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# Organotellurium Compounds in Organic Synthesis

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The review gives a systematic account of the survey of data on the application of organic compounds of tellurium in the synthesis of hydrocarbons, halogeno-derivatives, and carbonyl compounds.
The bibliography includes 94 references.

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## I. INTRODUCTION

The chemistry of organotellurium compounds has developed extremely vigorously during the last 10–15 years. It is sufficient to point out that the number of studies published during these years exceeded the number of publications during the entire preceding 130 years of the development of organotellurium chemistry. The synthesis of organotellurium compounds, their reactivity, and their structures in the crystalline state and in solution have been considered in a number of monographs[1,2] and reviews.[3–11] As the chemistry of organic compounds of tellurium has developed, their applications in preparative organic chemistry for the synthesis of various classes of organic compounds have expanded vigorously, although in this respect tellurium compounds are so far inferior to organoselenium compounds.[12–14]

The wide variety of applications of tellurium compounds in organic synthesis is based on a number of their specific features, among which the following may be included: (1) the ease of converting tellurium(II) derivatives into tellurium(IV) derivatives and vice versa; (2) the high nucleophilicity of the $RTe^-$ and $Te^{2-}$ anions; (3) the much higher stability of derivatives of tetracoordinate tellurium (σ-telluranes) of the type $RTeX_3$, $R_2TeX_2$, and $Ar_4Te$ compared with the analogous sulphur and selenium compounds; (4) the relative ease of eliminating the tellurium atom from tellurium(II) derivatives.

A series of new data on the application of organic derivatives of tellurium in the synthesis of a wide variety of organic compounds are described systematically and surveyed in the present review.

## II. SYNTHESIS OF HYDROCARBONS

One of the most thoroughly investigated applications of organotellurium compounds in preparative organic chemistry involves their use for the preparation of hydrocarbons. This applies in the first place to unsaturated compounds and biaryls. The only reaction described hitherto in which organotellurium reactants have been used to synthesise benzene derivatives is based on the oxidation of arylhydrazines by di(*p*-methoxyphenyl)tellurium oxide,[15,16] leads to arenes in comparatively low yields, and can hardly be regarded as of preparative importance.

### 1. Saturatated Hydrocarbons

Saturated hydrocarbons are readily formed in 70–90% yields on reduction of organyltellurides (I) with triphenyltin tetrahydroborate in benzene at 20–80 °C [17] (judging from the analogous reaction with selenides,[17] $R^2TeSnPh_3$ is probably a side product):

$$\underset{(I)}{R^1TeR^2} \xrightarrow{Ph_3SnH} R^1H;$$

$R^2$=Me, $R^1$=$C_{12}H_{25}$; $R^1$=Ph, $R^1$=$C_{12}H_{23}$, $C_9H_{19}CH_2CH$ (Me), $C_8H_{17}CH$ (OH) $CH_2$, $C_8H_{17}CH$ (OCOMe) $CH_2$, Me $(CH_2)_2$ CH (OH) CH $(CH_2)_2$ Me.

The reduction does not involve functional groups such as OH, OCOR, and C=O, which makes it possible to obtain also the corresponding substituted derivatives in high yields.[17]

It is noteworthy that diorganyltellurium dichlorides are reduced more readily than tellurides, but the reason for this is not clear since tellurium dichlorides are reduced via the formation of tellurides:[17]

$$RTeCl_2Ph \xrightarrow{Ph_3SnH} RH;$$
$$R=C_{12}H_{25},\ C_9H_{19}CH_2CH\ (Me).$$

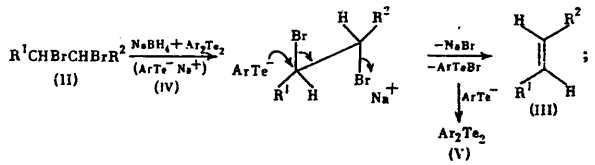
### 2. Olefins and Acetylenes

Various types of organotellurium compounds are used to obtain unsaturated compounds—olefins and acetylenes: derivatives of monocoordinate tellurium—tellurolate[18] and phosphorotellurolate anions;[19,20] derivatives of dicoordinate tellurium—diaryltellurides,[21,22] phenoxatellurin,[23,24] and diaryl ditellurides;[25] derivatives of tricoordinate tellurium—telluroxides,[12,26–29] and tellurium imides;[30,31] derivatives of tetracoordinate tellurium (σ-telluranes)—diaryltellurium dihalides[32] and organyltellurium trihalides.[32,33]

#### *(a) Catalytic Reactions with Particiation of Derivatives of Monocoordinate Tellurium*

One of the most important and promising applications of organotellurium reagents in organic synthesis involves the possibility of using them under catalytic conditions. The application of diaryl ditellurides (V) [for di(2-thienyl) ditelluride as an example] as catalysts of the debromination of vicinal dibromides (II) in the presence of $NaBH_4$, which leads to the unsaturated compound (III) in high yields,

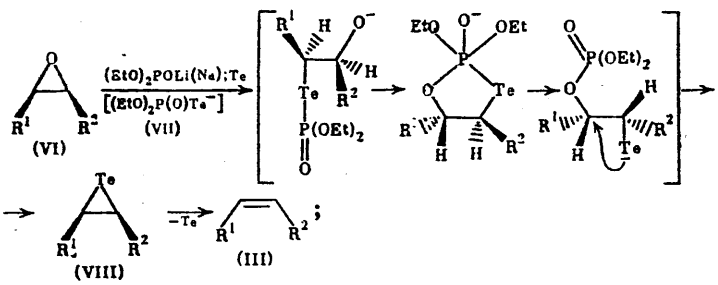
may serve as a typical illustration:[18]



Ar = 2-thienyl; $R^2$ = Ph, Me, $CO_2Et$; $R^1$ = H, $R^2$ = $C_6H_{17}$; $R^1$ = Ph, $R^2$ = COOH; $R^1$ = H, $R^2$ = COOH; —$(CH_2)_6$—; (II) = 5α, 6β-dibromocholestan-3β-ol.

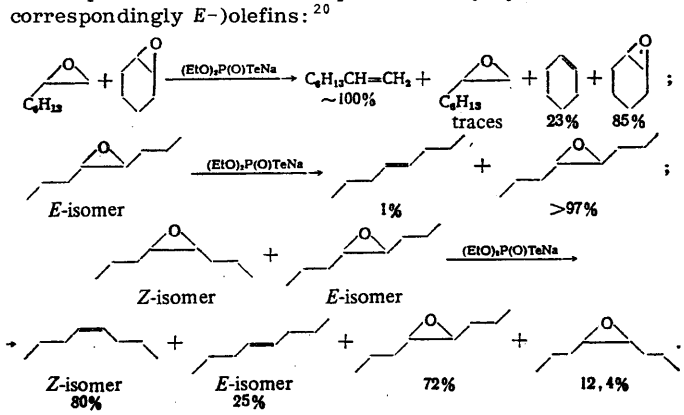
It has been suggested[18] that the main active species in this catalytic cycle is the tellurophenoxide anion (IV), formed on reduction of a diaryl ditelluride, whose halogenophilic attack on the bromine atom is accompanied by the anti-elimination of a second halogen atom with formation of the olefin (III). The course of this reaction (carried out in an atmosphere of nitrogen) is readily followed from the change in the colour of the solution from dark red (ditelluride) to colourless (tellurophenoxide anion).

Alkali metal *OO*-diethyl phosphorotellurolates (VII), among which the lithium derivative is the most active, are extremely effective reagents, which make it possible to convert the epoxides (VI) into olefins in high yields.[19,20] The deoxygenation of the epoxides as well as the dehalogenation of dibromides described above are carried out catalytically by adding tellurium (0.1–0.25 mmol) to a solution of diethyl phosphite (1–2 mmol) and epoxide (1 mmol).[19] The probable reaction mechanism includes the formation of unstable epitellurides (VIII):[20]



$R^1 = C_6H_{13}$, $R^2$ = H; $R^1 = C_8H_{17}$, $R^2$ = H; $R^1 = C_{18}H_{37}$, $R^2$ = H.

Compared with their selenium analogues, compounds (VII) are much more reactive and participate in catalytic deoxygenation reactions much more actively. Among epoxides, the terminal derivatives react most readily and among these the most reactive are the *Z*-isomers, which has been confirmed by the competing reactions shown below, with participation of the corresponding 1 : 1 mixtures of the epoxides. The deoxygenation with the aid of *OO*-diethyl phosphorotellurolates is stereospecific and *Z*- (or *E*-)epoxides always yield the *Z*- (or correspondingly *E*-)olefins:[20]



*(b) Derivatives of Dicoordinate Tellurium*

When a series of different diaryl tellurides (I, $R^1 = R^2 = Ar$) react with vicinal dibromides (II), the olefins (III) and diaryltellurium dihalides (IX) are obtained in high yields:[21]

$$\underset{\text{(II)}}{R^1CHXCHXR^2} + \underset{\text{(I)}}{Ar_2Te} \rightarrow \underset{\text{(III)}}{R^1CH{=}CHR^2} + \underset{\text{(IX)}}{Ar_2TeX_2};$$

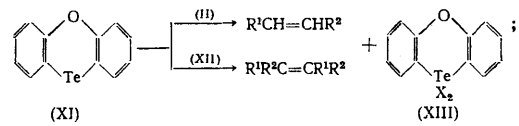
X=Br, Cl.

The reaction of diphenyl telluride (I, $R^1 = R^2$ = Ph) with 1,2-dibromoethane (II, $R^1 = R^2$ = H, X = Br) under mild conditions (refluxing for 30 min) affords a 74% yield of 1,2-bis(diphenyltelluronia)ethane dibromide (X), whose recrystallisation from glacial acetic acid produces diphenyltellurium dibromide (IX) and ethylene. The possibility of the intermediate formation of telluronium derivatives of type (IX) in reactions with participation of the substituted dibromides (II), arising in this connection, has not so far been investigated:

$$2Ph_2Te + CH_2BrCH_2Br \rightarrow \underset{\text{(X)}}{Ph_2\overset{+}{T}eCH_2CH_2\overset{+}{T}ePh_2}\ 2Br^- \xrightarrow{AcOH,\Delta} \underset{\text{(IX)}}{Ph_2TeBr_2} + CH_2{=}CH_2.$$

Another dehalogenating agent in the series of derivatives of dicoordinate tellurium is phenoxatellurin (XI).[23,24] Its interaction with vicinal [compound (II)] and geminal [compounds (XII)] organic dichlorides and dibromides results in the formation of the corresponding olefins and 10,10-dihalogenophenoxatellurins (XIII) in high yields.

Presumably in the series of vicinal dibromides the reactions proceed via the intermediate formation of telluronium salts of type (X) and in the case of the geminal dibromides via carbenes:



(XI)
X=Cl, Br.

The reactions with participation of diaryl tellurides and phenoxatellurin are not, however, general, because the number of vicinal and geminal dihalides, such as 1,2-dichlorocyclohexane[23] and benzylidene chloride and bromide,[24] are not dehalogenated under the conditions indicated.

Phenoxatellurin is a more active dehalogenating agent than phenothiatellurin, which is in its turn superior to phenoxaselenin.[24] Phenoxatellurin is used also for the dehalogenation of unsaturated vicinal di-iodides, which makes it possible to obtain the corresponding acetylenes in high yields:[23]

$$PhCX{=}CXR + (XI) \rightarrow PhC{\equiv}CR + (XIII);$$

X=I, R=H (80%), COOH (87%).

Together with diaryl tellurides and phenoxatellurin, diaryl ditellurides (V) are also used as dehalogenating agents.[25] The interaction of these compounds with the dibromide (II) is accompanied by the elimination of elemental tellurium with formation of the olefins (III) and the symmetrical diaryl tellurium dibromides (IX).

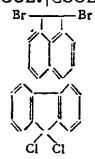
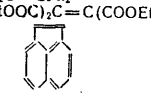
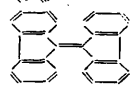
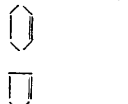
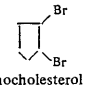
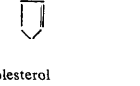
The possible ways of obtaining unsaturated compounds via the dehalogenation of vicinal and geminal dihalides by various organic derivatives of tellurium (II) are presented in the Table.

*(c) Derivatives of Tricoordinate Tellurium*

*Telluroxides.* Like selenoxides[12–14] telluroxides are now beginning to be used in the synthesis of olefins having different structures.[12,26–29] The possibility of employing

telluroxides for the preparation of olefins was first investigated by Sharpless et al.[12] When alkyl phenyl tellurides were oxidised by t-butyl hydroperoxide in benzene, a mixture of olefins, probably formed via the *syn*-elimination of the intermediate telluroxides, was obtained in a low yield.[12]

The synthesis of olefins from diorganyl dihalides and organic derivatives of tellurium(II).

| Dihalides (III) and (XII) | | | Te(II) derivative | Olefin | Yield, % | Refs. |
|---|---|---|---|---|---|---|
| $R^1$ | $R^2$ | X | | | | |
| (III), Ph | H | Br | (XI) | $PhCH=CH_2$ | 77 | [23] |
| (III), Ph | Ph | Br | $Ph_2Te$ | PhCH = CHPh-*trans* | 94 | [21] |
| (III), Ph | Ph | Br | $(p\text{-}MeOC_6H_4)_2Te_2$ | PhCH = CHPh-*trans* | 90 | [25] |
| (III), Ph | Ph | Br | $(p\text{-}EtOC_6H_4)_2Te_2$ | PhCH=CHPh | 100 | [25] |
| (III), Ph | COOH | Br | $Ph_2Te$ | PhCH=CHCOOH | 100 | [21] |
| (III), Ph | COOH | Br | (XI) | PhCH=CHCOOH | 93 | [23] |
| (III), Ph | COOH | Br | $(p\text{-}MeOC_6H_4)_2Te_2$ | PhCH = CHCOOH-*trans* | 68 | [25] |
| (III), Ph | COOH | Br | $(p\text{-}EtOC_6H_4)_2Te_2$ | PhCH=CHCOOH | 85 | [25] |
| (III), Ph | COOEt | Br | (XI) | PhCH=CHCOOEt | 89 | [23] |
| (III), COOH | COOH | Br | $(p\text{-}MeOC_6H_4)_2Te_2$ | HOOCCH = CHCOOH-*trans* | 73 | [25] |
| (III), COOH | COOH | Br | $(p\text{-}EtOC_6H_4)_2Te_2$ | HOOCCH = CHCOOH-*trans* | 86 | [25] |
| (III), Me | COOH | Br | (XI) | MeCH=CHCOOH | 75 | [23] |
| (XII), Ph | Ph | Cl | (XI) | $Ph_2C=CPh_2$ | 73 | [24] |
| (XII), COOEt | COOEt | Br | (XI) | $(EtOOC)_2C=C(COOEt)_2$ | 52 | [24] |
|  | | | (XI) |  | 23 | [25] |
|  | | | (XI) |  | 97 | [24] |
|  | | | (XI) |  | 62 | [25] |
|  | | | (XI) |  | 83 | [25] |
| Dibromocholesterol | | | $Ph_2Te$ | Cholesterol | 93 | [21] |

Subsequent studies[26–29] showed that the thermal decomposition of telluroxides can be used for the synthesis of olefins of different structures and compositions. The conditions in the thermolysis of telluroxides are determined by the structure of the alkyl group. Alkyl phenyl telluroxides (XIV), containing secondary alkyl groups, rapidly decompose at room temperature with formation of a mixtures of olefins in high yields.[29] Thus s-octyl phenyl telluroxides (XIV, R = $C_5H_{11}$) gives rise on decomposition to a mixture of oct-1-ene and *cis*- and *trans*-oct-2-enes in 80% yield together with a small amount of 2-octanol and 2-octanone. Telluroxides containing s-alkyl groups, such as 2-dodecyl, 2-tetradecyl, cycloheptyl, cyclo-octyl, and cyclododecyl, combined with other alkyl groups behave analogously.[29] On the other hand, cyclohexyl phenyl telluroxide (XVI) is extremely stable and decomposes only at 200–290 °C with formation of cyclohexane in a yield exceeding 70%;[29] however the causes of the increased resistance of this telluroxide to heating are not clear.

$$\underset{\substack{|\\ PhTe{=}O\cdot H_2O}}{RCH_2CHMe} \xrightarrow{\Delta} RCH_2CH{=}CH_2 + RCH{=}CHMe\,.$$
(XIV)

In contrast to telluroxides with s-alkyl groups, those containing primary alkyl groups [compound (XIVa)] decompose under more severe conditions.[26,29] Thus n-dodecyl phenyl telluroxide (XIVa, R = $C_{10}H_{21}$, Ar = Ph) is cleaved with formation of dodec-1-ene (50%) at 1-dodecanol (11%)[29] at 200–240 °C, while n-dodecyl 4-methoxyphenyl telluroxide (XIVa, R = n-$C_{10}H_{21}$, Ar = 4-$MeOC_6H_4$) affords a mixture of dodec-1-ene and the telluride (I) in proporations of 1 : 1 and 1.4 : 1 after refluxing for 24 h in $CCl_4$ or 12 h in toluene respectively.[26] The authors[26,29] believe that the primary intermediate in the decomposition reaction of telluroxide is tellurinic acid (XV), which reduces half of the telluroxide (XIV) to the telluride (I) in the next stage of the process. At the same time there is also a possibility of the disproportionation of this acid at a high temperature leading to the diaryl ditelluride (V):[26]

$$\underset{\substack{\|\\ O}}{RCH_2CH_2TeAr} \xrightarrow{\Delta} RCH{=}CH_2 + \underset{(XV)}{ArTeOH}\,;$$

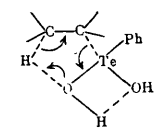
(XIVa), R = n-$C_{10}H_{21}$, Ar = 4-$MeOC_6H_4$;

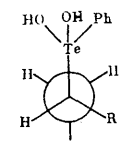
$$ArTeOH + RCH_2CH_2TeAr \rightarrow RCH_2CH_2TeAr + ArTeO_2H\,;$$

$$\underset{(XV)}{ArTeOH} + \underset{\substack{\|\\ O}}{\underset{(XIVa)}{RCH_2CH_2TeAr}} \rightarrow \underset{(I)}{RCH_2CH_2TeAr} + ArTeO_2H$$

$$3\,ArTeOH \xrightarrow{\Delta} \underset{(V)}{Ar_2Te_2} + ArTeO_2H + H_2O\,.$$

It is believed[29] that the causes of the difference between the reactivities of telluroxides with primary [compounds (XIVa)] and secondary [compounds (XIV)] alkyl groups, which exist in the form of dihydroxytelluranes, are determined by the difference between the stabilities of the carbonium ions formed on cleavage of the C–Te bond (A) and also be the difference between the steric environments of these two types of telluroxides (B):

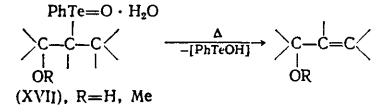

(A)

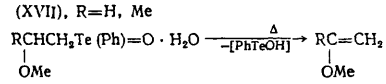

(B)

(XIV), R = Alk; (XIVa), R = H.

In the case of telluroxides elimination takes place in such a way that terminal olefins are formed preferentially.[29] Thus the ratio of the mono- and di-substituted olefins [formed on decomposition of the telluroxides (XIV, R = n-$C_5H_{11}$ or n-$C_7H_{15}$], amounting to (2.48–2.50) : 1, is much higher than in the elimination reactions of the analogous selenoxides (1.56 : 1)[34] and sulphoxides (1.5 : 1).[35]

Like alkyl phenyl and cycloalkyl phenyl telluroxides, their analogues containing hydroxy- and methoxy-groups [compounds (XVII) and (XVIII)] are also capable of undergoing thermal decomposition; their decomposition leads to allyl alcohols and allyl and vinyl ethers in high yields:[27–29]


(XVII), R=H, Me


(XVIII)

Bearing in mind the relative ease of synthesis of alkyl phenyl telluroxides of the type of compounds (XIV) and (XVII)–(XVIII), there are good prospects that the reactions examined in this Section will be applied in organic synthesis.

*Tellurimides.* It has been shown recently that olefins may be formed also on decomposition of tellurimides (XIX), which are believed tentatively to arise *in situ* on interaction of alkyl phenyl tellurides with an excess of chloramine T

(*N*-chloro-4-methyl-*N*-sodiobenzenesulphonamide) in boiling tetrahydrofuran (THF):[30]

$$RCH_2CH(R')TePh + p\text{-}MeC_6H_4SO_2NClNa \xrightarrow[-NaCl]{} [RCH_2CH(R')TePh \;\; NSO_2C_6H_4Me\text{-}n\ (XIX)] \xrightarrow{\Delta} RCH{=}CHR' + PhTeNHSO_2C_6H_4Me\text{-}p;$$

R′ = H; R = n-$C_8H_{17}$, n-$C_{10}H_{21}$, n-$C_{12}H_{25}$, n-$C_{13}H_{27}$; R′ = Me, R = n-$C_{11}H_{23}$ (molar ratio n-$C_{12}H_{25}CH{=}CH_2$/*trans*-n-$C_{11}H_{23}CH{=}CHMe$ = 2.5 : 1.0).

The tellurimides (XIXa), a scheme for the synthesis of which is presented below, afford fairly satisfactory yields of alkylvinylsilanes in the form of a 1 : 1 mixture of the *Z*- and *E*-isomers on pyrolysis *in situ* in boiling THF:[31]

$$PhTeCH_2SiMe_3 \xrightarrow[2)\ RCH(Me)X]{1)\ C_6H_5Li,\ TMEDA} PhTe{-}CH(R){-}CH_2{-}SiMe_3 \xrightarrow[-NaCl]{n\text{-}MeC_6H_4SO_2NClNa}$$

$$\longrightarrow PhTeCH(R){-}CH_2{-}SiMe_3\ (NSO_2C_6H_4Me\text{-}p;\ XIXa) \xrightarrow{\Delta} RCH{=}CHSiMe_3 + PhTeNHSO_2C_6H_4Me\text{-}p;$$

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

### *(d) Arylation of Olefins*

Like arylmercury chlorides[36,37] and arylthallium(III) derivatives[38] as well as the phenyl derivatives of magnesium (ArMgX),[39] Group IV elements ($Ph_4Sn$,[36] $Ph_4Pb$[36]), and Group V element ($Ar_3P$,[40] $Ph_3As$,[41,42] $Ph_3Sb$,[41,42] and $Ph_3Bi$[41,42]), the σ-telluranes $Ar_2TeX_2$ and $ArTeX_3$[32] can be used to arylate olefins by carrying out the reaction in the presence of stoichiometric amounts of $PdCl_2$/MeCOONa. Mainly products with the *trans*-configuration (XX) together with small amounts of the biaryls (XXI) (1–6%) are then formed:[32]

$$Ar_2TeCl_2 + RCH{=}CH_2 \xrightarrow{Pd(II)} \underset{(XX)}{\overset{Ar}{\overset{H}{C{=}C}}\!\!\overset{H}{\overset{R}{}}} + \underset{(XXI)}{Ar{-}Ar};$$

Ar=Ph, R=Ph, COOMe, CN, CHO, COMe, $CH_2OCOMe$; R=Ph, Ar=4-$MeC_6H_4$, 4-$BrC_6H_4$, 4-$MeOC_6H_4$.

The most varied olefins enter into the reaction: styrene, acrylic acid esters, acrylonitrile, methacrylonitrile, acroleine, methyl vinyl ketone, allyl alcohols, and allyl halides. In the reaction involving acrylonitrile, a 1 : 3 mixture of the *cis*- and *trans*-isomers was obtained while that of methacrylonitrile gave rise to a mixture of compounds (XX)–(XXIV) in proportions of 1 : 1 : 1.5:[32]

$$Ph_2TeCl_2 + CH_2{=}C(Me)CN \rightarrow \underset{(XXII)}{Ph(H)C{=}C(Me)CN} + \underset{(XXIII)}{Ph(H)C{=}C(CN)Me} + \underset{(XXIV)}{H_2C{=}C(CN)CH_2Ph}.$$

In the reactions of allyl alcohol and allyl bromide, the main products formed are β-phenylpropionaldehyde and allylbenzene respectively, as in the interaction of these compounds with phenylmercury derivatives.[37] The use of *p*-substituted diaryltellurium dihalides in this reaction leads (in the reaction involving styrene) to lower yields of *trans*-stilbenes than in the reaction with diphenyltellurium dichloride. The replacement of a chlorine atom by the acetoxy-group at the tellurium atom does not influence appreciably the yields of the arylated olefins. The reaction proceeds analogously also when rhenium(III) and rhodium(III) chlorides are used, but the yields of the olefins (XX) are then somewhat lower. Like diaryltellurium dihalides, aryltellurium trichlorides (XXV) give rise to *trans*-stilbenes on interaction with styrene:[32]

$$\underset{(XXV)}{ArTeCl_3} + H_2C{=}CHPh \xrightarrow{Pd(II)} \underset{(XX)}{\overset{Ar}{\overset{H}{C{=}C}}\!\!\overset{H}{\overset{Ph}{}}} + \underset{(XXI)}{Ar{-}Ar};$$

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

The olefin arylation reactions can be carried out also in catalytic amounts of $PdCl_2$, provided that a suitable oxidant is added to the reaction mixture: t-butyl hydroperoxide or copper(II) chloride (which is especially effective in solution in acetic acid). As in the case of mercury derivatives,[36,37] the arylation of olefins by organotellurium compounds proceeds via reactive arylpalladium intermediates (XXVI), which can either add to the double bond with subsequent β-elimination of HPdX (or BrPdX in the case of allyl bromides) or undergo reactive dimerisation with formation of biaryls (XXI). Both these reactions pathways can be illustrated in relation to the arylation of methacrylonitrile by diphenyltellurium dichloride in the presence of palladium(II) salts:[32]

$$Ph_2TeCl_2 \xrightarrow{PdX_2} \underset{(XXVI)}{[PhPdX]} \xrightarrow{H_2C{=}C(CN)Me} CH_2{-}C(CN)(Me){-}CH(Ph){-}PdX \xrightarrow{-HPdX} (XXII){-}(XXIV).$$

$$[PhPdX] \rightarrow \underset{(XXI)}{Ph{-}Ph}$$

Analogously to σ-telluranes, the interaction of diphenyl telluride with ethyl acrylate in the presence of $Pd(OCOCH_3)_2$ leads to ethyl cinnamate together with a certain amount of biphenyl.[22]

### *(e) Geometrical Isomerisation of Olefins*

An interesting application of organyltellurium trichlorides is their use for the geometrical isomerisation (inversion) of olefins by coupling *cis*-tellurotrichlorination and *trans*-dechlorotelluration processes.[33] When olefins interact with one equivalent of $TeCl_4$ in acetonitrile or chloroform,[33,43–45] 2-chloroalkyltellurium trichlorides (XXVII) are formed in high yields. The reduction of these compounds with an aqueous solution of $Na_2S$ leads to the liberation of elemental tellurium and the reformation of the initial olefin, but this time in the form of a mixture of *E*- and *Z*-isomers with the inverted form predominating. Thus the reaction involving *E*-but-2-ene yielded but-2-ene with the isomer ratio *Z* : *E* = 97 : 3.[33] The ratio of the isomers formed depends on the nature of the olefin and the solvent employed.

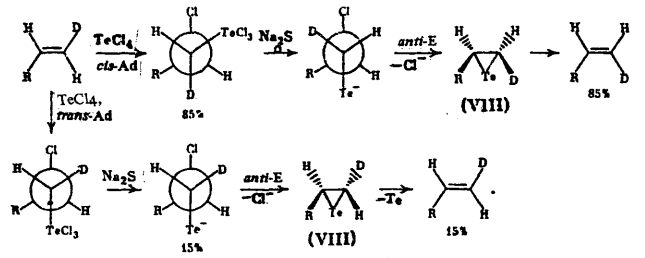
$$\underset{(III)}{\overset{H}{\overset{R}{}}\!\!\overset{R'}{\overset{H}{C{=}C}}} + TeCl_4 \rightarrow \underset{(XXVII\ a\text{-}c)}{RCHClCHR'TeCl_3} \xrightarrow{Na_2S} \underset{(III)}{\overset{H}{\overset{R}{}}\!\!\overset{H}{\overset{R'}{C{=}C}}};$$

a) R = *n*-$C_8H_{17}$, R′ = H; b) R = n-$C_8H_{17}$, R′ = D; c) R = R′ = Me.

The preferential *cis*-addition to the olefin has been demonstrated by studying the $^1H$ NMR spectra of the products of the addition of the $TeCl_4$ to *E*-[1-D]dec-1-ene.[33]† When this mixture is reduced with an aqueous solution of $Na_2S$, a mixture of the *Z*- and *E*-[1-D]dec-1-enes (85 : 15) is formed in

† The formation of 15% of the *trans*-adduct can be explained according to the authors[33] by the contribution of the electrophilic addition of $TeCl_4$, having the structure $TeCl_3^+Cl^-$ according to Krebs et al.[47]

conformity with stereospecific anti-elimination, which probably proceeds via the epitelluride (VIII):

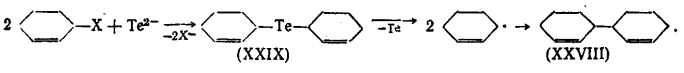


*(f) Synthesis of 1,5-Dienes*

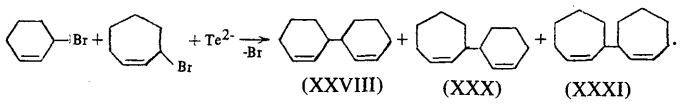
When diphenyl telluride is heated with allyl bromide at 180 °C in a sealed tube, diphenyltellurium bromide and diallyl are formed:[21]

$$Ph_2Te + H_2C{=}CHCH_2Br \rightarrow Ph_2TeBr_2 + H_2C{=}CHCH_2CH_2CH{=}CH_2 .$$

However, a more promising method of synthesis of 1,5-dienes of type (XXVIII) involves the interaction of alkyl halides of the allyl type with lithium telluride in boiling THF or a dioxant–THF mixture.[48] According to the data of Clive et al.,[48] the reaction proceeds via the initial formation of dialkenyl tellurides of type (XXIX) with their subsequent decomposition into radicals of the allyl type, which then dimerise:



This mechanism has been confirmed by the finding that the interaction of a mixture of 3-bromocyclohexene and 3-bromocycloheptene with the $Te^{2-}$ anion yields an almost statistical mixture of 2,2′-bicyclohexenyl (XXVIII), 3-(2′-cyclohexenyl)-cycloheptene (XXX), and 2,2′-bicycloheptenyl (XXXI) in proportions of 1 : 1.2 : 1:[33]



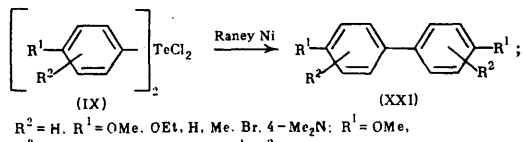
In contrast to dicycloalkenyl tellurides (XXIX), their selenium analogues are extremely stable. Thus the interaction of 3-bromocyclohexene with the $Se^{2-}$ anion under conditions analogous to those examined above leads mainly to the selenium analogue of compound (XXIX); in addition, a small amount of 2,2′-bicyclohexenyl (2%) is formed.[33]

### 3. Biaryls

One of the first examples of the application of organotellurium compounds in organic synthesis is in the synthesis of biaryls by the reductive cleavage of derivatives of tetracoordinate[32,49,50] and dicoordinate tellurium.[22,49–51] Although biaryls are formed (together with diaryl tellurides) also on thermal decomposition of tetra-aryltellurium derivatives $Ar_4Te$ (Ar = Ph,[52,53] $C_6F_5$,[54] or 4-$MeC_6H_4$ [53]), the latter reaction cannot be regarded as of preparative significance because the starting compounds for the synthesis of the tetra-aryltellurium derivatives are diaryltellurium dichlorides, from which biaryls can be obtained directly (see below).

*(a) Reactions of Derivatives of Tetracoordinate Tellurium with Raney Nickel*

When diaryltellurium dichlorides (IX, X = Cl) are treated with degassed Raney nickel in methylcellosolve, the biaryls (XXI) are obtained in good yields (58–91%).[49] The use instead of degassed Raney nickel of a catalyst obtained by boiling commercial nickel in 2-methoxyethyl ether or ethylene glycol gives rise to lower and less reproducible yields of biaryls:[49]



(IX) (XXI)

$R^2$ = H, $R^1$ = OMe, OEt, H, Me, Br, 4-$Me_2N$; $R^1$ = OMe, $R^2$ = 3-Me, 3-OMe, 2-OMe; $R^1$, $R^2$ = 3,4-$C_4H_4$.

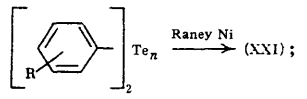
Aryltellurium trichlorides (XXV) are less suitable for the synthesis of biaryls,[49] although in the case of 2-naphthyltellurium trichloride, the yield of 2,2′-binaphthyl is 98%.[50]

*(b) Reactions of Derivatives of Tetracoordinate Tellurium with Palladium(II) Salts*

It was already mentioned above that, when olefins are arylated by diphenyl telluride[22] and σ-telluranes[32] in the presence of palladium(II) salts, the biaryls (XXI) are formed as side products together with arylated olefins. If the reactions of σ-telluranes (1 mol) with palladium(II) salts (2 mols) are carried out in the absence of olefins, then the arylpalladium intermediates (XXVI) undergo reductive dimerisation and the biaryls (XXI) are formed as sole products in moderate yields.[32]

*(c) Reactions of Derivatives of Dicoordinate Tellurium with Raney Nickel*

Like σ-telluranes,[49,50] the diaryl tellurides (I, $R^1 = R^2 = Ar$) and diaryl ditellurides (V) are converted into the biaryls (XXI) in high yields (60–90%) on treatment with degassed Raney nickel:



(I), $n = 1$; (V), $n = 2$

R = 4-OMe, H, 4-Me, 4-OEt, 4-Br.

*(d) Reactions of Diaryl Tellurides with Organomagnesium Compounds*

Another way of using diaryltellurides (I) in the synthesis of the biaryls (XXI) involves their treatment of Grignard reagents in ether or THF in the presence of phosphine complexes of nickel and cobalt [$NiCl_2(PPh_3)_2$, $NiCl_2(Ph_2PCH_2CH_2.PPh_2)$, and $CoCl_2(PPh_3)_2$], which leads to the cross-coupling products (XXXII) and the homo-coupling products (XXXIII) together with the biaryls:[51]

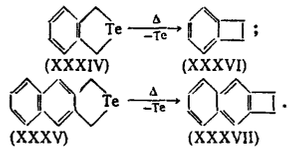
$$\underset{(I)}{Ar_2Te} + RMgBr \xrightarrow{Ni(II)\text{ or }Co(II)} \underset{(XXXII)}{Ar{-}R} + \underset{(XXI)}{Ar{-}Ar} + \underset{(XXXIII)}{R{-}R} .$$

The reaction mechanism proposed by Uemura and Fukuzawa[51] includes the formation of diorganylnickel (or diorganylcobalt) complexes, their subsequent conversion, on treatment

with diaryl tellurides, into aryltelluronickel (or the corresponding cobalt) complexes, and the decomposition of the latter with the elimination of tellurium and the formation of the final products.

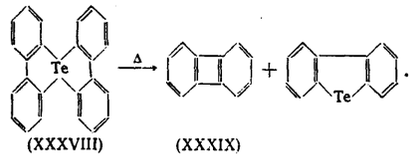
### 4. Cyclic Hydrocarbons

The synthesis of cyclic hydrocarbons of various types with the aid of organotellurium compounds is based on the ease of elimination of elemental tellurium from the corresponding tellurium-containing heterocycles.[55,56] For example, the thermal decomposition of compounds (XXXIV) and (XXXV) leads to benzo[*b*]cyclobutene (XXVI) and naphtho[*b*] cyclobutene in high yields:[55]



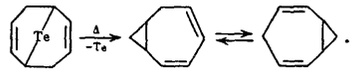
(XXXIV) (XXXVI) (XXXV) (XXXVII)

Like cyclic tetra-aryltellurium derivatives,[52–54] bis(diphenylene)tellurium(XXXVIII) gives rise on thermolysis to a heterocyclic diaryl telluride—dibenzotellurophen (yield 96%) and biphenylene (XXXIX) (yield 52%).[57,58] Together with the latter compound, also traces of polyphenylenes were detected in this reaction:



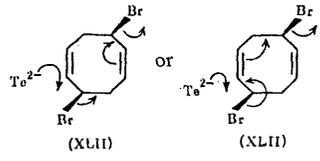
(XXXVIII) (XXXIX)

In certain cases processes of the type considered are accompanied by rearrangements. Thus, when 9-telluria-bicyclo[3.3.1]nona-2,6-diene (XL) is heated in deuteriotoluene (in a sealed tube) at 175 °C, bicyclo[5.1.0]octa-2,5-diene (XLI) is formed in a quantitative yield[56] and is in equilibrium with its isomeric diene (XLIa):



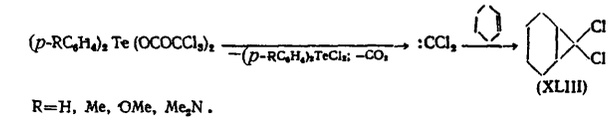
(XL) (XLI) (XLIa)

It is noteworthy that compound (XLI) is capable of being formed (in 20% yield) [together with compound (XL) in 18% yield] also under conditions ruling out the possibility of the thermal decomposition of compound (XL), on interaction of the dibromide (XLII) with $Na_2Te$ in dimethylformamide (DMF), which the authors[56] explain by the following scheme



(XLII) (XLII)

Diaryltellurium bis(trichloroacetate) (IX, X = $OCOCCl_3$) decomposes on heating with formation of diaryltellurium dichlorides (IX, X = Cl), carbon dioxide, and dichlorocarbene,[59] which makes it possible to employ them for the synthesis of dichlorocyclopropanes. When compound (IX) is refluxed in the presence of cyclohexene in *p*-xylene (or diglyme, 2,2-dichlorobicyclo[4.1.0]heptane (XLIII) is formed in low yields (20–30% together with diaryltellurium dichlorides (60–70%):[59]



(XLIII)

R=H, Me, OMe, $Me_2N$.

## III. SYNTHESIS OF HALOGENO-DERIVATIVES

The formation of mono- and di-halogeno derivatives of various types is frequently observed in reactions involving σ-telluranes.[43,44,60–65] However, these processes are by no means equivalent as regards preparative importance and some of them, for example, the formation of alkyl halides on thermal decomposition of alkylphenyltellurium dihalides[60] and di(chloroalkyl)- and di(chlorocycloalkyl)-tellurium dichlorides,[43,44,61] are relatively unpromising. Indeed alkyl phenyl tellurides, which are the starting materials in the synthesis of alkylphenyltellurium dihalides, are obtained by the reaction of tellurophenoxide anions with alkyl halides, while the pyrolysis of di(chloroalkyl)- and di(chlorocycloalkyl)-tellurium dichlorides results in the formation of a series of side products together with halogeno-derivatives of different structure.

### 1. Aromatic Halogeno-derivatives

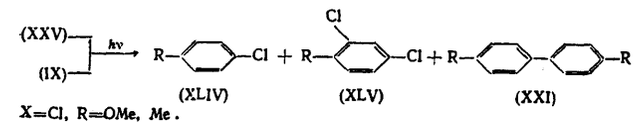
Aromatic halogeno-derivatives are formed on photolytic[62] or hydroperoxide-induced α-elimination[63] and also on elimination of tellurium halides (by treatment with bromine or iodine) from σ-telluranes of the type $Ar_2TeX_2$ and $ArTeX_3$.[64]

#### (a) *Photolytic α-Elimination from σ-Telluranes*

Reactions involving photolytic α-elimination of organyl halides from σ-telluranes are fairly general and lead to the formation of aromatic monohalogeno-derivatives and also dihalogeno-derivatives of cyclic and ethylenic hydrocarbons[62] (see below).

*p*-Chloroanisole (XLIV, R = OMe, X = Cl) is formed in a high yield (70%) together with small amounts of 2,4-dichloroanisole (XLV, R = OMe, X = Cl) and 4-methoxybiphenyl (XXI) (1%) on photolysis of *p*-anisyltellurium trichloride (XXV, R = OMe, X = Cl) in benzene. Metallic tellurium is liberated during the reaction probably as a consequence of the disproportionation of the $TeCl_2$ formed initially.[62] Other aryltellurium dichlorides behave analogously. In the reactions of diaryltellurium dichlorides, the yield of aryl halides is reduced; instead of elemental tellurium, a mixture of inoganic and organic tellurium compounds of unknown structure is produced and the amount of asymmetric biaryls increases.

*p*-Anisyltellurium tribromide, di(*p*-anisyl)tellurium diacetate, and *p*-anisyltellurium triacetate [obtained *in situ* from di(*p*-anisyl) ditelluride and lead tetra-acetate] enter into analogous reactions, which lead to *p*-anisyl bromide and *p*-anisyl acetate in yields of 30% and 6 and 15% respectively:[62]



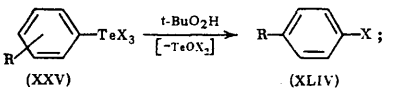
(XLIV) (XLV) (XXI)

X=Cl, R=OMe, Me.

The selective formation of the C–X bond (X = Hal) in the *unco*-positions [2- and 4-positions (Ed.of Translation)] in the molecule and the limited involvement of the solvent (benzene) in the formation of products (low yield of biaryls) suggest that the photolysis of σ-telluranes considered here does not entail the formation of free radicals. This is also indicated by the finding that the ratio of the reaction products does not change significantly in the photolysis of *p*-anisyltellurium trichloride or di(*p*-anisyl)tellurium dichloride in the presence of t-butyl peroxide.[62]

### *(b) α-Elimination Induced by Hydroperoxides*

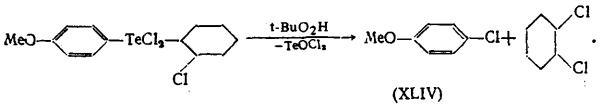
After the acetic acid solution of *p*-anisyltellurium trichloride (XXV, R = *p*-Ome, X = Cl) (1 mol) and t-butyl hydroperoxide (2 mols) has been refluxed for a short time, *p*-chloroanisole (XLIV) is obtained in 53% yield.[63] Tellurium is then converted into tellurium oxide chlorides, although the structure of the inorganic products has not been accurately established:[63]




(XXV) (XLIV)

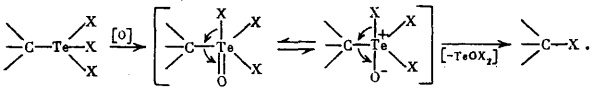
X = Cl, R = OMe, 4-Me, 2.3-$C_4H_4$; X = Br, R = 4-OMe.

When 2-chlorocyclohexyl-*p*-methoxyphenyltellurium dichloride is treated with t-butyl hydroperoxide in acetic acid, a mixture of *p*-chloroanisole (22%) and 1,2-dichlorocyclohexane (55%) (configuration not indicated) is formed, which indicates a greater liability of the $C_{Alk}$–Te bonds in the α-elimination reactions compared with $C_{Ar}$–Te:



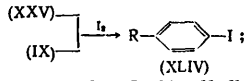

(XLIV)

The authors[63] suggest that organyl halides are formed via a mechanism involving the 1,2-tellurium halide shift in an instable hexacoordinate tellurium derivative formed on oxidation of σ-telluranes:




### *(c) Reactions Involving the Halogen-induced Elimination of Tellurium from σ-Telluranes*

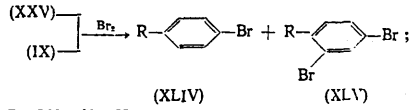
When *p*-anisyltellurium trichloride (XXV) reacts with iodine in boiling acetonitrile, *p*-iodoanisole (XLIV, X = I) is formed in 13% yield;[64] the presence of the *o*- and *m*-isomers was not detected under these conditions. The introduction of potassium, caesium, or ammonium fluorides into the reaction mixture increases the yield of *p*-iodoanisole to 85%. Treatment of diaryl tellurium dichlorides (IX, X = Cl) under analogous conditions also leads to aryl iodide, but in lower yields. On passing from *p*-anisyl- to phenyl- and *p*-bromphenyl-tellurium trichlorides, the yields of aryl iodides fall sharply, which indicates the electrophilic character of the process. The nature of the electronegative substituents at the tellurium atom (Cl, OCOMe, and $OCOCF_3$) does not have a significant influence on the yields of aryl iodides:[64]




(XLIV)

X=Cl, R=OMe, Me, H; X=OAc, R=OMe, H; X=$OCOCF_3$, R=H.

Somewhat different results have been obtained in the study of the elimination of tellurium bromide from σ-telluranes.[64] In the reaction of *p*-anisyl-tellurium trichloride with bromine in different solvents (actonitrile, dioxan, acetic acid), mainly 2,4-dibromoanisole (XLV, R = OMe, X = Br) and a small amount of *p*-bromoanisole (XLIV, R = Ome, X = Br) are formed. The preferential formation of the dibromo-derivatives (XLV) from *p*-anisyltellurium trichloride is the result of the ready bromination of the monoaryl bromides (XLIV) formed initially in the presence of tellurium(IV) derivatives playing the role of catalysts of electrophilic substitution in the aromatic ring. As in the elimination of tellurium iodide, the weakening of the electron-donating properties of the substituent in the arene rings (phenyl- and *p*-bromophenyl-tellurium trichlorides) leads to a sharp decrease of the yield of aryl bromide even in the presence of caesium and ammonium fluorides:[64]




(XLIV) (XLV)

R=OMe, Me, H.

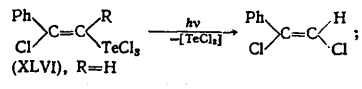
The chlorine-induced elimination of tellurium from aryltellurium trichlorides by reaction with chlorine, $SbCl_5$, and t-butyl hypochlorite affors very low yields of aryl chloride even in the case of *p*-anisyltellurium trichloride (not more than 5%). The cyanide-induced elimination of tellurium from aryltellurium trichlorides by reaction with copper(I) cyanide in DMF proceeds in approximately the same manner (yield 8%).[63]

## 2. Dihalogeno-derivatives of Olefinic and Cyclic Hydrocarbons

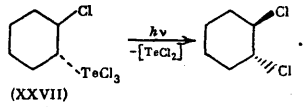
The formation of derivatives of organic compounds of these classes has been observed in the same reactions as the formation of aryl halides: photolytic[62] and hydroperoxide-induced α-elimination from σ-telluranes[63] and also halogen-induced elimination of tellurium from 2-chlorovinyltellurium trichlorides.[65]

### *(a) Photolytic α-Elimination*

Irradiation of a benzene solution of *Z*-2-chlorovinyl-2-phenyltellurium trichloride (XLVI, R = H) with UV light leads to *Z*-1,2-dichloroethylene (yield 39%); the composition and structure of other reaction products were not established; this may indicate that the α-elimination proceeds in this case with retention of configuration.[62] The photolysis of *trans*-2-chlorocyclohexyltellurium trichloride (XXVII) results in the formation of *trans*-1,2-dichlorocyclohexane in 28% yield[62] (the formation of the *cis*-isomer was not observed):



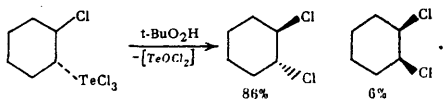

(XLVI), R=H




(XXVII)

*(b) α-Elimination Induced by Hydroperoxides*

Dihalogeno-derivatives of the types considered can be formed also by the hydroperoxide-induced α-elimination of organic halides from organyltellurium trihalides.[63] Thus, when *trans*-2-chlorocyclohexyltellurium trichloride is briefly refluxed with two equivalents of t-butyl hydroperoxide, a mixture of *trans*- and *cis*-1,2-dichlorohexanes is formed in yields of 86% and 6% respectively:

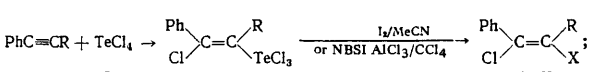



The analogous reaction with *trans*-2-chlorocyclohexyltellurium triiodide, which leads to only *trans*-1,2-chlorodiiodocyclohexane (64%), takes place also when t-butyl hydroperoxide is replaced by hydrogen peroxide, cumenyl hydroperoxide, and *m*-chloroperbenzoic acid, but the yields are then appreciably lower.[63]

*Z*-1,2-dichloroethylenes are formed together with small amounts of the *E*-isomers (ratio approximately 9 : 1) in the reaction involving *Z*-2-chlorovinyltellurium trichlorides (XLVI, R = H or Ph).[63]

*(c) Halogen-induced Elimination of Tellurium from 2-Chlorovinyltellurium Trichlorides*

The halogen-induced elimination of tellurium from 2-chlorovinyltellurium trichlorides (XLVI), whose *Z*-isomers are readily obtained (in 80–90% yield) by the addition of $TeCl_4$ to substituted acetylenes, has been used to synthesise 1,2-dihalogenoethylenes. Thus the iodine-induced elimination of tellurium from compounds (XLVI) by treatment with iodine (in acetonitrile or methanol) and the bromine-induced elimination of tellurium by treatment with *N*-bromosuccinimide (NBSI) (NBSI/$AlCl_3$ in $CCl_4$ or NBSI/$CuBr_2$ in acetonitrile) proceeds with retention of configuration, as for many β-substituted vinyl organometallic compounds investigated previously, and leads to *Z*-1,2-chloroiodo(or bromo)ethylenes (XLVII) in high yields:[65]



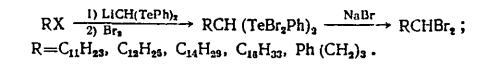

(XLVI) (XLVII)

X=I, R=H, Me, Et, Ph; X=Br, R=H, Ph.

Bearing in mind that, in contrast to other reagents (for example $HgCl_2$ [66]), which give rise to *E*-isomers as a result of *trans*-attack, the addition of $TeCl_4$ to substituted acetylenes always leads to *Z*-isomers (XLVI) and that the elimination of tellurium from the latter proceeds with retention of configuration, the above reaction sequence can be regarded as a convenient method of synthesis of *Z*-chloro(or bromo)-alkanes from alkynes.

*(d) Dihalogeno-derivatives of Saturated Hydrocarbons*

A single example of the synthesis of dihalogeno-derivatives of this type in reactions of organotellurium compounds has been described, namely the formation of 1,1-dibromoalkanes in high yield or thermal decomposition of 1,1-bis(phenyldibromotelluro)alkanes in the presence of sodium bromide in DMF.[63] The initial compounds are obtained in 80–85% yield by the reaction of alkyl halides with bis(phenyltelluro)methyllithium[67] and subsequent bromination of the intermediate bistellurides:

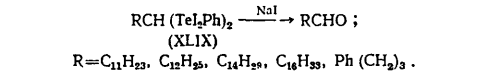



## IV. SYNTHESIS OF CARBONYL COMPOUNDS

Carbonyl compounds of different classes, namely aldehydes,[60,68,69] ketones,[15,16,70–72] and carboxylic acids[72,73] and their derivatives (esters[15,16,70,74–76] and anhydrides[59,77,78]) can be formed in reactions of monocoordinate,[71,72] dicoordinate,[69] tricoordinate,[15,16,70,76,78] and tetracoordinate[59,68,73–75,77] derivatives of tellurium.

*1. Aldehydes*

Benzaldehyde (together with other compounds) is formed in the photochemical oxidation of dibenzyl telluride or dibenzyl ditelluride.[69] Bis(*p*-methoxyphenyl)tellurone $(p\text{-}RC_6H_4)_2.TeO_n$ (XLVIII, R = OMe, *n* = 2)—the first reliably characterised representative of tellurone obtained by the oxidation of bis(*p*-methoxyphenyl) telluroxide (XLVIII, *n* = 1) with sodium periodate, is an effective oxidant oxidising various substituted benzyl alcohols to the corresponding benzaldehydes.[68] Thus the oxidation of piperonyl and veratryl alcohols by compound (XLVIII, *n* = 2) gave 70–80% yields of piperonyl and veratryl aldehydes.[68] Aldehydes have also been obtained in 70–93% yield by treating bis(phenyldiiodotelluro)alkanes (XLIX)[60] with NaI in DMF under mild conditions (60 min, 20 °C):

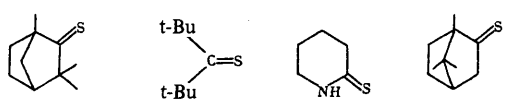



*2. Ketones*

Ketones are formed when thioketones (L) are oxidised[15,16,70] by diaryl telluroxides (XLVIII, *n* = 1) and on reduction of α-halogenoketones with *OO*-diethyl phosphorotellurolates (VII)[71] or alkali metal tellurophenoxides (IV).[72]

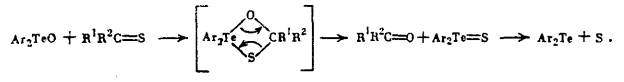
*(a) Oxidation of Thiocarbonyl Compounds by Diaryl Telluroxides*

Thioketones with a wide variety of structures (L a–d) can be selectively oxidised to ketones with the aid of diaryl telluroxides[15,16,70] (under the formula of each thiocarbonyl compound given below, the yield of its oxo-analogue is indicated). Together with oxo-compounds, sulphur and diaryl tellurides are formed in these reactions in almost quantitative yields:

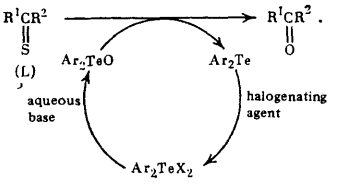



(La) (23%) (Lb) (100%) (Lc) (87%) (Ld) (10%)

According to Ley et al.,[16] the mechanism of this reaction can be represented schematically as follows:



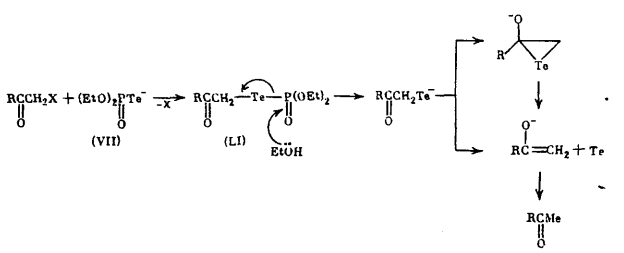
The oxidation of thioketones and thioacid esters (see below) to the corresponding oxo-derivatives has also been achieved with the aid of the catalytic oxidation-reduction cycle,[16,70] which requires the presence of a mild and effective halogenating agent into convert diaryl tellurides (I) into diaryltellurium dihalides (IX) and an aqueous solution of a base capable of converting the latter into diaryl telluroxides (XLVIII, $n = 1$). The most suitable brominating agent for tellurides is 1,2-dibromotetrachloroethane, which converts them into tellurium dibromides (IX, X = Br) in high yields at room temperature. Other reagents, namely hexachloroacetone, tetrabromoethane, and the dibromide of Meldrum's acid were much less effective in the above catalytic cycle. Among bases, an aqueous solution of potassium carbonate proved the most effective.[16,70] The optimum conditions in this reaction are stirring at room temperature in chloroform of a mixture of the carbonyl compound, 1.5% of the telluride (tellurium dihalides) or telluroxide, an excess of 1,2-dibromotetrachloroethane, and an aqueous solution of $K_2CO_3$:




The study of the influence of the nature of organic groups in the molecules of diaryltellurium dichloride $R^1C_6H_4TeCl_2$. $.C_6H_4R^2$ used in this catalytic cycle showed that, as the electron-donating properties of the ring substituents $R^1$ and $R^2$ in the *p*-positions with respect to the tellurium atom are enhanced, the rate of the oxidation reaction increases in the following sequence: H,H < 4-MeO,4′-MeO < 4-MeO,4′-$NMe_2$ < 4$NMe_2$,4′-$NMe_2$.

*(b) Reduction of Ketones with Functional-group Substituents in the α-Position*

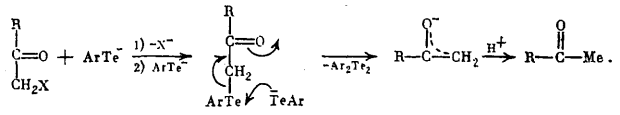
Sodium *OO*-diethyl phosphorotellurolate (VII) is a mild dehalogenating reagent for various α-halogenoketones.[71] Best results have been achieved in this reaction using stoichiometric amounts of the reactants in ethanol or THF (20° to 80 °C):




The mechanism proposed for this reaction, where the involvement of the intermediate compounds of type (LI) in the dehalogenation of α-halogenoketones is postulated, is based on the fact that the analogous reaction of 2,4′-dibromoacetophenone with sodium *OO*-diethyl phosphoroselenolate entails the formation of the selenium analogue of compound (LI), which does not, however, undergo further reactions.[71]

The readily available lithium and sodium thiophen-2-tellurolates, obtained by the reaction of 2-lithiothiophen with tellurium in THF or by the reduction of di(2-thienyl) ditelluride in an alkaline solution of $NaBH_4$ in alcohol, are extremely convenient, in the preparative sense, dehalogenating agents for various α-halogenoketones.[72]

The interaction of tellurophenoxides (2 mols) with α-halogenoketones (1 mol) results in reduction and the formation in high yields of the corresponding ketones and di(α-thienyl) ditelluride. In contrast to the reactions of α-halogenoketones with thiolate and selenolate anions, which usually give rise to a mixture of reduction and substitution products,[79,80] the use of the thiophen-2-tellurolate anion results in the formation of only the reduction products. However, it is possible that nucleophilic substitution with formation of intermediates of type (LII) is an intermediate stage in the reduction of α-halogenoketones by tellurolate anions. An indirect confirmation of this is provided by the interaction of α-bromoacetanilide (in excess) with sodium thiophen-2-tellurolate in alcohol, which results in the isolation of α-(2-thienyltelluro)acetanilide in 64% yield. This confirms the possibility, in principle, of the formation of the intermediate substitution product (LII) also in the reaction of $ArTe^-$ with α-halogenoketones and suggests the following two-stage reduction mechanism:[72]



A number of other electronegative substituents, for example, the MeCOO, $MeSO_2O$, and PhS groups, can also be readily removed from the α-position in acetophenones on treatment with alkali metal thiophen-2-tellurolates.[71]

In many cases α-halogenoketones may be reduced by employing sodium tetrahydroborate as the reducing agent in the presence of catalytic amounts of di(2-thienyl) ditelluride,[72] similarly to the formation of olefins by the reduction of vicinal dibromides examined above.[18]

## 3. Quinones

The formation of quinones with the aid of organotellurium compounds is based on the oxidation of dihydric phenols by diaryl telluroxides (XLVIII, $n = 1$)[15,16] or diaryl tellurones (XLVIII, $n = 2$).[68] Thus the oxidation of hydroquinone,[16] 1,4-dihydronaphthalene,[16] and 3,5-di-t-butyl-1,2-dihydroxybenzene[15,16] by di(*p*-anisyl) telluroxide leads to *p*-benzoquinone, 1,4-naphthoquinone, and 3,5-di-t-butyl-o-benzoquinone in 65, 97, and 80% yields respectively. In the case of di(*p*-anisyl)tellurone, the yield of *p*-benzoquinone is smaller, amounting to only 39%.[68]

## 4. Carboxylic Acids

*(a) Carbonylation of σ-Telluranes*

One of the possible ways of obtaining carboxylic acids from organotellurium compounds is based on the interaction of diaryltellurium dichlorides or aryltellurium trichlorides with

nickel carbonyl in DMF at 70 °C and subsequent treatment with water:[73]

$$Ar_2TeCl_2 + Ni(CO)_4 + 2H_2O \rightarrow 2ArCOOH + NiTe + 2HCl + 2CO;$$
$$ArTeCl_3 + 2Ni(CO)_4 + H_2O \rightarrow ArCOOH + NiCl_2 + NiTe + HCl + 7CO.$$

Together with carboxylic acids, diarylketones and diaryl tellurides are formed in this instance as side products.

By analogy with familiar reactions of this type involving other metallic compounds, their possible mechanisms can be described by the following schemes:[73]

(1) Aryltellurium trichlorides:

$$ArTeCl_3 + Ni(CO)_4 \rightarrow NiCl_2 + ArTeNi(CO)_2Cl \xrightarrow[ArTeCl_4]{\text{arylation}} Ar_2Te, \quad (1)$$

$$ArTeNi(CO)_2Cl + Ni(CO)_4 \rightarrow NiTe + ArNi(CO)_2Cl, \quad (2)$$

$$ArNi(CO)_2Cl + Ni(CO)_4 \xrightarrow{\text{insertion}} ArCNi(CO)_2Cl \begin{cases} \xrightarrow{\text{arylation}} Ar_2CO, \\ \xrightarrow[H_2O]{} ArCOOH. \end{cases} \quad (3)$$

(2) Diaryltellurium dichlorides

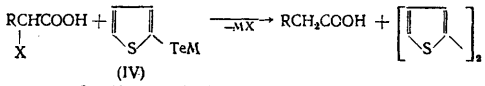
$$Ar_2TeCl_2 + Ni(CO)_4 \rightarrow ArNi(CO)_2Cl + ArTeNi(CO)_2Cl,$$

followed by reactions (1), (2), and (3).

Aliphatic tellurium dichlorides, in particular di(2-chloropropyl)tellurium dichloride, decompose under analogous conditions with formation of alkenes (in the given instance, propene), $NiCl_2$, and NiTe.[73] When $Ni(CO)_4$ is replaced by $Fe_2(CO)_9$, carbonylation does not take place. Thus the reaction of *p*-anisyltellurium trichloride with $Fe_2(CO)_9$ results in the formation of only di(*p*-anisyl) ditelluride, apparently as a consequence of the reduction of the trichloride by iron carbonyl.[73]

### *(b) Reduction of Carboxylic α-Halogenoacids*

Like α-halogenoketones (see above), carboxylic α-halogenoacids are reduced in high yields by lithium and sodium thiophen-2-tellurolates (IV) to the corresponding carboxylic acids:[72]



(IV)

M=Li, Na; R=Ph (99%), 1-$C_{10}H_7$ (97%), $(Ph)_2$ (98%).

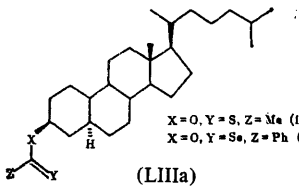
## 5. Derivatives of Carboxylic Acids

Organotellurium compounds have been used to obtain derivatives of carboxylic acids such as esters[15,16,70,74–76] and anhydrides.[77,78]

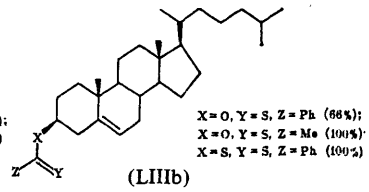
### *(a) Esters*

Esters have been synthesised from derivatives of tricoordinate tellurium (diaryl telluroxides[15,16,70] and telluronium ylides[76]) and derivatives of tetracoordinate tellurium—diaryltellurium diacylates.[74,75]

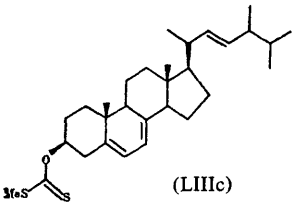
*Diaryl telluroxides.* Like ketones (see above), many esters were obtained in high yield by the oxidation of the corresponding thio- and selenocarbonyl compounds (LIIIa–e) with diaryl telluroxides:[15,16,70]



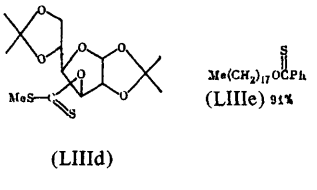

(LIIIa)




(LIIIb)



(LIIIc)




(LIIId) (LIIIe) 91%

*Telluronium ylides.* An effective method of synthesis of αβ-unsaturated acid esters is the interaction of carbonyl compounds with dialkyltelluronium ethoxycarbonylmethylylides (LV) obtained *in situ* by treating dibutylethoxycarbonylmethyltelluronium bromides (LVI) with potassium t-butoxide in THF. This reaction proceeds with high stereoselectivity, especially with aldehydes, and leads mainly to *E*-isomers:[76]

$$(C_4H_9)_2Te^+CH_2COOEt\ Br^- \xrightarrow[THF]{Me_3COK} (C_4H_9)_2Te^+-\bar{C}HCOOEt \xrightarrow[-(C_4H_9)_2TeO]{R^1R^2C=O} R^1R^2C=CHCOOEt.$$
(LV) (LIV)

The reaction is also applicable to cyclic and αβ-unsaturated ketones and aldehydes. The sharp difference between the reactivities of the telluronium ylides (LV) and the corresponding sulphonium ylides is noteworthy. Thus dimethylsulphonium ethoxycarbonylmethylide does not react with simple ketones and aldehydes, while its reaction with αβ-unsaturated carbonyl compounds yields cyclopropanes.[81]

*Diaryltellurium diacylates.* The methyl esters of carboxylic acids are formed in 85–90% yields on hearing diaryltellurium diacylates (IX) with methyl iodide in sealed tubes at 100 °C:[75]

$$(p\text{-}RC_6H_4)_2Te(OCOMe)_2 + MeI \rightarrow (p\text{-}RC_6H_4)_2TeI_2 + MeCOOMe;$$
(IX)

R=H, Me, OMe.

When diphenyltellurium diacetate reacts with chlorotrimethylsilane, diphenyltellurium dichloride is formed in a high yield (it is probably accompanied by trimethylsilyl acetate):[74]

$$Ph_2Te(OCOMe)_2 + 2Me_3SiCl \rightarrow Ph_2TeCl_2 + 2MeCOOSiMe_3.$$

### *(b) Acid Anhydrides*

Carboxylic acid anhydrides have been obtained in 80–95% yields by the reaction of diaryltellurium diacylates (IX) with acyl chlorides:[59,77]

$$(p\text{-}R^1C_6H_4)_2Te(OCOR^2)_2 + 2R^2COCl \rightarrow (p\text{-}R^1C_6H_4)_2TeCl_2 + (R^2CO)_2O;$$
(IX)

$R^1$=H, $R^2$=Me; $R^1$=Me, $R^2$=Ph; $R^1$=OMe, $R^2$=Et; $R^1$=OMe, $R^2$=$CH_2Cl$.

The high yields make it possible to regard this reaction as a preparative method of synthesis of the anhydrides of both aliphatic and aromatic carboxylic acids. The attempts to use

it for the synthesis of mixed anhydrides were, however, unsuccessful. Thus, although treatment of di(p-anisyl)-tellurium bis(trifluoroacetate) with acetyl chloride afforded di(p-anisyl)tellurium dichloride in a yield exceeding 90%,[59,77] the asymmetric anhydride, namely acetyl trifluoroacetate, was not isolated, which can probably be accounted for by its disproportionation under the reaction conditions.

Anhydrides are also formed in the reaction of diaryl telluroxides with carboxylic acid chlorides, apparently via the intermediate formation of diaryltellurium chloroacylates:[78]

$$(p\text{-MeOC}_6\text{H}_4)_2\text{TeO} + \text{MeCOCl} \rightarrow \left[(p\text{-MeOC}_6\text{H}_4)_2\text{Te}\begin{matrix}\text{Cl}\\ \text{OCOMe}\end{matrix}\right] \xrightarrow{\text{MeCOCl}} (p\text{-MeOC}_6\text{H}_4)_2\text{TeCl}_2 + (\text{MeCO})_2\text{O}.$$

## V. CONCLUSION

The data presented in the review demonstrate the likely usefulness of the application of organotellurium compounds in the synthesis of various classes of organic compounds and in the first place unsaturated and cyclic hydrocarbons, halogeno-derivatives of various types, and carbonyl compounds. Among these reactions, special interest attaches to catalytic reactions with participation of organotellurium compounds: tellurolate and phosphorotellurolate anions and diaryl telluroxides. In many instances the reactions which proceed readily when organotellurium reagents are used do not occur with selenium compounds having analogous structures (the synthesis of 1,5-dienes).

Further prospects for the application of organotellurium compounds in organic synthesis is as follows: (1) in the search for new possibilities of using organic derivatives of tellurium in order to obtain organic compounds, (2) in the study of conditions permitting an increase in the stereospecificity of the reactions, (3) in the development of new catalytic processes, and (4) in the elucidation of the specific features of organotellurium compounds compared with the analogous sulphur and selenium derivatives and in using these features in organic synthesis. The solution of the above problems is indissolubly linked to the expansion of studies connected with the development of methods of synthesis of organotellurium compounds using readily available starting materials and to the study of the reactivity of these compounds.

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During the preparation of this review for publication, a series of new reports on the application of organotellurium compounds in organic synthesis appeared. Uemura and Fukuzawa[82] gave a systematic account of and discussed the results of studies on the reaction involving α-elimination of organic halides from σ-telluranes of various types, published previously in a number of communications.[62,63,65] Olefins of different structure have been obtained in the decomposition of alkyl phenyl telluroxides synthesised either by the hydrolysis of the corresponding tellurium dibromides[83] or by the oxidation of alkylphenyl tellurides by hydrogen peroxide,[83] sodium periodate,[83] and *m*-chloroperbenzoic acid[83,84] and also by the catalytic debromination of vicinal dibromides by diaryl tellurides under the conditions of interfacial catalysis.[85] Catalytic debromination of 1,4-dibromoalk-2-enes by sodium thiophen-2-tellurolate has been used to obtain 1,3-dienes.[86] Oxidation of allyl phenyl tellurides by the oxidants enumerated above and also by t-butyl hydroperoxides leads to allyl alochols in high yields,[87] probably via the [2,3]-sigmatropic rearrangement of the alkyl phenyl telluroxides formed as intermediates.

New methods have been proposed for the synthesis of carboxylic acids on the basis of the decomposition of tellurones formed in the oxidation of ethylene ketals of aryl α-tellurophenylethyl ketones[88] and of the insertion (in the presence of $PdCl_2$) of the CO group in the Te–C bond in diorganyl tellurides and σ-telluranes.[89] New examples of the application of organotellurium reagents in the organic synthesis have been presented: the synthesis of αβ-unsaturated epoxides by the reaction of dialkyltelluronium allylides with aldehydes,[90] the synthesis of chlorohydrin ethers by the elimination of tellurium from the products of the addition of $TeCl_4$ to allyl ethers by treatment with Raney nickel,[91] and the formation of alkyl method ethers by the oxidation of alkyl phenyl tellurides with *m*-chloroperbenzoic acid in methanol.[92] Diaryl telluroxides proved to be effective catalysts of aldol condensation reactions[93] and diorganyl tellurides were found to catalyse the reactions of tosyl azide with aldehydes, which is due to the intermediate formation of tellurimides (from tosyl azide and diorganyl tellurides).[94]

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