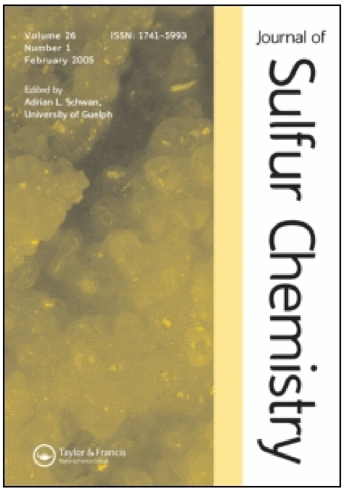

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Five-Membered Tellurium-Containing Heterocycles

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FIVE-MEMBERED TELLURIUM-CONTAINING HETEROCYCLES

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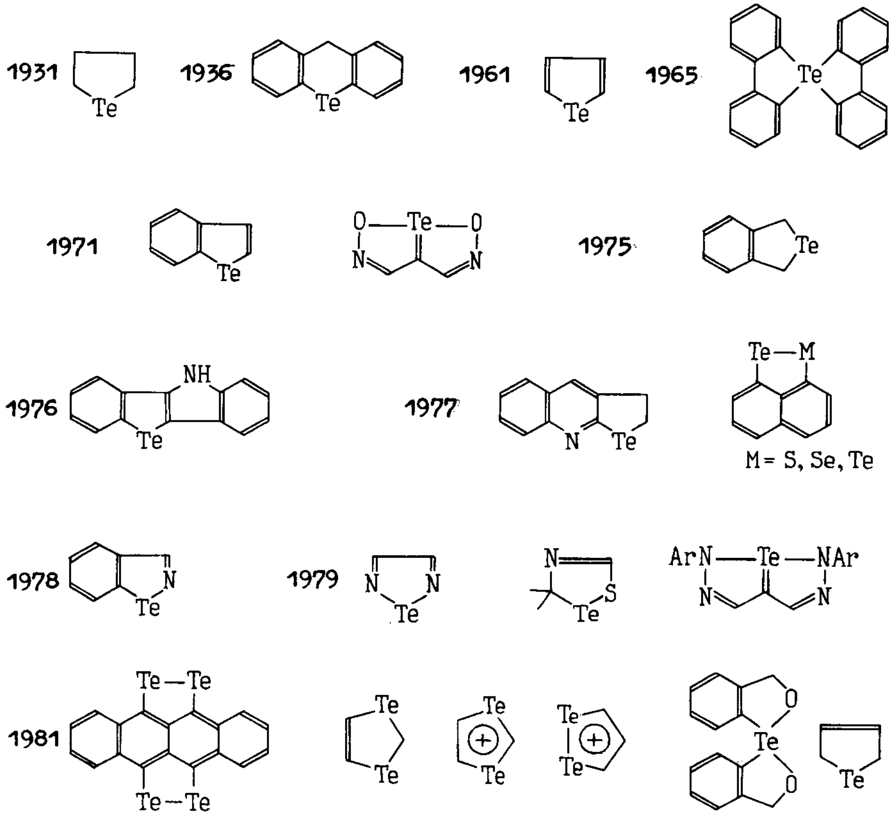
This reviews deals with five-membered tellurium-containing heterocyclic compounds the major part of which was unknown before 1977. Their synthesis, reactivity, and structure are presented in a systematic and generalized manner. Special attention is given to the pecularities in synthetic approaches to tellurium heterocycles and their reactivity as compared to the analogous sulfur and selenium compounds.

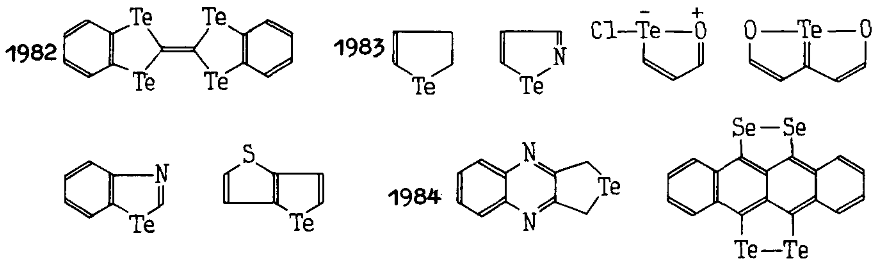
CONTENTS

I. INTRODUCTION

The rapid development of organotellurium chemistry in the last 10–15 years has been accompanied by an equally rapid increase in the number of publications on the chemistry of six- and five-membered heterocyclic tellurium compounds. While preparation and reactions of six-membered tellurium-containing heterocyclic compounds have been recently surveyed[1], no comprehensive review on syntheses, structure, and reactivity of their five-membered analogs, with the exception of the tellurophene chemistry considered in reviews, e.g., Refs. 2 and 3, has appeared in the literature until now. Meanwhile the progress in this area is very impressive.

Up to the sixties there had been described only two five-membered tellurium heterocycles, tetrahydrotellurophene[4] and dibenzotellurophene[5]. The synthesis of tellurophene[6,7] (in 1961 and 1965) and the study of the structure and reactivity of these novel heteroaromatic compounds possessing peculiar properties (Fringuelli *et al.*[2]) promoted drastically further investigation of the five-membered tellurium heterocycles. The major part of the heterocycles of this type has been prepared after 1977 as seen from the following scheme showing the chronology of the synthesis of various five-membered tellurium-containing heterocycles the chemistry of which is considered in the present review.





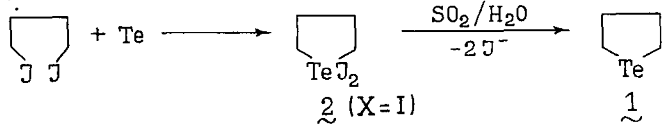
Thus the number of five-membered tellurium-containing heterocycles has already exceeded thirty and goes on growing. One should, however, note a certain disproportion between the development of synthetic procedures and the investigation of the structure and reactivity of tellurium heterocycles. Of the five-membered tellurium heterocycles described to date, only tellurophene[2,3] and benzo[b]tellurophene[8] have been studied fairly well, though not as extensively as their sulfur and selenium analogs. Therefore further progress in the chemistry of five-membered tellurium heterocycles can be envisaged in the following two general directions. (1) Development of novel methods of synthesis of tellurium heterocycles since only single synthetic procedures are known now for many of them resulting frequently in low yields of the desired compounds. Moreover, many systems are represented now by only one or few derivatives. (2) A substantial extension of the study into the structure and reactivity of these heterocycles which in many respects are sharply different from the properties of sulfur and selenium compounds. In this review tellurophene is not considered since it was the subject of other review articles[2,3]. Here we only list major publications on tellurophene which have appeared in recent years. They deal with the synthesis[9-14], reactivity[15,16], coordination chemistry[17], photochemistry[18], with the study of spectra (infrared[19], photoelectron[20,21], NMR[22-25], mass[26]) and of dipole moments[27].

II. HETEROCYCLES WITH ONE TELLURIUM ATOM

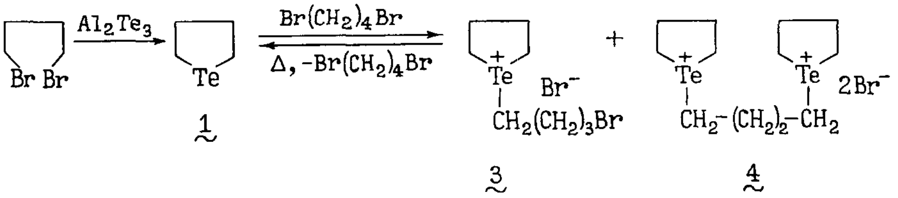
2.1. *Tetrahydrotellurophene and its derivatives*

The simplest representative of the five-membered tellurium-containing heterocyclic system, tetrahydrotellurophene (1-telluracyclopentane) is prepared by methods similar to those used for the preparation of its six-membered analog, 1-telluracyclohexane.[1] The general procedures are based on the following reactions: (1) interaction between 1,4-dithalobutanes and metallic tellurium or metal tellurides (Na_2Te, Al_2Te_3); (2) electrophilic addition of tellurium tetrachloride to appropriate diolefins.

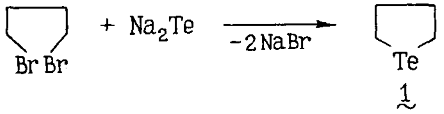
Tetrahydrotellurophene **1** was first obtained by Morgan via reaction of 1,4-diiodobutane with amorphous tellurium at 130–140 °C. The subsequent reduction of the initially formed 1-telluracyclopentane 1,1-diiodide **2** (X = I) with sulfur dioxide led to compound **1**[4,28].



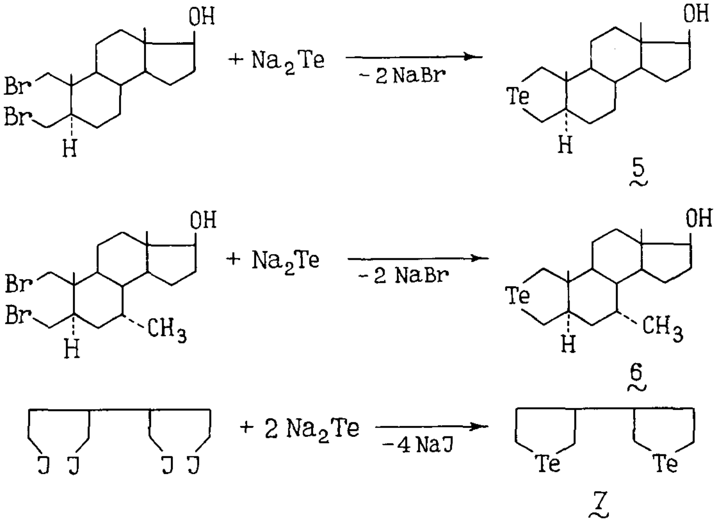
Another method for the synthesis of this heterocycle is based on the reaction of 1,4-dibromobutane with aluminum telluride at 125 °C[4]. The tellurium salts **3** and **4** emerging from the alkylation of the intermediate **1** with excess 1,4-dibromobutane are the final products of the reaction. Like other telluronium salts[29], compounds **3** and **4** upon heating above their melting points eliminate readily 1,4-dibromobutane to form tetrahydrotellurophene.



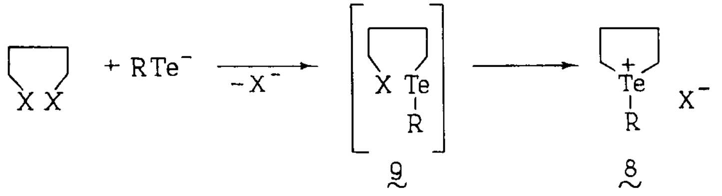
The most convenient one-pot synthesis of 1-telluracyclopentane is accomplished by treatment of 1,4-dibromobutane with sodium telluride obtained by the rongalite method.[30]



This reaction was also successfully used to obtain the steroid derivatives **5** and **6** containing the tetrahydrotellurophene moiety[31] and 3,3′-bis(tetrahydrotellurophenyl)[32,33] **7**.

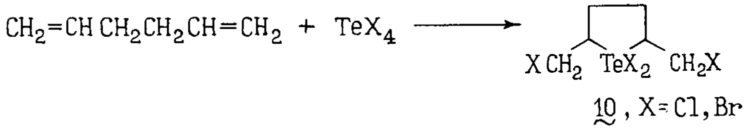


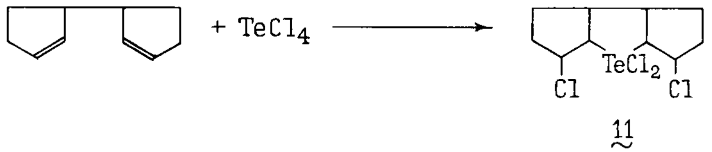
The reactions of tellurolate anions with 1,4-dihalobutanes give rise to the telluronium salts **8**[34]. The reactions proceed, apparently, via an intermediate compound **9** the quaternization of which is completed much faster than the second nucleophilic attack by RTe^{-}[34].



X = Cl, Br; R = p−$EtOC_6H_4$

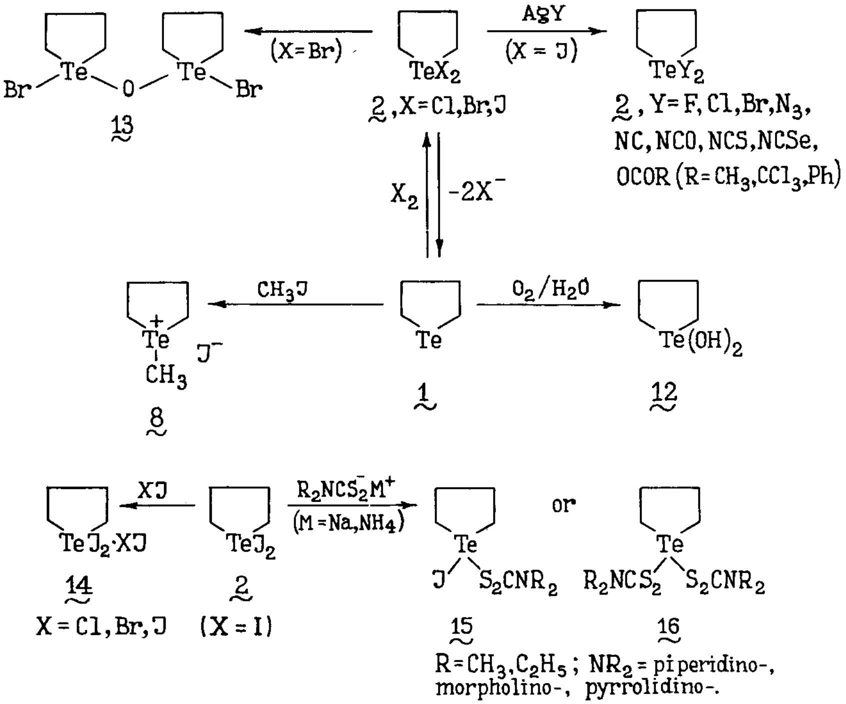
A number of tetrahydrotellurophene derivatives has been obtained through electrophilic addition of tellurium tetrahalides to the corresponding olefins. The reaction was found to proceed contrary to Markovnikov's rule. Thus, reaction of 1,5-hexadiene with TeX_4 (X = Cl, Br) results in 2,5-bis(halomethyl)-1-telluracyclopentane 1,1-dihalides **10**[35]. Similarly, $TeCl_4$ reacts with 2,2′-bicyclopentenyl to form compound **11**[36]





The chemical behavior of tetrahydrotellurophene is typical of all dicoordinated tellurium derivatives. Halogens and alkyl halides can be readily added to **1** to form the tetra- and tricoordinated tellurium derivatives **2** and **8** (R = CH_3, X = I). Oxidation with air oxygen converts **1** to 1-telluracyclopentane 1-oxide which is stable as the 1 : 1 H_2O adduct **12**. An analogous 1 : 1 complex compound has been prepared by treatment of **1** with mercuric chloride[4]. 1-Telluracyclopentane 1,1-dibromide **2** (X = Br), when reacting with one equivalent of compound **12** or upon treatment with one equivalent of NaOH (Na_2CO_3), is converted to bis(1-bromo-1-tellurocyclopentyl) oxide **13**[4]. Through reactions with various anions the diiodide **2** (X = I) readily gives σ-telluranes **2** (X = F, Cl, Br, N_3, NC, NCO, NCS, NCSe, OCOR) which in some cases are not easily accessible by other methods.[37] The compounds **2** are monomeric in solution and behave as non-electrolytes. In the dipseudohalides **2** (X = NCO, NCS, NCSe) and the dicyanide (X = NC) where the anionic component contains two various donor sites, only TeN type coordination is present as was evidenced by IR spectra.[37] When reacting with compounds of the XI type (X = Cl, Br, I), 1-telluracyclopentane 1,1-diiodide **2** (X = I) forms the adducts **14**[38], while the reaction with sodium and ammonium diorganyl dithiocarbamates gives rise to the compounds **15** and **16**.[39]

The reactions described above are given in Scheme 1.



SCHEME 1. Reactions of 1-Telluracylcopentane

1-Telluracyclopentane 1,1-diiodide **2** (X = I) is a valuable precursor of hexacoordinated tellurium derivatives containing a tetrahydrotellurophene fragment. The preparation of a series of compounds of this type with the general formula $(R_4M^+)_2[C_4H_8TeX_2X'_2]$ **17** (R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_7H_{15}; M = N, P, As, Sb; X = I, Cl, Br, NCO, NCS, N_3)[40] has been accomplished by the following reactions:

$$2\,R_4M^+X^- + C_4H_8TeI_2 \longrightarrow \underset{\mathbf{17}}{(R_4M^+)_2[C_4H_8TeI_2X_2]^{2-}}$$

M = N; R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_6H_{13}, C_7H_{15}; X = Cl, Br, I; M = P, As, Sb; R = C_6H_5; X = Cl, Br

$$[C_4H_8TeX_4]^{2-} + 4\,Y^- \longrightarrow [C_4H_8TeY_4]^{2-} + 4\,X^-$$

X = Cl, Br, I; Y = I, F, CNO, CNS, N_3

$$[C_4H_8TeI_2X_2]^{2-} + 2Y^- \longrightarrow [C_4H_8TeI_2Y_2]^{2-} + 2X^-$$

X = Cl, Br, I; Y = NCO, NCS

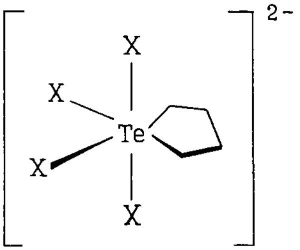
Judging from the molar conductivities and the molecular weights in methanol, acetonitrile, and nitrobenzene, compounds **17** behave like 2/1 electrolytes dissociating in solutions into 3 ions.[40]

TABLE I

Dipole Moments (D) of Compounds 19

M	$\mu(CCl_4)$	$\mu(C_6H_6)$
O	1.82[41]	1.66[41], 1.75[42]
S	1.98[41]	1.89[42], 1.85[41], 1.81[43]
Se	1.64[41]	1.81[41,42]
Te	–	1.63[42-44]

Tetrahalotelluracyclopentane dianions possess the octahedral structure **18**[40]



18

The structural and physical characteristics of tetrahydrotellurophene have been investigated by dipole moment measurements[41-44] and by ^1H NMR[41,45], photoelectron (PES)[46], IR[47] and mass spectroscopy.[28] The results of these studies have been compared with the data for other 1-chalcogenacyclopentanes **19**. The dipole moments of tetrahydrotellurophene and of the related heterocycles **19** containing VI A group atoms are listed in Table I.

Of all the saturated five-membered heterocycles **19**, tetrahydrotellurophene has the smallest dipole moment. As is the case with tetrahydrofuran, -thiophene, and -selenophene, the dipole moment vector is directed from the center of the ring to the heteroatom with the latter as the negative pole.[42,45] The magnitudes of the dipole moments for compounds **19** do not manifest any correlation with the electronegativities of the heteroatoms which is due to the differences in the geometries of the heterocycles substantially affecting the magnitudes of the dipole moments.[45]

The chemical shifts of the α- and β-protons of the heterocycles **19** in various solvents[45] are presented in Table II.

The signals of the α-hydrogen atoms appear upfield of the β-H signals. While the chemical shifts of the β-protons increase from oxygen to tellurium, with α-protons such a relationship is not fulfilled. It is surprising that the chemical shifts for tetrahydroselenophene listed in Ref. 41 ($\delta_\alpha = 3.41$ ppm, $\delta_\beta = 2.04$ ppm) do not follow the general rule. The identical trends of chemical shift displacements in tetrahydroselenophene and tetrahydrotellurophene coinciding with those in tetrahydrofuran and tetrahydrothiophene, for which the direction of the dipole moment vectors was determined earlier, may be considered as evidence for the assumption that the dipole moment in the first two heterocycles is directed from the ring to the heteroatom.[45].

TABLE II

Chemical Shifts (δ, ppm) of α- and β-Protons in Compounds 19[45]

	CCl_4		C_6D_6		C_6F_6	
M	α-H	β-H	α-H	β-H	α-H	β-H
O	3.61	1.79	3.57	1.43	3.51	1.84
S	2.75	1.91	2.54	1.47	2.71	1.99
Se	2.79	1.96	2.65	1.64	2.83	2.04
Te	3.10	2.03	2.91	1.69	3.18	2.10

TABLE III

Lower Ionization Potentials (eV) and Assignment of MO in Compounds 19[46]

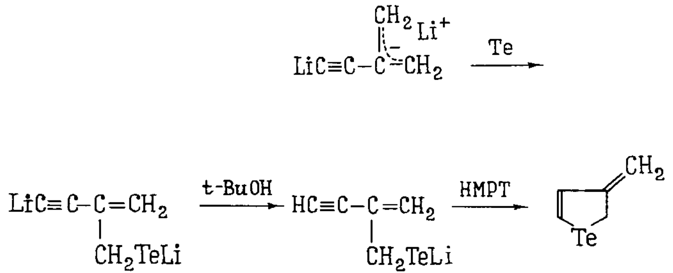
M	$n_\pi(b_1)$	C_2M (a_1)	C_2M (b_2)
O	9.53, 9.65	11.4	13.0 ± 0.5
S	8.42	10.9	$\geqslant 11.9$
Se	8.14	10.5	$\geqslant 11.4$
Te	7.73	10.0	$\geqslant 10.7$

The first three ionization potentials of compounds **19** determined by PES[46] are given in Table III.

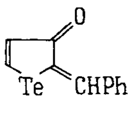
A detailed analysis of the IR spectra of tetrahydrochalcogen derivatives has been undertaken by Giorgini *et al.*[47] A thorough description of the fragmentation of **19** in mass spectra has also been presented[28]. The most interesting fact established in the latter work is the enhancement of the ability of the heteroatom to stabilize the molecular ion in the order O < S < Se < Te.

2.2. Derivatives of 2,3-Dihydrotellurophene

A representative of the 2,3-dihydrotellurophenes, 3-methylene-2,3-dihydrotellurophene **20** was prepared by reaction of the dilithium derivative of 2-methyl-1-buten-3-yne with tellurium and subsequent treatment of the reaction mixture with *t*-butanol and with hexamethylphosphotriamide (HMPT)[48]



20 (51%)

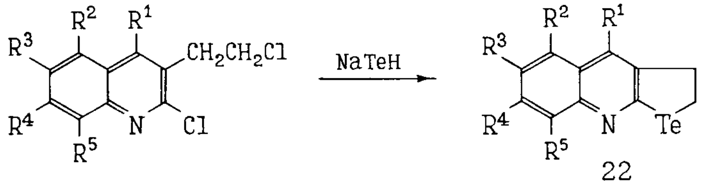


21

Compound **20** when heated in tetrahydrofuran solution containing *t*-BuOH, *t*-BuOK and HMPT is converted to 3-methyltellurophene in high yield (90 %).[48]

The 2,3-dihydrotellurophene derivative **21** is obtained as a by-product when diacetylene ketones react with lithium telluride in tetrahydrofuran.[49]

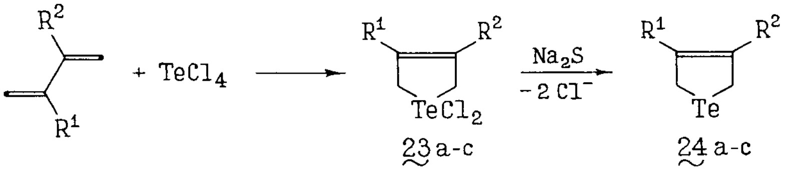
The quinoline analogs of 2,3-dihydrotellurophene, 2,3-dihydrotellurolo[2,3-b]quinolines **22** were prepared in moderate yields by reaction of 2-chloro-3(2′-chloroethyl)-quinolines with sodium hydrotelluride obtained from tellurium and $NaBH_4$ in ethanol[50]



$R^1 = R^2 = R^3 = R^4 = R^5 = H$; in the following only $R \neq H$ are given: $R^2 = CH_3$, $R^1 = Ph$, $R^5 = CH_3$

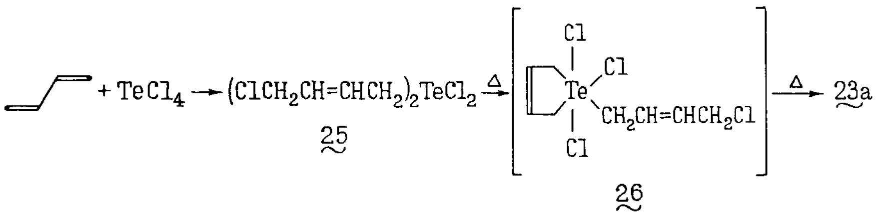
2.3. 2,5-Dihydrotellurophene and its Benzo Analogs

The 2,5-dihydrotellurophene 1,1-dichlorides **23a–c** have been prepared in 46–62% yield by electrophilic addition of tellurium tetrachloride to 1,3-butadiene and its isomers, isoprene, and 2,3-dimethyl-1,3-butadiene, in acetonitrile.[51] It should be noted that 2,3-diphenyl-1,3-butadiene and *cis,trans*-2,4-hexadiene do not undergo this reaction under analogous conditions. Reduction of **23** with aqueous Na_2S leads to the substituted 2,5-dihydrotellurophenes **24** in almost quantitative yields[51]

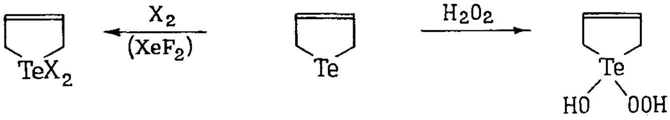


(a) $R^1 = R^2 = H$ (62%); (b) $R^1 = H$, $R^2 = CH_3$ (46%); (c) $R^1 = R^2 = CH_3$ (53%)

The nature of the products obtained by reaction of butadiene with $TeCl_4$ depends on the solvent. Thus, when CCl_4 is used, only bis (4-chloro-2-butenyl)tellurium dichloride **25** is formed.[52] However, on boiling the latter compound in toluene, it is readily converted to 2,5-dihydrotellurophene 1,1-dichloride **23a**, probably via reductive elimination from the intermediate **26**[51]



2,5-Dihydrotellurophene is comparatively unstable and slowly eliminates tellurium upon storage at ambient temperature. Its oxidation with bromine, iodine, or XeF_2 leads to the corresponding σ-telluranes. Upon treatment with hydrogen peroxide in tetrahydrofuran 2,5-dihydrotellurophene converts to compound **27**[51]

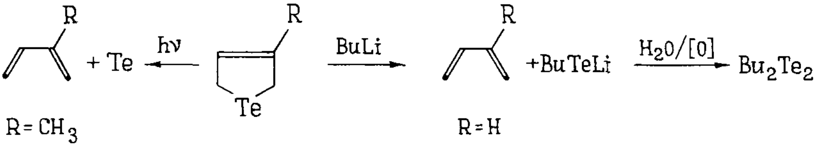


27

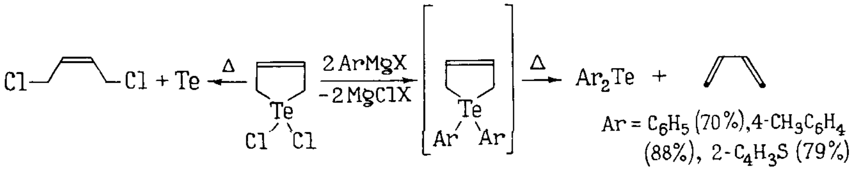
X = Br, I, F

Ring-opening reactions, which were not observed in the case of tetrahydrotellurophene, are characteristic of 2,5-dihydrotellurophene.

Opening of the dihydrotellurophene ring occurs when compounds **24** are treated with butyllithium in ether or upon photolysis at 300 nm. In the former case, the final products of the reaction are butadienes and dibutyl ditelluride, in the latter elemental tellurium and butadienes[51].



Opening of the ring takes place, too, in the reactions of 2,5-dihydrotellurophene 1,1-dichloride; other tellurium dihalides can apparently undergo such reactions as well. When 2,5-dihydrotellurophene 1,1-dichloride **23a** is treated with a Grignard reagent, the corresponding diaryl tellurides and butadiene are formed in high yield.[51] The reaction proceeds, probably, via tetracoordinated derivatives of tellurium **28** which, like other tetraorganyltelluranes,[29] undergo thermal decomposition to form the above-mentioned compounds. Pyrolysis of **23a** at 250 °C leads to elemental tellurium and 1,4-dichloro-2-butene.[51] This reaction indicates promising possibilities to prepare various 1,4-disubstituted 2-butenes by thermolysis of 2,5-dihydrotellurophenes containing various substituents (CN, OCOR and others) at the tellurium atom.[51]



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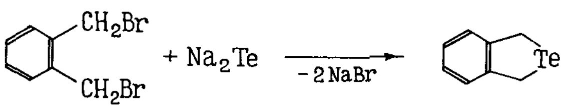
The methods of preparation and the structure of 2,5-dihydrobenzo[c]tellurophene and its derivatives **29** have been studied fairly well. The routes leading to the heterocycle construction are in this case identical to those used for the synthesis of tetrahydrotellurophene **1**. Compound **29** was first prepared by Guthbertson[53] via reaction of α,α′-dibromo-*o*-xylene with sodium telluride in DMF.



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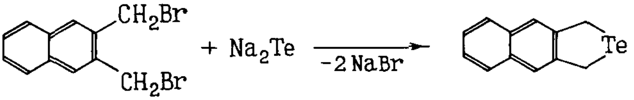
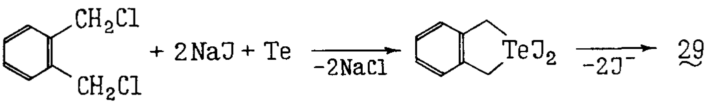
A similar reaction scheme was successfully employed for the preparation of the naphtho analog of 2,5-dihydrotellurophene **30**.[53]



30

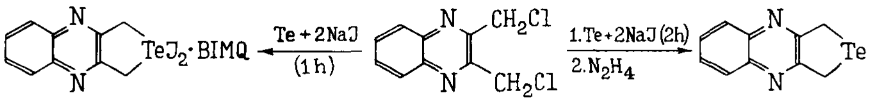
Another approach to the synthesis of 2,5-dihydrobenzo[c]tellurophene was suggested by Ziolo[54] who prepared 2,5-dihydrobenzo[c]-tellurophene 1,1-diiodide **31** by reaction of metallic tellurium with α,α′-dichloro-*o*-xylene and sodium iodide in 2-methoxyethanol in 83% yield. Since aliphatic dichlorides do not react with metallic tellurium it seems reasonable to suggest that the initial step of the reaction is nucleophilic substitution at the aliphatic carbon atom. This results in the formation of α,α′-diiodo-*o*-xylene which undergoes cyclization to diiodide **31** through reaction with tellurium. A transformation to the desired **29** can be achieved by reduction of diiodide **31** with $NaBH_4$[54,55], hydrazine hydrate,[56] or $Na_2S \cdot 9H_2O$[57].



31

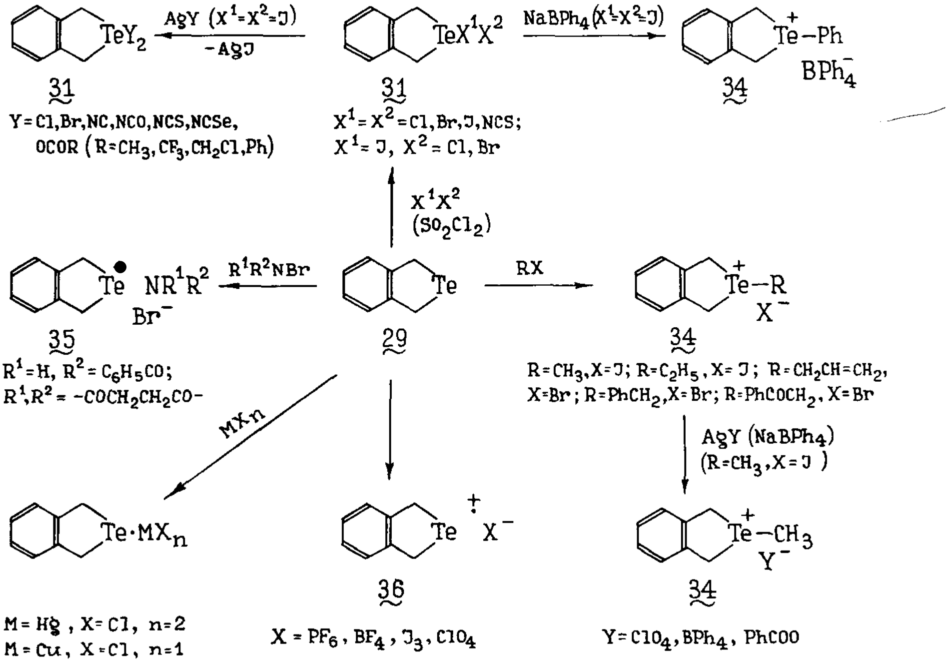
The reaction with α,α′-dibromo-*o*-xylene proceeds likewise.[57]

A similar reaction including the intermediate formation of 2,3-bis(iodomethyl)-quinoxaline was employed to prepare 1,3-dihydrotellurolo[3,4-b]quinoxaline **32**.[58] Shortening the reaction time leads to the formation of the stable 1 : 1 adduct of 1,3-dihydrotellurolo[3,4-b]quinoxaline 2,2-diiodide with 2,3-bis(iodomethyl)quinoxaline (BIMQ) **33**. Its structure was proven by an X-ray diffraction study.[58] Unlike the reaction of 2-chloro-3(2′-chlorethyl)quinoline with sodium hydrotelluride leading to **22**[50], 2,3-bis-(bromomethyl)quinoxaline is reduced by NaTeH to 2,3-dimethylquinoxaline.[58]



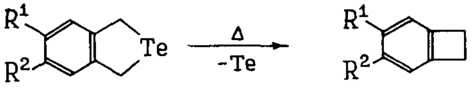
33 32

Similar to other cyclic tellurides considered above, 2,5-dihydrobenzo[c]tellurophene can be readily oxidized with bromine, iodine, sulfuryl chloride, and thiocyanogen to form the corresponding σ-telluranes **31**[56,57] A number of other derivatives of this type has been obtained by exchange reactions of 2,5-dihydrobenzo[c]tellurophene 1,1-diiodide **31** (X = I) with silver salts.[57] Through interaction of compound **29** with alkyl halides, phenacyl bromide,[55] and *N*-bromosuccinimide[57] the telluronium salts **34** and the azatelluronium salts **35** are formed. Some other telluronium salts **34** have been obtained by exchange reactions, and the salt **34** (X = BPh_4) was prepared by the method developed by Ziolo[59], i.e., through interaction of diiodide **31** with $NaBPh_4$.[55] In the presence of tetrabutylammonium salts, 2,5-dihydrobenzo[c]tellurophene is oxidized electrochemically to the cation-radical salts **36**.[60] Compound **29** forms with metal salts ($HgCl_2$, CuCl) molecular 1 : 1 complexes. With tetracyanoquinodimethane (TCNQ) it produces a charge-transfer complex $[C_8H_8Te]^{+}[TCNQ]^{-}$ [60]. Some important reactions of compound **29** and its derivatives are listed in Scheme 2.



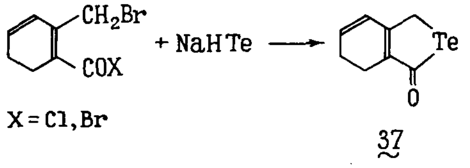
SCHEME 2. Reactions of 2,5-Dihydrobenzo[c]tellurophene and its Derivatives

Extrusion of the tellurium atom from the heterocycle is one of the typical transformations of compounds **29** and **30**. In argon at 500 °C, **29** and **30** eliminate tellurium forming the corresponding cyclobutene derivatives in fairly high yields.[53]

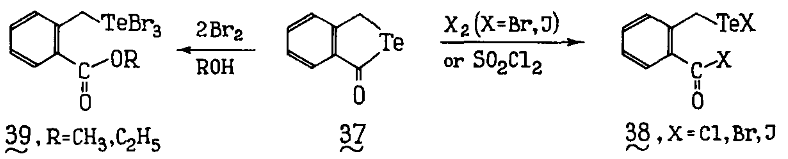


$R^1 = R^2 = H$; $R^1,R^2 = 3,4\text{-}C_4H_4$

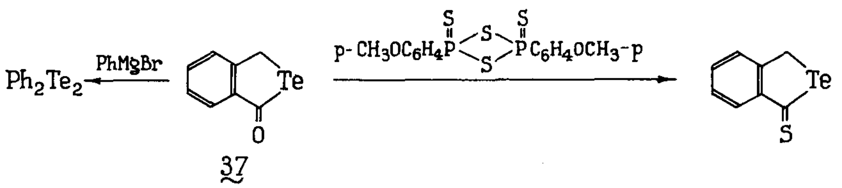
The synthesis and some properties of oxo derivatives of **29** have been described. They have been prepared by interaction of the appropriate benzoyl chlorides with NaTeH or Na_2Te. Two research groups have reported the synthesis of 2,5-dihydrobenzo[c]tellurophene-2-one **37** via reactions of *o*-bromomethylbenzoyl chloride[61,62] or bromide[62] with NaHTe. The phase transfer catalysis technique was found to be very effective in this case.



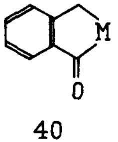
When compound **37** reacts with equimolar amounts of SO_2Cl_2, Br_2, or I_2 at low temperature, the tellurenyl halides **38** are formed instead of the expected σ-telluranes as was the case with 2,5-dihydrobenzo[c]telluorphene **29**.[56] The Te–C bond cleavage in this reaction is evidently due to the effect of the carbonyl group. Compounds **38** are the first representatives of aliphatic tellurenyl halides with the Te atom attached to a C_{sp^3}-center (arenetellurenyl halides have been studied rather well and are utilized in the synthesis of diaryl tellurides[63]). Treatment of **37** in CCl_4 with two equivalents of Br_2 in the presence of methanol or ethanol leads to the corresponding tellurium tribromides **39**.



Unlike **29**, compound **37** is thermally stable even at high temperature. Attempts to obtain benzocyclobutenone by heating **37** at 500 °C did not result in the extrusion of tellurium[62], though 2,5-dihydrobenzo[c]tellurophene readily reacts in this way under these conditions.[53] A likely explanation of the unexpected properties of **37** is based on the assumption of a strong Te–C=O conjugation which results in a significant polarization of the C=O bond. Compound **37** does not add phenylmagnesium bromide which rather provokes the destruction of the molecule resulting finally in the formation of diphenyl ditelluride. However, with Lawesson's reagent there occurs transformation of **37** to the corresponding thione as usual for carbonyl compounds.[62]



The ^{13}C NMR spectra of **40** (M = O, S, Se, Te) give clear evidence in favor of enhanced carbonyl bond polarization in this series.

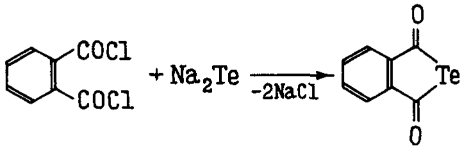


40

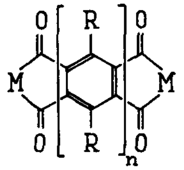
M	$\delta_{C=O}$, ppm	δ_{CH_2}, ppm
O	171.0	69.6
S	197.8	34.6
Se	199.9	29.5
Te	200.3	13.9

In spite of the "heavy atom" effect, the most downfield chemical shift for the carbonyl C atom is observed for the tellurium derivative **37** which indicates the largest positive charge at the C atom in this compound. On the contrary, the methylene carbon chemical shifts in **40** follow the opposite order.[61]

A dioxo derivative of 2,5-dihydrobenzo[c]tellurophene, 2,5-dihydrobenzo[c]tellurophene-2,5-dione **41**, was synthesized by Bergman[64] via interaction of phthaloyl chloride with sodium telluride using the transfer catalysis technique.



41



42

M=S,Se,Te; R=H,Hal; n=1-3

It is noteworthy that this compound, when treated with chlorine in CCl_4 solution, eliminates tellurium and converts to phthaloyl chloride.[62]

Analogs of **41**, the compounds **42**, obtained by reaction of **42** (M = O) with Na_2Te (Na_2Se, Na_2S), have been found to be effective photosensitizers.[65]

A number of publications deal with the structure of 2,5-dihydrobenzo[c]tellurophene **29** and its derivatives both in solution[54-56] and in the crystal[54,57,66,67].

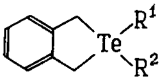
Measurements of the electric conductivity and the molecular weight of tellurium diiodide **31** in methylene chloride, acetone, and methyl ethyl ketone did not reveal ionic dissociation. In DMF, however, diiodide **31** behaves like an 1/1 electrolyte which proves the telluronium salt structure $[C_8H_8TeI]^+I^-$.[54] The electric conductivity and the molecular weights of the telluronium salts **34** containing a 2,5-dihydrobenzo[c]tellurophene moiety show that in solvents with low polarity ($CHCl_3$) they are associated to dimers. However, more solvating solvents of the DMSO type break down the weak intermolecular bonds. Compounds **34** in these solvents possess an electric conductivity typical of 1/1 electrolytes.[55]

These conclusions were arrived at by studies of the ^1H and ^{125}Te NMR spectra of compounds **31** and **34**. Some data from these spectra are presented in Tables 4 and 5.

The methylene proton signals of derivatives of di- and tetracoordinated tellurium (compounds **29** and **31** (X = I), respectively) are sharp singlets shifting downfield on passing from the di- to the tetracoordinated tellurium derivatives.[54,55] In the case of the telluronium salts **34**, the methylene proton signals appear as AB type multiplets which was to be expected for the pyramidal environment of the tellurium atom in these compounds.[55] The deshielding effect of solvents on the methyl protons in the CH_3 group attached to the tellurium atom decreases in the following order of solvents $CDCl_3$ > DMF > DMSO whereas their solvating power increases in the same order.

TABLE IV

^{1}H NMR Spectra of Compounds

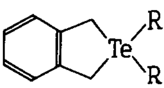


R^1	R^2	Solvent	δ, ppm[a]		$^2J(^1H-^{125}Te)$, Hz	Reference
–	–	$CDCl_3$	CH_2-4.65(s)		22.26(CH_2)	55
–	–	DMSO-d_6	CH_2-4.46(s)		22.3(CH_2)	55
–	–	DMF-d_5	CH_2-4.59(s)		–	54
I	I	DMSO-d_6	CH_2-4.75(s)		24.0(CH_2)	55
I	I	DMF-d_5	CH_2-4.99(s)		–	54
CH_3	I	$CDCl_3$	CH_3-2.42(s),	CH_2-4.28, 5.00[b]	24.6(CH_3)	55
CH_3	I	DMSO-d_6	CH_3-1.98(s),	CH_2-3.96, 4.26[b]	24.0(CH_3)	55
CH_3	I	DMF-d_7	CH_3-2.25(s),	CH_2-4.20, 4.60[b]	23.8(CH_3)	55
CH_3	ClO_4	DMSO-d_6	CH_3-1.98(s),	CH_2-3.99, 4.29[b]	22.4(CH_3)	55
CH_3	BPh_4	DMSO-d_6	CH_3-2.05(s),	CH_2-4.05, 4.28[b]	18.6(CH_3)	55
CH_2CH_3	I	DMSO-d_6	CH_3-1.26(tr), CH_2-4.07, 4.37	CH_2CH_3-2.72(q),	18.0(CH_2)	55

[a] Aromatic proton signals appear as multiplets at 6.8–7.5 ppm.
[b] The spin–spin coupling constants are 15 Hz.

TABLE V

^{125}Te NMR Spectra of Compounds



R^1	R^2	Solvent	$\delta(^{125}Te)$[a] ppm	Reference
–	–	DMF-d_7	268	56
Cl	Cl	DMF-d_7	993	56
Br	Br	DMF-d_7	939	56
I	I	DMF-d_7	829	56
CH_3	I	$CDCl_3$	652	55
CH_3	I	DMSO-d_6	651.4	55
CH_3	I	DMF-d_7	657.2	55
CH_3	OCOPh	$CDCl_3$	687	55
CH_2CH_3	I	$CDCl_3$	706.4	55
CH_2CH_3	I	DMSO-d_6	708.9	55
$CH_2CH{=}CH_2$	Br	DMSO-d_6	688.3	55
CH_2Ph	Br	DMSO-d	722.3	55
CH_2COPh	Br	DMSO-d_6	693.5	55
CH_2COPh	Br	DMF-d_7	680.1	55

[a] Chemical shifts are given relative to $(CH_3)_2Te$.

This is in accordance with the presence of strongly solvated $[C_8H_8TeR]^+$ cations in DMSO. The type of anion (I^-, ClO_4^-, BPh_4^-) does not essentially affect the proton chemical shifts.

The chemical shifts of ^{125}Te in compounds **31** and **34** given in Table V exemplify still rare direct measurements of ^{125}Te chemical shifts in tellurium organic compounds.

The ^{125}Te chemical shift values are strongly influenced by the oxidation number of the tellurium atom in the molecule, they are quite sensitive to variation of the molecular structure. The known range of ^{125}Te chemical shifts comprises 3500 ppm. Judging by the spectra of methyltelluronium salts, the chemical shifts of tellurium depend comparatively little on the solvent.[55] However, they noticeably vary with the nature of the substituent covalently linked with the tellurium atom (see data of Table V on telluronium salts containing the Br ligand).

2,5-Dihydrobenzo[c]tellurophene diiodide **31** exists in two crystalline modifications, which may be obtained via recrystallization from 2-methoxyethanol.[54] The less stable orange–red (β) modification transforms to the second yellow–orange (α) modification upon heating. Different electronic absorption and IR spectra in the region below 200 cm^{-1} of the (α) and (β) modifications were observed. The crystal and molecular structures of the two modifications differ in the type and the degree of the secondary Te . . . I and I . . . I interactions in which heavy atoms are involved. It is a change in such interactions which is responsible for the coloring of tellurium diiodides R_2TeI_2 which changes in the crystal state from yellow–orange (intermolecular Te . . . I bonds) to dark-violet appearing with I . . . I secondary interactions.[68–72] So far, the molecular and crystal structure of only the α-modification of **31** (X = I) has been documented by an X-ray diffraction study[66] (Fig. 1).

The tellurium atom in **31** (α-modification) possesses a distorted octahedral bond configuration with two iodine atoms in the axial positions. The angle I–Te–I is slightly less than 180°, i.e. 176.5°, as is also the case with other σ-telluranes.[29] The hydrocarbon fragment and the two iodine atoms of neighboring molecules occupy equatorial positions. The Te–C and Te–I bond lengths are typical of bonds of this type. The five-membered ring in **31** is practically planar; the C(1) atom suffers the greatest deviation from the plane (0.04 Å), the deviation of the tellurium atom is merely 0.03 Å. The angle C(1)–Te–C(8) (86.0°) is larger than those in dibenzotellurophene (81.7°)[73] and dibenzotellurophene diiodide (81.8°).[72]

The crystal and molecular structure of telluronium salts containing the dihydrotellurophene moiety **34a–c**, (a) R = $CH_2CH{=}CH_2$, X = Br; (b) R = CH_2COPh, X = Br; (c) R = CD_3, X = I, has been studied in Ref. 67.

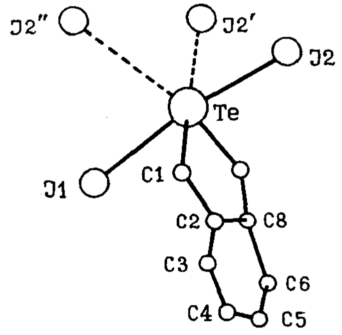


FIGURE 1. The Geometry of 2,5-Dihydrobenzo[c]tellurophene 1,1-Diiodide.

Crystals of these salts contain $C_8H_8Te^+R$ cation units with pyramidal tellurium. Three secondary bonds with anions can be traced leading to a distorted octahedral configuration of the tellurium center of **34** in the crystal with the dihydrotellurophene fragment lying in the plane perpendicular to the R–Te bond.

The salts **34a** and **34b** have almost identical structural parameters with the Te–C bond lengths in the range of 2.115 to 2.185 Å. The lengths of the Te–Br bonds in the range of 3.292–3.391 Å lie between the sums of the covalent and the van der Waals radii (2.51 and 4.15 Å).

The molecular structure of the iodide **34c** is different from that of the bromides. The lengths of the Te–C ring bonds in each of the two crystallographically independent $C_8H_8Te^+CD_3$ cations are in the range of 2.104–2.160 Å which is close to that in the bromides **34a,b**. However, in both cases one of the Te–I distances is considerably greater than the two others. Four Te–I distances are in the region of 3.596–3.688 Å and two others are 3.870 and 4.112 Å. These values, as in the case of the bromides, lie between the sums of the covalent and van der Waals radii (2.70 and 4.35 Å), but even the shortest of the Te–I distances is closer to the van der Waals distances. This indicates the different nature of the Te–Br and Te–I bonds in compounds **34a–c** which explains the diverse picture of the molecular association of these compounds in crystals.

It is interesting to note that unlike the diiodide **31**,[66] the dihydrobenzotellurophene fragment in the salts **34a–c** is non-planar. While the carbon atoms lie approximately in the common plane (the maximum deviation is 0.07 Å), the tellurium atoms deviate from the plane by 0.46 Å for **34a**, 0.27 Å for **34b** and 0.38, 0.30 Å for **34c**.[67]

Non-planar is the dihydrotellurophene ring also in 1,3-dihydrotellurolo[3,4-b]-quinoxaline **32**[74] (Fig. 2, where only the data for the tellurium-containing fragment are given). In this compound, the tellurium atom deviates from the plane of the practically planar quinoxaline residue by 0.68 Å. The angle C–Te–C (80.7°) is much smaller than in 2,5-dihydrobenzo[c]tellurophene 1,1-diiodide (86°)[66], but it is close to the angles in other five-membered heterocycles, dibenzotellurophene[73] and dibenzotellurophene diiodide.[72] The crystal structure of the quinoxaline derivative **32** shows intermolecular bonds in which tellurium atoms are involved. These bonds with the lengths of 3.791 and 3.898 Å are shorter than the sum of the van der Waals radii of Te atoms (4.40 Å). According to Ref. 74 such an association in the crystal is responsible for the very high melting point and low solubility of compound **32**. Results of the investigation of IR, Raman, PES, ^1H and ^{13}C NMR spectra of 2,5-dihydrobenzo[c]tellurophen-2,5-dione **41** have also been presented.[75]

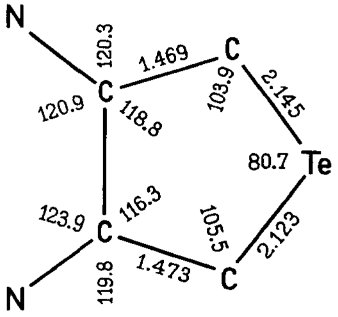


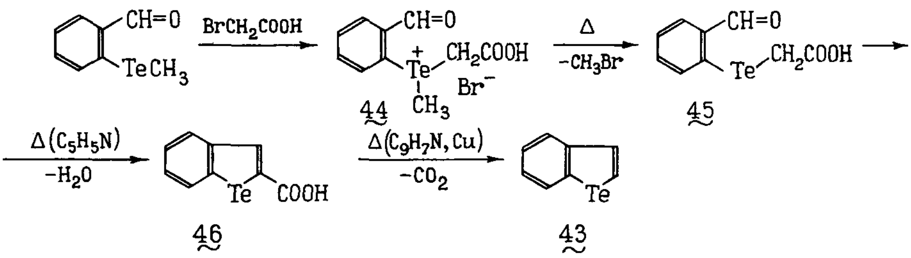
FIGURE 2. The Geometry of 1,3-Dihydrotellurolo[3,4-b]quinoxaline.

2.4. *Benzo[b]tellurophene and its Derivatives*

In contrast to its analogs, benzo[b]thiophene and benzo[b]selenophene, benzo[b]tellurophene and its derivatives have been studied comparatively little.[8]

The first report on the synthesis of a benzo[b]tellurophene derivative, viz. telluroindoxyl, by cyclization of 2-carboxyphenyltelluroacetic acid[76] could not be reproduced[77,78] and proved to be erroneous. All the methods developed to synthesize benzo[b]tellurophene and its derivatives are based on the cyclization of the corresponding organotellurium compounds. These can be divided into two main groups which differ in the way of closing the tellurophene ring and, consequently, in the structure of the starting organotellurium compounds. In the first group of reactions (cyclization of the C^2–C^3 and C^2–Te type), difficultly accessible phenyl methyl tellurides with an *o*-carbonyl function are used as starting materials whereby the unsubstituted or 2- and 3-substituted benzo[b]tellurophenes respectively, are formed. These reactions are analogous to those employed for obtaining the corresponding sulfur- or selenium-heterocyclic compounds. The second group of reactions leading to 3-halogenobenzo[b]tellurophenes (cyclization of the Te–$C_{ar.}$ type) is based on the use of the readily accessible tellurium trichlorides. These may be prepared either prior to the reaction or *in situ*. These reactions may be considered as specific of tellurium-organic chemistry.

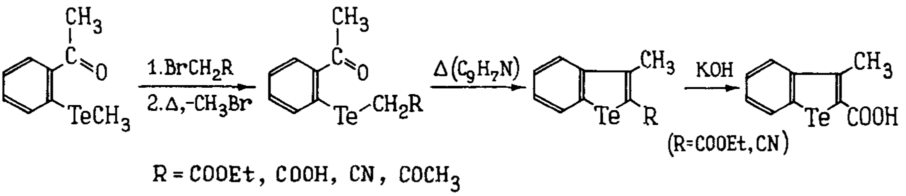
The parent benzo[b]tellurophene **43** was prepared by Piette[78] according to the following four-step reaction sequence with *o*-(methyltelluro)-benzaldehyde[79] as the starting compound.



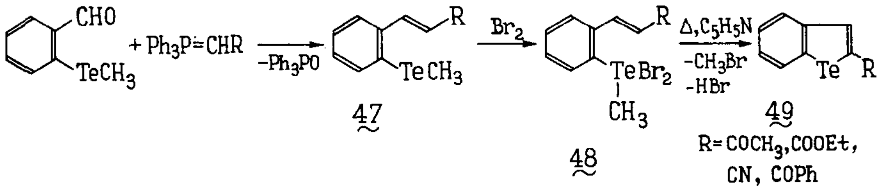
Interaction of the aldehyde with bromoacetic acid affords the telluronium salt **44**, which upon heating eliminates methyl bromide and is converted to acid **45**. Compound **45** undergoes cyclization to 2-carboxybenzo[b]tellurophene **46** which loses CO_2 upon refluxing in quinoline in the presence of copper powder to afford the desired heterocycle **43** in a total yield of 54%.[78]

An analogous reaction with bromoacetone gives rise to 2-acetylbenzo[b]tellurophene in very low yield.[80]

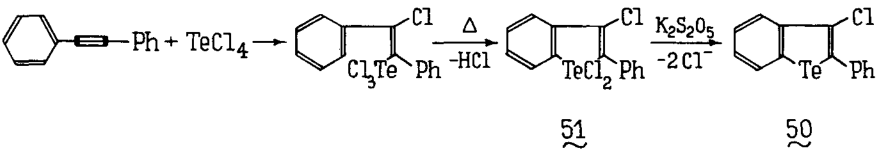
When *o*-(methyltelluro)-acetophenone is used as the initial compound, this reaction affords 2-substituted 3-ethylbenzo[b]tellurophenes in low yields.[80,81]



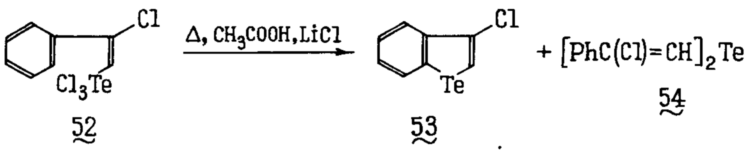
Another approach to 2-substituted benzo[b]tellurophene derivatives is based on the reaction of *o*-(methyltelluro)-benzaldehyde with stabilized phosphoranes. The reaction leads to *o*-(methyltelluro)-vinylbenzenes **47**[80] bromination of which produces the readily isolable telluride dibromides **48**. The latter compounds upon heating in pyridine undergo cyclization to 2-R-benzo[b]tellurophenes[80].



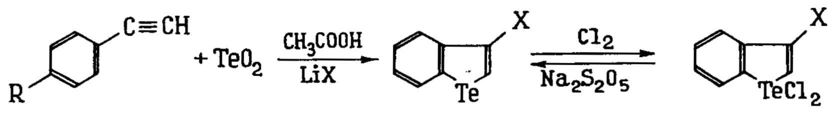
The synthesis of 3-halogenobenzo[b]tellurophenes is based on intramolecular electrophilic cyclization of the corresponding tellurium trichlorides. Analogous reactions are widely used in the preparation of six-membered tellurium-containing heterocycles.[1] The first representative of 3-halobenzo[b]tellurophenes, 2-phenyl-3-chlorobenzo[b]-tellurophene **50**[82], was obtained by cyclization of 1,2-diphenyl-2-chlorovinyltellurium trichloride through refluxing its solution for two hours in 1,2,4-trichlorobenzene and subsequent reduction of the intermediate 1,1,3-trichloro-2-phenylbenzo[b]tellurophene **51** with $K_2S_2O_5$.[82] The initial tellurium trichloride was prepared by electrophilic addition of $TeCl_4$ to diphenylacetylene.[83]



Compounds **50** and **51** were the very first examples of benzo[b]tellurophene derivatives. It is noteworthy that attempts at cyclization of 2-chloro-2-phenylvinyltellurium trichloride **52**[83] to the corresponding benzo[b]tellurophene failed.[8] But upon refluxing this compound in acetic acid in the presence of LiCl, along with bis(2-chloro-2-phenylvinyl)-telluride **54**, 3-chlorobenzo[b]tellurophene **53** is formed in 38% yield.[84]



A promising method for the synthesis of 3-halobenzo[b]tellurophenes **53** was developed by Bergman *et al.*[84–86] Various 3-halobenzo[b]tellurophenes were obtained in 21–92% yield upon reaction of TeO_2 with the appropriate phenylacetylene in acetic acid in the presence of lithium halides. Upon treatment of the reaction mixture with chlorine, the tellurium dichlorides **55** were isolated and then reduced with aqueous $Na_2S_2O_5$ to **53**.[84]

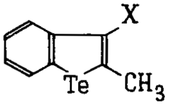


53 55

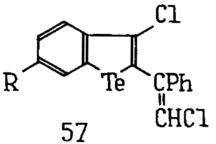
R = H: X = Cl, Br, I; R = CH_3: X = Cl; R = Br, X = Cl

Disubstituted acetylenes, *e.g.*, 1-phenyl-1-propyne, can also undergo these reactions giving rise to 3-bromo- and 3-chlorobenzo[b]tellurophenes **56** in 49 and 28 % yield, whereas diphenylacetylene and diphenyldiacetylene do not react in this way.[84]

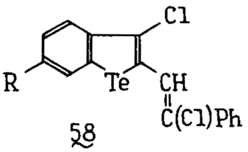
When LiCl is used as the source of halogen, compounds **57** and **58** are formed as by-products in amounts depending on the concentration of LiCl.[84]



56
X = Cl, Br



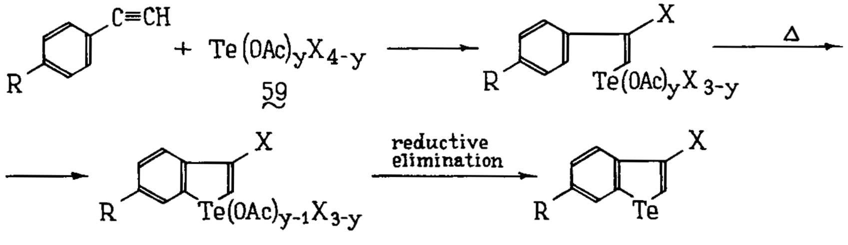
57



58

R = H, CH_3, Br

The authors of Refs. 84–86 suggest the following mechanism for the formation of 3-halobenzo[b]tellurophenes **53**. In the initial step there occurs an electrophilic addition of the tellurium acylates **59** (the structure of which is not exactly known) to the triple bonds of the phenyl acetylenes.

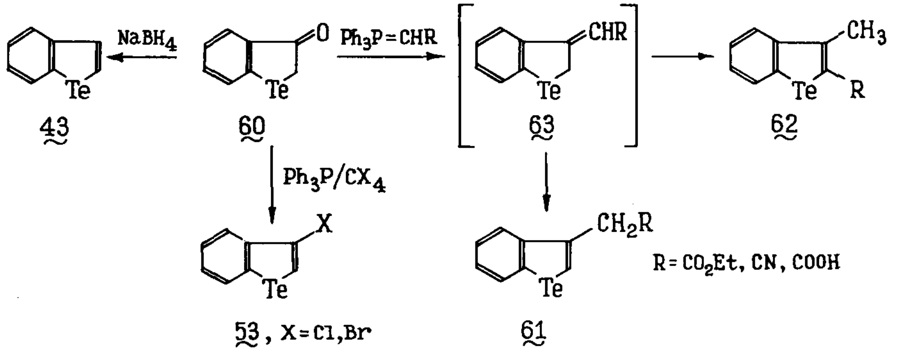


53

It is interesting to note that 3-bromobenzo[b]tellurophene can also be obtained via interaction of acetophenone semicarbazone with TeO_2 in acetic acid in the presence of LiBr.[84] Apparently, TeO_2, similarly to SeO_2,[87] oxidizes the semicarbazone to phenylacetylene which reacts as shown above. The yield of 3-bromobenzo[b]tellurophene does not, however, exceed 9 %. Semcarbazones of other ketones cannot be involved in this reaction at all.[84]

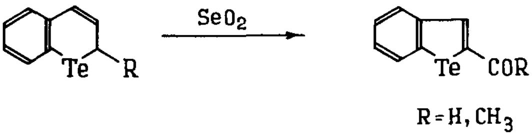
Benzo[b]tellurophene and some of its derivatives have also been prepared from compounds already possessing a five-membered tellurium-containing ring, in particular, 3-oxo-2,3-dihydrobenzo[b]tellurophene (telluroindoxyl) **60**. The synthesis of this compound is described below. Its reduction with $NaBH_4$ gives benzo[b]tellurophene,[88] and its interaction with CX_4 (X = Cl, Br) and Ph_3P gives rise to 3-chloro- and 3-bromobenzo[b]tellurophenes in 25 and 30 % yield, respectively.[81] A number of other

3-substituted benzotellurophenes **53** has been obtained from telluroindoxyl by the Wittig reaction.[81] In this case, along with the expected compounds **61**, formation of the isomeric compounds **62** was observed. The relative amounts of the isomers **61** and **62** depend on the kind of phosphorane used and the conditions of the experiment. The reaction proceeds, apparently, via the intermediate **63** which undergoes either a hydrogen 1,3-sigmatropic shift resulting in the formation of **61** or a tellurium 1,3-sigmatropic shift to methylene carbon leading to isomer **62**.[81]



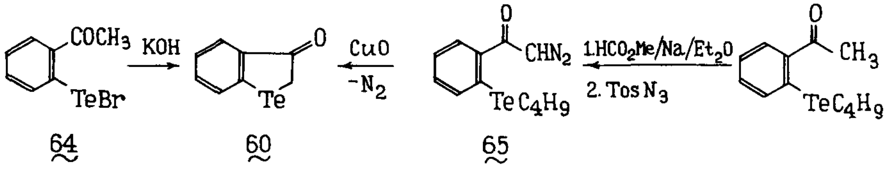
The latter isomerization is specific of telluroindoxyl and does not occur in the cases of the seleno- and oxa-analogs of **60**.

The preparation of 2-carbonyl derivatives of benzo[b]tellurophene by oxidation of tellurochromenes-1 with selenium dioxide[89,90] can scarcely be of any use in synthesis.

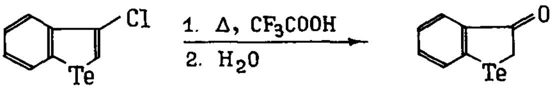


3-Oxo-2,3-dihydrobenzo[b]tellurophene **60** is one of the most important derivatives of benzo[b]tellurophene. The synthesis of **60** was accomplished by various methods.

Originally, compound **60** was obtained by Renson[88] through interaction of α-bromotellurenylacetophenone **64** with KOH in ethanol. Instead of KOH, ammonia[91] and potassium acetate[92] were also used. Another route leading to telluroindoxyl is the intramolecular cyclization of *o*-butyltelluro-ω-diazoacetophenone **65**[93] for which *o*-butyltelluroacetophenone serves as an appropriate precursor.

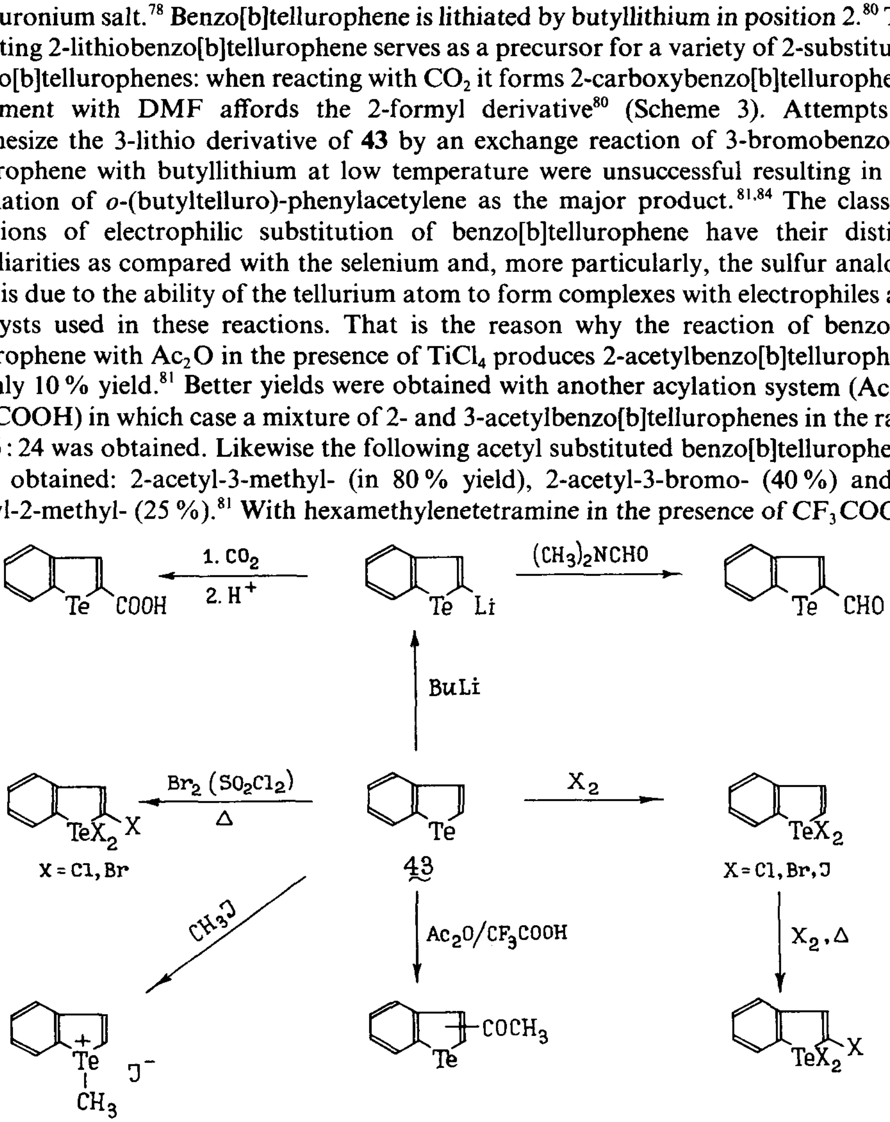


Compound **60** was also synthesized by Bergman[84] in 84 % yield by refluxing 3-chlorobenzo[b]tellurophene **53** in trifluoroacetic acid. 3-Bromobenzo[b]tellurophene gives telluroindoxyl in only 7 % yield.



53 60

Not so many reactions of benzo[b]tellurophene have been described in the literature until now. Like other compounds of dicoordinated tellurium,[29] **43** and its derivatives readily add halogens to form 1,1-dihalides.[78,80,84–86] Reaction with methyl iodide produces a telluronium salt.[78] Benzo[b]tellurophene is lithiated by butyllithium in position 2.[80] The resulting 2-lithiobenzo[b]tellurophene serves as a precursor for a variety of 2-substituted benzo[b]tellurophenes: when reacting with CO_2 it forms 2-carboxybenzo[b]tellurophene, treatment with DMF affords the 2-formyl derivative[80] (Scheme 3). Attempts to synthesize the 3-lithio derivative of **43** by an exchange reaction of 3-bromobenzo[b]tellurophene with butyllithium at low temperature were unsuccessful resulting in the formation of *o*-(butyltelluro)-phenylacetylene as the major product.[81,84] The classical reactions of electrophilic substitution of benzo[b]tellurophene have their distinct peculiarities as compared with the selenium and, more particularly, the sulfur analogs. This is due to the ability of the tellurium atom to form complexes with electrophiles and catalysts used in these reactions. That is the reason why the reaction of benzo[b]tellurophene with Ac_2O in the presence of $TiCl_4$ produces 2-acetylbenzo[b]tellurophene in only 10% yield.[81] Better yields were obtained with another acylation system (Ac_2O/CF_3COOH) in which case a mixture of 2- and 3-acetylbenzo[b]tellurophenes in the ratio of 76 : 24 was obtained. Likewise the following acetyl substituted benzo[b]tellurophenes were obtained: 2-acetyl-3-methyl- (in 80% yield), 2-acetyl-3-bromo- (40%) and 3-acetyl-2-methyl- (25%).[81] With hexamethylenetetramine in the presence of CF_3COOH,



SCHEME 3. Reactions of Benzo[b]tellurophene

43 gives the 2-formyl derivative in only 10 % yield.[81] At room temperature, halogens are readily added to the tellurium atom in benzo[b]tellurophene affording 1,1-dihalides. At higher temperatures, however, the reaction proceeds further. Refluxing of the *o*-dichlorobenzene solution of **43** containing halogens or SO_2Cl_2 gives rise to 1,1,2-trichloro(bromo)benzo[b]tellurophenes in 50–80 % yield. Their reduction with hydrazine hydrate leads to 2-halobenzo[b]tellurophenes. The use of excess bromine does not result in further bromination of 1,1,2-tribromobenzo[b]tellurophene whereas its 1,1,3-isomer under these conditions converts to 1,1,2,3-tetrabromobenzo[b]tellurophene which upon reduction gives rise to 2,3-dibromobenzo[b]tellurophene.[81]

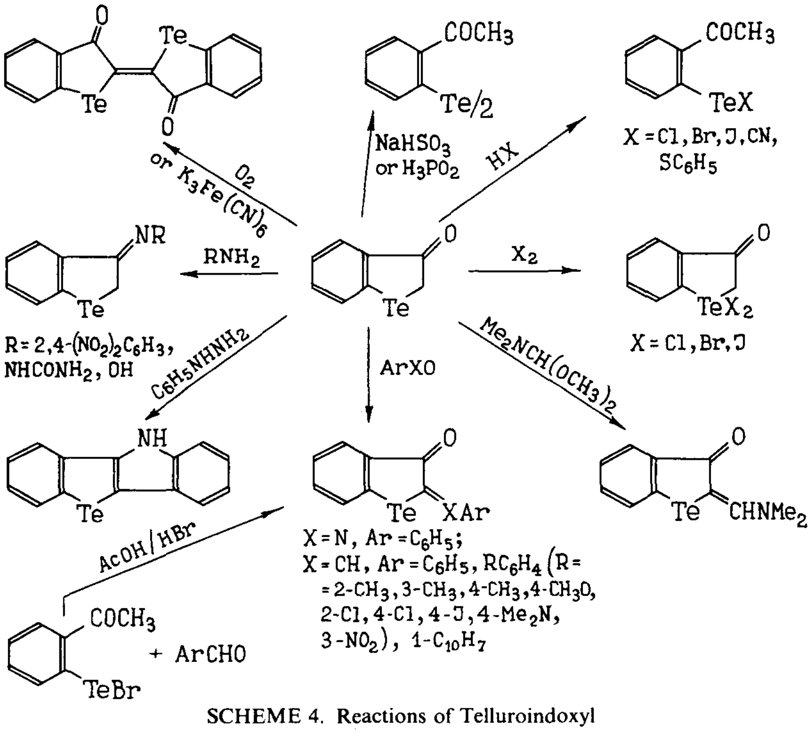
Substituted benzo[b]tellurophenes, viz. acids, aldehydes, ketones, and nitriles can undergo transformations typical of these compounds and have been utilized in the synthesis of various substituted benzo[b]tellurophenes.[80,81]

Some important reactions of telluroindoxyl **60** typical of compounds containing the C–Te–C fragment, and active methylene and carbonyl groups,[88,92,94,95] are shown in Scheme 4.

The molecular structure of benzo[b]tellurophene and of some of its derivatives has been investigated by ^{1}H NMR,[96,97] ^{125}Te NMR,[98] photoelectron,[99] mass[100] and IR spectra.[101]

The parameters of the ^{1}H NMR spectra of benzo[b]tellurophenes and of some related systems containing VI A group elements are listed in Table VI.[96,97]

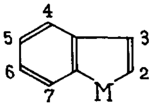
It may be concluded from the data in Table VI[97] that: (1) Annelation of the benzene ring with the heterocycle affects only insignificantly the chemical shifts of the H-2 and



SCHEME 4. Reactions of Telluroindoxyl

TABLE VI

Chemical Shifts (ppm) and Coupling Constants (Hz) in the ^{1}H NMR Spectra of the Compounds[97]



δ and I	M = O	M = S	M = Se	M = Te
H-2	7.52	7.27	7.79	8.55
H-3	6.66	7.19	7.42	7.84
H-4	7.49	7.70	7.69	7.71
H-5	7.13	7.25	7.24	7.26
H-6	7.19	7.22	7.14	7.03
H-7	7.42	7.77	7.77	7.82
$I_{2,3}$	2.19	5.57	5.57	6.95
$I_{3,5}$	0.87	0.86	0.65	0.43
$I_{4,5}$	7.89	8.09	7.97	7.97
$I_{4,6}$	1.28	1.16	1.02	1.07
$I_{4,7}$	0.80	0.73	0.48	0.51
$I_{5,6}$	7.27	7.22	7.22	7.24
$I_{5,7}$	0.92	1.17	1.17	1.08
$I_{6,7}$	8.43	8.06	8.27	8.00

H-3 protons. (2) H-2 nuclei are more deshielded than H-3 nuclei which may be considered as an indication that C-3 possesses higher electronic density than C-2.

The ^{125}Te chemical shifts of some monosubstituted benzo[b]tellurophenes have been studied in Ref. 98 (Table VII).

TABLE VII

^{125}Te Chemical Shifts (ppm)[a] of 2- and 3-Substituted Benzo[b]tellurophenes[98]

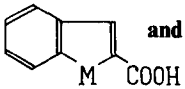
R	Position R 2	3	J_{Te-H_2} (Hz)	R	Position R 2	3	J_{Te-H_2} (Hz)
H	0	0	99.6	COCl	42	–	–
Cl	140.5	−5.5	91.6	CO_2CH_3	48.3	–	–
Br	184	34.9	93.6	$CO_2C_2H_5$	46.9	–	–
SCH_3	102.8	–	–	$CONH_2$	36.7	–	–
CH_3	22.6	−67.9	100.3	$CONHCH_3$	37.5	–	–
CH_2OH	−5.9	−43.7	98.8	$CON(CH_3)_2$	103.6	–	–
CHO	0	22.5	80	CN	224.5	59.9	86.7
$COCH_3$	24	–	–	CH_2CO_2H	–	−47.1	97.8
COC_6H_5	58.9	–	–	CH_2CN	–	−17.6	97.3
CO_2H	36.5	–	–				

[a] Chemical shifts are given with respect to benzo[b]tellurophene.

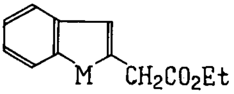
Comparison of the data in Table VII with those on tellurophenes and benzo[b]selenophenes[98] leads to the following conclusions: (1) Substituents substantially affect the chemical shift of ^{125}Te in substituted benzo[b]tellurophenes. (2) The chemical shifts of ^{125}Te are approximately 2.4 times more sensitive to the nature of the substituents

TABLE VIII

pK$_a^a$, ν_{CO} of Acids



and Solvolysis Rate (Ref. 103) Constants in 30% C_2H_5OH at 60°



M	pK$_a^b$	ν_{CO}^c	$k \cdot 10^5$ (sec^{-1})	k_X/k_T^d	$k_{Bi}/k_{Mo} \cdot 10^{3e}$
O	4.20(4.54)	1758(1755)	0.945	1.50	4.78
S	4.67(5.05)	1733(1734)	0.629	1	9.62
Se	4.79(5.14)	1731(1728)	1.044	1.66	9.56
Te	5.13(5.48)	1716(1721)	3.256	5.18	8.85

[a] Ionization constants were determined potentiometrically in H_2O–C_2H_5OH mixture (1 : 1).[102]

[b] In parentheses, pK$_a$ of monocyclic acids are given.

[c] In parentheses, ν_{CO} of monocyclic acids[102] are given.

[d] Ratio between solvolysis rate constants for the appropriate heterocycle and 1-(2-benzo[b]thienyl)ethyl acetate.

[e] Ratio between solvolysis rate constants for benzoannellated and monocyclic ethyl acetates.

than those of ^{77}Se. (3) Benzoannelation results in some deshielding of the Te nuclei as compared to analogous tellurophenes. A good linear correlation between the chemical shifts of ^{125}Te in benzotellurophenes and tellurophenes points to a similarity in the mechanism of substituent effect transmission to the tellurium center in both heterocycles.

Examination of the photoelectron spectra of benzotellurophene and analogous compounds containing VI A group elements shows that the first four bands are due to ionization of π-orbitals. The highest occupied MO of benzo[b]tellurophene is localized to a considerable degree at the heteroatom.[99]

Upon electron impact, the fragmentation of benzotellurophene[100] proceeds similarly to the fragmentation of benzothiophene and benzoselenophene. The main peak corresponds to a detellurated product, probably benzocyclobutene.

Ionization constants of benzo[b]tellurophene-2-carboxylic acid and its analogs[102] as well as solvolysis rates of 1-(2-benzo[b]heteryl)ethyl acetates[103] are presented in Table VIII.

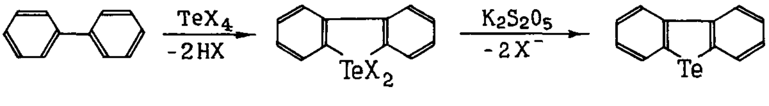
The pK values depend strongly on the electronegativity of the heteroatom indicating significant decrease in the heteroatom inductive effect from oxygen to tellurium. Benzoannelation enhances the strength of all acids almost equally regardless of the nature of the heteroatom.

Kinetic data on the solvolysis of the ethyl acetates show that the reactivity of the compounds decreases in the following order: benzotellurophene > benzoselenophene > benzofuran > benzothiophene[103].

^{13}C and ^{125}Te NMR spectra of telluroindoxyl and its analogs have been studied in refs. 104 and 105.

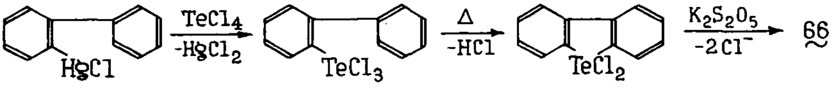
2.5. *Dibenzotellurophene*

The first derivative of dibenzotellurophene **66**, dibenzotellurophene dibromide **67** (X = Br) was isolated in very low yield by Courtot[5] when heating diphenyl with tellurium tetrabromide at 225–240° C. Better yields were achieved when tellurium tetrachloride was used. Upon treatment with $K_2S_2O_5$ the compounds **67** are readily reduced to dibenzotellurophene.[5]



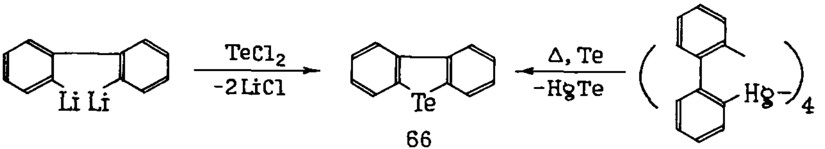
67, X=Cl, Br 66

The reaction proceeds probably via intermediate formation of *p*-diphenyltellurium trichloride and the subsequent migration of the $TeCl_3$ group into the *o*-position (as is the case when diphenyl ether interacts with tellurium tetrachloride to give phenoxatellurine 10,10-dichloride[106] and the cyclization of *o*-diphenyltellurium trichloride **68** to compound **67** (X = Cl). A more convenient route to heterocycle **66** developed by McCullough[107] includes cyclization of compound **68** (svnthesized from tellurium tetrachloride and 2-chloromercurybiphenyl or 2-lithiobiphenyl, in 76 % and 16 % yield, respectively) at 210 °C leading to compound **67** (X = Cl) in quantitative yield.



68 67

In two other methods for the preparation of dibenzotellurophene **66** less accessible *o,o′*-dilithiobiphenyl[108–110] and tetrameric *o*-biphenylenemercury **69** are used. 2,2′-Dilithiobiphenyl when reacting with $TeCl_2$ forms bibenzotellurophene in 52 % yield, and compound **69** upon heating with tellurium converts to the same heterocycle in 82 % yield.

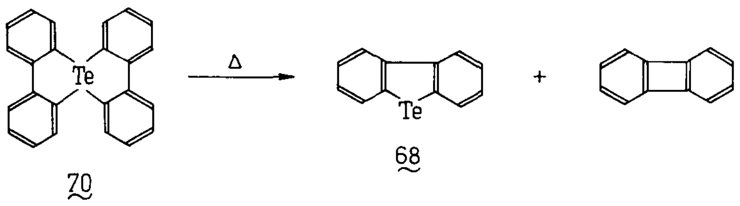


66 69

Dibenzotellurophene can also be obtained through thermal decomposition of the spirane **70**[108–111]. This reaction is, however, of no synthetic value, since compound **70** is obtained from 2,2′-dilithiobiphenyl which can be converted straight to dibenzotellurophene without the step of compound **70** formation (see above).

A peculiar method for the synthesis of dibenzotellurophene which, apparently, can be used in the preparation of other tellurium-containing heterocycles as well, consists in the reaction of dibenzothiophene 5,5-dioxide **71** with tellurium at elevated temperature.[112]

The SO_2–Te interchange is achieved also upon heating of thianthrene 5,5,10,10-tetroxide **72** with tellurium.[113]



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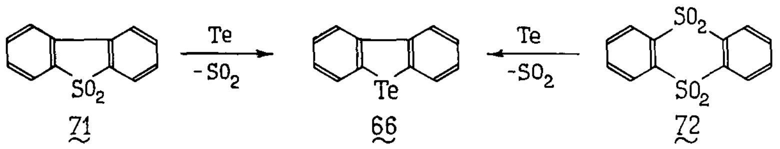
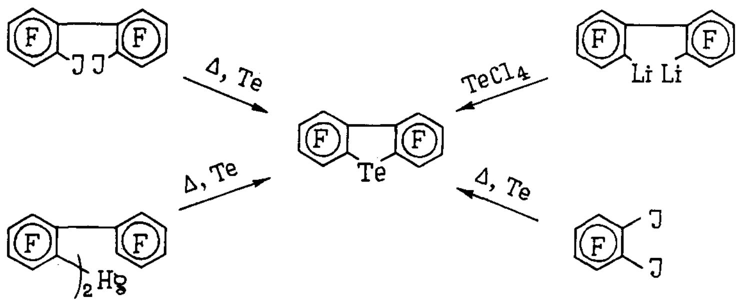


71

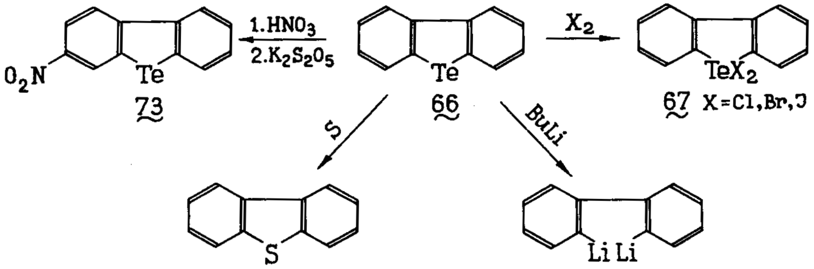
66

72

Some specific methods have been suggested for the preparation of dibenzotellurophenes containing perfluorinated benzene moieties.[114–117] The following reactions of metallic tellurium give rise to octafluorodibenzotellurophene: with 2,2′-diiodooctafluorobiphenyl at high temperature (in 66 % yield[114]), with bis(2-nonafluorobiphenylmercury) (in 10 % yield[115]) (this reaction proceeds, apparently, via initial formation of bis-(nonafluorobiphenylyl) telluride undergoing cyclization at elevated temperatures), with 1,2-diiodotetrafluorobenzene (in 17 % yield[115,117]). The same compound can also be obtained through reaction of 2,2′-dilithiooctafluorobiphenyl with $TeCl_4$ (17 % yield[114,117]). A detailed study of the mass spectrum of octafluorodibenzotellurophene has been reported in ref. 118.



Dibenzotellurophene interacts with halogens to form the dibenzotellurophene 5,5-dihalides **67**.[107,110] When dibenzotellurophene is treated with concentrated HNO_3, initially 2-nitrodibenzotellurophene 5,5-dinitrate is produced. Upon reduction, it readily forms 2-nitrodibenzotellurophene **73**.[113] Reaction of compound **66** with butyllithium leads to ring fission and to the formation of 2,2′-dilithiobiphenyl, but when **66** is heated at elevated temperature with sulfur, the tellurium atom is replaced by sulfur.[5] Reaction of dibenzotellurophene with picric acid gives the 1 : 1 adduct which according to γ-resonance spectra[119] possesses a sandwich structure formed by interaction between the π-electron system of the heterocycle and the picric acid. Reactions of dibenzotellurophene are outlined in Scheme 5.



SCHEME 5. Reactions of Dibenzotellurophene

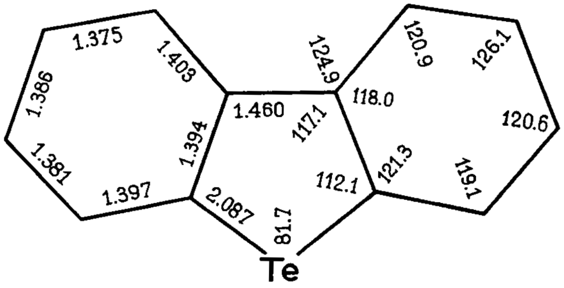


FIGURE 3. The Geometry of Dibenzotellurophene.

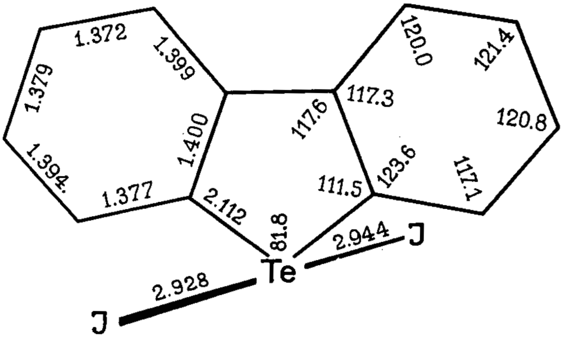


FIGURE 4. The Geometry of Dibenzotellurophene 5,5-Diiodide.

The molecular and crystal structure of dibenzotellurophene **66**[73] (Fig. 3) and of dibenzotellurophene 5,5-diiodide **67** (X = I)[72] (Fig. 4) have been examined by X-ray diffraction.

The dibenzotellurophene molecule is almost planar; the dihedral angles between the heterocycle and the benzene rings are 1.4° and 0.6°.

The angle C–Te–C in **66** (81.7°) has, as is also the case with acyclic diaryl chalcogenides[29], the minimal value among the related heterocyclic systems containing VI A group elements.[73]

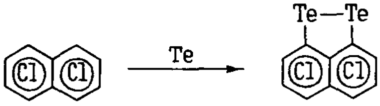
Somewhat greater is the distortion of the dibenzotellurophene 5,5-diiodide molecule **67** (X = I) in the crystal, the angle between the benzene rings being 3.3°[72]. This leads to a lack of coplanarity of the central five-membered heterocyclic ring. The iodine atoms lie in the axial plane and the angle I–Te–I equals 181.5°. The tellurium atom forms intermolecular bonds with the iodine atoms of each of the two neighboring molecules so that it acquires an octahedral configuration. The secondary Te . . . I bonds connect the molecules to extended chains. The absence of intermolecular I . . . I bonds in the crystals explains the red color of this compound. (Details see in Section 2.3.)

III. HETEROCYCLES WITH TWO HETEROATOMS

Five-membered tellurium heterocycles containing two heteroatoms are of considerable interest, since various electron-donor components of the charge-transfer complexes or cation radical salts (the so-called organic metals, i.e., organic solids with electric conductivity comparable to metals) can be obtained on the basis of compounds containing tellurium in combination with other VI A group elements such as S, Se, Te. This, apparently, explains the special attention given lately to the problems of synthesis, structure and reactivity of these compounds.

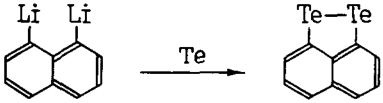
3.1. Derivatives of 1,2-ditellurole and its analogs

Of 1,2-ditellurole derivatives only *peri*-bridge systems have been described to date. The first representative of these compounds, 3,4,5,6,7,8-hexachloronaphtho[1,8-cd]-1,2-ditellurole **74** was obtained by heating octachloronaphthalene with tellurium at 350 °C[120]



74

Later Meinwald[121,122] synthesized naphtho[1,8-cd]-1,2-ditellurole **75** as well as its sulfur and selenium analogs via interaction of 1,8-dilithionaphthalene with powdered chalcogens in very low yields (8–12%)[121,122]



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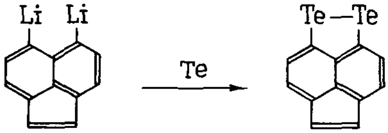
In an analogous way, acenaphtho[5,6-cd]-1,2-ditellurole **76** was prepared[123]



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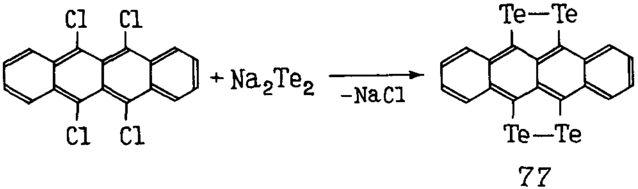
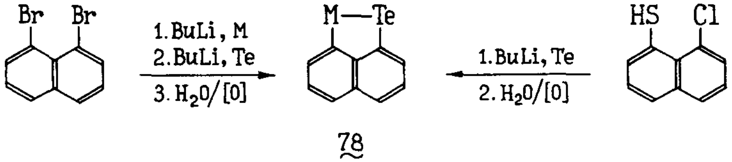
The compound containing two *peri*-condensed 1,2-ditellurole rings, 5,6,11,12-tetratelluratetracene **77**, was synthesized by reaction of 5,6,11,12-tetrachlorotetracene with sodium ditelluride[124]



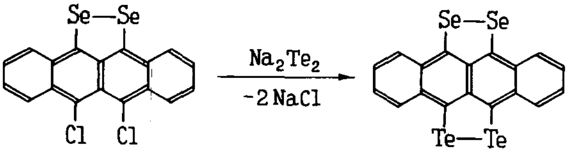
77

The synthesis of the 1,2-chalcogenatelluroles **78**, naphtho[1,8-cd]-1,2-tellurathiole **78** (M = S) and -1,2-telluraselenole **78** (M = Se) has also been described.[122,125] These compounds were obtained by successive treatment of 1,8-dibromonaphtalene with butyllithium and a chalcogen (sulfur or selenium) and then with the second equivalent of butyllithium and tellurium, subsequently subjecting derivatives containing MLi groups (M = S, Se, Te) to hydrolysis and air oxidation of the MH functions to compounds **78**. Very low yields of these heterocycles, 2 % (M = S) and 4 % (M = Se), were achieved. An alternative approach leading to compound **78** (M = S) is based on the reaction of 8-chloronaphthalene-1-thiol with two equivalents of butyllithium and with tellurium. The yield of the heterocycle reaches in this case 60 %.[125]



78
M=S, Se

A mixed selenium–tellurium-containing heterocycle, 5,6-ditellura-11,12-diselenatetracene **79** was synthesized through interaction of 5,6-diselena-11,12-dichlorotetracene with sodium ditelluride.[126]



Compounds **75**–**79** form with tetracyanoquinodimethane (TCNQ) deeply colored charge-transfer complexes with acetonitrile or acetone solutions of the components are mixed.[121,125] It is interesting to note that the electric conductivity of the complexes of the compounds **78** with TCNQ increases in the order: M = S (10^{11} ohm · cm), M = Se (2×10^7 ohm · cm) < M = Te (50 ohm · cm).[122] Metallic properties (electric conductivity Ω = 1–2 $ohm^{-1} \cdot cm^{-1}$) at room temperature are exhibited by the complex **76** as well as by the ion-radical salt formed when tetratelluratetracene is oxidized by anhydrous copper(II) halides.[127]

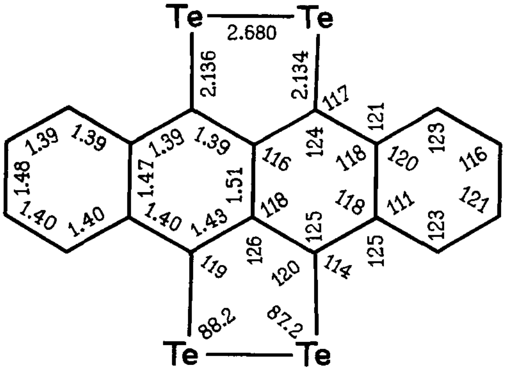
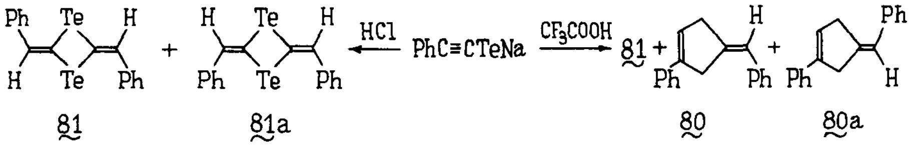


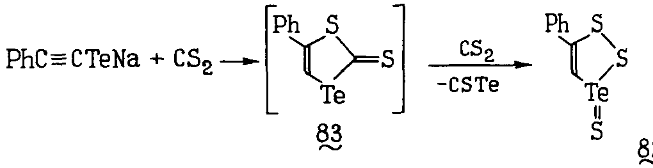
FIGURE 5. The Geometry of Tetratelluratetracene.

The molecular and crystal structure of tetratelluratetracene was determined by X-ray diffraction[128] (Fig. 5). The molecules in the crystal are packed in layers, neighbouring layers being connected by short intermolecular Te . . . Te bonds equal to 3.71 Å.

3.2. *1,3-Ditelluroles and tetratellurafulvenes*

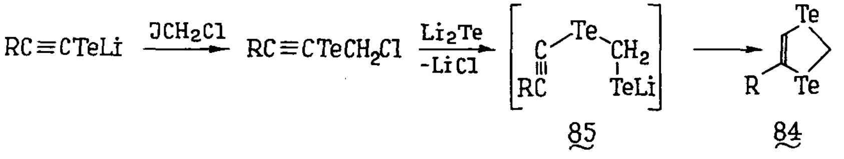
Petrov *et al.* were the first to report the preparation of 1,3-ditellurole.[129] When sodium phenylacetylenides react in DMSO with Te and then are treated with an ether solution of HCl, compounds are formed which were assigned the structure of 2-(*p*-X)-benzylidene-4*H*-[2*H*-(1,3-ditelluroles)] **80**. This report proved, however, erroneous, as the subsequent work of the same authors[130] and of others[131,132] showed (using X-ray structural analysis, among other methods) that the actual structures of the reaction products were *cis*-**81** and *trans*-isomers of the 1,3-ditelluretane **81a**. As shown in ref. 131, when HCl is replaced with another proton donor, CF_3COOH, one obtains along with 1,3-ditelluretane **81** (1 %) a mixture of the *cis*- **80** (5 %) and *trans*-isomers **80a** (7 %) of 1,3-ditellurole.





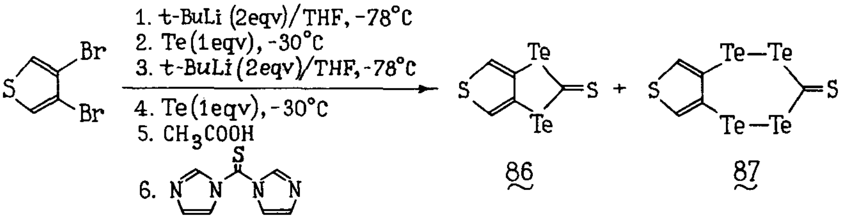
An attempt to synthesize a derivative of 1,3-thiatellurole by a reaction similar to the one used for the preparation of 1,3-dithiole[133], viz. via interaction of sodium 2-phenylethynyltellurolate with CS_2 led to the trithione **82**.[130] Apparently, this compound is formed via the intermediate 1,3-thiatellurole-2-thione **83** which upon reaction with CS_2 gives compound **82**.[130]

An effective method for the synthesis of 1,3-ditelluroles and its derivatives was developed by Detty.[134] It is based on an intramolecular nucleophilic addition to the triple bond of compound **85** formed *in situ* as shown below:

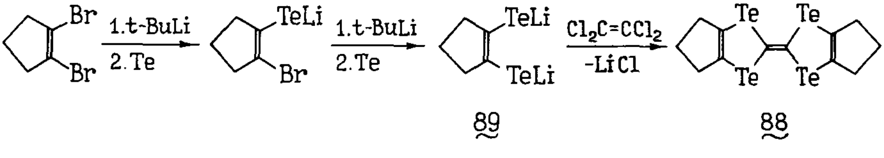


The yield of the unsubstituted heterocycle **84** is 65 % whereas substituted 1,3-ditelluroles have been obtained in yields from 4 % (R = CH_3) to 49 % (R = C_6H_5). As by-products, symmetric tellurides $(RC{\equiv}C{-}CH_2)_2Te$ are formed.[134]

The thiophene-annellated tellurole **85** is described in ref. 135. The scheme of the synthesis of this compound starting from 3,4-dibromothiophene is given below. The seven-membered tellurium heterocycle **86** is formed as a by-product of this reaction.[135]

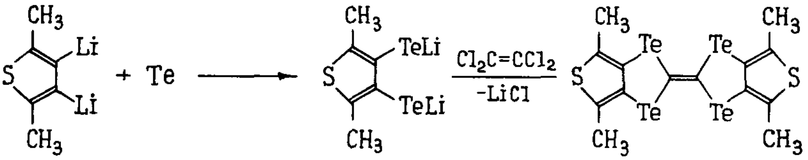


Tetratellurafulvalenes and their benzo analogs are of particular interest among derivatives of 1,3-ditellurole. Bis-(trimethylene)-tetratellurafulvalene **88** was synthesized by Wudl in 32 % yield.[136] Substitution of bromine by lithium under the action of *t*-butyllithium and subsequent treatment of the lithio derivative with tellurium leads to tellurolate **89** the reaction of which with tetrachloroethylene gives rise to the tetratellurafulvalene **88**.[136]

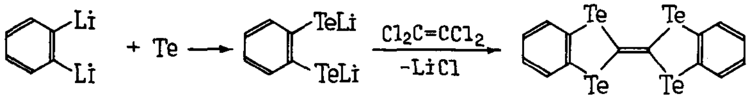


Treatment of 3,4-dilithio-2,5-dimethylthiophene with tellurium and tetrachloroethylene affords the tetratellurafulvalene **90** in over 70 % yield.[137]

Similarly to this, by reaction of *o*-dilithiobenzene with tellurium and subsequent treatment with tetrachloroethylene, the synthesis of dibenzotetratellurafulvalene **91** has been accomplished in 10 % yield.[138]



90



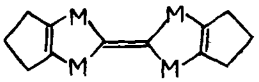
92

91

TABLE IX

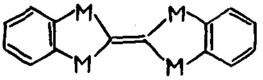
Oxidation Potentials and UV Spectra

of tetrachalcogenafulvalenes



88

and of their benzo analogs (ref. 136)



91

Compound type	δ_{max}, nm	$E_1^{1/2}$(V)	$E_1^{1/2}$(V)	ΔE
88, S	315, 327, 473	0.24	0.73	0.49
88, Se	299, 508, 534	0.42	0.81	0.39
88, Te	320, 335, 410, 610, 635	0.40	0.69	0.29
91, S	–	0.71	1.14	0.43
91, Se	–	0.78	1.17	0.39
91, Te	–	0.71	1.05	0.34

The extremely high nucleophilicity of the tellurolate anions **89** and **92** makes their reaction with tetrachloroethylene in THD possible even at room temperature. It is interesting to note in this connection that the selenium analog of compound **88** cannot be produced under similar conditions.[136]

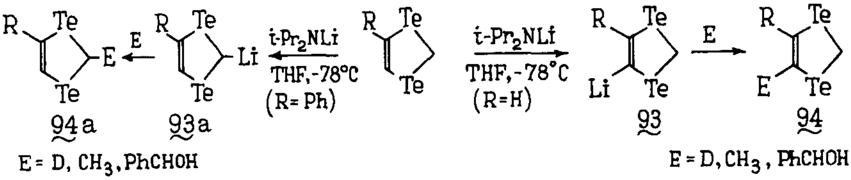
An important characteristic of compounds **88** and **91** are their oxidation potentials.[136,138,139] These constants, together with analogous data for sulfur and selenium compounds,[136] and UV-spectral characteristics are listed in Table IX.

Considering the decrease in the values of $\Delta E = E_2^{1/2} - E_1^{1/2}$ in the series of compounds **88** from sulfur to tellurium, the authors of ref. 136 suggested that ionization in the case of the sulfur analog proceeds from the π-orbitals of **88**, while in the tellurium analog it occurs from the lone electron pair of tellurium.

Compound **88** with TCNQ[136] and other acceptors[139] forms charge-transfer complexes possessing a high electric conductivity.

The reactivity of 1,3-ditelluroles has been investigated so far very inadequately. Of interest are results of the lithiation of the heterocyclic system of 1,3-ditellurole **84**

(R = H) and 4-phenyl-1,3-ditellurole **84a** (R = Ph) reported by the authors of ref. 140. Treatment of compounds **84** and **84a** with lithium diisopropylamide in THF at −70 °C leads to 4-lithio-1,3-ditellurole **93** (R = H) and 2-lithio-4-phenyl-1,3-ditellurole **93a** (R = Ph), respectively. The structure of the lithio derivative was established in both cases on the ground of their reactions with electrophiles leading, respectively, to compounds **94** (R = H) and **94a** (R = Ph)[140]



The unusual course of the lithiation reaction of the 1,3-ditelluroles **84** and **84a** was explained in ref. 140 by steric hindrance created by the phenyl group for the nucleophilic attack of lithium diisopropylamide on the C-5 position.

The molecular structure of bis-(trimethylene)-tetratellurafulvalene **88** was investigated in an X-ray diffraction study[141] (Fig. 6) and shown to be similar to that of bis-(trimethylene)-tetraselenafulvalene. The bond lengths and angles in the carbocyclic rings of compound **88** practically coincide with those in its sulfur and selenium analogs. On the other hand, the angles in the heteroring of the tetratellurafulvalene **88** differ significantly from those in the analogous selenium derivative. The length of the double bond (1.356 Å) somewhat exceeds its typical value, but is close to the length of the corresponding bond in tetramethyltetraselenafulvalene (1.352 Å) and bis-(trimethylene)tetraselenafulvalene (1.383 Å). Compound **88** differs from its selenium analog in its packing in the crystal. It does not form uniform stacks and is characterized by two intermolecular contacts between tellurium atoms which are shorter than the sum of the van der Waals radii of these atoms. By means of the shorter contacts (3.583 Å) there takes place interaction between neighbouring molecules in the same plane whereas interaction between molecules in the perpendicular planes is revealed in the longer contacts.

3.3. 1,3-Ditellurolylium cations

Derivatives of 1,3-ditellurolylium cation **95** have not yet been isolated in analytically

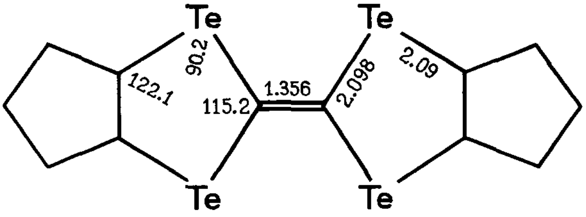
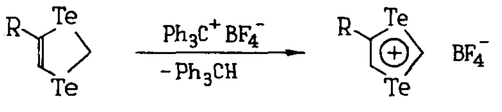


FIGURE 6. The Geometry of Bis-(trimethylene)-tetratellurafulvalene.

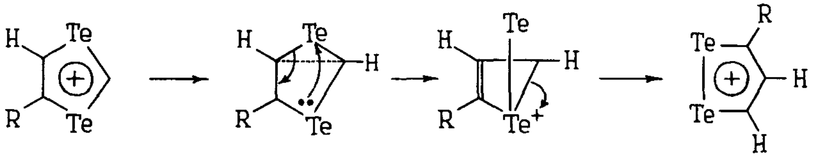
pure form. Their formation in solution when 1,3-ditelluroles **84** are treated with $Ph_3C^+BF_4^-$ can be inferred from the NMR spectra[134]



84 **95**

R = H(a), CH_3(b), $CH_3(CH_2)_3$(c), C_6H_5(d)

At room temperature in CD_3CN solution, a two-proton doublet is observed in the ^1H NMR spectrum of compound **95a** at 11.81 ppm (J = 1.2 Hz), and at 15.0 pp, (J = 1.2 Hz) a one-proton triplet is seen. At 30 °C this spectrum, however, changed rapidly and new signals appeared, a two-proton doublet at 13.8 ppm (J = 6.9 Hz) and a one-proton triplet at 10.3 ppm (J = 6.9 Hz). The last spectrum corresponds, in the opinion of the authors of ref. 134, to the 1,2-ditellurolylium salts **96a** formed by rearrangement of **95a** as shown below:

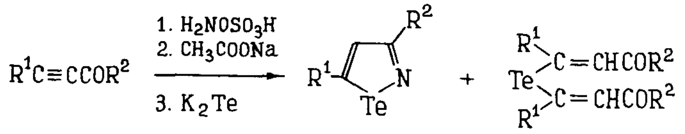


95 **96**

Upon further storage of the solution at room temperature, the ditllurolylium salt **96a** decomposes and metallic tellurium is extruded. The rearrangement is accelerated by alkyl and aryl substituents. Upon treatment of substituted 1,3-ditelluroles with $Ph_3C^+BF_4^-$, the formation of 1,2-ditellurolylium cations is observed in the NMR spectrum.[134]

3.4. *Isotellurazoles and their benzo analogs*

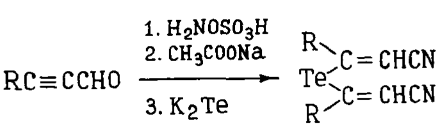
Derivatives **97** of the five-membered heteroaromatic system isotellurazole have been synthesized quite recently.[142] They are obtained by the reaction of alkynyl ketones with hydroxylamine-*O*-sulphonic acid and K_2Te in aqueous solution containing CH_3COONa. The reaction is always accompanied by formation of by-products, the bis-(ketoalkenyl) tellurides **98**, and the yields of isotellurazoles **97** are very low (4–10 %).



97 **98**

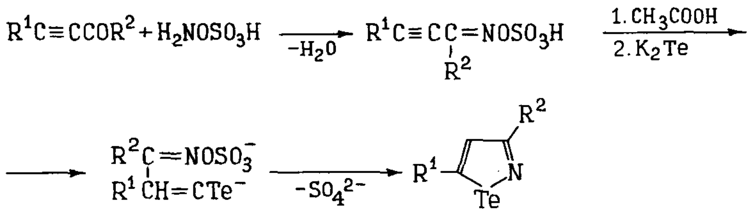
R^1 = H, R^2 = CH_3, C_2H_5, C_3H_7; R^1 = R^2 = CH_3; R^1 = C_6H_5, R^2 = CH_3.

When the alkynyl aldehydes are used instead of ketones, only the cyanovinyl tellurides **99** are obtained in low yield[142].



99

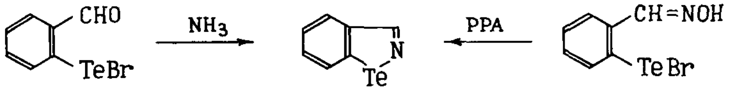
A possible reaction mechanism includes conversion of a keto group to an oxime-*O*-sulfonic acid followed by nucleophilic addition of tellurolate anion to the C≡C triple bond.[142]



97

The isotellurazoles **97** are characterized by high melting points and are easily sublimed. Their fragmentation under electronic impact proceeds similarly to that of the corresponding isothiazoles resulting in the loss of $R^1C{\equiv}CH$ and R^2CN.[142]

The benzo analog of compounds **97**, benzoisotellurazole **100**, was obtained by Renson using two reaction schemes, from *o*-bromotellurenylbenzaldehyde and from the corresponding oxime.[91] Both compounds were converted to the heterocycle **100**, the former upon treatment with ammonia, the latter with polyphosphoric acid. It is interesting to note that interaction of *o*-bromotellurenylacetophenone with ammonia produces not 3-methylbenzoisotellurazole, but telluroindoxyl.[91]



100

In the UV spectrum of compound **100** (δ_{max}, nm; log ε): 207 (4.27), 242 (4.15), 344 (3.65) a considerable bathochromic shift of absorption bands is observed as compared to its selenium 203 (4.15), 228 (4.30), 318 (3.67) and sulfur 204 (4.19), 222 (4.36), 303 (3.57) analogs.[91] In the ^{1}H NMR spectrum, the H-3 proton (δ = 10.16 ppm) is most deshielded in the case of compound **100**. (For the selenium and sulfur analogs, the signals of the corresponding proton are observed at substantially higher fields, 9.15 and 8.75 ppm, respectively).[91]

Benzoisotellurazole possesses a very high melting point (173 °C) as compared to benzoisoselenazole (57 °C) and benzoisotellurazole (39 °C) and is poorly soluble in common organic solvents. This peculiarity can be explained by short intermolecular bonds Te . . . N (2.40 Å)[143] in the tellurium-containing heterocycle **100**, the geometry of which is shown in Fig. 7 (mean values of bond lengths and angles are given).

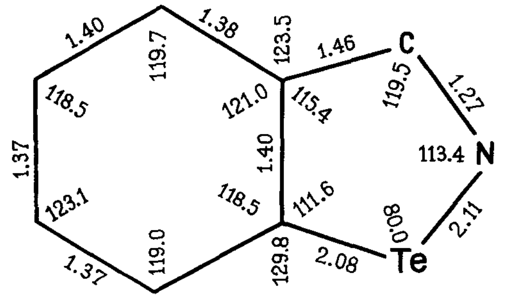
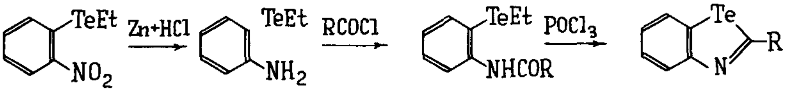


FIGURE 7. The Geometry of Benzoisotellurazole.

3.5. *Benzotellurazole*

Of all 1,3-tellurazoles only derivatives of 1,3-benzotellurazole **101** have been synthesized so far.[144] The starting substance for the synthesis of this heterocyclic system is *o*-nitrotellurophenetole.[145] This is readily reduced to *o*-aminotellurophenetole which can be acylated with acyl chlorides under usual conditions giving rise to the corresponding anilides **102**. Formylation of the amino group is achieved by the use of the system HCOOH-dicyclohexylcarbodiimide. By action of $POCl_3$, the anilides **102** are cyclized to the benzotellurazoles **101**, though in very low yields (2 % in the case of the parent compound **101** (R = H).[144]



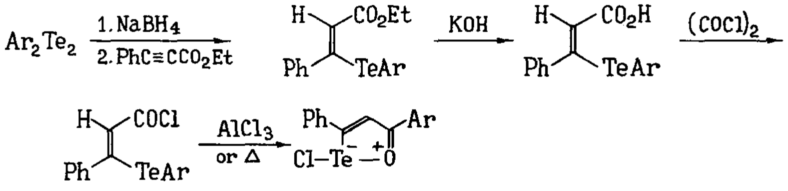
102

101

R=H(2%), CH_3(11%), C_6H_5 (15%), CO_2Et(13%), COPh(2%)

3.6. *1,2-Oxatellurol-1-ium chlorides*

Derivatives of the new tellurium-containing heterocyclic cation 1,2-oxatellurol-1-ium **103** were synthesized by Detty[146] via cyclization of *β*-aryltelluro(acryloyl)- or -cinnamoyl chlorides. Under the action of Lewis acids ($AlCl_3$) or upon heating, the (*β*-aryltelluro)-cinnamoyl chlorides **104** the synthesis of which is outlined in the Scheme below undergo *ipso*-acylation to form 3-phenyl-5-aryl-1,2-oxatellurol-1-ium chlorides.



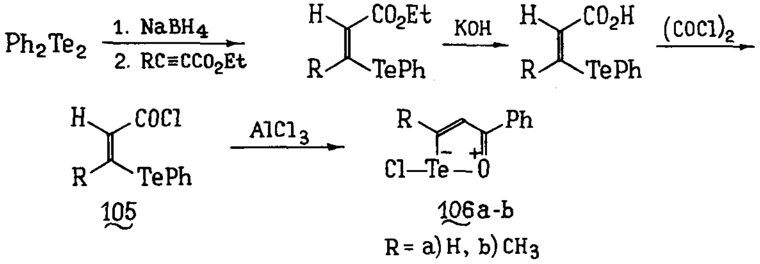
104

103 a-f

Ar = (a) C_6H_5 (81 %), (b) *p*-$CH_3C_6H_4$ (92 %), (c) *p*-$CH_3OC_6H_4$ (96 %), (d) *p*-$CH_3COC_6H_4$ (50 %), (e) *o*-$CH_3C_6H_4$ (75 %), (f) 1,2-C_4H_4 (82 %)

Both the thermal and the catalytic rearrangement rate depend to a great extent on the electronic nature of the substituents in the aryl ring.[146] Thus, with Ar = p-$CH_3OC_6H_4$, the reaction proceeds at room temperature leading to 1,2-oxatellurol-1-ium chloride **103c** in quantitative yield. When Ar = p-$CH_3C_6H_4$, the reaction proceeds in boiling $CDCl_3$ with the half period of transformation $\tau_{1/2}$ of one hour. In the case of Ar = C_6H_5, $\tau_{1/2}$ rises to 30 hours. An introduction of the electron-acceptor p-$COCH_3$ group into the benzene ring of benzoyl chloride led to complete inhibition of the reaction. Thus, refluxing **104d** in $CDCl_3$ for 72 hours left the initial β-aryltellurocinnamoyl chloride unchanged.

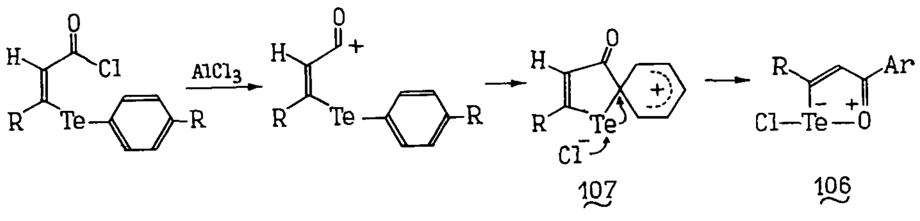
Cyclization of β-(aryltelluro)acryloyl chlorides **105** occurs in a similar way. Upon treatment with $AlCl_3$, they are converted to 1,2-oxatellurol-1-ium chlorides **106** in high yields.



In the opinion of the authors of ref. 146, the rearrangement of cinnamoyl (acryloyl) chlorides into the heterocycles **103** and **106** takes place via intramolecular attack of the electrophilic carbonyl carbon at the aromatic carbon atom bound to tellurium (*ipso*-acylation) leading to the spirocyclic σ-complex **107**. Subsequent nucleophilic attack of the chloride ion at the tellurium produces 1,2-oxatellurol-1-ium chlorides. An alternative route involves a concerted reaction implying direct attack on the Ar–Te bond by the carbonyl carbon without formation of the spirocyclic intermediate **107** (Scheme 6).

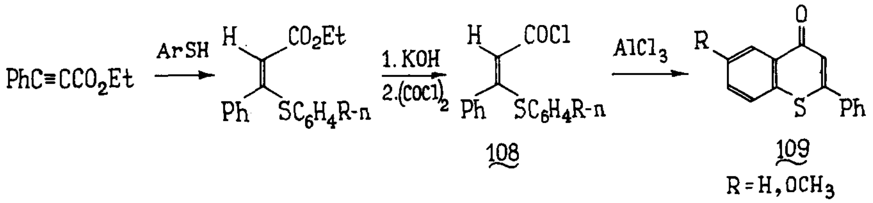
The crucial dependence of the rearrangement rate on the nature of the p-substituents of the aryl nuclei (according to a rough evaluation based on only two points, the reaction constant ϱ equals -6) is evidence for a mechanism involving *ipso*-acylation.

Thus, regardless of the nature of the p-substituents in the aryl ring, β-(aryltelluro)-propenoyl chlorides undergo *ipso*-acylation under the action of either Lewis acids or heating at high temperature. In this connection, Detty's data[147] on the *ipso*- or *ortho*-cyclization of (β-arylchalcogeno)propenoyl chlorides and its dependence on the chalcogen are of interest.

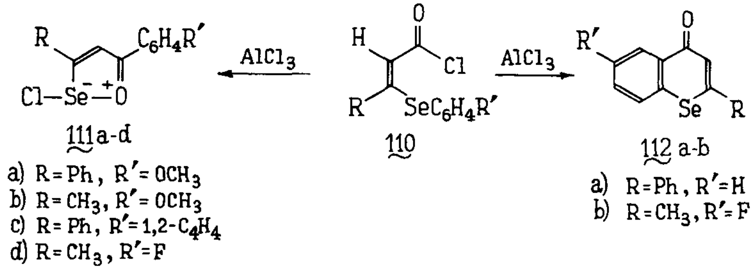


SCHEME 6. The mechanism of rearrangement of cinnamoyl(acryloyl) chlorides

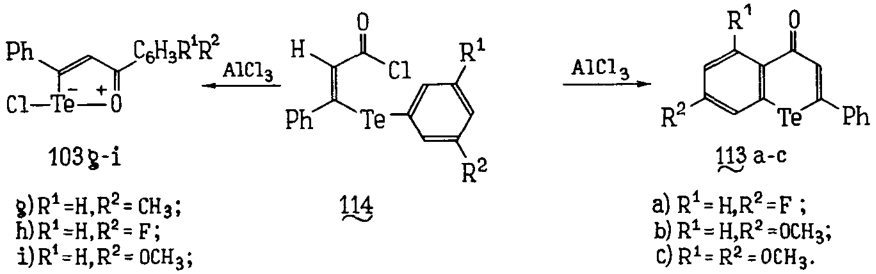
β-(Arylthio)cinnamoyl chlorides **108**, the preparation of which is described below, undergo only *o*-acylation when treated with $AlCl_3$ to form thioflavones **109** in good yield.



The cyclization of *β*-(arylseleno)propenoyl chlorides **110** upon treatment with $AlCl_3$ proceeds depending on the nature of R and of the substituents in the aryl ring (R′), through either *ipso*-acylation leading to 1,2-oxaselenol-1-ium chlorides **111** or *o*-acylation in which case selenoflavones **112** are obtained. In some cases both these reactions can proceed simultaneously. When R = Ph, R′ = H, only the selenoflavone **112a** is formed. When R = Ph, R′ = OCH_3; R = CH_3, R′ = OCH_3 as well as with R = Ph, R′ = 1,2-C_4H_4 only the 1,2-oxaselenol-1-ium chlorides **111 a–c** are obtained under the action of $AlCl_3$ or through heating. However, when R = CH_3 and R′ = F, both the 1,2-oxaselenol-1-ium chloride **111d** (36%) and the selenoflavone **112b** (24%) were isolated.

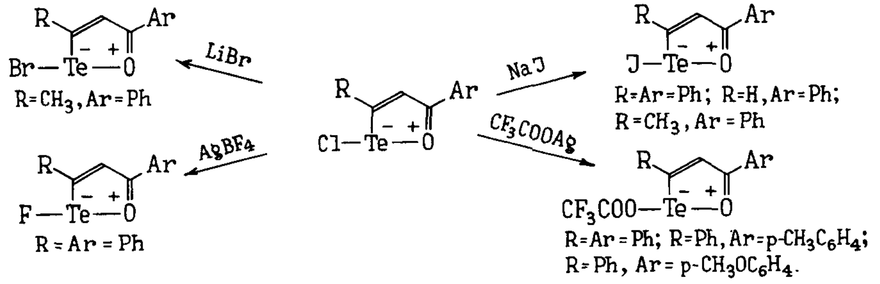


On the other hand, all *p*-substituted *β*-(aryltelluro)propenoyl chlorides undergo only *ipso*-acylation leading to 1,2-oxatellurol-1-ium chlorides as noted above. However, appropriate choice of substituents in (aryltelluro)-propenoyl chlorides activating the *o*-positions of the aryl rings making them susceptible to electrophilic attack and preventing *ipso*-acylation results in cyclization with the predominant formation of telluroflavones **113**. *m*-Substituted *β*-(aryltelluro)cinnamoyl chlorides **114** have been shown to be just the proper compounds. Upon treatment with $AlCl_3$ at −78 °C, they give rise to products of *ipso*- and/or *o*-acylation the ratio between which is determined by the nature of R. Thus, with R^2 = CH_3 (R^1 = H), only the product of *ipso*-attack **103g** is formed, when R^2 = F (R^1 = H), both *ipso*- and *o*-attack products (**103h** and **113e**, respectively) are obtained in the ratio of 16 : 1. When R^2 = OCH_3 (R^1 = H), also a mixture of *ipso*- and *o*-attack products (**103i** and **113b**, respectively) is formed in the ratio of 1 : 23 whereas with R^1 = R^2 = OCH_3 only the telluroflavone **113c** is produced in 90% yield[147].



Thus, the intramolecular rearrangement of β-(arylchalcogeno)propenoyl chlorides is very sensitive to the nature of the substituents. In the case of arylthio groups, only *o*-acylation occurs and thioflavones are formed., Arylseleno and aryltelluro groups, depending on the nature and position of the substituents, may undergo both *ipso*- and *o*-acylation giving rise to either 1,2-oxachalcogenol-1-ium chlorides or chalcogenoflavones or to a mixture of both.

The 1,2-oxatellurol-1-ium chlorides **103** and **106** are stable to air and light both in the crystal state and in solution, are thermally stable and may be heated without decomposition up to 300 °C.[146] The Te–Cl bond in these compounds possesses a highly ionic character and the chlorine atom can be readily replaced by other ions such as Br^-, I^-, or CF_3COO^-. Interestingly, 1,2-oxatellurol-1-ium chlorides treated with $AgBF_4$ form not borofluorides, as might be expected, but 1,2-oxatellurol-1-ium fluorides

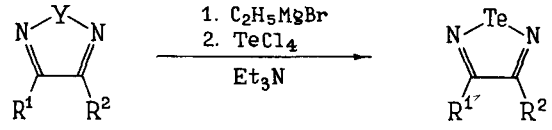


IV. HETEROCYCLES WITH THREE AND MORE HETEROATOMS

4.1. 1,2,5-Telluradiazoles

The parent heterocycle and its derivatives **115** were obtained by Bertini[148,149] through reaction sequences including the treatment of 1,2,5-thiadiazoles **116** (Y = S) or selenadiazoles **116** (Y = Se) successively with ethylmagnesium bromide, H_2SO_4, and $TeCl_4$ in the presence of triethylamine.

Of all 1,2,5-thiadiazoles only substituted derivatives were converted to tellurium analogs. The yields of compounds **115** are much lower than in the case where the corresponding 1,2,5-selenadiazoles are involved. The mechanism for the transformation of the heterocycles **116** into **115** is described by the following scheme:[149]

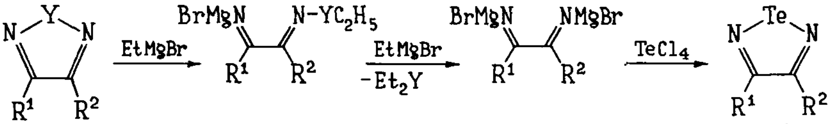


116

Y=S: $R^1=R^2=CH_3,Ph$;
Y=Se: $R^1=R^2=CH_3,H,Ph$;
$R^1=H$, $R^2=CH_3$; $R^1=H,R_2=$
$=Ph$

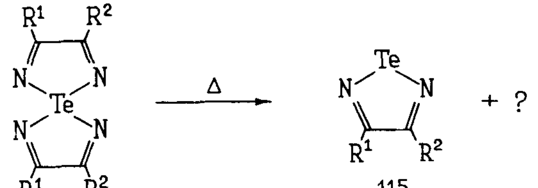
115

$R^1=R^2=H$ (20%)(Y=Se); CH_3(12%)(Y=Se),
(6%)(Y=S); Ph(79%)(Y=Se), (39%)(Y=S);
$R^1=H,R^2=CH_3$(26%)(Y=Se); $R^1=H$, $R^2=$
$=Ph$(60%)(Y=Se)



116 **115**

According to ref. 149, this mechanism is confirmed by the following fact: If prior to adding $TeCl_4$ the reaction mixture is treated with H_2SO_4 which transforms magnesium salts into free bases, the yields of **115** increase. This view is, however, open to doubt, since the imines shown in the Scheme would in the first place form complexes with $TeCl_4$ rather than undergo cyclization. The same is true of Schiff bases[150] as well as of nitrogen heterocycles containing an N atom of the pyridine type.[29] Moreover, this mechanism does not explain why the compounds of Te(II), but not Te(IV) are formed upon reaction with $TeCl_4$. Apparently, the reaction proceeds via tetracoordinated tellurium compounds **117** which, similarly to tetraaryltelluranes[115], are decomposed to form compounds **115** and some by-products the structure of which has not been elucidated yet.



117 **115**

The 1,2,5-telluradiazoles **115** are characterized by high melting points and low solubility in the common organic solvents. They are sensitive to sun light and are readily hydrolyzed in aqueous acid solutions. The treatment of **115** with such solutions results in their decomposition with the formation of metallic tellurium and 1,2-dicarbonyl compounds.[149] However, **115** are fairly stable to water and even to alkaline solutions

$$\mathbf{115} + H_3O^+ \rightarrow R^1COCOR^2 + NH_4^+ + Te + H_2TeO_3$$

The fragmentation of **115** under electron impact proceeds similarly to that of their sulfur and selenium analogs resulting in the appearance of $RCNTe^+$, $HCNTe^+$, and Te^+ ions.[149]

A comparison of some properties of 1,2,5-chalcogenadiazoles is given in Table X.[149]

TABLE X

Comparison of the properties of 1,2,5-chalcogenadiazoles 116 (R = H)[149]

Y	M.p., °C	UV[a] (δ_{max})	NMP ^{1}H, δ, ppm
O	−28	b	8.66
S	−50	253 (10100)	8.89
Se	21	285 (6600)	9.47
Te	185–188	336 (390)	10.81

[a] In THF.

[b] Absorption in the far UV region.

The molecular and crystal structures of 1,2,5-telluradiazole have been determined.[152] The bond lengths and the valence angles for this molecule are given in Fig. 8. As with benzoisotellurazole[143], secondary intermolecular bonds between Te and N atoms (2.764 Å) were also found in 1,2,5-telluradiazole. These bonds connect each Te atom with two N atoms belonging to neighboring molecules in the crystal. This leads to a polymeric ribbon type structure which is responsible for the anomalous physical properties (m.p., solubility) as compared to other 1,2,5-chalcogenadiazoles. The C–N and C–C bond lengths in 1,2,5-telluradiazole being equal to 1.273 and 1.421 Å, respectively, are close to the standard values for C=N and C–C bonds which indicates a weak aromaticity of this heterocycle.[152]

4.2. Δ^4-1,2,4-Thiotellurazolines

Compound **118**, the only known representative of compounds of this class, has been obtained by heating Sb_2Te_3 (or In_2Te_3) at 80–90 °C over a period of many days with 2*H*-1,3-thiazete **119** which above 80 °C exists in equilibrium with its valence tautomer **120**[153].

The yield of the heterocycle **118** amounts to 15 %. It reacts readily with phosphites and compounds containing multiple bonds eliminating tellurium which allows one to consider **118** as an equivalent of a hetero-1,3-diene in cycloaddition reactions.[153]

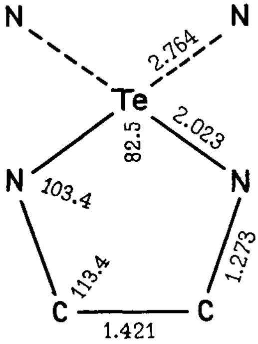
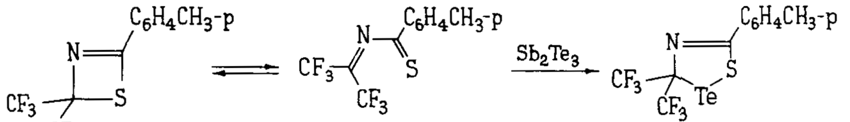


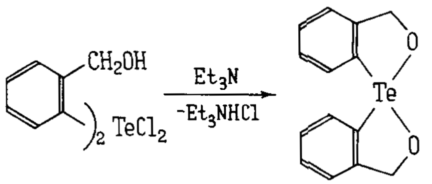
FIGURE 8. The Geometry of 1,2,5-Telluradiazole.



119 120 118

4.3. 1,1-Spiro[3H-2,1-benzoxatellurole]

A spirobicylic compound, 1,1-spiro[3*H*-2,1-benzoxatellurole] **121** was obtained in almost quantative yield[154] by treatment of bis-[2-hydroxymethyl]phenyltellurium dichloride with triethylamine in benzene.

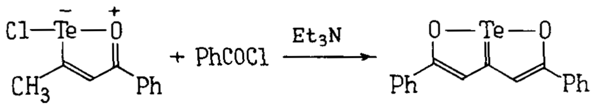


121

In contrast to the corresponding sulfurane[155], the methylene protons of this spirane appear in the ^{1}H NMR spectra at room temperature as sharp single peaks (in deuterochloroform at 5.28 ppm and in nitrobenzene at 5.34 ppm). This indicates a substantially lower energy barrier for the polytopal rearrangement of bisphenoidal tellurium-containing structures as compared to the analogous sulfur and selenium derivatives which is in agreement with predictions based on quantum mechanical calculations.[156]

4.4. 1,6-Dioxa-6a-tellurapentalene

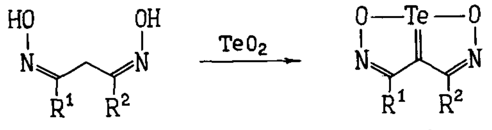
The only known representative of 1,6-dioxa-6a-tellurapentalenes, 2,6-diphenyl-1,6-dioxa-6a-tellurapentalene **122** has been prepared via interaction of 3-methyl-5-phenyl-1,2-oxatellurol-1-ium chloride **106b** with benzoyl chloride in the presence of triethylamine in 39 % yield.[157]



106b 122

More numerous are the aza analogs of compound **122**, i.e. the 2,5-diaza-1,6-dioxa-6a-tellurapentalenes **123**[158,159]. They have been synthesized by treatment of the dioximes of 2-unsubstituted 1,3-diketones with tellurium dioxide.

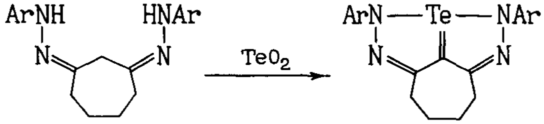
The use of tellurium tetrachloride instead of tellurium dioxide in this reaction results in decreasing yields of the compounds **123**.[159]



123

$R^1 = R^2 = H$ (25 %), CH_3 (20 %); $R^1 = H$, $R^2 = C_6H_5$ (5 %), $R^2 = p\text{-}CH_3C_6H_4$ (5 %); $R^1 = H$, $R^2 = p\text{-}ClC_6H_4$ (4 %); $R^1 = CH_3$, $R^2 = CO_2C_2H_5$ (5 %); R^1, $R^2 = -(CH_2)_3$ (30 %); $-(CH_2)_4-$ (45 %); $-CH_2C(CH_3)_2CH_2-$ (30 %); $\underbrace{CH_2-CH_2-CH-(C}H_2)_2$ (60 %): $\underbrace{CHC(CH_3)_2-C(CH_3)-(C}H_2)_2$ (50 %)

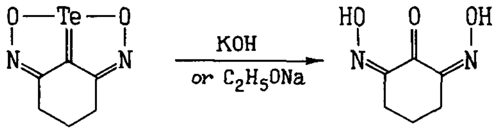
A representative of the third type of compounds possessing the 6a-tellurapentalene framework, 1,2,5,6-tetraaza-6a-tellurapentalene **124**, has been obtained in 2 % yield via reaction of the bis(2,4-dinitrophenyl)hydrazone of 1,3-cycloheptandione with tellurium dioxide[160]



Ar = 2,4-$(NO_2)_2C_6H_3$

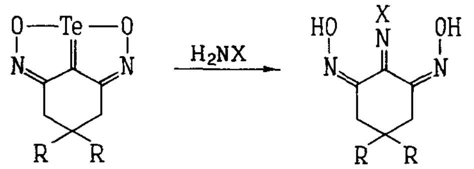
124

The reactivity of 6a-tellurapentalenes **122** and **123** has not been yet studied in detail. Compound **122** is fairly stable to acids and alkali whereas its aza analogs **123** readily react with ethanol solutions of KOH and C_2H_5ONa affording 1,2,3-triketone 1,3-dioximes.[159]



123

Interaction of **123** with hydroxylamine, hydrazine and phenylhydrazine also proceeds with the elimination of the tellurium atom leading to the corresponding derivatives of 1,2,3-tricarbonyl compounds.[159]



123

X = OH, NH_2, NHPh

The difference in behavior between these two types of tellurapentalenes is clearly revealed in their reactions with halogens. 2,5-Diphenyl-1,6-dioxa-6a-tellurapentalene reacts at low temperature with bromine and chlorine to form the tellurium adducts **125**.[157] At higher temperature, halogenation of the ring occurs and compounds **126** are

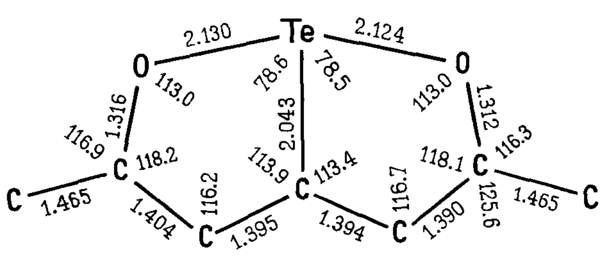
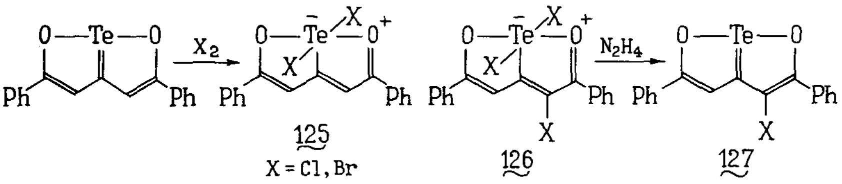


FIGURE 9. The Geometry of 2,5-Diphenyl-1,6-dioxa-6a-tellurapentalene.

formed. Their reduction with hydrazine produces new 6a-tellurapentalenes **127** in high yield.



125
X = Cl, Br
126
127

As regards 2,5-diaza-1,6-dioxa-6a-tellurapentalenes, these compounds could not be involved in any of the usual electrophilic substitution reactions, such as halogenation, nitration, sulfonation, Vilsmeyer formylation and Friedel–Crafts acylation.[159] The reasons for the inability of compounds **123** to react with halogens are not, however, quite clear in view of the well-known feasibility of oxidative addition of halogens to the tellurium atom of Te(II) compounds.[29]

The molecular and crystal structures of **122** (Fig. 9) and **125** (X = Br) have been studied by X-ray diffraction.[157] The molecule of the former compound is planar, the C–C bond lengths are close to those of the aromatic type whereas the lengths of the C–O bonds are intermediate between those for double and single bonds.

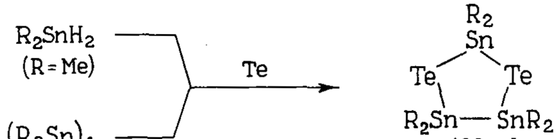
Mass spectra of 2,5-diaza-1,6-dioxa-6a-tellurapentalenes as well as spectra of their sulfur and selenium analogs have been reported.[161]

4.5. Tellurium–tin- and -germanium-containing heterocycles

Bearing in mind the definition of the heterocyclic compounds, the substances considered in this section, without any carbon atoms, would be more correctly referred to as cyclic tellurium-elementoorganic compounds.

Two main methods have been employed for the preparation of tellurium- and tin-containing rings. In the first, dialkylstannane dihydrides[162] or dialkylstannane oligomers[163,164] react with metallic tellurium to give compounds with the Sn_3Te_2 moiety, **128a, b**. Evidently, when dialkylstannane dihydrides are used, the reaction also proceeds via oligomers subsequently oxidized by tellurium.[162]

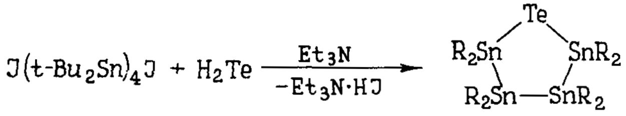
Compound **128a** is also a by-product of the reaction of dimethyltin chloride with NaHTe[165] and compound **128b** is formed together with the four-membered ring Sn_2Te_2.[164]



128a-b

R= a) CH_3; b) t-Bu

The second method consists of the reaction of 1,4-diiodo-1,1,2,2,3,3,4,4-octa-(*t*-butyl)-tetrastannane with H_2Te in the presence of triethylamine leading to the formation of another five-membered ring, Sn_4Te **129a.**[164]

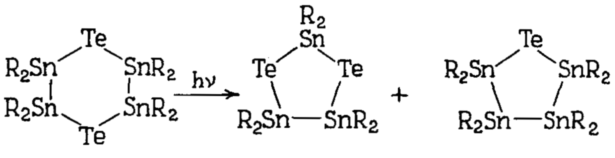


129a

R = t-Bu

This compound can also be obtained by reaction of tetrametric bis-(*t*-butyl)tin with Te. Its yield is, however, small in this case, and it is isolated concomitantly with **128b** and the four-membered ring Sn_2Te_2.[164]

Furthermore, compounds **128a** and **129b**, a methyl analog of **129a**, can be produced when 2,2,3,3,5,5,6,6-octamethyl-1,4-ditellura-2,3,5,6-tetrastannane **130** is UV-irradiated with xenon lamp light in C_6D_6.[165] The formation of these compounds has been confirmed by ^1H NMR spectroscopy.[166]

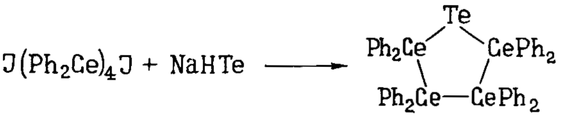


130 R=Me **128a** **129b**

The stability of tellurium-tin ring compounds with respect to oxygen, light and heating is, generally, not high; it is determined by both the type of the ring and the structure of the alkyl substituents. Compound **128a** is very unstable, **128b** decomposes after several days of storage in air, whereas **129a** does not undergo decomposition in air over a very long period of time.[165]

An X-ray structural study of compound **129a** has been performed[164], and the ^{119}Sn NMR spectrum of compound **128a** has been studied.[166]

The only tellurium and germanium-containing ring **131** has been obtained by reaction of 1,4-diiodo-1,1,2,2,3,3,4,4-octaphenyltetragermane with NaHTe.[167]



131

This heterocycle is so unstable that no satisfactory elemental analysis could be obtained owing to its rapid oxidation to the oxygen analog.

REFERENCES

1. I. D. Sadekov, V. I. Minkin, and A. D. Garnovskii, *Sulfur Rep.* **4**, 63 (1985).
2. F. Fringuelli, G. Marino, and A. Taticchi in: *Advances in Heterocyclic Chemistry*, Vol. 21, p. 119. Academic Press, New York, 1977.
3. S. Gronowitz, *Adv. Heterocycl. Chem.*, **1**, 67 (1980).
4. G. T. Morgan and F. H. Burstall, *J. Chem. Soc.*, **1931**, 180.
5. C. Courtot and M. G. Bastani, *C. R. Acad. Sci.*, **203**, 197 (1936).
6. E. H. Braye, W. Hubel, and J. Caplier, *J. Am. Chem. Soc.*, **83**, 4406 (1961).
7. W. Mack, *Angew. Chem.*, **77**, 260 (1965).
8. M. Renson, *Chem. Scr.* **A8**, 29 (1975).
9. W. Lohner and K. Praefcke, *Chem. Ber.*, **111**, 3745 (1978).
10. C. Backes, D. Cagniant, and P. Cagniant, Abstracts of papers of the IIIrd Intern. Symp. on Chemistry of Se and Te (Metz, Fr., 1979, p. 90).
11. G. Kirsch, P. Cagniant, D. Cagniant, and C. Backes, *Phosphorus Sulfur*, **6**, 161 (1979).
12. A. Scheller, W. Winter, and E. Müller, *Liebigs Ann. Chem.*, **1976**, 1448.
13. A. Ulman, J. Manassen, F. Florow, and D. Rabinovich, *Tetrahedron Lett.* 1885 (1978).
14. K. Ramasamy, M. Murugesan, and P. Shanmugan, *Synthesis*, **1978**, 842.
15. E. Luppold, E. Müller, and W. Winter, *Z. Naturforsch.*, **31b**, 1654 (1976).
16. F. Fringuelli, B. Serena, and A. Taticchi, *J. Chem. Soc., Perkin Trans. II*, **1980**, 971.
17. K. Chkor, C. Pommier, J. F. Berar, and G. Galvarin, *M. Diot. Mol. Cryst. Liq. Cryst.*, **71**, 3 (1981).
18. J. Martens and K. Praefcke, *J. Organometal. Chem.*, **198**, 321 (1980).
19. G. Paliani and R. Cataliotti, *Spectrochim. Acta*, **37A**, 707 (1981).
20. G. De Alti, and P. Decleva, *Chem. Phys. Lett.* **77**, 413 (1981).
21. V. Galasso, *Theochem.*, **3**, 231 (1982).
22. M. L. Martin, M. Trierweiler, V. Galasso, F. Fringuelli, and A. Taticchi, *J. Magn. Res.*, **42**, 155 (1981).
23. W. Lohner and K. Praefcke, *J. Organometal. Chem.*, **208**, 43 (1981).
24. M. L. Martin, M. Trierweiler, V. Galasso, F. Fringuelli, and A. Taticchi, *J. Magn. Res.*, **47**, 504 (1982).
25. M. A. Natiello, G. E. Scuseria, and R. H. Contreras, *Theochem.*, **14**, 233 (1983).
26. F. Fringuelli and A. Taticchi, *J. Heterocycl. Chem.*, **15**, 137 (1978).
27. H. Lumbroso, C. Liegeois, N. Dereu, and L. Christiaens, *J. Mol. Struct.*, **67**, 251 (1981).
28. A. M. Duffield, H. Budzikiewicz, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 2920 (1965).
29. I. D. Sadekov, A. A. Maksimenko, and V. I. Minkin, *The Chemistry of Tellurium-Organic Compounds*, Rostov University Press, 1983.
30. W. V. Farrar and J. M. Gulland, *J. Chem. Soc.*, **1945**, 11.
31. G. Zanati, G. Gaare, and M. E. Wolf, *J. Med. Chem.*, **17**, 561 (1974).
32. E. Buchta and K. Greiner, *Z. Naturwiss.*, **46**, 532 (1959).
33. E. Buchta and K. Greiner, *Chem. Ber.*, **94**, 1311 (1961).
34. K. G. K. de Silva, Z. Monsef-Mirzai, and W. R. McWhinnie, *J. Chem. Soc., Dalton Trans.*, **1983**, 2143.
35. Yu. V. Migalina, I. M. Balog, V. G. Lendel, A. S. Kosmin, and N. S. Zefirov, *Khim. Geterotsikl. Soed.*, **1978**, 1212.
36. M. Albeck and T. Tamary, *J. Organometal. Chem.*, **164**, C23 (1979).
37. T. N. Srivastava, R. C. Srivastava, and H. B. Singh, *Ind. J. Chem.*, **18A**, 367 (1979).
38. T. N. Srivastava, R. C. Srivastava, and M. Singh, *Ind. J. Chem.*, **17A**, 615 (1979).
39. T. N. Srivastava, R. C. Srivastava, and A. Bhargava, *Ind. J. Chem.* **18A**, 263 (1979).
40. T. N. Srivastava, R. C. Srivastava, and M. Singh, *J. Organometal. Chem.*, **157**, 405 (1978).
41. E. T. Strom, B. S. Snowden, H. C. Custard, D. E. Woesner, and J. R. Norton, *J. Org. Chem.*, **33**, 2555 (1968).
42. H. Lumbroso and D. M. Bertin, *J. Chem. Soc., Chem. Comm.*, **1973**, 342.
43. H. Lumbroso, D. M. Bertin, F. Fringuelli, and A. Taticchi, *C. R. Acad. Sci.*, **277C**, 203 (1973).
44. H. Lumbroso, D. M. Bertin, F. Fringuelli, and A. Taticchi, *J. Chem. Soc., Perkin Trans. II*, **1977**, 775.

45. F. Fringuelli, S. Gronowitz, A. Hörnfeldt, and A. Taticchi, *J. Heterocycl. Chem.*, **11**, 827 (1974).
46. S. Pignataro and G. Distefano, *Chem. Phys. Letters*, **26**, 356 (1974).
47. M. G. Giorgini, G. Paliani, and R. Cataliotti, *Spectrochim. Acta*, **33A**, 1083 (1977).
48. W. Kulik, H. D. Verkruijsse, R. L. P. de Jong, H. Hommes, and L. Brandsma, *Tetrahedron Lett.* **24**, 2203 (1983).
49. M. R. Detty, B. J. Murray, and M. D. Seidler, *J. Org. Chem.*, **47**, 1968 (1982).
50. K. Ramasamy and P. Shanmugan, *Z. Naturforsch.*, **32b**, 605 (1977).
51. J. Bergman and L. Engman, *J. Am. Chem. Soc.*, **103**, 2715 (1981).
52. H. J. Arpe and H. Kuckertz, *Angew. Chem., Int. Ed. Engl.*, **10**, 73 (1971).
53. E. Guthbertson and D. D. MacNicol, *J. Chem. Soc., Chem. Comm.*, **1975**, 1893.
54. R. F. Liolo and W. H. H. Gunther, *J. Organometal. Chem.*, **146**, 245 (1978).
55. A. Z. Al-Rubaie, W. R. McWhinnie, P. Granger, and S. Chapelle, *J. Organomet. Chem.*, **234**, 287 (1982).
56. N. Lumbulyadis and H. J. Gysling, *J. Organometal. Chem.*, **192**, 183 (1980).
57. T. N. Srivastava, R. C. Srivastava, and R. Kumar, *J. Ind. Chem. Soc.*, **59**, 186 (1982).
58. H. B. Singh, W. R. McWhinnie, T. A. Hamor, and R. H. Jones, *J. Chem. Soc., Dalton Trans.*, **1984**, 23.
59. R. F. Liolo, C. Thornton, and A. E. Smith, *J. Organometal. Chem.*, **190**, C64 (1980).
60. H. B. Singh and W. R. McWhinnie, *J. Organometal. Chem.*, **264**, 305 (1984).
61. M. Loth-Compere, A. Luxen, P. Thibaut, L. Christiaens, M. Guillaume, and M. Renson, *J. Heterocycl. Chem.*, **18**, 343 (1981).
62. L. Engman and M. P. Cava, *J. Org. Chem.*, **46**, 4194 (1981).
63. N. Petragnani, L. Torres, K. J. Wynne, *J. Organometal. Chem.*, **92**, 185 (1975).
64. J. Bergman and L. Engman, *Org. Prep. Proced. Int.*, **10**, 289 (1978).
65. Yu. P. Popov, G. F. Belikh, USSR Pat. 549,465; *Bull. Izobr.*, No. 9, p. 96 (1977).
66. C. Knobler and R. F. Ziolo, *J. Organometal. Chem.*, **178**, 423 (1979).
67. R. H. Jones and T. A. Hamor, *J. Organometal. Chem.*, **269**, 11 (1984).
68. G. Y. Chao and J. D. McCullough, *Acta Cryst.*, **15**, 887 (1962).
69. H. Hope, C. Knobler, and J. D. McCullough, *Inorg. Chem.*, **12**, 2665 (1973).
70. C. Knobler, J. D. McCullough, and H. Hope, *Inorg. Chem.*, **9**, 797 (1970).
71. J. D. McCullough, *Inorg. Chem.*, **12**, 2669 (1973).
72. J. D. McCullough, *Inorg. Chem.*, **14**, 1142 (1975).
73. J. D. McCullough, *Inorg. Chem.*, **14**, 2639 (1975).
74. A. E. McCarthy and H. B. Singh, *J. Organometal. Chem.*, **275**, 57 (1984).
75. A. Bigotta, V. Galasso, G. Pelizer, G. Distefano, G. C. Pallalardo, J. Bergman, and L. Engman, *Spectrochim. Acta*, **38A**, 185 (1982).
76. F. P. Mazza and E. Melchionna, *Rend. Acad. Sci. Napoli*, **34**, 54 (1928); *C.A.*, **23**, 2955 (1929).
77. W. V. Farrar, *Research*, **4**, 177 (1951).
78. J. L. Piette and M. Renson, *Bull. Soc. Chim. Belges*, **80**, 521 (1971).
79. J. L. Piette and M. Renson, *Bull. Soc. Chim. Belges*, **79**, 367 (1970).
80. J. L. Piette, J. M. Talbot, J. C. Genard, and M. Renson, *Bull. Soc. Chim. France*, **1973**, 2468.
81. J. M. Talbot, J. L. Piette, and M. Renson, *Bull. Soc. Chim. Belges*, **89**, 763 (1980).
82. I. D. Sadekov and V. I. Minkin, *Khim. Geterotsikl. Soed.*, **1971**, 138.
83. M. de M. Campos, and N. Petragnani, *Tetrahedron*, **18**, 527 (1962).
84. J. Bergman and L. Engman, *J. Organometal. Chem.*, **199**, 377 (1980).
85. J. Bergman and L. Engman, *Tetrahedron Lett.* **1979**, 1509.
86. J. Bergman and L. Engman, Abstracts of papers of IIIrd Intern. Symp. on Chemistry of Se and Te (Metz, Fr., 1979, p. 16).
87. J. Lalezari, A. Shafiee, and H. Golgolab, *J. Heterocycl. Chem.*, **10**, 655 (1973).
88. J. M. Talbot, M. Renson, and J. L. Piette, *Bull. Soc. Chim. France*, **1976**, 294.
89. J. van Coppenolle, J. L. Piette, and M. Renson, *Chem. Scr.* **A8**, 116 (1975).
90. N. Dereu and M. Renson, *J. Organometal. Chem.*, **258**, 163 (1983).
91. R. Weber, J. L. Piette, and M. Renson, *J. Heterocycl. Chem.*, **15**, 865 (1978).
92. W. Lohner and K. Praefcke, *J. Organometal. Chem.*, **208**, 35 (1981).
93. W. Lohner and K. Praefcke, *J. Organometal. Chem.*, **194**, 173 (1980).
94. J. L. Piette, P. Andre, and M. Renson, *C. R. Acad. Sci.*, **276C**, 1035 (1973).
95. R. Weber, L. Christiaens, and M. Renson, *Chem. Scr.* **A8**, 116 (1975).
96. G. Llabres, M. Baiwir, J. Denoel, J. L. Piette, and L. Christiaens, *Tetrahedron Lett.* **1972**, 3177.
97. P. Faller and R. Weber, *Bull. Soc. Chim. France*, **1972**, 3193.

98. T. Drakenberg, A. B. Hörnfeldt, S. Gronowitz, J. M. Talbot, and J. L. Piette, *Chem. Scr.*, **13**, 152 (1978–1979).
99. J. F. Müller, *Helv. Chim. Acta*, **58**, 2646 (1975).
100. N. P. Buu-Hoi, M. Mangane, M. Renson, and J. L. Piette, *J. Heterocycl. Chem.*, **7**, 219 (1970).
101. G. Mille, M. Guilliano, T. Jammal, and J. Chouteau, *Spectrochim. Acta*, **39A**, 1033 (1983).
102. F. Fringuelli and A. Taticchi, *J. Heterocycl. Chem.*, **10**, 89 (1973).
103. S. Clementi, F. Fringuelli, P. Linda, G. Marino, G. Savelli, A. Taticchi, and J. L. Piette, *Gazz. Chim. Ital.*, **107**, 339 (1977).
104. W. Lohner and K. Praefcke, *J. Organometal. Chem.*, **208**, 39 (1981).
105. M. Baiwir, G. Llabres, L. Christiaens, A. Luxen, and J. L. Piette, *Spectrochim. Acta*, **39A**, 693 (1983).
106. H. D. K. Drew, *J. Chem. Soc.*, **1926**, 223.
107. J. D. McCullough, *Inorg. Chem.*, **14**, 2285 (1975).
108. D. Hellwinkel and G. Fahrbach, *Tetrahedron Lett.* **1965**, 1823.
109. D. Hellwinkel and G. Fahrbach, *Liebigs Ann. Chem.*, **712**, 1 (1968).
110. D. Hellwinkel, *Ann. N. Y. Acad. Sci.*, **192**, 158 (1972).
111. D. Hellwinkel and G. Fahrbach, *Chem. Ber.*, **101**, 574 (1968).
112. N. M. Cullinane, A. G. Ress, and C. A. Plummer, *J. Chem. Soc.*, **1939**, 151.
113. R. Passerini and G. Purello, *Ann. Chim.* **48**, 738 (1958); *C.A.*., **53**, 8144 (1959).
114. S. C. Cohen, M. L. N. Reddy, and A. G. Massey, *J. Organometal. Chem.*, **11**, 563 (1968).
115. C. M. Woodward, G. Hughes, and A. G. Massey, *J. Organometal. Chem.*, **112**, 9 (1976).
116. S. C. Cohen, M. L. N. Reddy, and A. G. Massey, *J. Chem. Soc., Chem. Comm.*, **1967**, 451.
117. S. C. Cohen and A. G. Massey, in *Advances in Fluorine Chemistry*, Vol. 6, p. 83. Butterworths, London.
118. S. C. Cohen, A. G. Massey, G. F. Lathier, and G. M. Miller, *Org. Mass Spectr.*, **6**, 373 (1972).
119. N. J. Dance and C. H. W. Jones, *Can. J. Chem.*, **56**, 1746 (1978).
120. E. Klingsberg, U.S. Pat. 3,769,276; *C.A.*, **80**, 70810 (1974).
121. J. Meinwald, D. Dauplaise, F. Wudl, and J. J. Hauser, *J. Am. Chem. Soc.*, **99**, 255 (1977).
122. D. Dauplaise, J. Meinwald, J. C. Scott, H. Temkin, and J. Clardy, *Ann. N. Y. Acad. Sci.*, **313**, 382 (1978).
123. L. Y. Chiang and J. Meinwald, *Tetrahedron Lett.* **1980**, 4565.
124. D. J. Sandman, J. C. Stark, and B. M. Foxman, *Organometallics*, **1**, 739 (1982).
125. J. Meinwald, D. Dauplaise, and J. Clardy, *J. Am. Chem. Soc.*, **99**, 7743 (1977).
126. K. A. Balodis, R. S. Medna, and O. Ya. Neyland, *Zh. Org. Khim.*, **20**, 891 (1984).
127. E. B. Yagubskii, N. D. Kunu, A. D. Zvorykina, and O. Ya. Neyland, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1981**, 1432.
128. R. P. Shibaeva and V. F. Kaminskii, *Cryst. Struct. Common.*, **10**, 663 (1981).
129. M. L. Petrov, V. Z. Laishev, and A. A. Petrov, *Zh. Org. Khim.*, **15**, 2596 (1979).
130. V. Z. Laishev, M. L. Petrov, and A. A. Petrov, *Zh. Org. Khim.*, **17**, 2064 (1981).
131. M. V. Lakshmikantham, M. P. Cava, M. Albeck, and L. Engman, *J. Chem. Soc., Chem. Commun*, **1981**, 828.
132. S. L. Bender, N. F. Haley, and H. R. Luss, *Tetrahedron Lett.* **22**, 1495 (1981).
133. R. Mayer and T. Gebhardt, *Chem. Ber.*, **97**, 1298 (1964).
134. S. L. Bender, M. R. Detty, and N. F. Haley, *Tetrahedron Lett.* **23**, 1531 (1982).
135. L. Y. Chiang, P. Shu, D. Holt, and D. O. Cowan, *J. Org. Chem.*, **48**, 4713 (1983).
136. F. Wudl and E. Aharon-Shalon, *J. Am. Chem. Soc.*, **104**, 1154 (1982).
137. K. A. Lerstrup and D. O. Cowan, *J. Phys. Colloq.*, **1983**, 1247; *C.A.*, **100**, 68230 (1984).
138. K. A. Lerstrup, D. Talham, A. Bloch, T. Poehler, and D. O. Cowan, *J. Chem. Soc., Chem. Comm.*, **1982**, 336.
139. G. Saito, T. Enoki, and H. Inokuchi, *Chem. Lett.* **1983**, 503.
140. S. L. Bender, M. R. Detty, M. W. Fichter, and N. F. Haley, *Tetrahedron Lett.*, **24**, 237 (1983).
141. R. J. Carrol, M. v. Lakshmikantham, M. P. Cava, F. Wudl, E. Aharon-Shalon, and S. D. Cox, *J. Chem. Soc., Chem. Commun.*, **1982**, 1316.
142. F. Lucchesini and V. Bertini, *Synthesis*, **1983**, 824.
143. H. Campsteyn, L. Du Pont, J. Lamotte-Brasseur, and M. Vermeire, *J. Heterocycl. Chem.*, **15**, 745 (1975).
144. M. Mbuyi, M. Evers, G. Tihange, A. Luxen, and L. Christiaens, *Tetrahedron Lett.* **24**, 5873 (1983).
145. A. Luxen and L. Christiaens, *Tetrahedron Lett.*, **23**, 3905 (1982).
146. M. R. Detty, B. J. Murray, and D. L. Smith, *J. Am. Chem. Soc.*, **105**, 875 (1983).

147. M. R. Detty and B. J. Murray, *J. Am. Chem. Soc.*, **105**, 883 (1983).
148. V. Bertini, F. Lucchesini, and D. De Munno. Abstracts of papers of IIIrd Intern. Symp. on Chemistry of Se and Te (Metz, Fr., 1979; p. 14).
149. V. Bertini and F. Lucchesini, *Synthesis* **1982**, 681.
150. V. G. Tkalenko, A. P. Amarskaya, Yu. V. Kolodyazhniy, I. D. Sadekov, V. I. Minkin, and O. A. Osipov, *Zh. Obshch. Khim.*, **43**, 1943 (1973).
151. G. Wittig and H. Fritz, *Liebigs Ann. Chem.*, **577**, 39 (1952).
152. V. Bertini, P. Dapporto, F. Lucchesini, A. Sega, and A. De Munno, *Acta Cryst., Sect. C: Cryst. Struct. Commun.*, **40C**, 653, (1984).
153. K. Burger, R. Ottlinger, A. Provoksch, and J. Firl, *J. Chem. Soc., Chem. Commun.*, **1979**, 80.
154. I. D. Sadekov, A. A. Maksimenko, and V. I. Minkin, *Khim. Getrotsikl. Soed.*, **1981**, 122.
155. V. J. Adzima and J. C. Martin, *J. Org. Chem.*, **42**, 4006 (1977).
156. V. I. Minkin and R. M. Miniaev, *Zh. Org. Khim.*, **11**, 1993 (1975).
157. M. R. Detty and H. R. Luss, *J. Org. Chem.*, **48**, 5149 (1983).
158. M. Perrier and J. Vialle, *Bull. Soc. Chim. France*, **1971**, 4591.
159. M. Perrier and J. Vialle, *Bull. Soc. Chim. France*, **1979**, 199.
160. M. Perrier and J. Vialle, *Bull. Soc. Chim. France*, **1979**, 205.
161. M. Perrier, R. Pinel, and J. Vialle, *J. Heterocycl. Chem.*, **12**, 639 (1975).
162. B. Mathiasch, *Z. Anorg. Alg. Chem.*, **432**, 269 (1977).
163. H. Puff, R. Gattermayer, R. Hundt, and R. Zimmer, *Angew. Chem.*, **89**, 556 (1977).
164. H. Puff, A. Bongartz, W. Schuh, and R. Limmer, *J. Organometal. Chem.*, **248**, 61 (1983).
165. B. Mathiasch, *J. Organometal. Chem.*, **194**, 37 (1980).
166. A. Blecher and M. Dräger, *Angew. Chem.*, **91**, 740 (1979).
167. L. Ross and M. Dräger, *J. Organomettal. Chem.*, **194**, 23 (1980).