

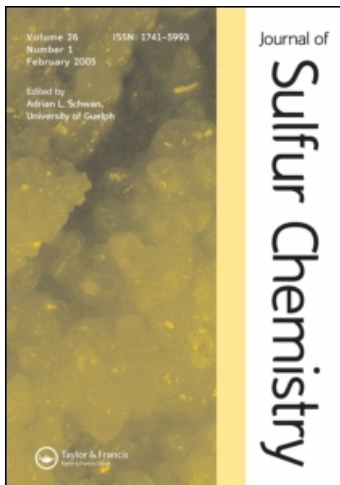
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π -Telluranes: Synthesis, Structure and Reactivity

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π -TELLURANES: SYNTHESIS, STRUCTURE AND REACTIVITY

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(Received May 8, 1987)

A comprehensive up-to-date review of the synthesis, structure and reactivity of the tricoordinated organotellurium compounds diaryl telluroxides, diaryl tellurimides and telluronium ylides (π -telluranes) is presented. Similarities and differences in structure and reactivity of π -telluranes and their sulfur and selenium analogs are traced.

Key words: Diaryl tellurimides, diaryl telluroxides, π -telluranes, telluronium ylides

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I. INTRODUCTION

π -Telluranes represent tricoordinated organotellurium compounds containing formal

Te=X double bonds with the general formula $R_2Te=XR_n$ (where X = O, N, C and n = 0, 1, 2, respectively). These compounds have been investigated to a much lesser degree as compared to selenium¹ and particularly sulfur² analogs, though diaryl telluroxides were obtained as early as the end of the last century.³ On the other hand, telluronium ylides⁴ and tellurimides⁵ were first prepared only in 1970 and 1977, respectively.

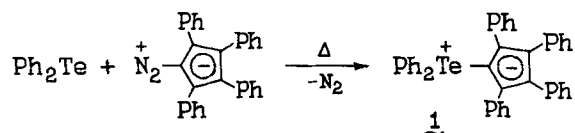
So far there exist only two reviews^{6,7} partly dealing with telluronium ylides and telluroxides. However, the appearance, in the last years, of many papers devoted to π -telluranes, the growing application of these compounds in the synthesis of other organotellurium compounds and various organic compounds and the peculiarity of their reactivity in comparison to π -sulfuranes and π -selenuranes has made it expedient to generalize and systematize the data about these organotellurium compounds.

II. SYNTHESIS OF π -TELLURANES

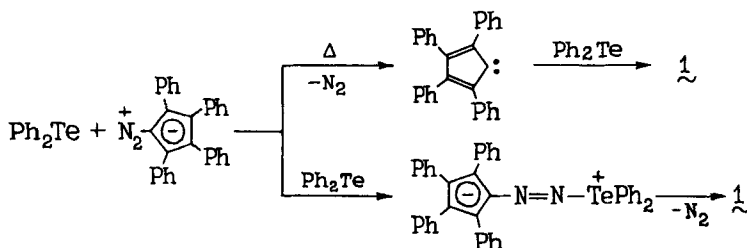
II.1. Diorganyltelluronium Ylides

The methods of synthesis of telluronium ylides (and their stability) are determined essentially by the nature of the substituents at the carbanionic center which may be involved in the negative charge delocalization.

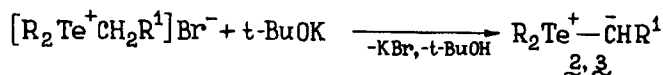
The first described telluronium ylide, diphenyltelluronium tetraphenylcyclopentadiene ylide **1**, was obtained by Lloyd by thermolysis of tetraphenyl diazocyclopentadiene in excess diphenyl telluride^{4,8}



This reaction may proceed via the addition of thermally generated carbene in its singlet electronic state to the tellurium atom (as in the case of diorganyl sulphides),⁹ or via an intermediate tellurazine as in the case of the interaction between phosphines and diazo compounds:¹⁰



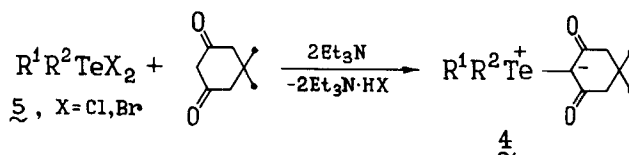
Unstabilized telluronium ylides, e.g. dialkyltelluronium allyl ylides **2**,¹¹ and ylides containing one π -acceptor substituent at the carbanionic center, e.g. dialkyltelluronium carbethoxymethylides **3**,¹² have only been prepared in situ by the standard (for the synthesis of ylides of VIA group elements) reaction,⁷ based on the interaction of appropriate telluronium salts with potassium *t*-butoxide in tetrahydrofuran.



2, R¹ = CH=CH₂; R = CH₃, *n*-C₄H₉, *iso*-C₄H₉, *cyclo*-C₆H₁₁

3, R¹ = COOC₂H₅; R = CH₃, *n*-C₄H₉

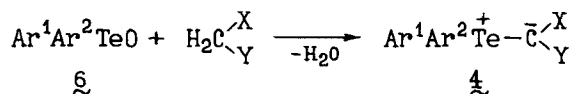
The methods of synthesis of telluronium ylides **4**, containing two π-acceptor substituents at the carbanionic center, have received a special attention. For the first time they were obtained by the treatment of various σ-telluranes **5** with dimedone in the presence of two equivalents of triethylamine.¹³⁻¹⁵



R¹ = R² = CH₃, C₆H₅, 4-CH₃C₆H₄, 4-CH₃OC₆H₄, 4-C₂H₅OC₆H₄, 4-(CH₃)₂NC₆H₄, 4-BrC₆H₄, 4-FC₆H₄; R¹ = CH₃, R² = C₆H₅, 4-CH₃C₆H₄, 4-CH₃OC₆H₄, 4-C₂H₅OC₆H₄; R¹ = 4-CH₃OC₆H₄, R² = C₆H₅CH₂, 4-(CH₃)₂CHC₆H₄

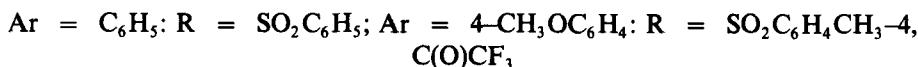
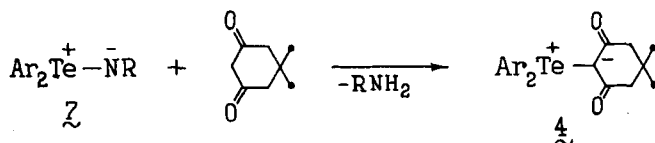
However, other compounds with active methylene groups (acetylacetone, malonodinitrile, acetoacetic ester, malonic ester) do not form ylides under similar conditions.^{14,15} This can be related to decreasing CH-acidity when passing from dimedone to the above-mentioned compounds with active methylene groups.

The method for the synthesis of telluronium ylides **4**, based on the interaction between diaryl telluroxides **6** and compounds containing active methylene groups¹⁵⁻¹⁷ is of more general use. Unlike sulfonium and selenonium ylides, the formation of which requires the use of strong dehydrating agents (acetic anhydride, dicyclohexylcarbodiimide, phosphoric acid anhydride, thionyl chloride and the like),⁷ the reaction with telluroxides proceeds upon boiling of equimolar quantities of the reagents in chloroform or benzene with simultaneous distillation of the water formed in the course of the reaction.

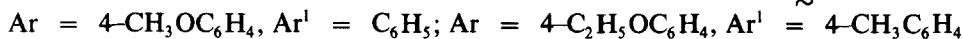
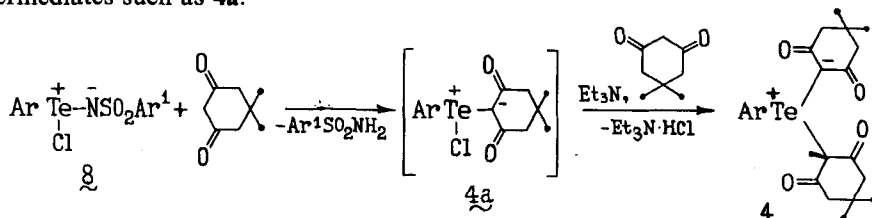


Ar¹ = Ar² = 4-CH₃OC₆H₄; X = Y = COOC₂H₅; X = NO₂, Y = COOC₂H₅; X, Y = *o*-COC₆H₄CO; X, Y = COCH₂(CH₃)₂CH₂CO; Ar¹ = Ar² = C₆H₅; X = Y = CN; X = CN, Y = COOCH₃; X = CN, Y = COOC₂H₅; X, Y = COCH₂C(CH₃)₂CH₂CO

It is unlikely that the formation of ylides **4** by the interaction of tellurimides **7** with dimedone¹⁸ will become the general route to these ylides, since tellurimides are prepared from telluroxides or σ-telluranes which can be transformed directly to the ylides as mentioned above.



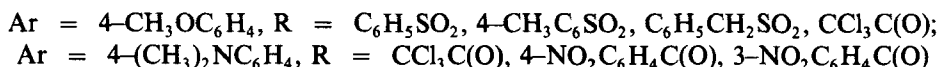
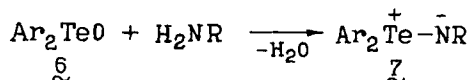
The method based on the interaction of *N*-sulfonyl-*Te*-aryl-*Te*-chlorotellurimides **8** with dimedone in the presence of triethylamine is also specific yielding only aryl(dimedonyl)telluronium dimedone ylides. The reaction probably proceeds via unstable intermediates such as **4a**.¹⁹



II.2 Tellurimides

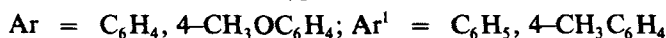
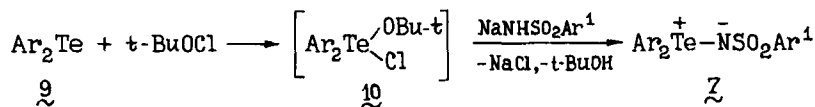
All tellurimides known to date contain a strongly electron-accepting substituent (a sulphonyl or acyl group) at the nitrogen atom.

The first stable tellurimides, *N*-sulfonyl diaryl tellurimides **7**, were prepared by the condensation of diaryl telluroxides **6** and sulfonamides.^{5,20}

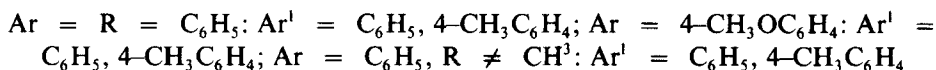
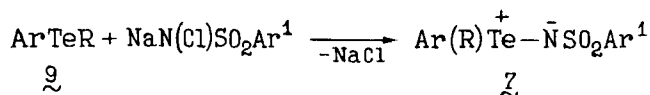


It was shown later that this method is also suitable for the synthesis of *N*-acyltellurimides with strong electron acceptor groups in the *N*-acyl moiety.^{20,21} Donor substituents in the aryl nuclei of telluroxides which increase their basicity and acceptor substituents in amides enhancing NH-acidity, both promote formation of tellurimides.

The second method for the synthesis of tellurimides **7** based on the use of diaryl tellurides **9** consists in the latter's treatment with *t*-butyl hypochlorite with subsequent addition of the sodium sulfonamide salts. The reaction proceeds apparently via oxidation of the tellurides to *t*-butoxy(diaryl)tellurium chlorides **10**, which under the action of sodium sulfonamide salts form the tellurimides **7**.^{20,21}

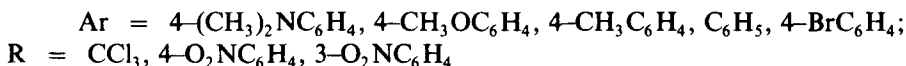
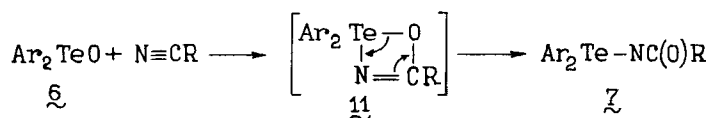


The intermediate formation of *N*-(*p*-toluenesulfonyl)-*Te,Te*-2,2'-diphenyltellurimide at the interaction of dibenzotellurophen with chloramine-T was proposed by Hellwinkel²² in 1968. However, *N*-sulfonyltellurimides **7** were prepared via reaction of tellurides **9** with chloramine-B and -T only recently²³

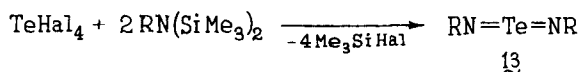
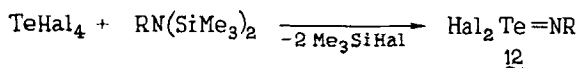


This reaction was performed in benzene with anhydrous chloramines and catalytic amounts of crown ethers.

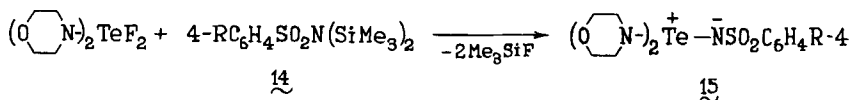
Of special interest is the synthesis of *N*-acyl tellurimides **7** based on the interaction between diaryl telluroxides **6** and nitriles. The reaction very likely proceeds via intermediate **11**²⁴



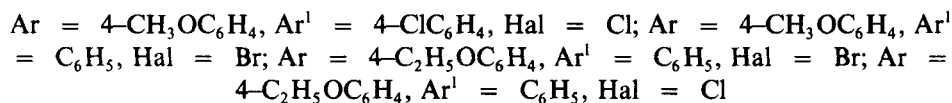
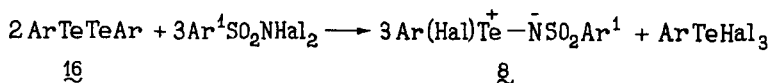
Tellurimides **12**, containing halogen atoms at tellurium, and diimides **13** were prepared by the interaction of *N,N*-disilylamides and -sulfonamides with tellurium tetrahalides²⁵



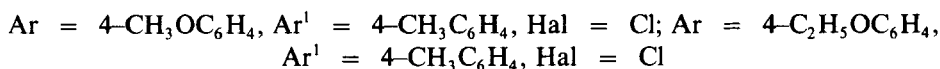
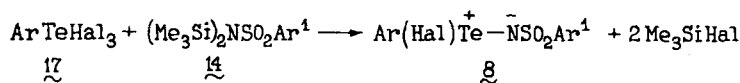
The reaction of di(*N*-morpholyl)tellurium difluoride and *N,N*-bis(trimethylsilyl)sulfonamides **14** yields tellurimides with three Te-N bonds **15**²⁶



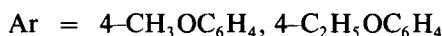
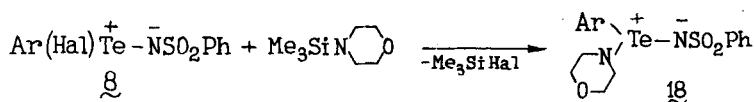
Tellurimides **8**, containing one halogen atom at the tellurium center, have been obtained¹⁹ through reaction of diaryl ditellurides **16** with *N,N*-dihaloarenesulfonamides in the ratio 2:3.



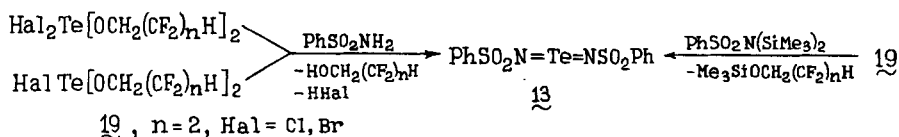
The compounds **8** can also be obtained by the reaction of aryltellurium trichlorides **17** with *N,N*-disilylsulfonamides **14**¹⁹



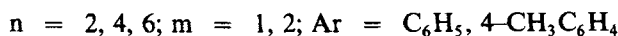
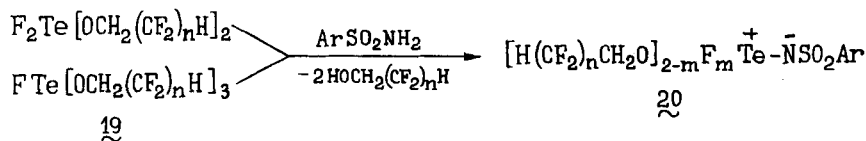
When heated in benzene, tellurimides **8** and trimethylsilylmorpholine form tellurimides **18** containing the morpholine ring at the tellurium atom.¹⁹



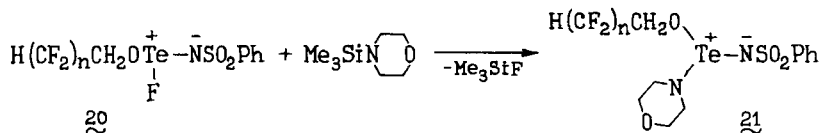
Tellurimide **13** (R = C₆H₅) has also been prepared by interaction of polyfluoroalkoxy(halo)telluranes **19** with benzenesulfonamide or *N,N*-disilyl derivatives **14** by simultaneous cleavage of Te-Hal and Te-O bonds.²⁷



Tellurimides **20** containing fluorine atoms or polyfluoroalkoxy groups at the tellurium atom have been obtained from polyfluoroalkoxy(fluoro)telluranes **19**.²⁸ In these compounds, unlike their chlorine and bromine analogs, either the Te-F or the Te-O bond is cleaved depending on the nature of the sulfonamide. In the interaction of telluranes **19** (Hal = F) with sulfonamides the reaction proceeds only at the Te-O bonds and in the case of disilylated sulfonamides one affects the Te-F bonds.



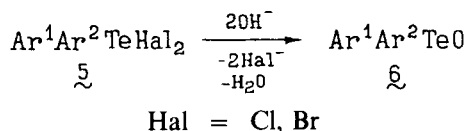
Tellurimides **20** when treated with *N*-trimethylsilylmorpholine are transformed to *Te*-morpholyl tellurimides **21**²⁸



II.3. Diaryl Telluroxides

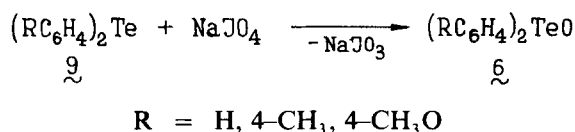
Among the diorganyl telluroxides only the diaryl derivatives **6** are true telluroxides, because dialkyl and alkyl aryl telluroxides are always isolated as hydrates which are assigned the structure of either a hydrogen-bonded complex $\text{R}_2\text{TeO} \cdot \text{H}_2\text{O}$ or a σ -tellurane $\text{R}_2\text{Te}(\text{OH})_2$. Three methods for the synthesis of telluroxides **6** in which use is made of tetra- (σ -telluranes **5**) and dicoordinated (diaryl tellurides **9**) tellurium derivatives are known so far.

The most general method for the synthesis of various diaryl telluroxides **6** is the hydrolysis of diaryltellurium dihalides **5** in the presence of ammonia^{29,30} or dilute alkali solution^{3,31-38}



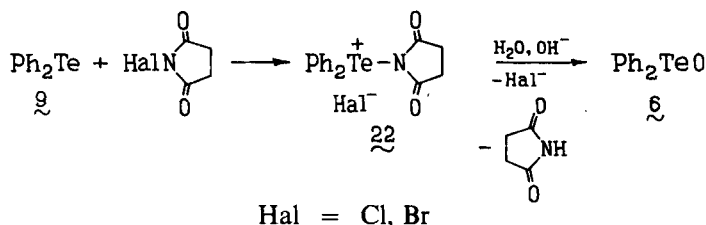
The use of dichlorides and dibromides yields the best results. Diiodides are not readily hydrolyzed. The application of difluorides is not recommended due to their limited accessibility (as compared to other tellurium dihalides). The hydrolysis of other types of σ -telluranes (diaryltellurium diacylates $\text{Ar}_2\text{Te}(\text{OCOR})_2$,³⁹ diorganyl tellurium oxyhalides $\text{Ar}_2\text{Te}(\text{OH})\text{Hal}$ or their anhydrides $(\text{Ar}_2\text{TeHalH}_2\text{O})^{40,41}$) is of no practical value.

From the dicoordinated tellurium derivatives (diorganyl tellurides **9**), diaryl telluroxides **6** can be obtained in two ways. The first of these is to oxidize tellurides with sodium periodate⁴²



Other oxidizing agents such as atmospheric oxygen and hydrogen peroxide produce mixed products.^{43,44}

An alternative method of using diaryl tellurides **9** for the synthesis of telluroxides **6** is the oxidation of the former with *N*-halosuccinimide followed by hydrolysis of the azatelluronium salts **22** with aqueous solutions of NaOH, Na₂CO₃, or NaHCO₃.⁴⁵ The best results are achieved with *N*-chlorosuccinimide without isolation of the intermediate salts **22**.



It is very convenient to use *t*-butyl hypochlorite as a source of positively charged halogen because the initially formed (*t*-butoxy)diaryltellurium chlorides are readily hydrolyzed to oxides.⁴⁵

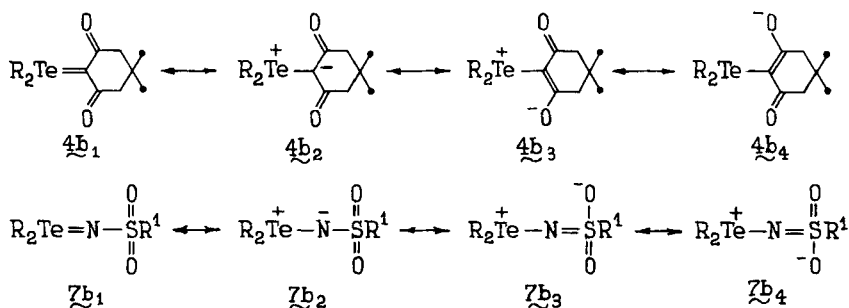
III. STRUCTURE AND PHYSICOCHEMICAL PROPERTIES

III.1. Molecular and Crystal Structure

To date the molecular and crystal structures of the following three π -telluranes have been investigated by X-ray diffraction: di(*p*-methoxyphenyl)telluronium-4,4-dimethyl-2,6-dioxocyclohexane ylide **4b**,⁴⁶ *N-p*-toluenesulfonyl-*Te,Te*-di(*p*-methoxyphenyl)-tellurimide **7b**⁴⁷ and diphenyl telluroxide **6a**⁴⁸ (Table 1).

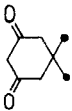
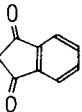
All above-listed compounds possess the structure of a trigonal pyramid with the tellurium atom at the vertex. The angle of pyramidalization of the tellurium atom of these π -telluranes is lower than in the corresponding π -sulfurane and π -selenurane. This is explained by the pure *p*-orbital character of the bonds to tellurium. It should be pointed out that diphenyl telluroxide in the crystalline state has a dimeric structure which is due to secondary bonds Te . . . O (3.171 Å) as distinct from the ylide and the imide.

An analysis of the bond lengths in the dimedone moiety of telluronium ylide **4b** and of the NSO₂ group of tellurimide **7b** leads to the conclusion of delocalization of negative charge over the bond systems of the groups -C[C(O)-]₂ and NSO₂, respectively. This indicates that the dipolar resonance structures **4b**₃, **4b**₄ and **7b**₃, **7b**₄ make major contributions to the ground state of telluronium dimedone ylides and *N*-sulfonyltellurimides, respectively.^{15,20,46,47}



A comparison between the N-S(VI) and S-O bond lengths in chalcogenimides (Table 2) allows one to conclude that the contribution of the resonance structures **7b**₃, **7b**₄ to

Table 1. Bond lengths (Å) and sums of the angles at the pyramidal vertex in compounds R^1R^2M-Z

Compd:	R^1	R^2	M	Z	M-C(R^1)	M-C(R^2)	M-Z	Sum of the angles at M:	Ref.
4b	4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	Te		2.08	2.15	2.07	299	46
21	C ₆ H ₅	C ₆ H ₅	Se	C(COCH ₃) ₂	1.906	1.926	1.83	313.3	49
22	CH ₃	CH ₃	S		1.784	1.787	1.71	312.1	50
7b	4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	Te	NSO ₂ C ₆ H ₄ CH ₃ -4	2.109	2.111	1.98	289.5	47
23	C ₆ H ₅	C ₆ H ₅	Se	NSO ₂ C ₆ H ₅	1.94	1.94	1.82	295.9	51
24	C ₆ H ₅	C ₆ H ₅	Se	NSO ₂ C ₆ H ₄ CH ₃ -4	1.933	1.933	1.787	307.2	52
25	C ₆ H ₅	C ₆ H ₅	S	NSO ₂ C ₆ H ₄ CH ₃ -4	1.769	1.80	1.63	308.5	53
6a	C ₆ H ₅	C ₆ H ₅	Te	O	2.122	2.127	1.87	289.5	48
26	C ₆ H ₅	C ₆ H ₅	S	O	1.76	1.76	1.47	309.7	54

the ground state of *N*-sulfonylchalcogenimides increases in the following order: S < Se < Te.

The molecules of tellurimide **7b** in the crystal are chiral⁴⁷ as in the case of *N*-sulfonylsulfimides^{53,55-58} and -selenimides **23**.⁵¹ They may be represented as the Newman projections along the S-N bond of **27a** and **27b**. Though the first attempts to prove the existence of such enantiomers in solution failed,^{20,59} the use of chiral shift reagents in ¹H NMR spectroscopy (see Sect. III.2.3.)⁶⁰ gave evidence for the presence of stable enantiomeric tellurimides.

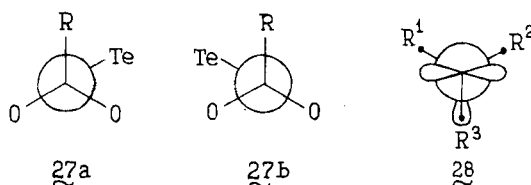


Table 2. Bond lengths (Å) in compounds $Ar_2M^+-N^-SO_2R$

Compound	Ar	R	M	M-N	N-S	S-O ¹	S-O ²	Ref.
7b	4-CH ₃ OC ₆ H ₄	C ₆ H ₄ CH ₃ -4	Te	1.980	1.573	1.453	1.453	47
23	C ₆ H ₅	C ₆ H ₅	Se	1.82	1.60	1.44	1.46	51
24	C ₆ H ₅	C ₆ H ₄ CH ₃ -4	Se	1.787	1.598	1.438	1.438	52
25	C ₆ H ₅	C ₆ H ₄ CH ₃ -4	S	1.628	1.598	1.430	1.435	53

In the crystalline state tellurimide **7b** and its selenium and sulfur analogs possess conformation **28** (shown in a Newman projection along the N–X bond (X = S, Se, Te)) in accordance with the predictions for the model sulfimide (H₂SNH) obtained by *ab initio* SCF MO⁶¹, EHMO and CNDO/2 methods.⁶²

III.2. Spectral Properties

III.2.1. IR spectra The IR spectra of telluronium dimedone ylides **4** exhibit characteristic absorptions in the region 1600–1500 cm⁻¹ (Table 3).

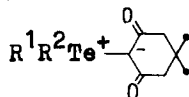
An assignment of the absorption bands to be attributed to carbonyl stretching in the dimedone moiety could not be carried out because of the strong overlapping by the ν_{CH} bands.^{14,15}

All *N*-sulfonyl-*Te,Te*-diaryltellurimides **7** have four strong characteristic IR absorption bands at around 1233–1215, 1140–1122, 1095–1082, and 994–960 cm⁻¹, respectively.^{5,20,21,59} (Table 4). The three bands at 1233–1215, 1440–1120, and 1095–1082 cm⁻¹, which are also present in the IR spectra of the analogous sulfimides^{63–69} and selenimides,^{21,70–74} have been assigned to $\nu_{\text{SO}_2}^{\text{as}}$, $\nu_{\text{SO}_2}^{\text{s}}$, and $\nu_{\text{S-C}}$, respectively.⁵⁹ From the X-structural data of *N*-sulfonyltellurimide **7b**⁴⁷ it follows that the N–S(VI) bond (1.573 Å) in this compound, as also in the selenimides **23** (1.60 Å)⁵¹ and **24** (1.598 Å)⁵² and sulfimide **25** (1.598 Å),⁵³ is much shorter than an ordinary bond (1.73–1.75 Å).⁷⁵ According to this observation as well as to the isotopic band shifts occurring in the IR spectrum of ¹⁵N-benzenesulfonyl-*Te,Te*-diphenyltellurimide, the band at 995–960 cm⁻¹ and the medium-intensity band at 650–645 cm⁻¹ are assigned to $\nu(\text{N-S}^{\text{VI}})$ and $\nu(\text{Te-N})$, respectively.⁷⁶

In the case of the *N*-arenesulfonyl-*Te*-halo-*Te*-aryltellurimides **8**, containing an acceptor halogen atom at tellurium, the band at 902 cm⁻¹ corresponds to $\nu(\text{N-S}^{\text{VI}})$ and the band at 688 cm⁻¹ to $\nu(\text{Te-N})$.¹⁹

In the IR spectra of *N*-acyltellurimides^{20,21,24,77} (Table 5) as well as other *N*-acylchalcogenimides^{78–81} a considerable shift of the carbonyl absorption band towards lower frequencies is observed as compared to the corresponding band of carbamides.

Table 3. Characteristic frequencies (cm⁻¹) in the IR spectra of the ylides:



R ¹	R ²	ν, cm^{-1}
4-(CH ₃) ₂ NC ₆ H ₄	4-(CH ₃) ₂ NC ₆ H ₄	1612, 1585, 1535
4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	1590, 1530
4-C ₂ H ₅ OC ₆ H ₄	4-C ₂ H ₅ OC ₆ H ₄	1565, 1510
C ₆ H ₅	C ₆ H ₅	1570, 1530, 1520
4-FC ₆ H ₄	4-FC ₆ H ₄	1584, 1545
4-BrC ₆ H ₄	4-BrC ₆ H ₄	1550
4-CH ₃ OC ₆ H ₄	CH ₃	1585, 1505
4-C ₂ H ₅ OC ₆ H ₄	CH ₃	1600, 1505
4-CH ₃ C ₆ H ₄	CH ₃	1585, 1520
CH ₃	CH ₃	1590, 1535

Table 4. Characteristic frequencies (cm⁻¹) in the IR spectra of *N*-sulfonyltellurimides (R¹C₆H₄)₂Te⁺-N⁻SO₂R²

R ¹	R ²	ν _(S-C)	ν _(N S)	ν _(SO₂) ^s	ν _(SO₂) ^{as}	ν _(SO₂)	Ref.
H	C ₆ H ₅	1095	966	1122	1233	1178	21
H	4-CH ₃ C ₆ H ₄	1090	985	1130	1225	1178	21
4-CH ₃ O	4-CH ₃ C ₆ H ₄	1082	968	1133	1220	1176	5
4-CH ₃ O	C ₆ H ₅	1090	980	1130	1225	1174	5
H	C ₆ H ₅ CH ₂	1095	986	1131	1220	1176	59
4-CH ₃	C ₆ H ₅ CH ₂	1088	995	1128	1228	1178	59
3-CH ₃	C ₆ H ₅ CH ₂	1090	970	1139	1228	1184	59
4-CH ₃ O	C ₆ H ₅ CH ₂	1090	995	1133	1215	1174	5, 59
4-(CH ₃) ₂ N	C ₆ H ₅ CH ₂	1085	980	1136	1220	1178	59
4-Cl	C ₆ H ₅ CH ₂	1095	980	1130	1226	1176	59
3-Cl	C ₆ H ₅ CH ₂	1095	972	1139	1229	1184	59
4-Br	C ₆ H ₅ CH ₂	1095	980	1131	1225	1178	59
3-Br	C ₆ H ₅ CH ₂	1090	970	1140	1228	1184	59

Owing to the major contribution of the dipolar resonance structure **7c₃** to the ground state of these compounds, the N-C bond is to a large extent a double bond.

This leads to the existence of *N*-acyltellurimides in the form of *E*- and *Z*-isomers.^{20,27}

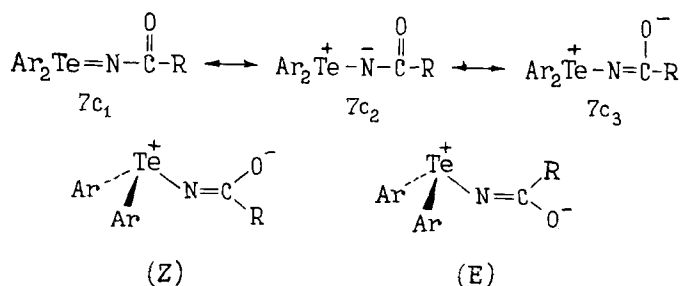


Table 5. Carbonyl group vibrational frequencies in the IR spectra of *N*-acyltellurimides (R¹C₆H₄)₂Te⁺-N C(O)R²

R ¹	R ²	ν _(CO) , cm ⁻¹
H	CCl ₃	1500 ²⁴
4-CH ₃ O	CCl ₃	1575 ²¹ , 1570 ²⁴
4-CH ₃	CCl ₃	1580 ²⁴
4-(CH ₃) ₂ N	CCl ₃	1580 ²¹ , 1575 ²⁴
4-Br	CCl ₃	1560 ²⁴
4-(CH ₃) ₂ N	3-NO ₂ C ₆ H ₄	1585 ²¹
4-(CH ₃) ₂ N	4-NO ₂ C ₆ H ₄	1575 ²¹
H	CF ₃	1655 ⁷⁷
4-CH ₃	CF ₃	1670 ⁷⁷
3-CH ₃	CF ₃	1654 ⁷⁷
4-CH ₃ O (<i>Z</i> -)	CF ₃	1683 ⁷⁷
4-CH ₃ O (<i>E</i> -)	CF ₃	1600 ⁷⁷
4-(CH ₃) ₂ N	CF ₃	1590 ⁷⁷
3-Cl	CF ₃	1665 ⁷⁷
4-Br	CF ₃	1670 ⁷⁷
3-Br	CF ₃	1655 ⁷⁷

For most *N*-trifluoroacetyl tellurimides only the *Z*-isomeric forms, stabilized by the proximity of the oppositely charged atomic centers, have been observed. The compounds are characteristic by virtue of their large carbonyl frequency shift, as compared to ν_{CO} of trifluoroacetamide, which amounts to $\sim 70 \text{ cm}^{-1}$ ($\nu_{\text{CO}} = 1683\text{--}1654 \text{ cm}^{-1}$). Variations in the electronic nature of the substituent of the aryl groups can change the positive charge at the tellurium atom, which in turn affects the relative stability of the *Z*- and *E*-isomers. Introduction of methoxy groups into the *p*-positions of aryl groups attached to the tellurium atom equalizes the stability of the *Z*- and *E*-isomeric forms, and the corresponding tellurimides have been obtained in two forms, the carbonyl bond vibrations of which appear at 1683 (*Z*) and 1600 (*E*) cm^{-1} . Introduction of a stronger donor (e.g. a dimethylamino group) into the *p*-position with respect to the tellurium atom strongly stabilizes the *E*-form of the corresponding tellurimide. The carbonyl frequency shift, which in this case is caused by intermolecular interaction of dipolar structures, amounts to 150 cm^{-1} ($\nu_{(\text{CO})} = 1599 \text{ cm}^{-1}$).⁷⁷

Also *N*-trifluoroacetyl-*Se*-aryl-*Se*-methylselenimides, containing a donor methyl group at the selenium atom, exist only in the *E*-form ($\nu_{(\text{CO})} = 1602\text{--}1580 \text{ cm}^{-1}$),⁸⁰ whereas all *N*-acylsulfimides for which X-ray structural data have been obtained exist in the *Z*-form.^{82,83}

III.2.2. UV spectra The UV spectra of telluronium dimedone ylides **4** are similar to those of the corresponding sulfonium and selenonium ylides (Table 6).

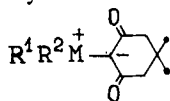
It has been noted^{14,15} that an increase in the donor ability of substituents attached to the onium tellurium center gives rise to a bathochromic shift in the long-wave absorption band.

A comparison between the UV spectra of telluronium ylides and of the sodium dimedone salt⁸⁴ has shown that the long-wave absorption originates from the electronic transitions in the carbanionic moiety.

A small bathochromic shift of the long-wave absorption band due to a significant decrease in the acceptor properties of the groups R_2M^+ in the series $\text{S} < \text{Se} < \text{Te}$ was observed on passing from sulfonium to telluronium ylides (Table 6).^{14,15}

N-Benzylsulfonyl- and *N*-trifluoroacetyl-*Te*,*Te*-diaryltellurimides with identical sub-

Table 6. UV spectra of chalcogenonium ylides:

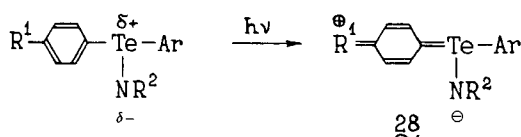


R ¹	R ²	M	λ_{max} , nm	Ref.
CH ₃	CH ₃	S	261	84
CH ₃	CH ₃	Te	270	14, 15
CH ₃	C ₆ H ₅	S	259	84
CH ₃	C ₆ H ₅	Se	261	85
CH ₃	C ₆ H ₅	Te	268	14, 15
C ₆ H ₅	C ₆ H ₅	S	250	84
C ₆ H ₅	C ₆ H ₅	Se	257	85
C ₆ H ₅	C ₆ H ₅	Te	262	14, 15

Table 7. UV spectra of tellurimides ($R^1C_6H_4)_2Te^+-N^-R^2$

R^1	R^2	λ_{max} , nm (lg ϵ) (CH ₃ OH)
H	SO ₂ CH ₂ C ₆ H ₅	222 (4.45), 274 (3.75)
4-CH ₃	SO ₂ CH ₂ C ₆ H ₅	244 (4.23), 267 (3.91)
3-CH ₃	SO ₂ CH ₂ C ₆ H ₅	219 (4.50), 272 (3.75)
4-CH ₃ O	SO ₂ CH ₂ C ₆ H ₅	250 (4.24), 273 (4.32)
		325 (3.83), 376 (4.07) (75% H ₂ SO ₄)
4-(CH ₃) ₂ N	SO ₂ CH ₂ C ₆ H ₅	317 (4.05)
4-Cl	SO ₂ CH ₂ C ₆ H ₅	244 (4.32), 274 (3.80)
3-Cl	SO ₂ CH ₂ C ₆ H ₅	220 (4.46), 280 (3.55)
4-Br	SO ₂ CH ₂ C ₆ H ₅	252 (4.46), 276 (4.14)
3-Br	SO ₂ CH ₂ C ₆ H ₅	222 (4.56), 280 (3.57)
H	C(O)CF ₃	222 (4.21), 273 (3.67)
4-CH ₃	C(O)CF ₃	235 (4.33), 273 (3.88)
3-CH ₃	C(O)CF ₃	218 (4.36), 278 (3.70)
4-CH ₃ O (Z-)	C(O)CF ₃	256 (4.24), 272 (4.30)
		323 (3.85), 372 (3.88) (75% H ₂ SO ₄)
4-CH ₃ O (E-)	C(O)CF ₃	246 (3.94), 269 (3.90)
4-(CH ₃) ₂ N	C(O)CF ₃	313 (4.46)
4-Br	C(O)CF ₃	253 (4.36), 275 (3.94)
3-Br	C(O)CF ₃	218 (4.56), 278 (3.74)
3-Cl	C(O)CF ₃	217 (4.46), 279 (3.71)

stituents on the aryl rings, as is also the case with selenimides^{72,80} and sulfimides,⁶⁵ have very similar UV spectra^{20,59,77} (Table 7). The UV spectra of unsubstituted and *m*-substituted tellurimides differ only slightly from the spectrum of benzene. In the case of *p*-substituted tellurimides, a bathochromic shift of the benzene bands was observed due to conjugation between the aryl nuclei and the substituents which includes electron transfer from the occupied p_π -orbitals of the aryl nuclei to the unoccupied d_π -orbital of tellurium^{59,77} (**28**).

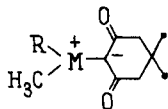


This phenomenon is most pronounced for tellurimides containing *p*-dimethylamino groups ($\lambda_{max} = 313$ and 317 nm) (Table 7).^{59,77} With protonation of this group (UV spectrum in 75% H₂SO₄) the p_π - d_π conjugation is interrupted and the spectra become similar to those of benzene.^{59,77}

The similarity of the spectra of *N*-sulfonyl- and *N*-acyltellurimides indicates that both compounds possess a dipolar structure with considerable positive charge at the tellurium atom.²⁰

A bathochromic shift of the long-wave band in the UV spectra of *N*-sulfonylchalcogenimides containing a dimethylamino group in the *p*-position of an aryl nucleus (S - 287 nm,⁶⁵ Se - 295 nm,⁷² Te - 317 nm)⁵⁹ suggests that the polarity of the chalcogen-nitrogen bond increases in the following order: S < Se < Te.

III.2.3. NMR spectra The aromatic protons of *p*-aryl substituted telluronium dimedone ylides **4** appear as an AA'BB' quartet, which is typical for the ¹H NMR spectra

Table 8. Proton chemical shifts of methyl protons in ylides:

R	M	δ_{CH_3} , ppm	Ref.
CH ₃	S	2.94	84
CH ₃	Te	2.40	14
C ₆ H ₅	S	3.34	84
C ₆ H ₅	Se	3.10	85
C ₆ H ₅	Te	2.65	14

of *p*-substituted benzene derivatives.^{14,15} The coupling constants for the *o,m*-protons are 7–9 Hz. The chemical shifts of the *o*-protons are only slightly affected by ring substitution, whereas for the *m*-protons there is a clearly defined correlation with the electronic nature of the *p*-substituents. Both *o*- and *m*-protons are shifted 0.20–0.25 ppm upfield as compared to the corresponding protons of *p*-substituted diaryl telluroxides **6**, indicating weaker deshielding by the telluronium dimedone moiety in comparison with the group Te–O.^{14,15}

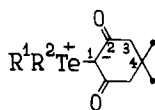
Substitution of one methyl group in dimethyltelluronium ylide by phenyl, as in the case of sulfonium ylides,⁸⁴ results in considerable deshielding of the methyl protons ($\Delta\delta = 0.25$ ppm, Table 8).^{14,15} The deshielding effect of the RM–C groups in methyl(R) chalcogenonium ylides decreases in the following order: S > Se > Te (Table 8) which is related partly to the heavy-atom effect.^{14,15}

In the ¹H NMR spectrum of *p*-methoxyphenylbenzyltelluronium dimedone ylide containing a prochiral group near the chiral center, the diastereotopic methylene protons of the benzyl group, as in the case of selenonium ylides,⁸⁶ appear as a typical AB quartet in nitrobenzene and as a single peak in methylene chloride.^{14,15} At the same time with *p*-methoxyphenyl(*p*-isopropylphenyl)telluronium dimedone ylide with the prochiral group far removed from the tellurium atom, the proton signal splitting was achieved only by using a chiral shift reagent, tris(3-fluoroacetyl-*d*-camphorato)europium, Eu(TFA-Camph)₃.^{14,15}

Investigation of the ¹³C NMR spectra of telluronium dimedone ylides (Table 9) has shown that substituents in the aryl groups practically do not affect the position of the ylide carbon signal.⁸⁷ Only on passing from the diaryl derivatives to the dimethyl compounds the chemical shift of the ylide carbon increases by 1.0 ppm. However, the magnitudes of the chemical shifts of such atoms are rather sensitive to the nature of the solvent and vary by about 1.5 ppm upon change from chloroform to acetone. In view of the absence of such solvent effects in the case of stabilized sulfonium ylides,⁸⁸ it has been suggested that the substantial dependence of the chemical shifts of the ylide carbon atoms in telluronium ylides on the type of solvent is due to their higher basicity as compared to sulfonium ylides.⁸⁶

The considerable upfield shift of the ¹³C NMR ylide carbon signal (52.6 ppm)⁸⁷ of dimethyltelluronium dimedone ylide in comparison to the corresponding sulfonium ylide signal (86.1 ppm)⁸⁹ is accounted for by the heavy-atom effect as well as by increased ylide bond polarity.^{15,87}

Table 9. ^{13}C NMR spectra of ylides:



R ¹	R ²	Chemical shift, δ , ppm							
		1	2	3	4	5	6 ^{a)}	9	7, 8
4-(CH ₃) ₂ NC ₆ H ₄	4-(CH ₃) ₂ NC ₆ H ₄ ^{b)}	51.3	190.9	49.4	30.1	26.7	102.9	149.9	137.6 111.1
4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	51.4	191.3	49.4	30.3	26.7	109.1	160.1	134.2 113.9
4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄ ^{c)}	52.3	189.8	49.8	30.1	26.7	110.7	160.0	134.7 113.6
4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄ ^{d)}	52.7	190.1	49.9	30.5	26.8	111.4	160.8	135.2 114.2
4-CH ₃ C ₆ H ₄	4-CH ₃ C ₆ H ₄	51.3	190.8	49.3	30.2	26.6	126.2	139.6	132.4 128.7
C ₆ H ₅	C ₆ H ₅	51.2	190.7	49.2	30.1	26.6	119.6	129.1	132.4 127.9
4-BrC ₆ H ₄	4-BrC ₆ H ₄	51.3	191.2	49.3	30.4	26.6	118.0	124.8	131.4 113.4
4-CH ₃ C ₆ H ₄	CH ₃ ^{e)}	51.3	191.6	49.2	30.3	26.6	116.1	139.6	131.2 128.8
C ₆ H ₅	CH ₃ ^{f)}	51.3	191.4	49.2	30.3	26.6	120.1	129.0	131.2 128.0
CH ₃	CH ₃ ^{g)}	52.6	192.3	50.3	31.7	27.9	—	—	— —

^{a)}The following numbering has been used for the phenyl ring carbons: $\delta_{\text{C}_{1-6}}$; ^{b)}chloroform as solvent; ^{c)}benzene as solvent; ^{d)}acetone as solvent; ^{e)}the chemical shift of the methyl group at Te is 2.04 ppm; ^{f)}the chemical shift of the methyl group at Te is 2.04 ppm; ^{g)}the chemical shift of the methyl group at Te is 1.22 ppm.

The small magnitude of the carbon chemical shift of the methyl group at the tellurium atom in aryl(methyl)telluronium dimedone ylides (1.2–3.0 ppm) as compared to the analogous sulfonium ylides (26.0–27.0 ppm)⁸⁸ is also explained⁸⁷ by the heavy-atom effect.

In the ^1H NMR spectra of *N*-benzylsulfonyl tellurimides the signal of the methylene protons of the benzyl group appears as a sharp singlet (Table 10) with the line shape unchanged both upon solvent change or temperature decrease (down to -40°C).⁵⁹ However, an addition of the chiral shift reagent $\text{Eu}(\text{TFA-Camph})_3$ leads to split methylene proton signals which proves the presence of the enantiomers **27a, b** in the solution.⁶⁰

The ^{19}F NMR spectra of *N*-trifluoroacetyltellurimides, existing in the *Z*-form, show a narrow singlet signal of the trifluoromethyl group, which is little affected by the nature

Table 10. Chemical shifts (ppm) of the methylene protons and ^{19}F nuclei in tellurimides ($\text{R}^1\text{C}_6\text{H}_4$)₂Te⁺-N⁻R²

R ¹	R ² = SO ₂ CH ₂ C ₆ H ₅ (δ_{CH_2})	R ² = C(O)CF ₃ ($\delta_{^{19}\text{F}}$) ^{a)}
H	4.10	73.87
4-CH ₃	4.17	73.86
3-CH ₃	4.17	73.92
4-CH ₃ O	4.17	73.67 (Z-form)
		68.69, 74.37 (E-form)
4-(CH ₃) ₂ N	4.10	68.57, 74.32 (E-form)
3-Cl	4.19	73.80
4-Br	4.25	73.72
3-Br	4.19	73.74

^{a)}Upfield ^{19}F chemical shifts with respect to CCl_3F .

of *p*-substituents of the aryl groups (Table 10).⁷⁷ At the same time, tellurimides for which the *E*-form has been established produce two broad signals of the CF₃ group in concentrated solution (Table 10). Upon dilution the low-field signals disappear and an increase in upfield signal intensity is observed. This has warranted the conclusion that the low-field signals are due to associates, the existence of which in solution has been established also with the aid of IR spectra whereas the upfield signals have been assigned to the *E*-form.^{20,77}

III.3. Dipole Moments

Unlike other chalcogenonium ylides,^{90,91} the telluronium dimedone ylides **4** have rather small dipole moments (2-5 D, Table 11). This is due to a compensation of the oppositely directed Te-C and C=O bond moments.^{14,15} Such a picture has also been observed in the case of diorganylsulfonium indanedione ylides.⁹²

The dipole moments of the ylides **4**^{14,15,87} have been calculated on the basis of conformation **29**. This conformation is supported by the results of quantum-chemical computations⁸⁷ of the relative stabilities of the most likely conformers of the model ylides (CH₃)₂M⁺-C⁻(CHO)₂ (M = S, Se) using the CNDO/2 method with an spd-basis in the parametrization⁹³ and also by X-ray data.⁴⁶

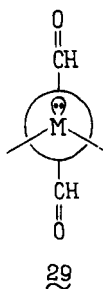


Table 11. Dipole moments (D) of ylides (C₆H₆, 30 °C):

R ¹	R ²	μ _{obs.}	μ _{calc.}
4-(CH ₃) ₂ NC ₆ H ₄	4-(CH ₃) ₂ NC ₆ H ₄	5.49	4.96
4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	4.16	3.95
4-C ₂ H ₅ OC ₆ H ₄	4-C ₂ H ₅ OC ₆ H ₄	4.26	4.09
4-CH ₃ C ₆ H ₄	4-CH ₃ C ₆ H ₄	3.58	3.58
C ₆ H ₅	C ₆ H ₅	3.16	3.16
4-BrC ₆ H ₄	4-BrC ₆ H ₄	1.74	1.68
4-FC ₆ H ₄	4-FC ₆ H ₄	2.06	1.82
CH ₃	CH ₃	3.18	--
CH ₃	4-CH ₃ OC ₆ H ₄	3.28	--
CH ₃	4-C ₂ H ₅ OC ₆ H ₄	3.42	--

Table 12. Dipole moments (D) of tellurimides (RC_6H_4)₂Te⁺-N⁻C(O)CF₃ (dioxane, 25°C)

R	$\mu_{\text{obs.}}$	$\mu_{\text{calc.}}$
H	6.02	6.02
4-CH ₃	6.25	6.25
4-CH ₃ O	5.92	6.35
4-Br	5.74	5.43

N-Trifluoroacetyltellurimides **7** possess rather high dipole moments in accordance with the dipolar structure of these compounds (Table 12).^{20,77}

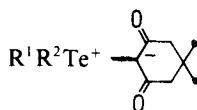
III.4. Mass Spectra

So far mass spectral investigations have only been carried out with the telluronium dimedone ylides **4** (Table 13).⁸⁷

In their mass spectral properties the telluronium ylides differ markedly from selenonium ylides. This is apparently due to a considerable increase in the polarity of the ylide chalcogen-carbon bond of the tellurium derivatives.

Unlike the selenonium analogs of compounds **4a** and **4b** (Table 13) where the intensities M⁺, characterizing the molecular resistance to electron impact, equal 14.8 and 25.9%, respectively,⁹⁴ the molecular ions of tellurium ylides possess very low intensities (0.1–0.3%) at full ion current). Only in the case of the dimethyl derivative **4b**, due to the positive inductive effect of the methyl groups, the intensity of the M⁺ peak reaches 1.8%.⁸⁷ Clearly even the minimum excess energy, received by the molecule at ionization, is used for ylide bond cleavage.

The rearrangement ions resulting from phenyl migration to the oxygen atom in the carbanionic moiety upon mass spectral fragmentation of selenium ylides produce rather intensive peaks (2.5–6.4% at full ion current).⁹⁴ However, tellurium ylide spectra have

Table 13. Relative intensities of ion peaks (in % to full ion current) in the mass spectra of telluronium ylides:

No.	R ¹	R ²	W_{M^+}	F ₁ R ¹ R ² Te	F ₂ R ² Te	F ₃ R ¹ R ²	F ₄ R ²	F ₅ HTe	F ₆ Te	F ₇ (83)	F ₈ (56)	F ₉ (55)	ΣTe
4b	CH ₃	CH ₃	1.8	38.9	18.4	—	14.1	1.3	2.8	3.7	2.8	5.8	64.6
4c	CH ₃	C ₆ H ₅	0.1	19.3	16.6	0.3	14.1	0.2	2.0	3.7	3.2	2.2	38.1
4d	CH ₃	4-C ₂ H ₅ OC ₆ H ₄	0.1	9.5	2.7	—	—	0.5	1.5	11.8	9.2	6.6	28.2
4e	C ₆ H ₅	C ₆ H ₅	0.2	10.1	4.2	15.7	26.6	0.2	0.5	5.3	3.7	2.8	15.2
4f	4-CH ₃ C ₆ H ₄	4-CH ₃ C ₆ H ₄	0.1	10.3	1.4	14.1	16.0	0.1	0.4	4.9	3.2	2.1	12.2
4a	4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	0.1	8.2	2.6	12.9	0.9	—	0.5	12.9	6.7	4.4	15.1
4g	4-FC ₆ H ₄	4-FC ₆ H ₄	0.3	10.8	6.9	17.2	11.6	0.3	1.2	5.9	2.9	2.0	19.2
4h	4-(CH ₃) ₂ NC ₆ H ₄	4-(CH ₃) ₂ NC ₆ H ₄	0.1	2.8	0.9	11.0	23.4	—	0.2	3.9	1.8	1.6	5.7

no or only low-intensity peaks corresponding to the above-mentioned rearrangement ions (less than 0.01% for the compounds **4g, h**).

The differences observed in the mass spectral fragmentations of selenonium and telluronium ylides are similar to those in thermolysis. Whereas selenonium ylides upon heating in inert solvents are subject to rearrangement with the migration of one of the substituents from the selenium to the oxygen atom in the carbanion moiety,⁹⁵ telluronium dimedone ylides undergo fragmentation with formation of the corresponding tellurides and the product of carbanion moiety trimerization.⁹⁶

III.5. The Basicity of Telluronium Ylides

The thermodynamic pK_{BH}^+ constants of the telluronium dimedone ylides **4** have been determined (Table 14).¹⁴ Compounds **4** constitute moderately strong bases comparable to aromatic amines.⁹⁷ A comparison of the basicity constants of analogous chalcogenonium ylides indicates that the basicity increases in the following sequence: S < Se < Te, which is parallel to a decrease in electronegativity of the onium atom and an increase in its size.

The best correlation of ylide **4** basicities is achieved by using σ° -constants which has been explained by the essentially inductive mechanism of the interaction between *p*-substituents of the aryl groups and the onium Te atom.^{14,15}

IV. REACTIVITY

The reactivity of π -telluranes has been studied to a much lesser degree than that of other π -chalcogenuranes. However, the data so far available point to important peculiarities in their reactions as compared to the reactions of their sulfur and selenium analogs.

The utilization of π -telluranes, and, especially, oxides and ylides for the preparation of various classes of organic compounds has been studied extensively in recent years

Table 14. Thermodynamic basicity constants (pK_a^T) of ylides $R^1R^2M^+ \begin{array}{c} \diagup \\ \text{C} \\ \diagdown \end{array} \begin{array}{c} \diagdown \\ \text{O} \\ \diagup \end{array}$ (acetonitrile, 25 °C)

R ¹	R ²	M	pK_a^T
4-(CH ₃) ₂ NC ₆ H ₄	4-(CH ₃) ₂ NC ₆ H ₄	Te	11.48 ^{a)}
4-CH ₃ OC ₆ H ₄	4-CH ₃ OC ₆ H ₄	Te	10.74
4-C ₂ H ₅ OC ₆ H ₄	4-C ₂ H ₅ OC ₆ H ₄	Te	10.86
4-CH ₃ C ₆ H ₄	4-CH ₃ C ₆ H ₄	Te	10.69
C ₆ H ₅	C ₆ H ₅	Te	10.59
4-BrC ₆ H ₄	4-BrC ₆ H ₄	Te	10.07
4-FC ₆ H ₄	4-FC ₆ H ₄	Te	10.22
CH ₃	C ₆ H ₅	Te	11.22
CH ₃	4-CH ₃ OC ₆ H ₄	Te	11.40
CH ₃	4-C ₂ H ₅ OC ₆ H ₄	Te	11.25
CH ₃	CH ₃	Te	12.07
C ₆ H ₅	C ₆ H ₅	Se	9.59
CH ₃	CH ₃	S	9.67

^{a)} The second pK_{BH}^+ value is equal to -6.61.

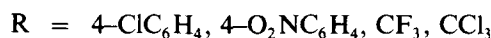
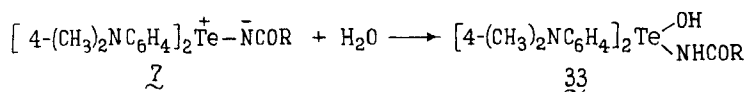
owing to the discovery of some of their characteristic reactions (in part recently reviewed).⁹⁸⁻¹⁰⁰

IV.1. Reactions with Nucleophiles

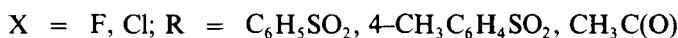
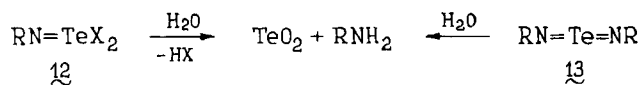
Interaction between π -telluranes and nucleophiles is determined mainly by the nature of the former and is accompanied in most cases by an increase in tellurium coordination number to 4 or its decrease to 2.

Diorganyl telluronium dimedone ylides **4** belong to those few π -telluranes which do not react with water or aqueous alkali^{14,15} (these compounds can be even recrystallized from water without decomposition). However, the unstabilized diphenyltelluronium tetraphenylcyclopentadiene ylide **1** is easily decomposed by the action of aqueous alkali.⁸

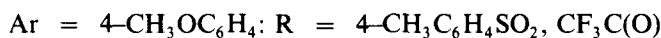
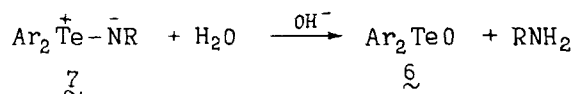
Unlike ylides **4**, *N*-acyl-*Te*, *Te*-di(*p*-dimethylaminophenyl)tellurimides **7** upon long standing in air or recrystallization from aqueous solvents forms the hydrates **33**.^{20,21} The formation of the latter has been confirmed by the appearance of an absorption band in the region 3320–3220 cm^{-1} not found in the IR spectra of the starting tellurimides.^{20,21} The wave number of the ν_{CO} band is shifted 90 cm^{-1} as compared to the corresponding absorption band in tellurimides.⁷



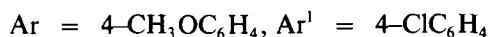
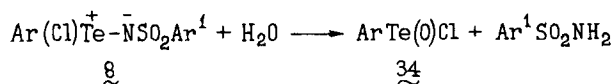
The tellurimides **12**, **13** are readily hydrolyzed by hot water with formation of tellurium dioxide and the corresponding amides.^{25,26}



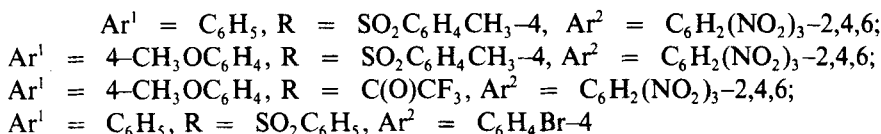
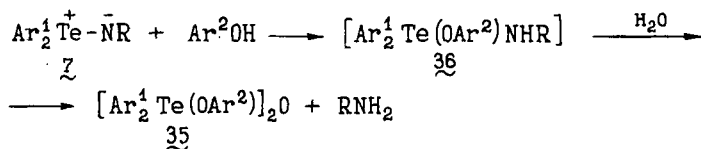
Both *N*-sulfonyl and *N*-acyl tellurimides **7** are hydrolyzed by aqueous alkali to give diaryl telluroxides and corresponding amides.²⁰ It should be noted that the corresponding reaction of selenimides proceeds under more severe conditions.¹⁰¹



In the tellurimide **8** only the $\text{Te}=\text{N}$ bond is involved in the hydrolysis whereas the $\text{Te}-\text{Cl}$ bond remains unchanged.¹⁹ In this respect tellurimides differ from the analogous sulfur¹⁰² and selenium¹⁰³ derivatives. The arenesulfonamide and the aryltelluroxo halide **34** are the products of the reaction.

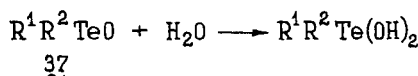


The tellurimides **7** react with phenols to give bis-[diaryl(aryloxy)tellurium] oxides **35** and the corresponding amides.¹⁰⁴



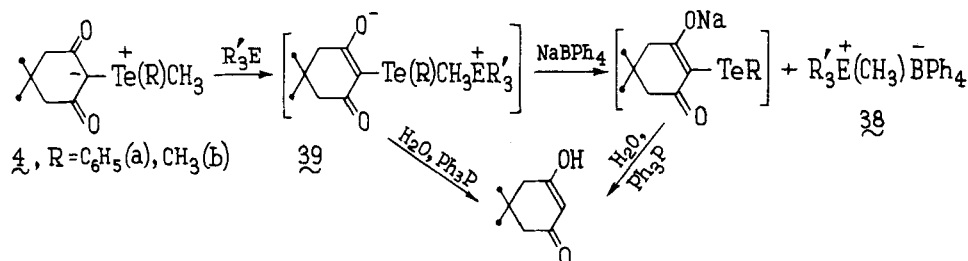
It seems likely that the reaction proceeds via formation of σ -telluranes **36**, which are hydrolyzed very easily to compound **35**. Such a mechanism is supported by the fact that the oxides **35** are formed in identical yields with a ratio of the reactants of 1:1 as well as of 1:2.

Similar to dialkyl and aryl alkyl selenoxides,¹ dialkyl and aryl alkyl telluroxides **37** readily react with water to give the compounds to which the structure of either telluroxide hydrates R₂TeO·H₂O or tetracoordinated diorganyltellurium dihydroxides R₂Te(OH)₂ has been assigned.^{40,41}



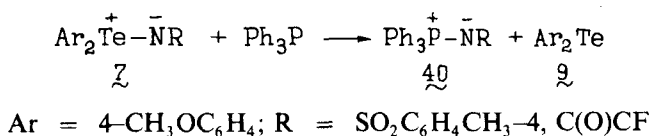
Diaryl telluroxides do not react with water.

Other nucleophiles involved in reactions with π -telluranes are triphenylphosphine and its analogs. Here too, there is a certain similarity in the behavior of diorganyl telluroxides and diorganyl tellurimides as distinct from diorganyltelluronium dimedone ylides **4**.¹⁰⁵ The latter react with triphenylphosphine and other derivatives of the group V elements, e.g. Et₃N, (Me₂N)₃P and Ph₃As. In the presence of NaBPh₄, as is also the case with sulfonium¹⁰⁶⁻¹¹⁰ and selenonium^{111,112} ylides, these compounds undergo dealkylation and in all cases except Ph₃As form the corresponding onium tetraphenylborates **38** in good yield. Apart from these, the ylides **4**, when treated with Ph₃P, give dimedone and trace amounts of Ph₃P=O. The poor yield of arsonium tetraphenylborate in the reaction of the ylides **4** with Ph₃As is explained by decomposition of the ylides at the high reaction temperature of 140–160 °C⁹⁶ (see Section IV.4).



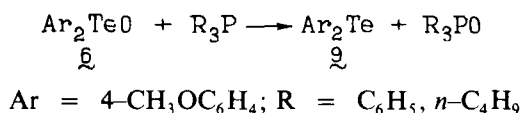
In the absence of NaBPh_4 the reaction between ylides **4** and Ph_3P results not in the expected methyl triphenylphosphonium-2-phenyl-telluryldimedonate **39** ($\text{E} = \text{P}$, $\text{R} = \text{Ph}$) as in the case of the sulfonium¹⁰⁸ and selenonium analogs,¹¹¹ but in a mixture of dimedone and $\text{Ph}_3\text{P}=\text{O}$. The reactions of telluronium ylides **4** with $(\text{Me}_2\text{N})_3\text{P}$ proceed like those with Ph_3P . For diphenyl- and di(*p*-methoxyphenyl)telluronium dimedone ylides, which cannot be dearylated with $(\text{Me}_2\text{N})_3\text{P}$ due to the difficulty of nucleophilic substitution at the sp^2 -hybridized carbon atom, one might expect the formation of telluranylphosphonium betaines, i.e. products of the addition of $(\text{Me}_2\text{N})_3\text{P}$ to the telluronium center. The ^{31}P NMR spectrum of the reaction mixture shows signals at δ_{p} 25 ppm, assigned to $(\text{Me}_2\text{N})_3\text{P}=\text{O}$, and at 50–52 ppm. A very strong band appears at 1000 cm^{-1} in the IR spectrum. These data are consistent with the concept of betaine formation in solution. However, attempts to isolate these betaines from the reaction mixture or to identify them by some other technique failed.¹⁰⁵

Tellurimides **7** behave in a different way. Their interaction with $\text{Ph}_3\text{P}^{113}$ affords, as in the case of sulfimides¹¹⁴ and selenimides,¹¹⁵ triphenylphosphinimides **40** and diaryl tellurides **9**.



The reactions with tellurimides proceed under milder conditions (at room temperature) as compared with sulfimides, which react with triphenylphosphine in *N,N*-dimethylformamide at $100\text{--}130^\circ\text{C}$.¹¹⁴

Diaryl telluroxides **6** oxidize triorganylphosphines to triorganylphosphine oxides and form diaryl tellurides **9**.¹¹⁶



IV.2. Reactions with Electrophiles

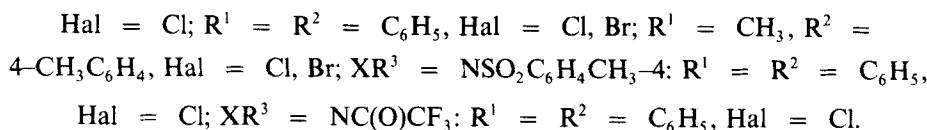
The reactions of π -telluranes with electrophiles reveal most clearly the peculiarities of their reactivity. In most cases, interaction between π -telluranes and electrophiles proceeds with an increase in the tellurium coordination number.

IV.2.1. Halogens Halogens cleave Te-X bonds in telluronium dimedone ylides and tellurimides under very mild conditions; σ -telluranes **5** and dihalide derivatives of dimedone^{15,117} or amides^{20,18} are formed.



$\text{XR}^3 = \text{CCOCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CO}$; $\text{R}^1 = \text{R}^2 = 4\text{-CH}_3\text{OC}_6\text{H}_4$; $\text{Hal} = \text{Cl}, \text{Br}, \text{I}$;

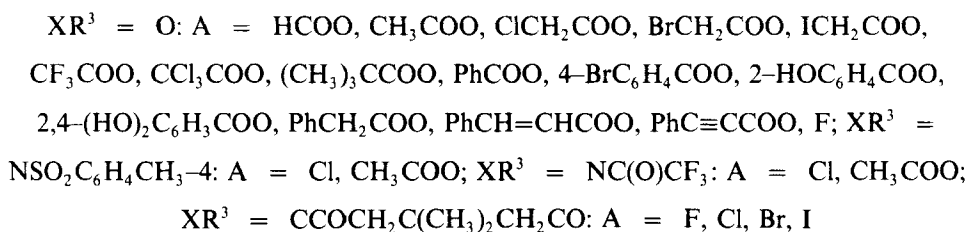
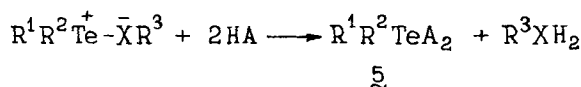
$\text{R}^1 = \text{R}^2 = 4\text{-(CH}_3)_2\text{NC}_6\text{H}_4$, $\text{Hal} = \text{Cl}, \text{Br}, \text{I}$; $\text{R}^1 = \text{R}^2 = 4\text{-CH}_3\text{C}_6\text{H}_4$,



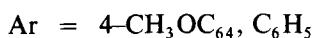
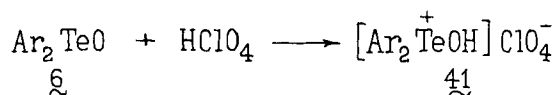
Tellurimides such as $\text{RN}=\text{TeHal}_2$ (**12**) and $\text{RN}=\text{Te}=\text{NR}$ (**13**) behave in a similar way. They react with chlorine to give tellurium tetrachloride and *N,N*-dichloroamides.^{25,26}

It should be noted that in the reactions with halogens sulfonium ylides stabilized by two electron acceptor groups form dihalide derivatives of the carbanionic moieties of the molecules as well as sulfides.¹¹⁹

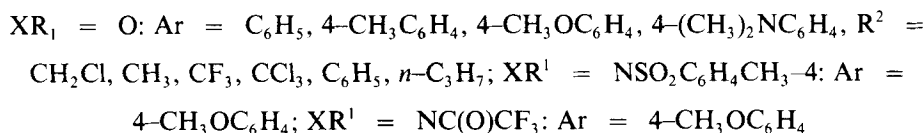
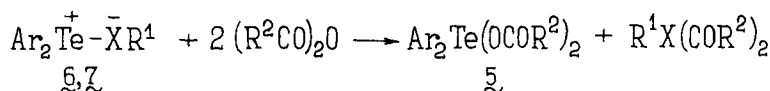
IV.2.2. Acids and their derivatives The reactions with acids are common to all π -telluranes. In all instances their interaction with acids containing sufficiently nucleophilic anions (HHal , HONO_2 , RCOOH) gives rise to the corresponding σ -telluranes **5**.^{15,20,34,117,118,120-125}



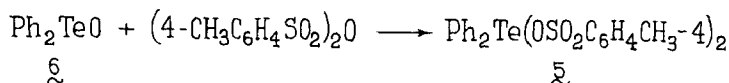
It is a different case with perchloric acid and its non-nucleophilic anion. Its interaction with diaryl telluroxides **6** produces diaryloxytelluronium perchlorates **41**, presumably of ionic structure.³⁴



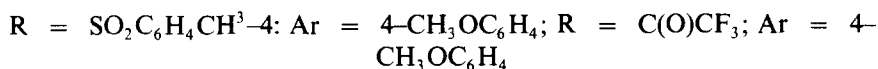
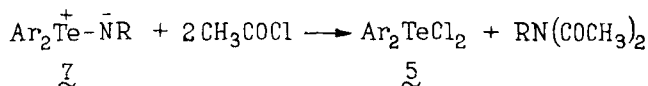
Diaryl telluroxides^{34,122,126} and tellurimides¹¹⁸ react easily with carboxylic acid derivatives such as carboxylic acid anhydrides and acyl chlorides. In reactions of compounds **6**, **7** with carboxylic acid anhydrides the corresponding diaryl tellurium diacylates **5** are formed in high yields (in the case of tellurimides **7** the secondary reaction products are *N,N*-diacylamides which during the work-up of the reaction mixtures are hydrolyzed to the corresponding monoacyl derivatives).



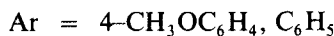
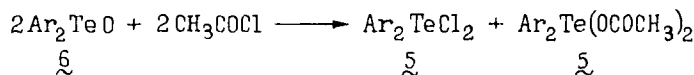
Diaryl selenoxides, similarly to diaryl telluroxides, react with acid anhydrides to give diarylselenium diacylates,³⁴ whereas diaryl sulfoxides do not undergo such reactions.³⁴ Diaryl telluroxides **6** react also with sulfonic acid anhydrides to form σ-telluranes **5**.¹²²



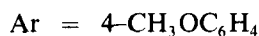
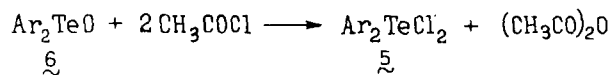
Interaction between tellurimides **7** and acyl chlorides,¹¹⁸ as in the case of anhydrides, proceeds via Te-N cleavage and formation of diaryltellurium dihalides **5** and *N,N*-diacylamide derivatives.



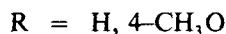
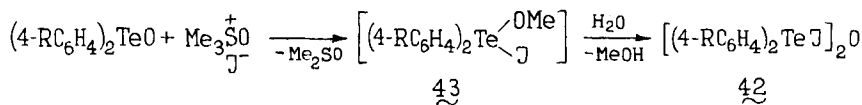
At the same time, in the reaction of diaryl telluroxides **6** with acetyl chloride (in the molar ratio 1:1) equimolar amounts of tellurium dichlorides and tellurium diacylates are formed.³⁴



With an excess of acyl chloride diaryltellurium dichlorides and the anhydrides of the corresponding acids are obtained in high yields.³⁴

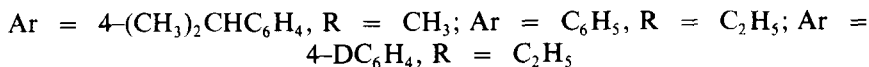
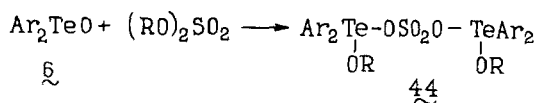


IV.2.3. Alkylating agents A number of recent investigations have been concerned with the reactions of one type of π-telluranes, the diaryl telluroxides **6**, with various alkylating agents: trimethylsulfoxonium iodide,¹²⁷ dialkyl sulfates¹²⁸ and methyl iodide.¹²⁹ Judging by the data obtained the structure of the final reaction products is determined primarily by the alkylating agents. The reactions of diaryl telluroxides **6** with trimethylsulfoxonium iodide lead to bis(diaryliodotellurium) oxides **42** in 60–70% yield. It is likely that this reaction proceeds via the intermediates **43**.¹²⁷



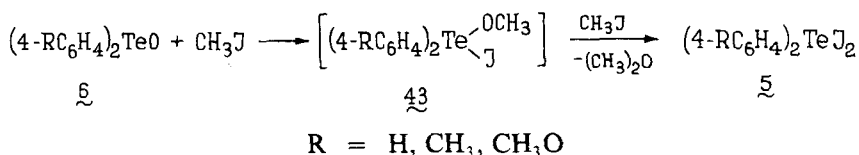
Another type of σ-telluranes, bis(diarylalkoxytellurium) sulfates **44**, have been ob-

tained by interaction of diaryl telluroxides **6** with dialkyl sulfates in the appropriate dry alcohols.¹²⁸



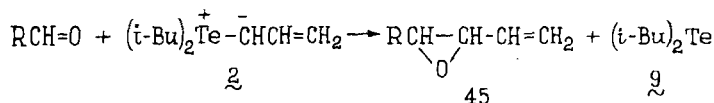
The structure of these recently synthesized compounds **44** has been established by means of their IR spectra (bands in the region of 1200 cm^{-1} , characteristic for the S=O bond vibration in covalent sulfates) and by their formation (similarly to other σ -telluranes) upon boiling in formamide of the corresponding diaryl tellurides.

Of special interest is the reaction of diaryl telluroxides with methyl iodide.¹²⁹ Unlike dimethyl sulfoxide,¹³⁰ heating of diaryl telluroxides with methyl iodide (in large excess) in a sealed tube at 100°C results in diaryltellurium diiodides **5** in 80–90% yield, probably via intermediates such as **43**.



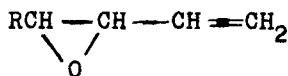
In addition to the diaryltellurium diiodides **5**, the corresponding diaryl tellurides were isolated in 10–15% yield. Further investigations are needed to account for the formation of these compounds.

IV.2.4. Aldehydes and ketones Telluronium ylides **4** do not react with aldehydes and ketones. At the same time unstabilized telluronium ylides such as the dialkyltelluronium allyl ylides **2**¹¹ and the monostabilized telluronium ylides, the dialkyltelluronium carbethoxymethylides **3**,¹² react readily with different aldehydes and ketones to give products the structure of which is determined by the nature of the telluronium ylides. Dialkyltelluronium allyl ylides **2** (the best results were achieved by using di(*iso*-butyl)-telluronium allyl ylide), the synthesis of which is described in Section II.1, in its reaction with aliphatic and aromatic aldehydes gives the α,β -unsaturated epoxides **45** in the form of a mixture of *cis*- and *trans*-isomers and di(*iso*-butyl) telluride.¹¹ As can be seen from Table 15, in the case of aromatic aldehydes the *cis/trans* ratio is determined by electronic as well as steric factors.



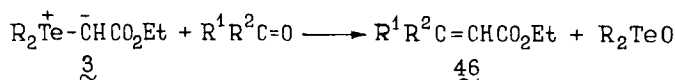
Telluronium ylides such as dialkyltelluronium carbethoxymethylides **3** (synthesis see Sect. II.1.), react with aldehydes and ketones to give α,β -unsaturated esters **46** in high yields (Table 16). Thus, the telluronium ylides **3** are distinct in their properties from unstabilized telluronium ylides as well as from the corresponding sulfonium ylides which

Table 15. Synthesis of α,β-unsaturated epoxides:



R	Yield %	cis/trans ratio	R	Yield %	cis/trans ratio
C ₆ H ₅	82	85:15	2-ClC ₆ H ₄	86	50:50
4-CH ₃ C ₆ H ₄	75	80:20	2,4,6-(CH ₃) ₃ C ₆ H ₂	58	57:43
4-CH ₃ OC ₆ H ₄	64	83:17	1-C ₁₀ H ₇	80	82:18
3,4-(CH ₃ O) ₂ C ₆ H ₃	65	88:12	cyclo-C ₆ H ₁₁	55	78:22
3-C ₅ H ₄ N	86	78:22	4-cyclo-C ₆ H ₉	57	80:20
4-ClC ₆ H ₄	80	75:25	C ₆ H ₁₃	38	68:32
4-O ₂ NC ₆ H ₄	94	58:42	C ₆ H ₅ CH ₂ CH ₂	30	64:36
2-CH ₃ C ₆ H ₄	65	60:40	C ₉ H ₁₉	35	65:35
2-CH ₃ OC ₆ H ₄	83	63:37	CH ₃ C(C ₆ H ₅)(CH ₃)	56	85:15

do not react with simple aldehydes and ketones and, by reaction with α,β-unsaturated carbonyl compounds, are converted to cyclopropanes.¹³¹



Also *N*-arenesulfonyltellurimides **7** undergo reaction with aldehydes to form *N*-arenesulfonylazomethines **47** and diaryl telluroxides **6** in low yields.¹³²

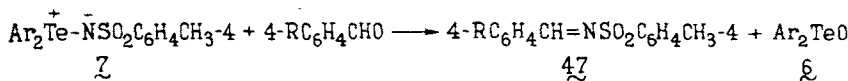
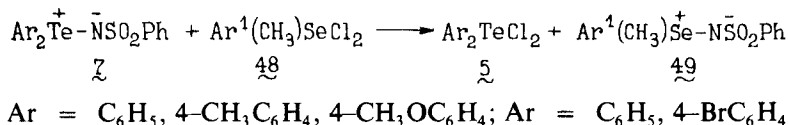


Table 16. Synthesis of α,β-unsaturated esters from ylides R₂Te⁺-C⁻HCO₂C₂H₅

Carbonyl compound	Yield of ester, %	E/Z isomer ratio
benzaldehyde	75	50:1
piperonal	73	50:1
3,4-dimethoxybenzaldehyde	76	50:1
2-bromo-4,5-methylenedioxybenzaldehyde	53	50:1
hexanal	52	19:1
cyclopentanone	52	
cyclohexanone	74	
2-methylcyclohexanone	84	12:1
3-methylcyclohexanone	83	1:1
4-methylcyclohexanone	81	
4-tert-butylcyclohexanone	90	
isophorone oxide	80	1:2
benzophenone	52	
2-hexanone	65	2.5:1
pinacone	55	50:1
trans-cinnamaldehyde	72	50:1
benzalacetone	56	2:1

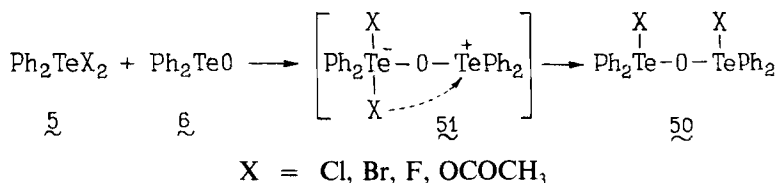
N-Trifluoroacetyltellurimides do not react with benzaldehydes. For the reaction of tellurimides with dimedone see Sect. II.1.).

IV.2.5. *Diorganylchalcogen dihalides* *N*-Sulfonyltellurimides **7**¹³³ react easily with diorganylselenium dichlorides **48** to form diaryltellurium dichlorides **5** and selenimides **49** in high yields.



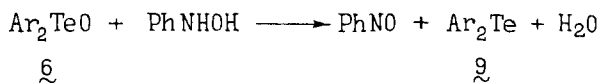
It is likely that the driving force of this reaction results from the enhanced propensity of tellurium towards formation of tetracoordinated derivatives.

A specific method for the preparation of bis(diarylhalotellurium) oxides **50** in high yields, which has no analogy in the chemistry of diaryl sulfoxides and diaryl selenoxides, is based on the interaction between diaryl telluroxides **6** and σ -telluranes **5**.¹³⁴ The reaction proceeds, in the authors' opinion, via pertellurane **51** with pentacoordinated tellurium.

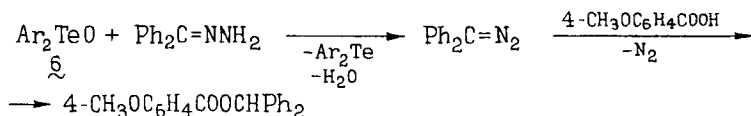


IV.3. Oxidative Properties of π -Telluranes

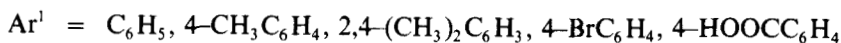
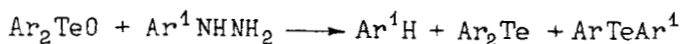
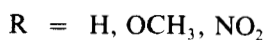
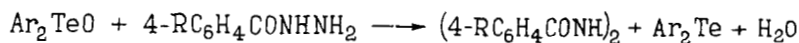
Some reactions with π -telluranes revealing their oxidative properties have been described above. Formally, the reaction of tellurimides with triphenylphosphine and of diaryl telluroxides with triorganylphosphines may be regarded as such. In addition to phosphines, diaryl telluroxides **6** readily oxidize other organic compounds; specifically, *N*-phenylhydroxylamine to nitrosobenzene and benzophenone hydrazone to diazodiphenylmethane.^{116,135}



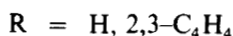
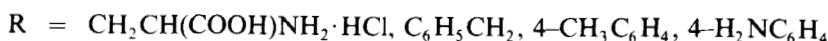
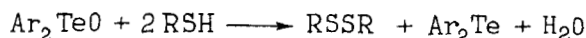
Ar is here and further on *p*-CH₃OC₆H₄



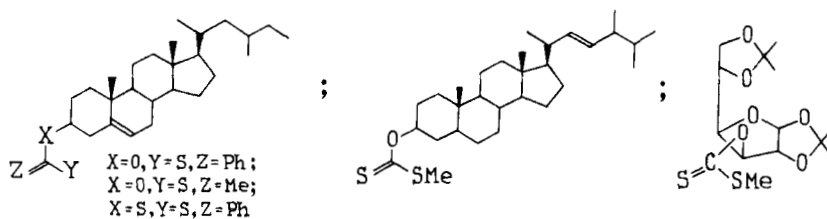
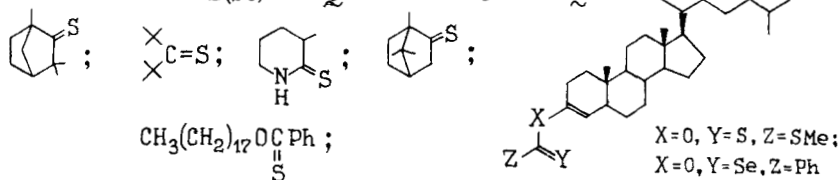
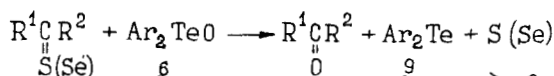
Under mild conditions diaryl telluroxides oxidize carboxylic acid hydrazides to diarrylhydrazides and phenylhydrazines to the corresponding arenes. In the latter case, along with the expected symmetrical telluride (*p*-CH₃OC₆H₄)₂Te, unsymmetrical diaryl tellurides are formed as the result of an aryl exchange of unclarified mechanism.^{116,135}



Diaryl telluroxides **6** are very effective for the oxidation of thiols to disulfides and of some phenols to the corresponding quinones.

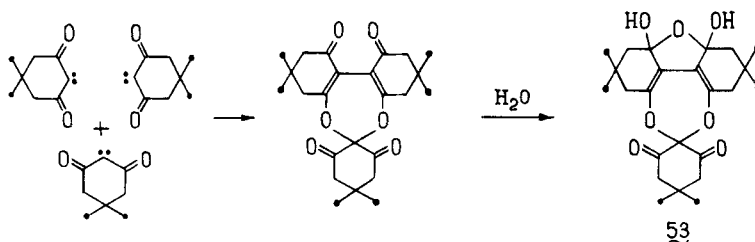
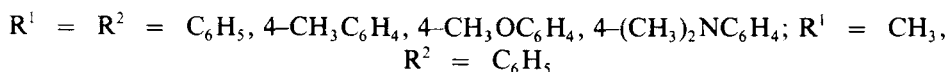
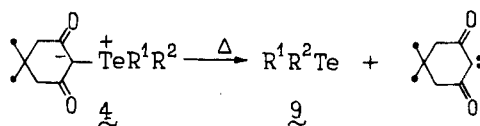


Diaryl telluroxides are also employed for the oxidation of thio(seleno)carbonyl compounds (thioketones, thioesters and their selenium analogs). In this case the corresponding carbonyl compounds, sulfur (selenium), and diaryl tellurides **9** are formed in high yields.^{116,135,136}



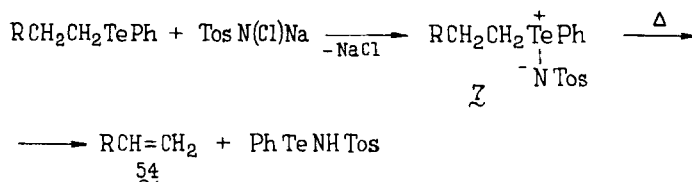
The oxidation of thiocarbonyl to carbonyl compounds has also been performed with the aid of an oxidative catalytic cycle which may become operative at any stage of the

spectra.⁹⁶ It is likely that this compound is formed via carbene generation according to the following scheme:



In contrast to the telluronium ylides **4** their selenium analogs when heated are subject to a rearrangement associated with Se→O migration of one of the groups attached to the selenium atom.⁹⁵

Unlike the telluronium ylides **4**, the tellurimides **7**, obtained via the reaction of phenyl alkyl tellurides with chloramine-T in boiling tetrahydrofuran (THF), decompose to give alkenes **54** in high yields.¹⁴⁰



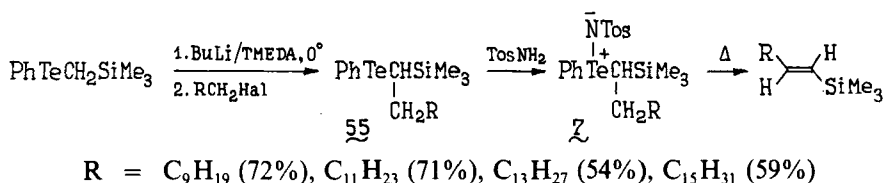
Some data on this reaction are given in Table 17.

Compounds **7** can be utilized for the preparation of vinylsilanes. *N*-Sulfonyltellurimides **7**, obtained through the reaction of compounds **55** with chloramine-T in 60–70% yield, when heated in THF, decompose easily to give vinylsilanes in high yields.¹⁴¹

Table 17. Synthesis of alkenes by reaction of phenyl alkyl tellurides with chloramine-T

Telluride	Alkene	Yield, %
<i>n</i> -C ₁₀ H ₂₁ TePh	<i>n</i> -C ₈ H ₁₇ CH=CH ₂	66
<i>n</i> -C ₁₂ H ₂₅ TePh	<i>n</i> -C ₁₀ H ₂₁ CH=CH ₂	78
<i>n</i> -C ₁₄ H ₂₉ TePh	<i>n</i> -C ₁₂ H ₂₅ CH=CH ₂	89
<i>n</i> -C ₁₅ H ₃₁ TePh	<i>n</i> -C ₁₃ H ₂₇ CH=CH ₂	75
<i>n</i> -C ₁₂ H ₂₅ CH(CH ₃)TePh	<i>n</i> -C ₁₂ H ₂₅ CH=CH ₂ (2.2) ^{a)}	93
	<i>trans</i> -C ₁₁ H ₂₃ CH=CHCH ₃ (1.0) ^{a)}	

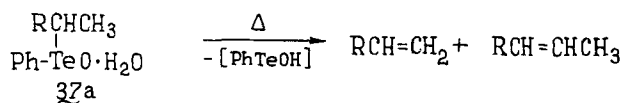
^{a)} molar ratio of isomers.



The reaction is stereospecific and leads to *E*-isomers only. The sulfur and selenium analogs of compounds **55** are decomposed in a similar manner at the thermolysis temperature depending on the chalcogen. Sulfonylselenimides decompose at room temperature whereas *N*-sulfonylsulfimides do so only at 100 °C.¹⁴¹

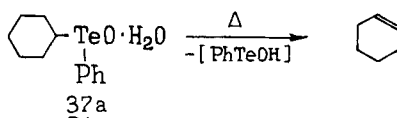
The decomposition of telluroxides upon thermolysis was first investigated by Sharpless.¹⁴² Upon oxidation of phenyl alkyl tellurides with *t*-butyl hydroperoxide in benzene the intermediate phenyl alkyl telluroxides **37** are decomposed with the formation of an alkene mixture.

The conditions necessary for the thermolysis of phenyl alkyl telluroxides **37**, obtained either by alkaline hydrolysis of phenylalkyltellurium dibromides^{35-38,143} or by oxidation of the corresponding tellurides with *m*-chloroperbenzoic acid,^{143,144} hydrogen peroxide,^{143,144} *t*-butyl peroxide,¹⁴⁴ or sodium periodate,¹⁴³ are determined by their structure. (It is interesting to note that upon oxidation with *m*-chloroperbenzoic acid products of the structure R(Ph)Te(OH)OCOR, R = *m*-ClC₆H₄, are obtained. These products result from the reaction between initially formed telluroxides and the *m*-chlorobenzoic acid produced in the course of reaction). Phenyl alkyl telluroxides **37a**, containing *sec*-alkyl groups decompose even at room temperature to give alkene mixtures in high yields. For example, a mixture of 1-octene (**54**, R = C₆H₁₃) and *cis*- and *trans*-2-octene (**56**, R = C₆H₁₃) in 80% yield with small amounts of 2-octanol and 2-octanone was obtained from *s*-octyl phenyl telluroxide **37a** (R = C₆H₁₃). 2-Dodecyl, 2-tetradecyl-, cycloheptyl-, cyclooctyl- and cyclododecyl phenyl telluroxides behave likewise.^{37,38}



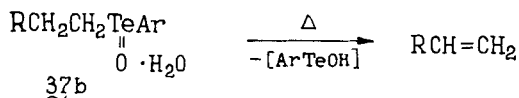
The ratio of isomers with a double bond at the first and second carbon atom in the case of linear alkenes (**54**, **56**) is much higher for telluroxides **37a** (2.28–2.50:1, R = C₆H₁₃, *n*-C₈H₁₇) than for selenoxides (1.56:1)¹⁴⁵ and sulfoxides (1.50:1).¹⁴⁶

Cyclohexyl phenyl telluroxide **37a** (R = *cyclo*-C₆H₁₁) is the most stable among the cycloalkyl phenyl telluroxides. It is decomposed only at 200–220 °C to give cyclohexene in 70% yield.^{36-38,144}

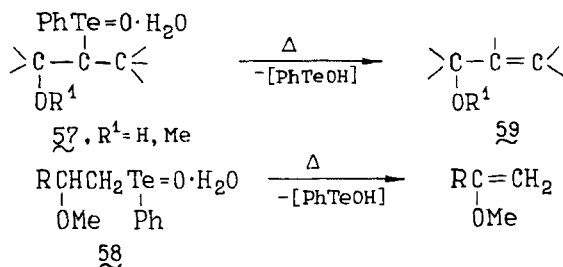


Telluroxides **37b** with primary alkyl groups are very stable too; they decompose under severe conditions. Thus, *n*-dodecyl phenyl telluroxide **37b** (R = C₆H₁₃, Ar = C₆H₅), when heated at 200–240 °C³⁸ gives alkene in 50% yield and *n*-dodecyl *p*-anisyl telluroxide

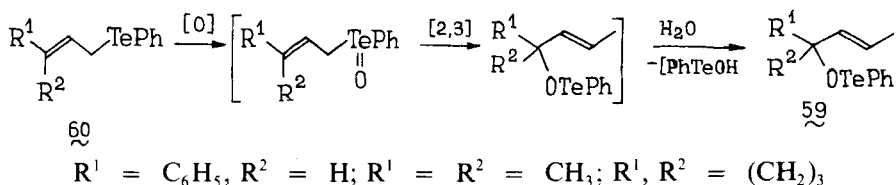
37b ($R = C_6H_{13}$, $Ar = p-CH_3OC_6H_4$) converts into an equimolar mixture of alkenes and telluride upon long refluxing in CCl_4 .³⁵



Similarly, phenyl alkyl telluroxides **37a, b** and their analogs with hydroxy and methoxy groups **57, 58** are decomposed to give allyl alcohols **59** or allyl (vinyl) ethers in high yields:^{37,38}

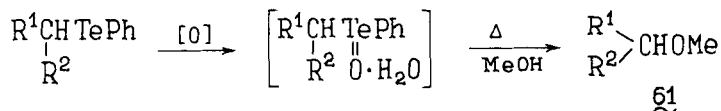


Allyl alcohols **59** are formed, too, via oxidation of phenyl allyl tellurides **60** in diethyl ether with oxidants such as H_2O_2 , $NaIO_4$, and *t*-butyl peroxide.¹⁴⁷ The formation of alcohols **59** proceeds, probably, via 2,3-sigmatropic rearrangement of the intermediate telluroxides. α,β -Unsaturated carbonyl compounds and allyl alcohols (isomers of compounds **59**) are formed.



Some data on the synthesis of alkenes and their derivatives by thermolysis of phenyl alkyl telluroxides are given in Table 18.

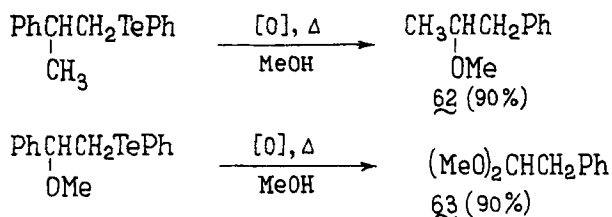
In the oxidation of phenyl alkyl tellurides (or the corresponding telluroxides **37**) by *m*-chloroperbenzoic acid in methanol also other than the above-mentioned compounds are formed.¹⁴⁸ In this case, alkyl methyl ethers **61** are obtained in high yields.



$R^1 = n-C_{12}H_{25}$, $R^2 = H$ (50%); $R^1 = C_6H_5CH_2CH_2$, $R^2 = H$ (67%);

$R^1 = n-C_{12}H_{25}$, $R^2 = CH_3$ (86%)

With the phenyl group in the vicinal position with respect to the phenyltelluro moiety, the substitution of the latter is accompanied by phenyl migration to give compounds **62, 63**.



Application of this reaction to the products of methoxytellation of cyclic alkenes³⁷ makes it possible to obtain dimethyl acetals of cyclic aldehydes **64**, **65** which are formed by ring contraction of the starting telluriumorganic compounds.

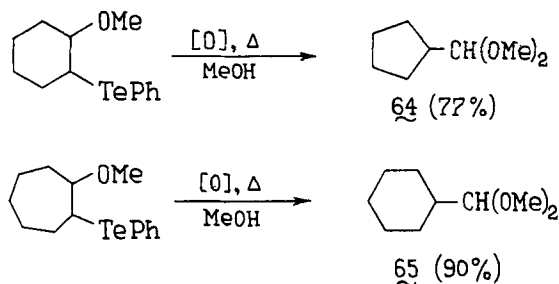


Table 18. Synthesis of alkenes, allyl and vinyl ethers and allyl alcohols by thermolysis of phenyl alkyl telluroxides






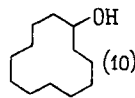

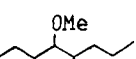
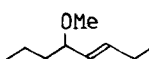
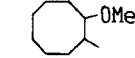
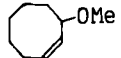
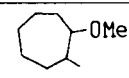
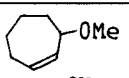
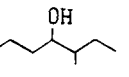
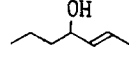
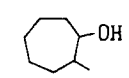
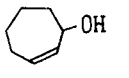
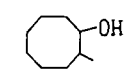
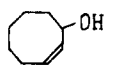
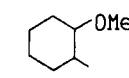
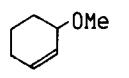

Telluroxide R	Reaction conditions	Products and yield (%)
37a , $n\text{-C}_6\text{H}_{13}$	a	1-octene (57), <i>trans</i> -2-octene (19), <i>cis</i> -2-octene (4), 2-octanol (10), 2-octanone (10)
37a , $n\text{-C}_8\text{H}_{17}$	a	1-decene (50), 2-decene (20), 2-decanol (2), 2-decanone (3)
37a , $n\text{-C}_{12}\text{H}_{25}$	a	1- and 2-tetradecene (80), tetradecanol (3), tetradecanone (4)
37a 	b	cyclohexene (72), cyclohexanol (2), cyclohexanone (traces)
37a 	a	cycloheptene (70), cycloheptanol (3), cycloheptanone (10)
37a 	a	cyclooctene (70), cyclooctanol (9), cyclooctanone (20)
37a 	a	 (80)  (10)  (10)
37b , $n\text{-C}_{10}\text{H}_{21}$	a	1-dodecene (50), 1-dodecanol (11)
57 	a	 (80)
57 	a	 (81)

Table 18. (Continued)

Telluroxide R	Reaction conditions	Products and yield (%)
57 	a	 (99)
57 	a	 (72)
57 	a	 (67)
57 	a	 (67)
57 	a	 (70)
57, $C_8H_{17}CHCH_2^-$ OMe	b	C_8H_{17}  (78)

^{a)} telluroxide decomposition proceeds at room temperature;

^{b)} telluroxide is decomposed at 200–240 °C.

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