5. Reactions with Electrophiles

Few reactions of diorganyl ditellurides with electrophilic reagents have been described. Treatment of diaryl ditellurides with excess methyl iodide leads to an equimolar mixture of arylmethyltellurium diiodide **61** and aryldimethyltelluronium iodide **62**.[102,105,110] The first stage of the reaction is probably methylation of the ditelluride leading to the intermediate aryltelluromethylaryltelluronium iodide **63** which decomposes subsequently to an aryl methyl telluride **3** and an arenetellurenyl iodide **34**. Subsequent interaction between the compounds formed and the excess of methyl iodide gives rise to **61** and **62** as shown in the scheme below.



The reaction of diorganyl ditellurides with phenylacetylene in the presence of methyl iodide which leads to alkyl phenylethynyl tellurides as final products proceeds most probably *via* formation of telluronium salts **63**.[307,308]

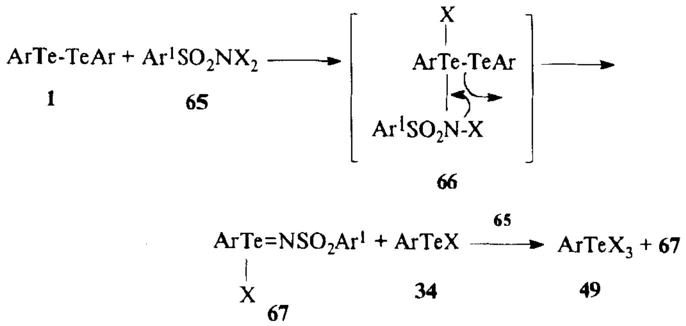
Electrophilic thiocarboxylation of diaryl ditellurides with acylsulphenyl bromides leads to arenetellurenyl bromides **34** together with earlier unknown derivatives of dicoordinated tellurium, namely arenetellurenyl thiocarboxylates **64**. The compounds were isolated in 20–70% yield.[309]



$$\underset{\textbf{1}}{RC(=O)SBr} + Ar_2Te_2 \longrightarrow \underset{\textbf{34}}{ArTeBr} + \underset{\textbf{64}}{ArTeSC(=O)R}$$

It should be noted that in contrast to their selenium analogs **64** are not desulfurized by triphenylphosphine.[310]

Similarly to diaryl disulfides and diaryl diselenides, diaryl ditellurides readily react with *N*,*N*-dihalogenoarenesulfonamides **65**.[311] Apparently, the reaction involves the intermediate formation of **66**, followed by further decomposition to haloanhydrides of arene-*N*-arylsulphonyliminotellurenic acids **67** and arenetellurenyl halides **34**. The reaction of the latter with excess **65** gives rise to **49** and **67**.



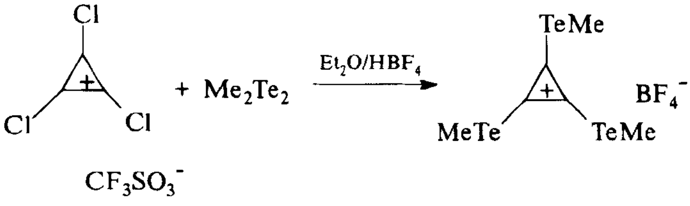
$$\underset{\mathbf{1}}{\mathrm{ArTe{-}TeAr}} + \underset{\mathbf{65}}{\mathrm{Ar^1SO_2NX_2}} \longrightarrow \left[\underset{\mathbf{66}}{\begin{matrix}\mathrm{X}\\ |\\ \mathrm{ArTe{-}TeAr}\\ |\\ \mathrm{Ar^1SO_2N{-}X}\end{matrix}}\right] \longrightarrow$$

$$\underset{\mathbf{67}}{\begin{matrix}\mathrm{ArTe{=}NSO_2Ar^1}\\ |\\ \mathrm{X}\end{matrix}} + \underset{\mathbf{34}}{\mathrm{ArTeX}} \xrightarrow{\mathbf{65}} \underset{\mathbf{49}}{\mathrm{ArTeX_3}} + \mathbf{67}$$

X = Cl, Br

This proposal is supported by the fact that the interaction between arenetellurenyl halides (generated *in situ* from diaryl ditelluride and halogen) and *N*,*N*-dihalogenosulfonamides **65** results in the formation of **67**.

Apart from the above reactions, fission of Te-Te bonds has been observed with dimethyl ditelluride where the action of trichlorocyclopropenylium salts results in the formation of salts of the tris(methyltelluro)cyclopropenyl cation **68**.[312] A second, poorly characterized product is probably the unstable methanetellurenyl chloride.



68

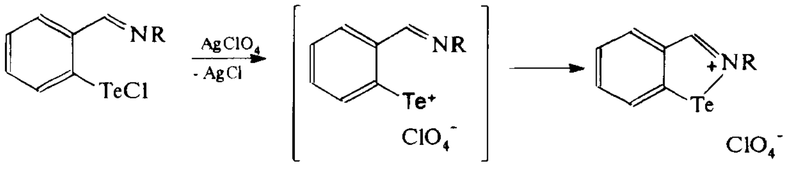
The cation **68**, in contrast to analogous chalcogen containing cations is rather unstable and rapidly loses elemental tellurium when heated above 90°C. It is worth nothing that aromatic ditellurides unlike diaryl disulfides and diselenides do not react with trichlorocyclopropenyl cations.

Diorganyl ditellurides also react with nitrosyl perchlorate or tetrafluoroborate forming tellurenyl cation salts **69** isolated as stable complexes with tributylphosphine.[313]

$$R_2Te_2 + NO^+X^- \xrightarrow[-NO]{} \left[\; RTe^+X^- \;\right] \xrightarrow{Bu_3P} \left[\; RTePBu_3 \;\right]^+ X^-$$

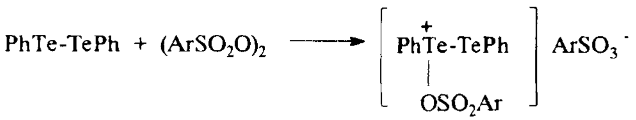
69

The synthesis of the cations **70**, especially those stabilized by intramolecular Te→N coordination, may be performed in a simpler manner by exchange reaction of the corresponding tellurenyl halide with $AgBF_4$ or $AgClO_4$. The preparation of benzoisotellurazolium perchlorates starting from *o*-(chlorotellurenyl)benzalanilines and $AgClO_4$ illustrates this approach.[170,314]



70

It has recently been shown[315] that the reaction of diphenyl ditelluride with *p*-nitrobenzylsulfonyl peroxide results in the formation of the highly reactive electrophilic intermediates **71**.

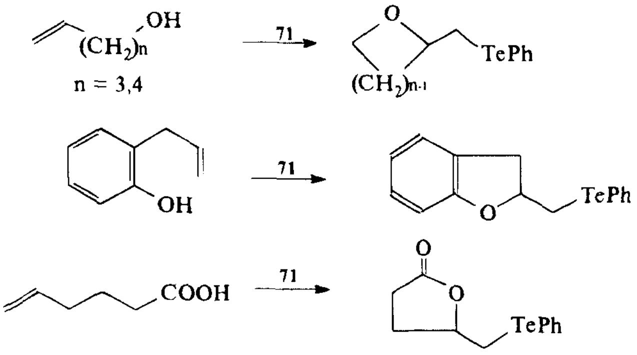


$$PhTe\text{-}TePh + (ArSO_2O)_2 \longrightarrow \left[\; \overset{+}{Ph}Te\text{-}TePh \atop \mid \atop OSO_2Ar \;\right] ArSO_3^-$$

71

$Ar = 4\text{-}O_2NC_6H_4$

Interaction between the cations **71** and unsaturated alcohols or acids leads to the formation of tetrahydrofuran, tetrahydropyran or lactone rings to which a phenyltelluromethyl group is attached (the yields 52–81%). Some examples of such processes are presented below.



3.6. Reactions Leading to Derivatives with Te-Element Bonds

Compounds containing Te-metal bonds with metal = Hg, Al, Sm, Yb have already been mentioned (see Sect. 3.1.). Reactions of diorganyl ditellurides leading to compounds containing Te-element bonds (where the element belongs to the Vth or IVth group of the periodic system) are considered in this Section.

Exchange reactions of diorganyl ditellurides with tetraorganyldipnictogens proceed under mild conditions and result in the formation of compounds with Te-element bonds **72** where the element is P,[207,316-318] As,[316,318] Sb[318-323] or Bi.[318,324-328]

$$R_2Te_2 + R^1_4El_2 \rightleftharpoons RTeElR^1_2$$

72

R = Me, Ph, 4-MeC$_6$H$_4$; E = P: R^1 = Me, *i*-Pr, *t*-Bu; E = As: R^1 = Me; E = Sb: R^1 = Me, Et; E = Bi: R^1 = Me, Pr, Ph

The position of the equilibrium in the above reactions depends mostly on the nature of the VA group element. While the equilibrium constants of the reactions of Me_2Te_2 and Me_4E_2 (E = P, As) are 63 and $3\ 10^{-2}$, respectively,[318] the equilibrium of the reactions of the same ditelluride with Me_4Sb_2 and Me_4Bi_2 are completely shifted to the right.[318] The positions of the equilibrium correlate with the bulk of the substituent at the VA group element. For example, interaction between $(4\text{-}CH_3C_6H_4)_2Te_2$ and $(i\text{-}C_3H_7)_4P_2$ or $(t\text{-}C_4H_9)_2P_2$ leads to **72**.[207,311]

Reactions of diorganyl ditellurides with antimonyorganic polymers result in formation of **73** in which two organyltelluro groups are linked to the antimony atom.[323]

$$(R^1Sb)_x + R_2Te_2 \longrightarrow \underset{\textbf{73}}{R^1Sb(TeR)_2}$$

$x = 4$, n; $R^1 = 2,4,6\text{-}Me_3C_6H_2$, Me, Et; R = Ph, $4\text{-}MeC_6H_4$

Organoelement hydrides from the IVA group cleave the Te-Te bond of diaryl ditellurides under mild conditions. Thus, interaction between diaryl ditellurides and triphenyltin hydride at 60–70 °C gives rise to aryltriphenylstannyl tellurides **74**[12] in 60–70% yield.

$$\underset{\textbf{1}}{Ar_2Te_2} + Ph_3SnH \xrightarrow[-H_2]{} \underset{\textbf{74}}{ArTeSnPh_3} \qquad \underset{\textbf{74a}}{ArTeER_3}$$

E = Ge, Sn, Pb

Since the present review is confined to the chemistry of diorganyl ditellurides only those approaches to compounds containing Te-element bonds are considered where diorganyl ditellurides serve as their precursors. It may be mentioned, however, that an extensive series of **74a** has been obtained *via* exchange reactions of tellurolate anions with halides R_3EX (E = Ge, Sn, Pb[187]).

The reactions of diaryl ditellurides with dialkylmercury compounds leading to dialkyl tellurides have already been described.[229] An analogous reaction between diethyl ditelluride and bis(triethylsilyl)mercury results in the formation of ethyltriethylsilyl telluride **74** in more than 70% yield.[329]

$$Et_2Te_2 + (Et_3Si)_2Hg \xrightarrow[-Hg]{\Delta} \underset{\textbf{74}}{EtTeSiEt_3}$$

3.7. Complexation Reactions

Similar to other diorganyl dichalcogenides, diorganyl ditellurides when reacting with metal salts may form metal complexes with either retention or cleavage of Te-Te bonds. Ditellurides form complexes with Hg(II),[231,330] Cu(I),[140,330-332] Cu(II),[140] Ag(I)[333] and Pd(II)[333] salts under mild conditions. The data concerning the stoichiometry of the complexes with Hg(II) and Cu(I) salts are quite contradictory. Whereas, L·MX_n (where L is the ditelluride molecule) stoichiometry has been generally attributed to these complexes,[140,231,331,332] the composition L·$2MX_n$ has been found in the case of some Cu(I) compounds.[330] McWhinnie has pointed out[330] that the varying composition of the complexes is due to the fact that different solvents (ethanol or propionitrile) were used in their preparation. Complexes of bis(2-aminophenyl) ditelluride with $AgNO_3$ and $PdCl_2$ have the L·MX_n composition[333] while the Schiff bases prepared from the same amine react with these salts (as well as with $SnCl_4$) forming complexes of the L·$2MX_n$ stoichiometry.[333] A spectral study[330] revealed that interaction between Cu(I) or Hg(II) halides and an equimolar mixture of two different diaryl ditellurides leads to complexes when the ligand is the unsymmetrical ditelluride.

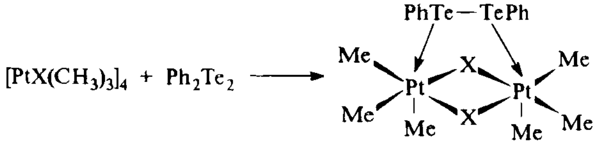
$$\mathrm{Ar_2Te_2 + Ar^1_2Te_2 + MX_n \longrightarrow ArAr^1Te_2 \cdot 2MX_n}$$

Ar = Ph, Ar^1 = 4-$EtOC_6H_4$, M = Hg: X = Cl, Br, n = 2; M = Cu: X = Cl, Br, n = 1

The 1:1 complex of diphenyl ditelluride and uranium pentachloride has been obtained by a ligand exchange reaction.[334,335]

$$\mathrm{UCl_5 \cdot Cl_2C{=}C(Cl)COCl + Ph_2Te_2 \xrightarrow[-\,Cl_2C{=}C(Cl)COCl]{} UCl_5{\cdot}Ph_2Te_2}$$

The Te-Te bond does not cleave in the reaction of diphenyl ditelluride with tetrameric halotrimethylplatinum; the reaction leads to a bridged metal complex **75**.[336]

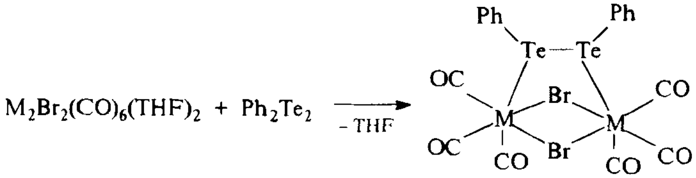


75

X = Cl, Br

It should be noted that unlike their tellurium analogs, diphenyl disulfide and diphenyl diselenide do not react with the tetranuclear platinum complexes.[336]

The Te-Te bonds of diorganyl ditellurides are also preserved in the reaction of diaryl ditellurides with halogenocarbonyl derivatives of Re(I)[337] and Mn(I).[338] According to an X-ray study[337] the Re or Mn atoms in **76** are bound to bridged bromine atoms as well as to Te-Te bridges. The length of the Te-Te bond in the rhenium complex is 2.794 Å[337] differing slightly from that of the free ligand diphenyl ditelluride (2.712 Å).[339]



76

M = Re, Mn

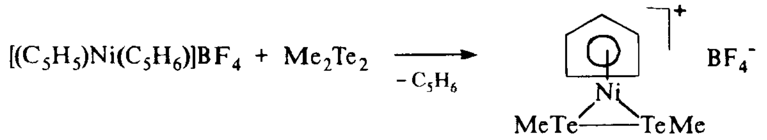
According to ligand exchange reactions[338] of diphenyl dichalcogenide complexes **76** (M = Mn) their kinetic stability increases in the order S < Se < Te.

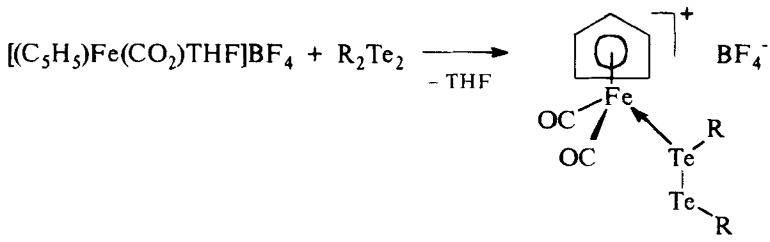
Interaction between diaryl ditellurides and iridium(I) chlorocarbonyl is accompanied by fission of the Te-Te bond.[340]

$$[Ir(CO)(Cl)L_2] + Ar_2Te_2 \longrightarrow [Ir(CO)(Cl)L_2(TeAr)_2]$$

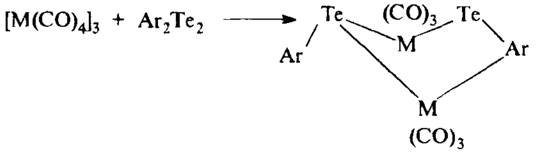
$L = PPh_3$

Other reactions not affecting the Te-Te bonds in diorganyl ditellurides are known; they are presented in the scheme below.[341,342] However, the bonding of the tellurium-containing ligands in these complexes has not been sufficiently characterized.





The rupture of Te-Te bonds takes place most often as a result of oxidative addition reactions of diorganyl ditellurides with substrates containing a metal center in its lowest oxidation state. The interaction between diaryl ditellurides and iron[120,343-345] or ruthenium[343] carbonyls leads to dinuclear compounds **77** where the metal atoms are bonded by bridging aryltellurium groups.



77

$[Ru(CO)_2(TePh)_2]_n$

78

M = Fe: Ar = Ph,[343] C_6F_5,[120,345] 4-$MeOC_6H_4$;[344] M = Ru: Ar = Ph[343]

However, in the case of ruthenium, the main products of the reaction are polymers **78**.[343] According to a mass-spectral study,[343] the strength of the chalcogen-iron bonds in the complexes **77** decreases in the order Te > Se > S.

At the same time no cleavage of the Te-Te bond occurs when the chromium pentacarbonyl complex with THF reacts with dimethyl ditelluride to give the complex **79**.[346]

$$Cr(CO)_5{\cdot}THF + Me_2Te_2 \xrightarrow[-THF]{} Cr(CO)_5{\cdot}Te_2Me_2$$

79

The product of the reaction of iron carbonylnitrosyl with bis(4-methoxyphenyl) ditelluride has a structure with bridged tellurium atoms similar to that of **77**.[347]

$$2\ Fe(NO)_2(CO)_2 + Ar_2Te_2 \xrightarrow[-CO]{} [Fe(NO)_2TeAr]_2$$

$Ar = 4\text{-}MeOC_6H_4$

The synthesis of arylselenium and aryltellurium carboxylic esters by reaction of the corresponding diaryl ditellurides (diselenides) with carbon monoxide in the presence of $Co_2(CO)_8$ has been described.[63,348] The proposed reaction mechanism includes an intermediate formed by cleavage of the chalcogen-chalcogen bonds by the cobalt carbonyl. No reactions of diaryl ditellurides with this carbonyl have been studied.

Reactions of diaryl ditellurides with iron,[349,350] molybdenum[351] and chromium[352] cyclopentadienyl carbonyls usually lead to complexes of three different types. Under mild conditions at ambient temperature, the mononuclear complexes **80** are formed. More severe conditions (reflux in benzene or heating to 60 °C in toluene) allow one to obtain the binuclear complexes **81**. These same compounds are also accessible by heating or UV irradiation of the mononuclear derivatives **80**. Usually only two isomers of the five possible for the binuclear complexes **81** are formed. Thus, two X-ray characterized complexes **81** have been isolated upon treatment of iron cyclopentadienyl carbonyl with bis(4-ethoxyphenyl)ditelluride.[350]

$$[CpM(CO)_n]_2 + Ar_2Te_2 \longrightarrow \underset{\mathbf{80}}{[CpM(CO)_nTeAr]} + \underset{\mathbf{81}}{[CpM(CO)_{n-1}TeAr]_2}$$

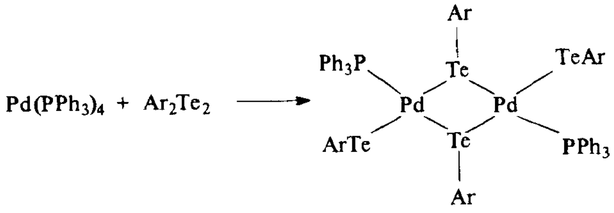
M = Fe: n = 2: Ar = Ph,[349] $4\text{-}EtOC_6H_4$;[350] M = Mo, Cr: n = 3: Ar = Ph[351,352]

Finally, the fully decarbonylated products **82** and **83** have been found to be characteristic for molybdenum[351] and chromium[352] derivatives. They were obtained by reflux of the reagents in xylene[351] or toluene.[352]

$$\underset{\mathbf{82}}{[CpMo(TePh)_2]_x} \qquad \underset{\mathbf{83}}{[CpCr(TePh)]_2Te}$$

Formation of **80** and **81** was also observed when molybdenum pentamethylcyclopentadienyl carbonyl reacted with diphenyl ditelluride.[353]

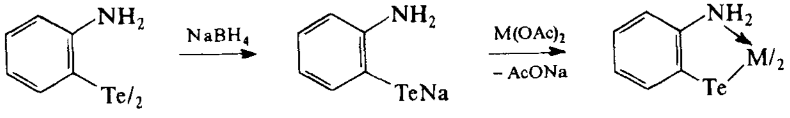
The complexes **84**, containing both bridged and terminal aryltellurium ligands, have been obtained by reaction of diaryl ditellurides with the triphenylphosphine palladium complex.[119]



84

Ar = 4-EtOC$_6$H$_4$, 2-C$_4$H$_3$S

Recently the synthesis of a number of telluriumorganic compounds, which may be considered as potential synthons for the preparation of various chelate complexes containing the MN$_2$Te$_2$ unit, has been performed. However, zinc and cadmium 2-aminobenzenetellurolates,[354] prepared as shown in the scheme below, are probably the only representatives of such chelates known today.



M = Zn, Cd

3.8. Extrusion of Tellurium

The decrease in the Te-Te and Te-C bond energies as compared with those of the analogous bonds formed by the lower chalcogens[355] conditions the relative ease of extrusion of one or both tellurium atoms from diorganyl ditellurides.

The elimination of a tellurium atom from dibenzyl ditelluride proceeds quite readily, especially upon UV irradiation.[260,356] It has been suggested[356] that during the first step of this transformation a photoinduced formation of organyltellurenyl radicals RTe$^\bullet$ takes place. The reaction rate increases substantially when triorganylphosphines are present in the solution. The phosphine tellurides **85** formed in this reaction readily decompose to the starting initial phosphine and elemental tellurium. A scheme illustrating the above transformation is given below.[356]

$$R_2Te_2 \xrightarrow{h\nu} RTe^{\bullet}$$

$$RTe^{\bullet} + R^1_3P \longrightarrow [R^1_3PTeR]^{\bullet}$$

$$[R^1_3PTeR]^{\bullet} \longrightarrow \underset{\mathbf{85}}{R^1_3PTe} + R^{\bullet}$$

$$R^1_3PTe \longrightarrow R^1_3P + Te$$

$$R_2Te_2 + R^{\bullet} \longrightarrow R_2Te + RTe^{\bullet}$$

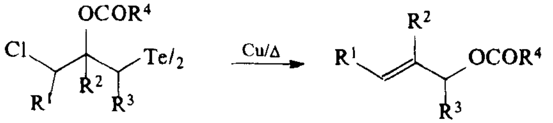
Tellurium is also easily eliminated from dibenzyl ditelluride upon heating to 120 °C,[260] while thermal elimination of selenium from dibenzyl diselenide proceeds only at 150 °C. By contrast, the thermally stable diaryl ditellurides withstand without decomposition prolonged boiling in xylene.[265] In the solid state their decomposition starts only at temperatures higher than 250 °C.[107,265] The complete decomposition of bis(4-alkoxyphenyl) ditellurides to the corresponding tellurides and tellurium proceeds only at 300 °C.[265] A preparatively more convenient method for the conversion of ditellurides to tellurides is reflux of the former compounds with copper in dry dioxan.[58,113,357-362] Heating of diaryl disulfides in *N,N*-dimethylacetamide in the presence of copper powder leads to copper(I) arenethiolates.[363]

$$\underset{\mathbf{1}}{(RC_6H_4)_2Te_2} \xrightarrow[-Te]{Cu/\Delta} (RC_6H_4)_2Te$$

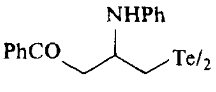
R = 4-Br,[357,358] 3-Br,[358] 4-Cl,[357,358] 3-Cl,[358] 4-F,[358] H,[357,359,360] 4-CF_3,[361] 4-Me,[357] 3-Me,[358] 4-NH_2,[362] 4-MeO,[357] 3-MeO,[360] 4-OH,[361] 4-MeNH,[362] 4-EtO,[357,358] 4-Me_2N,[362] 4-Me_3Si,[113] 4-$NO_{[2]}$,[358] 2,4,6-Me_3,[360] 3,4-C_4H_4,[358] 3-Me-4-H_2N,[362] 2-Me-4-H_2N,[362] 3-EtO-4-H_2N,[362] 3-F_3C-4-H_2N,[362] 3,5-Me_2-4-H_2N,[363] 3-MeOCO-4-H_2N,[362] 4-PhNH,[362] 2-C_6H_5[58]

Unlike diaryl ditellurides **1**, the ditellurides **86** when treated with copper powder, give (in 58–97% yield) dechlorotellurated compounds, namely substituted allyl benzoates, instead of the expected tellurides. The ditelluride **86a** is inert toward the action of copper powder.[126]

It should be noted that a Pd/C catalyst may also be used for the conversion of ditellurides to the corresponding tellurides.[362]



86



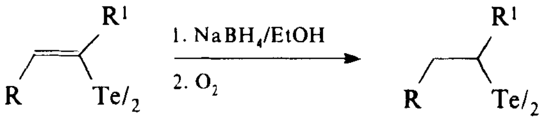
86a

Freshly prepared Raney nickel causes a more profound transformation of diaryl ditellurides. The latter when heated with this catalyst in diglyme eliminate both tellurium atoms to form the corresponding biaryls in high yields.[117]

Some known pyrolytic reactions successfully used in the preparation of sulfur and selenium heterocycles can not be applied in telluriumorganic chemistry due to the relatively low strength of the C-Te and Te-Te bonds. The synthesis of benzo[*b*]thiophene (85% yield[364]) as well as that of selenophene together with benzo[*b*]selenophene[365] is possible by high temperature reactions of diphenyl disulphide and diselenide with acetylene and propargyl alcohol, respectively. However, diphenyl ditelluride under similar conditions giving rise mainly to elemental tellurium. Benzo[*b*]tellurophene was only isolated in trace amounts (1–2%[364]).

3.9. Reactions of Functional Groups

Transformations of functional groups of diorganyl ditellurides with retention of the Te-Te bond have been scarcely studied. Thus, bis(4-acetylaminophenyl) ditelluride hydrolyzes under the action of NaOH in ethanol to give bis(4-aminophenyl) ditelluride[106] and the diethyl ketal of bis(2-acetylphenyl) ditelluride under acid conditions readily converts to bis(2-acetylphenyl) ditelluride in high yield.[29] Similarly to other acids containing dicoordinated tellurium atoms,[3,4,158] ditellurosalicylic acid affords the diacyl dichloride when treated with dichloromethyl butyl ether.[28] Finally, the reduction of C=C double bonds of divinyl ditellurides has been described.[61]



Acknowledgments

Financial support by the Russian Fund for Fundamental Research (grant 93-03-5000) and INTAS (grant 94-4675) is appreciated.

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