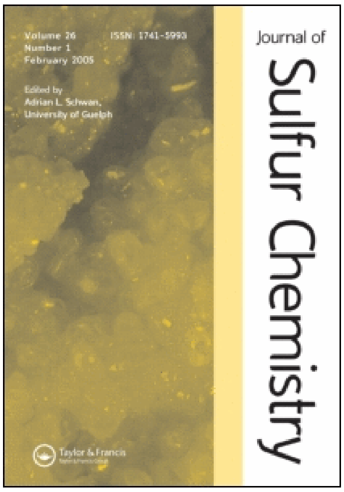

Journal of Sulfur Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926081

Six-Membered Tellurium-Containing Heterocycles

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To cite this Article Sadekov, Igor D. , Minkin, Vladimir I. and Garnovskii, Alexander D.(1985) 'Six-Membered Tellurium-Containing Heterocycles', Journal of Sulfur Chemistry, 4: 3, 63 — 108

To link to this Article: DOI: 10.1080/01961778508082470

URL: http://dx.doi.org/10.1080/01961778508082470

Sulphur Reports
Volume 4(3), January 1985, pp. 63–115

Printed in the United Kingdom

SIX-MEMBERED TELLURIUM-CONTAINING HETEROCYCLES

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This is a comprehensive up-to-date review of the syntheses and reactions and the structural and physical characteristics of the tellurium organic compounds mentioned in the title the major part of which has only recently been obtained and not yet been surveyed. Particular attention is given to the peculiarities in their structure and reactivity due to the tellurium site as compared to the properties of the analogous sulfur and selenium heterocyclic compounds.

CONTENTS

I. INTRODUCTION

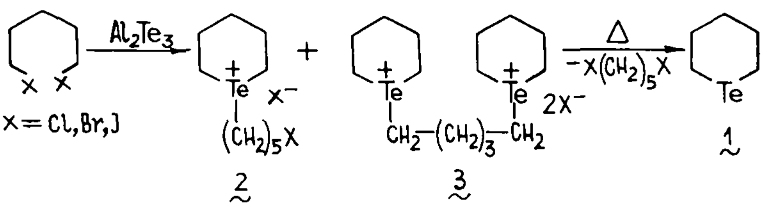
The last 10–15 years are characterized by an extremely rapid development of organotellurium chemistry. Special attention was paid to the elaboration of methods for preparing heterocyclic tellurium compounds and to the transformations of these compounds. This is especially true of six-membered tellurium-containing heterocycles whose number has more than doubled in the last 8–10 years. The aim of this review article is to describe the methods of preparation, the reactivity and synthetic potentialities of this class of heterocyclic compounds.

The methods of preparation and the chemical behavior of tellurium-containing heterocycles are in some instances basically different from those of the analogous sulfur and selenium derivatives so that existing methods for preparing the latter substances can very often not be applied to the synthesis of tellurium-containing heterocycles. So far there exists only one review dealing with six-membered tellurium-containing heterocycles in the shape of a chapter in the book by K. Irgolic "The Organic Chemistry of Tellurium"[1] (1974).

II. MONOCYCLIC SYSTEMS

2.1 1-Telluracyclohexane and Its Derivatives

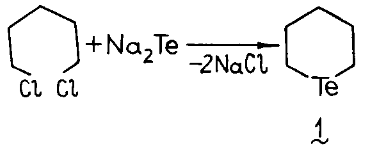
The most general way of preparing 1-telluracyclohexane **1** is the reaction of 1,5-dihalopentanes with aluminum[2] or sodium telluride.[3,4] However, in the case of aluminum telluride, the final product of the reaction is not the heterocycle **1**, but the telluronium salts **2** and **3** resulting from the alkylation of the initially formed 1-telluracyclohexane by excess pentamethylene dihalide.[2] The reaction of 1,5-dihalopentanes with Al_2Te_3 occurs most readily in the case of the diiodide (at 135–145° C). The reactions with the dibromide and the dichloride proceed at more elevated temperatures: 165° C and 175–185° C, respectively. In the reaction with the dibromide, apart from the salts **2** and **3** ($X = Br$), also some 1-telluracyclohexane 1,1-dibromide was isolated[2]. This substance forms, apparently, owing to the partial hydrolysis of Al_2Te_3, the decomposition of H_2Te and the reaction of the latter with 1,5-dibromopentane.[2] The Telluronium salts **2**,**3**, when heated in vacuum, easily lose the corresponding 1,5-dihalopentane and are converted to compound **1**.[2]



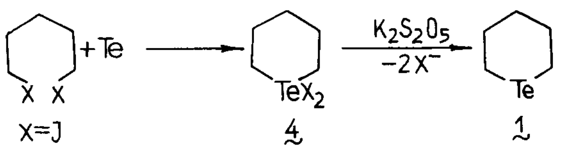
A simpler one-step method of preparing the heterocycle **1** is based on the interaction of 1,5-dichloropentane with sodium telluride synthesized by the rongalite method.[3,4]

This method was also employed to obtain deutero derivatives of **1**: 4,4-d_2- and 3,3,5,5-d_4-1-telluracyclohexane.[4]

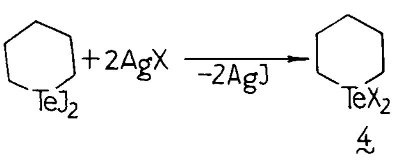
1-Telluracyclohexane may also be prepared via the reaction of 1,5-diidopentane with metallic tellurium at high temperatures.[2,3]



As in the case with alkyl iodides,[5] the reaction products are tellurium diiodides i.e. 1-telluracyclohexane 1,1-diiodide **4** (X = I) which is reduced in high yield to 1-telluracyclohexane by potassium metabisulfite.[3]



1-Telluracyclohexane possesses properties typical of diorganyl tellurides. It is easily oxidised by chlorine, bromine, and iodine to σ-telluranes, *i.e.* 1-telluracyclohexane 1,1-dihalides which in their turn may be reduced to the parent heterocycle.[2,3] This method is sometimes used to purify 1-telluracyclohexane.[3] 1-Telluracyclohexane 1,1-diiodide (**4**, X = I), when treated with appropriate silver salts, undergoes transformation to various σ-telluranes **4** containing the telluracyclohexane moiety.[6]

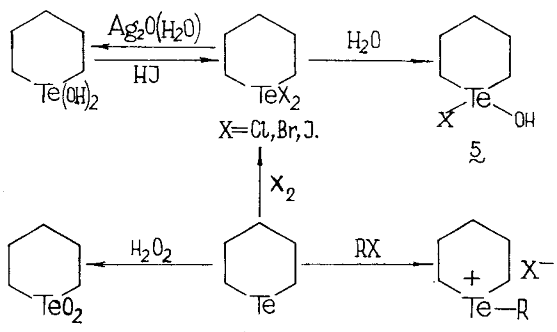


X = F, Cl, Br, CN, NCO, NCS, NCSe, CH_3COO, CCl_3COO, $C_6H_5CH_2COO$, C_6H_5COO, $CH_3(CH_2)_{12}COO$

The infrared spectra of tellurium dipseudohalides[6] (**4**, X = NCO, NCS, NCSe, CN) indicate that NCX groups (X = O, S, Se), as is also the case with acyclic σ-telluranes,[7] are attached to the tellurium atom via nitrogen (TeNCX) whereas the cyanide group connects via the carbon atom (TeCN).

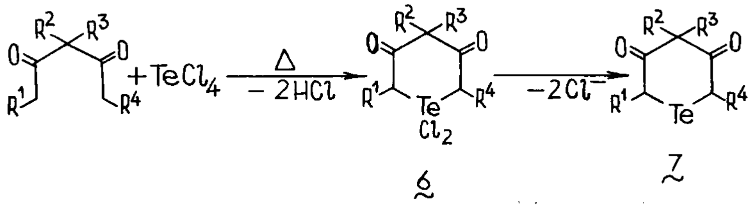
1-Telluracyclohexane can be fairly easily alkylated. Thus, when it is treated with 1,5-dihalopentanes, there are formed, depending on the reagent ratio, mono-(**2**) or ditelluronium salts **3**. According to Morgan,[2] when compound **1** is oxidized with hydrogen peroxide in methanol, 1-telluracyclohexane 1,1-dioxide is formed. This is a white amorphous powder insoluble in common solvents, exploding on heating, oxidizing hydrochloric acid to chlorine, decolorizing potassium permanganate solution. However, the elemental analysis agrees poorly with the proposed structure.

1-Telluracyclohexane 1,1-dibromide treated with silver oxide yields 1-telluracyclohexane 1,1-dihydroxide[8] which on reaction with HI produces the diiodide **4** (X = I). Hydrolysis of the dihalides **4** gives the 1-telluracyclohexane 1-hydroxy-1-halides **5**.[8] The reactions of 1-telluracyclohexane are summarized in Scheme I.



SCHEME I. Reactions of 1-telluracyclohexane

The most important derivatives of 1-telluracyclohexane are 1-tellura-3,5-cyclohexanediones 1,1-dichlorides which are produced by reaction of tellurium tetrachloride with 1,3-diketones in dry, rigorously purified chloroform.[9–18]



$R^1 = R^2 = R^3 = R^4 = H$;[9–11] $R^1 = R^2 = R^4 = H$, $R^3 = CH_3$,[11] C_2H_5,[11] n-C_3H_7,[14] iso-C_3H_7,[14] n-C_4H_9,[15] iso-C_4H_9,[15] $C_6H_5CH_2$,[17] Cl;[11] $R^2 = R^3 = R^4 = H$, $R^1 = C_2H_5$,[12] n-C_3H_7,[13] iso-C_3H_7,[13] n-C_4H_9,[15] iso-C_4H_9,[13] $C(CH_3)_3$,[11] C_5H_{11},[13–15,17] C_7H_{15},[17] $C_6H_5CH_2$,[18] C_8H_{17},[17] C_9H_{19},[15] $C_{10}H_{21}$;[18] $R^1 = R^4 = H$, $R^2 = R^3 = CH_3$,[16] $C_6H_5CH_2$;[17] $R^1 = R^4 = C_2H_5$, $R^2 = R^3 = H$;[13,17] $R^2 = H$, $R^3 = CH_3$;[17] $R^2 = H$, $R^3 = C_2H_5$;[13] $R^3 = R^4 = H$, $R^1 = C_2H_5$, $R^2 = CH_3$;[13] $R^1 = n$-C_3H_7, $R^2 = C_2H_5$;[13] $R^1 = R^2 = C_2H_5$;[14] $R^1 = C_2H_5$, $R^2 = n$-C_4H_9;[15] $R^1 = C_2H_5$, $R^2 = n$-C_3H_7;[18] $R^1 = C_2H_5$, $R^2 =$ iso-C_3H_7;[18] $R^1 = CH_3$, $R^2 = C_6H_5CH_2$;[18] $R^2 = R^3 = H$, $R^1 = C_2H_5$, $R^4 = C_3H_7$;[13] $R^1 = R^4 = C_3H_7$[14]

Only those 1,3-diketones which contain alkyl or aralkyl (benzyl) substituents can undergo this reaction. At the terminal carbon atoms of the 1,3-diketone systems there must be one hydrocarbon substituent whereas both one or two substituents may be attached to the C^3 atom.

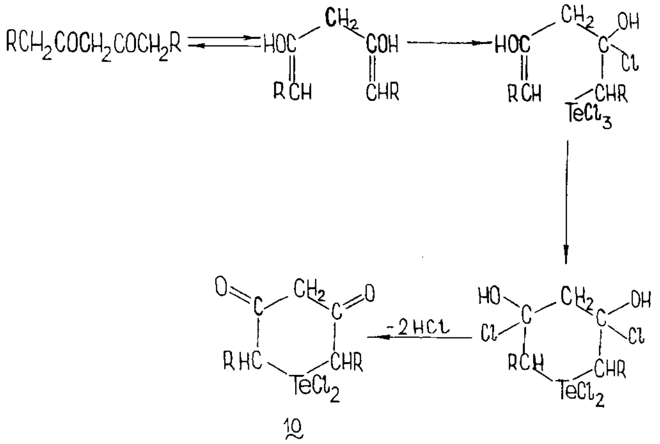
Depending on the nature of the substituents in 1,3-diketones, there can be produced either cyclic compounds **6** or acyclic ones of the type **8**[9–11,13] and **9**.[13–14,17] Branched hydrocarbon groups R^1, R^4 facilitate the formation of these compounds.

8: $(R^1COCH{=}C(OH)CHR^2)_2TeCl_2$

9: $(R^1\ COCH{=}C(OH)CHR^2\ TeCl_3$

Alkyl or aralkyl substituents attached to the C^3 atom of 1,3-diketones generally promote the formation of the cyclic products $6^{11,13,16,18}$. Notable exceptions are 3,3-bis (*p*-nitrobenzyl) acetylacetone which does not react with tellurium tetrachloride[17] and 3-chloroacetylacetone which forms **9** as the major product in its reaction with $TeCl_4$.[11]

Morgan[18] suggested the following scheme for the formation of **6** (Scheme II).

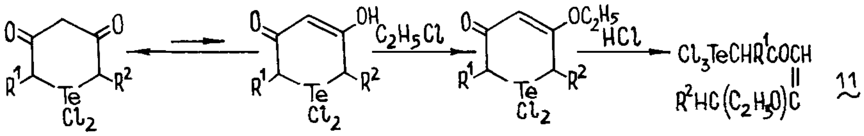


SCHEME II. Morgan's scheme of the formation of 1-tellura-3,5-cyclohexanediones 1,1-dichlorides

The structure of 1-tellura-3,5-cyclohexadione 1,1-dichlorides **6** and of the corresponding tellurides **7** was proven by chemical, spectral,[19] and X-ray structural data.[20–25]

1-Tellura-3,5-cyclohexadione 1,1-dichlorides **6** can be reduced in high yield with potassium metabisulfite or alkali metal bisulfites to 1-tellura-3,5-cyclohexadiones **7**. Chlorine, bromine, and iodine are easily added to the latter[10–12] producing 1-tellura-3,5-cyclohexanedione 1,1-dihalides.

1-Tellura-3,5-cyclohexanediones are decomposed by concentrated solutions of HCl, KOH, and by aluminum amalgam.[9] Upon treatment with ethyl chloride and HCl in chloroform solution they give rise to the tellurium trichlorides **11**. Compounds **11** may be obtained also in the course of the reaction of 1, 3-diketones with $TeCl_4$ in the presence of small amounts of ethanol as an ethyl chloride precursor.[10–14,17]



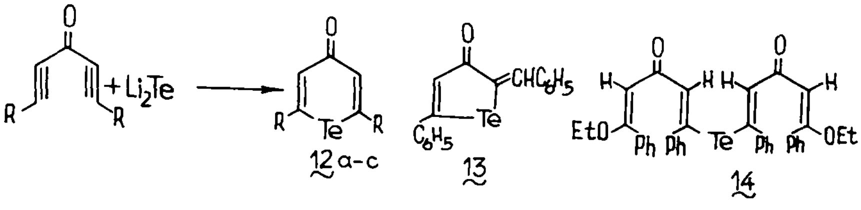
The diketones **7** form dioximes with hydroxylamine in dilute acetic acid.[16,17] In dilute acetic acid 2,4-dialkyl- and 4,4-dimethyl derivatives **7** produce monooximes, but in alkaline solutions dioximes are isolated as the major products.[16,17]

Compounds **7** possess bactericidal activity; however, their toxicity is rather high.[26–30] Merocyanine dyes containing 1-tellura-3, 5-cyclohexanediones with heterocyclic moieties are efficient photosensitizers.[31,32]

2.2. *Derivatives of 1-Tellura-2,5-Cyclohexadiene*

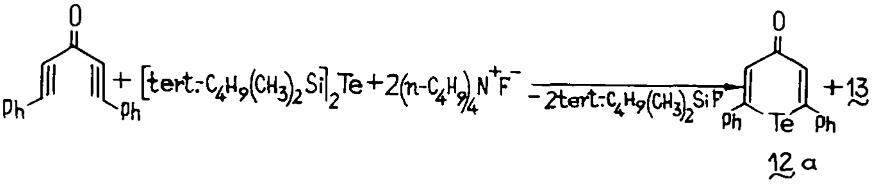
Derivatives of this heterocyclic system serve as synthons for donor components of charge-transfer complexes possessing high electric conductivity ("organic metals"). The first representatives of 1-tellura-2,5-cyclohexadienes, i.e. 2,6-diorganyl-4*H*-telluropyran-4-ones **12** like their sulfur[33] and selenium analogues[34] were obtained by nucleophilic addition of lithium telluride (from lithium triethylborohydride and tellurium in tetrahydrofuran) to diacetylenic ketones.[35,36]

To enhance the yield of 2,6-diphenyl-4*H*-telluropyran-4-one **12a** and to prevent the formation of the telluracyclopentene derivative **13** the reaction was performed under strongly basic conditions (ethanol-tetrahydroduran solution of sodium



R = a) C_6H_5, b) CH_3, c) $C(CH_3)_3$

ethoxide).[35] Compound **14** was isolated as a by-product in 10% yield. An alternative approach to the synthesis of **12a** is the interaction of bis(*t*-butyldimethylsilyl) telluride[37] with tetra-*n*-butylammonium fluoride in the presence of 1,5-diphenyl-1,4-pentadiyn-3-one.[35] However, significantly poorer yields (19% instead of 51% in the former reaction) have been obtained.

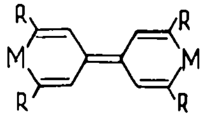


The diphenyl derivative **12a** when treated with Lawesson's reagent is converted to thione **15a**[38] which when refluxed in xylene self-condenses to $\Delta^{4,4'}$-2,2',6,6', tetraphenyl-4-telluropyranyl-4*H*-telluropyron **16a** in very low yield (less than 1%). The main products of the reaction are **17** and **18** in the ratio 45:55[38] which are formed because of the substitution of the tellurium atom in the six-membered ring by sulfur eliminated from **15a**. However, presence of copper powder in this reaction inhibits this exchange leading to the formation of **16a** in a yield of over 70%. The (telluropyranyl) telluropyrans **16b,c** were prepared from compounds **15b,c** by the same method in 32% and 22% yield, respectively.[36]

Compounds **16a,b** with tetracyanoquinodimethane (TCNQ) form charge transfer complexes with a composition of 1:1 and 2:3 (1:2), respectively. No individual crystalline complex was isolated in the reaction of TCNQ with **16c**. Some electrochemical and electric conductivity characteristics of **16**-TCNQ complexes compared to their oxygen, sulfur, and selenium analogs[36] are listed in Table I.

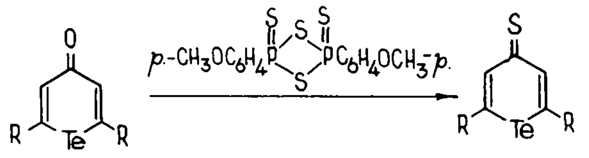
TABLE I

Redox potentials (E) of the compounds

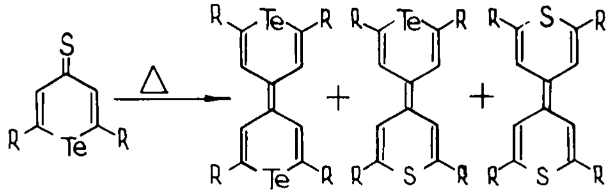


and their electrical conductivity of their complexes with TCNQ at 25 °C

M	R	Stoichiometry of complexes with TCNQ	E(V) E_1	E_2	σ $\Omega^{-1}cm^{-1}$
O	H	1:1	+0.21	+0.50	0.06
O	CH_3	1:1	+0.03	+0.42	10^{-6}
O	C_6H_5	1:1	+0.15	+0.47	1.7(40)
S	H	1:1	+0.20	+0.46	1−4(30)
S	CH_3	1:1	+0.09	+0.34	10^{-4}
S	CH_3	1:2			0.5
S	C_6H_5	1:1	+0.22	+0.41	10(250)
Se	C_6H_5	1:1	+0.33	+0.51	0.5
Te	CH_3	1:2	+0.22	+0.38	4
Te	CH_3	2:3			0.4
Te	C_6H_5	1:1	+0.34	+0.49	0.5



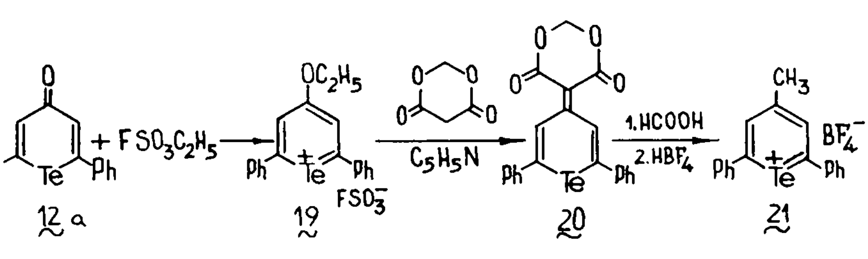
15a-c



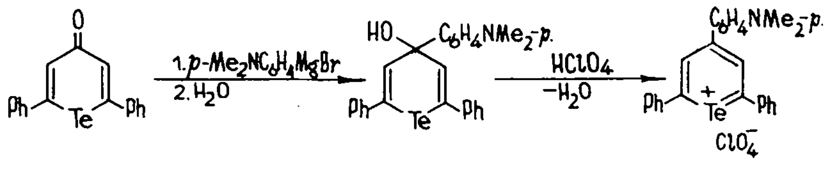
16a-c 17 18

2.3. *Telluropyrylium Cations*

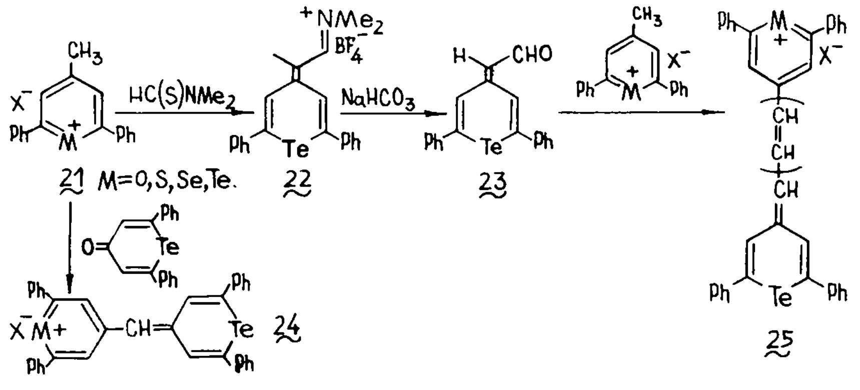
While the first reported representatives of six-membered tellurium heterocycles contained telluropyrylium units condensed in a telluraanthracene system (Chapt. 4.2), monocyclic derivatives of telluropyrylium, *viz.* 2,6-diphenyltelluropyrylium salts,[39] were obtained quite recently by methods which in principle do not differ from those used to prepare thiopyrylium and selenopyrylium salts. Treatment of 2,6-diphenyl-4*H*-telluropyran-4-one **12a** with ethyl fluorosulfate leads to 2,6-diphenyl-4-ethoxypyrylium fluorosulfate **19**, interaction of which with Meldrum's acid in pyridine produces compound **20**. When this compound reacts with formic acid CO_2 is released and 4-methyltelluropyrylium formate is formed. Treatment of the latter with fluoroboric acid gives rise to stable 4-methyl-2,6-diphenyltelluropyrylium tetrafluoroborate **21**.[39]



Another method for obtaining telluropyrylium salts is based on the conventional access of compounds of this type, *viz.* the interaction of appropriate alcohols (from ketone **12a** and aryl magnesium bromides) with perchloric acid.[40]



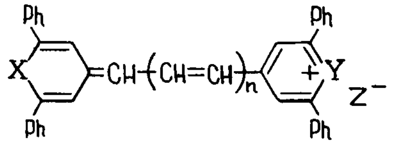
The reactivity of telluropyrylium salts resembles strongly that of pyrylium, thio-, and selenopyrylium salts. Thus, compound **21** (M = Te) is converted by *N*,*N*-dimethylthioformamide to the iminium salt **22**. This compound is hydrolyzed by aqueous $NaHCO_3$ to 4*H*-(2,6-diphenyltelluropyranilidene) acetaldehyde **23**.[39] Condensation of the salt **21** as well as its oxygen, sulfur, and selenium analogs with pyrone **12a** and aldehyde **23** leads to mono- (**24**) and trimethine (**25**) dyes.[39]



A substantial bathochromic shift in the long-wave absorption band is apparent in the tellurium-containing (M = Te) dyes **24** and **25** as compared to their oxygen,sulfur, and selenium analogs (Table II). This trend is explained[39] by the increasingly electropositive character of the heteroatoms from oxygen to tellurium. A similar trend also characterizes the electronic absorption spectra of 2,6-diphenyl-4-methylchalcogenopyrylium perchlorates: λ_{max} for the oxygen derivative is 550 nm, for the sulfur derivative 592 nm, for the selenium and tellurium derivatives it is 620 and 653 nm, respectively.[39]

TABLE II

UV spectra of bis(chalcogenopyrylo) methines and -polymethines with the structure



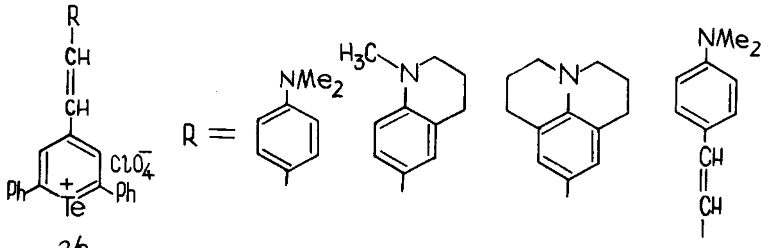
(CH_2Cl_2)

X	Y	Z	n	λ_{max}, nm	log ε	X	Y	Z	n	λ_{max}, nm	log ε
O	O	ClO_4	0	545		S	Se	ClO_4	1	782	
			1	686		S	Te	ClO_4	0	690	5.11
O	S	ClO_4	0	585					1	820	5.30
			1	725		Se	Se	ClO_4	0	667	
O	Se	ClO_4	0	605					1	795	
			1	743					2	910[a]	
O	Te	BF_4	0	650	5.14	Se	Te	ClO_4	0	722	5.00
			1	780	5.35				1	843	5.26
S	S	ClO_4	0	622		Te	Te	BF_4	0	759	5.20
			1	751					1	885	5.45
			2	879[a]					2	1010	5.18
S	Se	ClO_4	0	643							

[a] solvent: acetic acid

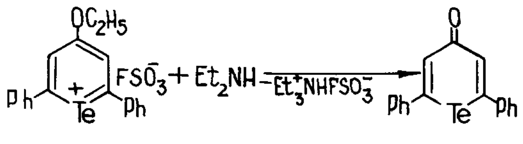
The synthesis of pentamethine and heptamethine dyes containing telluropyrylium fragments has also been described.[39]

2,6-Diphenyl-4-methyltelluropyrylium tetrafluoroborate as well as other pyrylium salts[40] when reacting with aldehydes in acetic anhydride form various styryl derivatives **26**.[39]



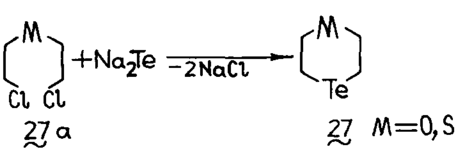
26

4-Ethoxy-2,6-diphenyltelluropyrylium fluorosulfate forms under the action of diethylamine not a substitution product, 4-(*N*,*N*-diethylamino)-2,6-diphenyltelluropyrylium fluorosulfate, but undergoes dealkylation producing the telluropyrone **12**.[39]



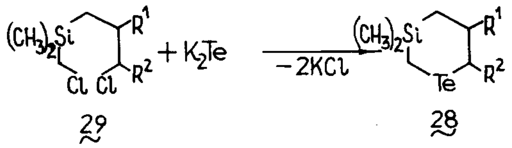
2.4. Saturated Heterocycles with Two Heteroatoms

The majority of known systems of this type contain heteroatoms in the positions 1 and 4. The only 1,3-system described to date is 1-sila-3-telluracyclohexane.[41] Saturated six-membered tellurium-containing heterocycles may be prepared by two methods. The first method is similar to one used earlier to prepare 1-telluracyclohexane. It is based on the interaction of the dichlorides **27a** with sodium telluride.[3,42] For instance, 1-oxa- (**27**, M = O) and 1-thia-4-telluracylohexanes (**27**, M = S) were obtained from the reaction of ethanol solutions of bis(2-chloroethyl) ether[3] or bis(2-chloroethyl) sulfide[42] with aqueous sodium telluride prepared by the rongalite method.



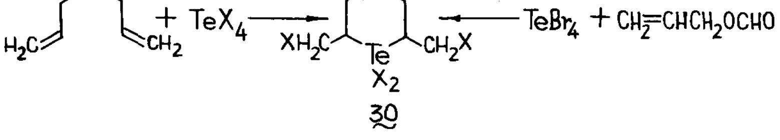
The yield of **27** (M = S) achieved is small (6.6 %) and is favored by dilution.[42] The purification of crude 1-oxa-4-telluracyclohexane was performed through its conversion to the dichloride, reduction with potassium metabisulfite and subsequent distillation of **27** (M = O).

Similarly to **27**, the unstable 1-sila-3-telluracyclohexanes **28** were synthesized from potassium telluride and **29**.[41]



R^1 = R^2 = H; R^1 = H, R^2 = CH$_3$; R^1 = C(CH$_3$)$_3$, R^2 = H

The second method is not as general as the first one permitting the preparation of only 3,5-bis(halomethyl) derivatives of the heterocycles **30**. This method consists of electrophilic addition of tellurium tetrahalides (which are formed from tellurium dioxide and HCl or HBr in aqueous solution) to diallyl ether, diallyl sulfide, and diallylamines.[43] The reaction proceeds contrary to Markovnikov's rule and leads to 3,5-bis(halomethyl)-1-oxa-(thia-, aza-)-4-telluracyclohexane 4,4-dihalides **30** in 35–80% yields. Compounds **30** are isolated as mixtures of *cis*-and *trans*-isomers. These were separated in the case of 3,5-bis(bromomethyl)-1-oxa-4-telluracyclohexane 4,4-dibromide by means of fractional crystallization.[43]

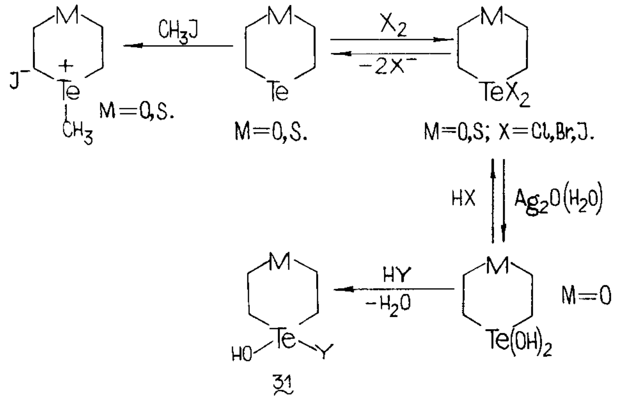


M = O, X = Cl, Br; M = S, X = Cl, Br; M = NH, X = Br; M = NCH$_3$, X = Cl, Br *cis*-3,5-Bis(bromomethyl)-1-oxa-4-telluracyclohexane 4,4-dibromide was also obtained *via* the reaction of allyl formate with tellurium tetrabromide in 9% yield.[43]

The synthesis of 1-oxa-4-telluracyclohexane by reaction of bis(2-iodoethyl) ether with powdered tellurium is not a promising procedure because of the decomposition of the ether in the course of the reaction.[3]

The chemical properties of 1-oxa and 1-thia-4-telluracyclohexanes (there are no data in the literature on the reactivity of other systems of this type) are determined mainly by the presence of a tellurium atom in the six-membered ring. They are, therefore, very similar to the reactions of 1-telluracyclohexane. Chlorine, bromine, and iodine are easily added to the tellurium site to form σ-telluranes.[42] Addition of methyl iodide to the tellurium atom leads to telluronium salts.[3,42] 1-Oxa-4-telluracyclohexane 4,4-dichloride is converted by wet silver oxide to 1-oxa-4-telluracyclohexane 4,4-dihydroxide which in turn upon treatment with HX (X = Cl, Br, I) gives 1-oxa-4-telluracyclohexane 4,4-dihalides; treatment with some other acids (nitric, picric, picrolonic) produces the hydroxy compounds **31**.[3]

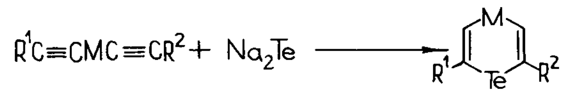
The reactions of compounds **27** are listed in Scheme IIII.



SCHEME III. Reactions of 1-oxa(thia)-4-telluracyclohexanes

2.5. *1-Hetera-4-Tellura-2,5-Cyclohexadienes*

The only method for the preparation of **32** known to date is based on nucleophilic addition of sodium telluride to the diacetylenes **32a**. Thus, from sodium telluride and dialkynyl sulfides (**32a**, M = S) in methanol[44] or in mixtures of liquid ammonia and methanol or of dimethylformamide and methanol,[45] from sodium telluride and dialkynyl sulphones (**32a**, M = SO_2) in methanol,[46] from sodium telluride and



32

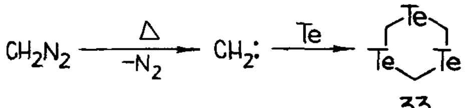
M = S, R^1 = H, R^2 = CH_3, C_2H_5, $CH_2 = C(CH_3)$, $C(CH_3)_3$; $R^1 = R^2$ = H, CH_3, $C(CH_3)_3$; M = SO_2, $R^1 = R^2$ = CH_3, $C(CH_3)_3$; M = $P(O)C_6H_5$, $R^1 = R^2$ = H, CH_3, $C(CH_3)_3$; M = $P(O)C_6H_{11}$-cyclo, $R^1 = R^2$ = H, CH_3, $C(CH_3)_3$

organyldialkynylphosphine oxides (**32a**, M = P(O)R) in methanol or in aqueous dimethylformamide[47] there were synthesized many derivatives of 1-hetera-4-tellura-2,5-cyclohexadiene **32**.

According to[44] the addition of sodium telluride to 1-alkynyl ethynyl sulfides proceeds as a result of the nucleophilic attack of Te^{2-} on the triple bond. This leads to the formation of $RC{\equiv}CSCH{=}CHTe^-$ and subsequent ring closure to **32**. The rate of the reaction depends both on the nature of R in the diacetylene and, to a considerable degree, on the chalcogen atom in the sodium chalcogenide. The reaction rate decreases in the following order: $Na_2Te > Na_2Se > Na_2S$ which coincides with the decreasing solvation of the anion X^{2-} (X = S, Se, Te).[45]

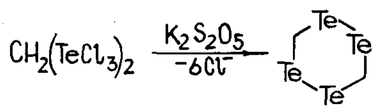
2.6. Heterocycles with More Than Two Tellurium Atoms

So far only three compounds of this type have been reported. 1,3,5-Tritelluracyclohexane **33** is prepared via the reaction of methylene (generated by thermal decomposition of diazomethane) with a tellurium mirror.[48] The structure of this compound was elucidated by means of MS and IR.



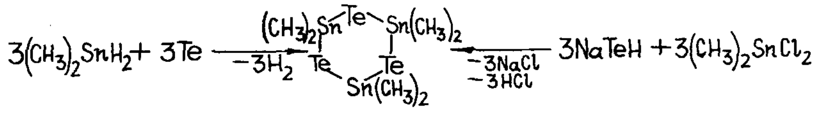
33

A heterocycle with four tellurium atoms in the ring, *i.e.* 1,2,4,5-tetratelluracyclohexane **34** was obtained when methylene bis(tellurium trichloride), a by-product of the reaction between tellurium tetrachloride and acetic anhydride,[49] was reduced with potassium metabisulfite.[49,50] This red-brown, poorly soluble compound melting within a wide temperature range (54–102 °C) was first isolated by Morgan[49] who assigned to it the structure of 1,2-ditelluracyclopropane. However, the examination of mass, ^1H NMR (the signal from the methylene protons appears at δ 3.34 in dimethyl sulfoxide), and γ-resonance spectra led to the conclusion that this compound had in fact the dimeric structure **34**.[50]



34

The tellurium- and tin-containing heterocycle, 1,1,3,3,5,5-hexamethyl-1,3,5-tristanna-2,4,6-tritelluracyclohexane **35** was first synthesized via the reaction of dimethylstannane with powdered tellurium.[51] A considerable amount of the corresponding five-membered heterocycle with two tellurium and three tin atoms is formed

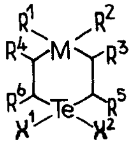


35

along with compound **35**.[52] Via the reaction of dimethyldichlorostannane with sodium hydrogentelluride (from tellurium and sodium borohydride in water), compound **35** could be obtained free of impurities.[52] Its structure was established by an X-ray determination.[52]

2.7. *Structures of Monocyclic Six-Membered Tellurium Heterocycles in the Crystalline State and in Solution*

Data concerning the structures of monocyclic six-membered tellurium heterocycles are relatively scarce. Molecular and crystalline structures of 1-phenyl-1-telluroniacyclohexane bromide[53] as well as of 1-tellura-3,5-cyclohexanediones,[20–25]1-oxa-[54] and 1-thia-4-telluracyclohexane 4,4-diiodides[55] were determined by X-ray analysis. Some data on bond lengths and valence angles in **36** are listed in Table III.



36

All compounds examined prefer the chair conformation. In derivatives of 1-tellura-3,5,-cyclohexanedione **36c–e** (Table III), methyl groups occupy axial positions[21,23,24] whereas in 1-phenyl-1-telluroniacyclohexane bromide **36a** the phenyl group is in the equatorial position.[53] In derivatives of acetylacetone **36b–e**, the molecules are associated as a result of Te...Te secondary interactions so that zigzag polymeric chains of tellurium atoms are formed. In these chains a weak interaction between the tellurium atoms is suggested by many authors to be a consequence of p-d overlap between neighboring tellurium atoms. The intermolecular contacts Te...Te in **36b**(3.97 Å), **36d**(4.04 Å), and **36e**(4.07, 3.95 Å) are shorter than in **36c**(5.05 Å) which explains the deeper yellow color of **36b,e** as compared to **36c**. The intermolecular Te...Te contacts (6.06 Å) are longest in phenoxatellurine,[56] which is therefore the least colored among similar heterocyclic derivatives of Te^{II}.

TABLE III

Bond lengths (Å) and valency angles in compounds 36

M	R^1	R^2	R^3	R^4	R^5	R^6	X^1	X^2	Te-C	Te-X	Angle C-Te-C	Angle X^1-Te-X^2
a) C	H	H	H	H	H	H	C_6H_5	Br	2.14[a]	—	91.6	—
b) C	H	H	=O	=O	H	H	none	none	2.16	—	89.5	—
c) C	CH_3	CH_3	=O	=O	H	H	none	none	2.17	—	86.4	—
d) C	H	CH_3	=O	=O	CH_3	H	none	none	2.18	—	88.4	—
e) C	H	H	=O	=O	CH_3	CH_3	none	none	2.19	—	89.7	—
f) C	H	H	=O	=O	H	H	Cl	Cl	2.16	2.49	95.5	188.2
g) O	H	H	H	H	H	H	I	I	2.16	2.92	94.1	182.9
h) S	H	H	H	H	H	H	I	I	2.16	2.91	100.0	185.0

[a] Mean values of the bond lengths for Te-C and Te-X are given.

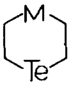
In the case of the σ-telluranes **36f–h**[22,54,55] the tellurium atom occupies the center of a trigonal bipyramid. The equatorial positions are taken up by two carbon atoms and a lone electron pair with two halogens in the axial positions. With the secondary interactions Te...I taken into account the tellurium atom acquires an almost octahedral environment. The Hal-Te bonds as is also the case for acyclic σ-telluranes,[57] suffer a greater repulsion by the lone electron pair, *i.e.* the angles Hal-Te-Hal exceed 180°: 182.8° for 1-oxa-,[54] 185° for 1-thia-4-telluracyclohexane 4,4-diiodide,[55] and 188.2° for 1-tellura-3,5-cyclohexanedione 1,1-dichloride.[22] Secondary Te ... I interactions are considered to be responsible for the deep color of the diiodides in the crystalline state.[58] Thus, in the case of 1-oxa-4-telluracyclohexane 4,4-diiodide, the intramolecular contacts Te ... I-Te have been found to cause the red color of this compound. In the violet 1-thia-4-telluracyclohexane 4,4-diiodide, there exist, along with intermolecular bonds Te-I ... Te, secondary I ... I bonds causing the extremely deep color of this compound in the crystalline state.

Telluracyclohexane as well as tellurium-containing heterocycles with two heteroatoms in the ring possess, both in solution and in the crystalline state, the chair conformation. The conformations of monocyclic six-membered heterocycles were characterized by means of their R-values[4] ($R = {}^3I_{tr.}/{}^3I_{cis}$). Judging from these, the conformation of 1-oxacyclohexane was found to be quite close to the ideal chair conformation of cyclohexane whereas in 1-chalcogenacyclohexanes the R's of which are in the range of 2.61 (for 1-thiacyclohexane) and 2.76 (for 1-telluracyclohexane), the chair is expected to be slightly distorted.[4]

Of special interest are results of a dynamic NMR study[59,60] of energy barriers of the chair-chair interconversions of the heterocycles considered. The activation energies of the ring inversion for 1-heteracyclohexanes[59] and 1-hetera-4-telluracyclohexanes are given in Table IV.

TABLE IV

Free activation energies (kcal/mol) of the ring inversion for compounds



X	M	Coalescence t °C	$\Delta G^{\ddagger}$ kcal/mol
CH_2	O	− 61	10.3
CH_2	S	− 81	9.4
CH_2	Se	−105	8.2
CH_2	Te	−119	7.3
CH_2	S=O	− 70	10.1
CH_2	Se=O	−102	8.3
CH_2	SO_2	− 63	10.3
CH_2	SeO_2	−133	6.7
O	S	—	11.0
O	Se	—	10.2

In the case of 1-heteracyclohexanes, the free activation energy decreases in the following order: O-S-Se-Te, which is in good correlation with the torsional potentials of the C-X bonds.[59]

The activation barriers ($\Delta G^\ddagger$) for the ring inversion of 1-oxa-4-thia- and 1-oxa-4-selenacyclohexane calculated from the coalescence temperatures of the methylene ring proton signals are greater for 1-oxa-4-telluracyclohexane than for 1-oxa-4-thiacyclohexane and for the respective selenium analog. 1-Oxa-4-telluracyclohexane possesses probably the lowest activation energy because cooling of the solution to −150 °C does not result in coalescence.[60] Thus, the increase in the length of the carbon-chalcogen bonds enhances the conformational mobility of the molecules[60] as is also the case with 1-heteracyclohexanes.

Examination of the ^{13}C NMR spectra of six-membered saturated heterocycles allows one to trace the effect of the heteroatom on the chemical shifts of the carbon ring atoms and to elucidate the influence of the orientation of substituents at the heteroatoms on the conformational equilibrium.[61,62] Chemical shift data for various 1-heteracyclohexane derivatives are given in Table V.

The chemical shifts of the α-carbon atoms are almost completely determined by the electronegativity of the heteroatom in position 1. An increase in the coordination number of the chalcogen atom (σ-chalcogenuranes, chalcogenium salts) leads to a downfield shift of the α-carbon atom signals.[61] The most significant shifts are observed in covalent trigonal bipyramidal tellurane structures; these shifts are much less if interaction with halogens leads to molecular complexes (sulfur derivatives, some selenium derivatives). The ^{13}C chemical shifts of the γ-carbon atoms correlate also with the electronegativity of the heteroatom in position 1, but, unlike those of the

TABLE V

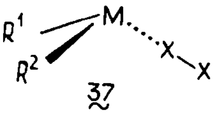
Chemical shifts (δ, ppm) in ^{13}C NMR spectra of compounds

M	Solvent	Chemical shifts			M	Solvent	Chemical shifts		
		α-C	β-C	γ-C			α-C	β-C	γ-C
O	—	68.0	26.6	23.6	$SeBr_2$	CH_2Cl_2	51.2	20.9	22.9
S	—	29.3	28.2	26.9	$TeBr_2$	CH_2Cl_2	36.9	20.3	25.9
Se	—	20.2	29.1	28.4	SI_2	CH_2Cl_2	33.3	25.9	—
Te	—	−2.1	29.9	30.9	SeI_2	CH_2Cl_2	29.7	25.7[a]	26.0[a]
SO (mixt.)	$CDCl_3$	49.0	19.3	25.3	TeI_2	CH_2Cl_2	33.2	21.4	25.5
SO (ax.)	$CDCl_3$	45.1	15.5	24.7	$HS^+FSO_3^-$	HSO_3F	31.2	24.1	21.8
SO (eq.)	CD_2Cl_2	52.1	23.3	24.7	$HSe^+FSO_3^-$	HSO_3F	41.2	23.8	22.5
SeO (mixt.)	CH_2Cl_2	42.1	18.6	26.3	$HTe^+FSO_3^-$	HSO_3F	24.0[a]	25.0[a]	25.8[a]
SeO (ax.)	CH_2Cl_2	39.4	16.8	25.1	$CH_3S^+I^-$	H_2O	37.8	20.5	22.7
SO_2	$CDCl_3$	52.6	25.1	24.3	$CH_3Se^+I^-$	H_2O	34.1	20.5	23.9
SBr_2	CH_2Cl_2	34.7	22.9	27.6	$CH_3Te^+I^-$	H_2O	—	20.7	27.7

[a] Assigments not clear

α-carbon atoms, they move upfield with increasing electronegativity of the 1-substituents. The chemical shifts of the β-carbon atoms depend, too, on the electronegativity of hetero groups in position 1, but in this case, the orientation (axial or equatorial) of the substituents at the heteroatom exerts also an important influence. The chemical shifts of the β-carbon atoms of 1-heteracyclohexanes are displaced upfield when the electronegativity of the heteroatom increases, but this upfield shift is weaker than with the γ-carbon atom. In general, the effect of the electronegativity of the heteroatom in position 1 on the chemical shifts of carbon ring atoms in six-membered saturated systems is as follows: α (50 ppm per unit of electronegativity) > γ (−5 ppm) > β (−2.5 ppm).

Determination of R values and conductometry have been used to elucidate the nature of the products resulting from the interaction of diorganyl chalcogenides (among them 1-chalcogenacyclohexanes) with halogens.[63] These compounds exist either as charge-transfer complexes (CCT) **37** in which the chalcogen atom is attached to one halogen atom and the angle M . . . X-X is close to 180° or as covalent trigonal bipyramidal structures (TB) **38**. The results of these studies are presented in Table VI.



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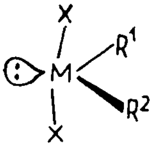

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TABLE VI

Structure of products resulting from the interaction of diorganyl chalcogenides R_2M with halogens X_2

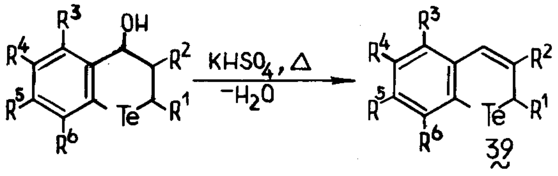
Halogen (X)	Chalcogen (M) M = S	 M = Se	 M = Te
Cl	(TB)	TB	TB
Br	CCT	TB	TB
I	CCT	CCT	TB

III. BICYCLIC SYSTEMS

Of possible bicyclic six-membered tellurium-containing heterocycles so far only compounds with one tellurium atom have been described. Practically all research work on compounds of this type, with the exception of telluroisochroman, has been done during the last 10–12 years.

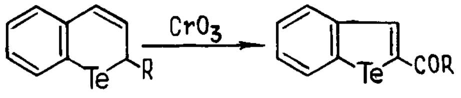
3.1. *Tellurochromenes*

The simplest representatives of bicyclic six-membered systems with the tellurium atom in position 1, the tellurochromenes (1-tellura-1,2-dihydronaphthalenes) **39** were prepared by distillation of the tellurochromanols (products of tellurochromanone reduction) over $KHSO_4$.[64]



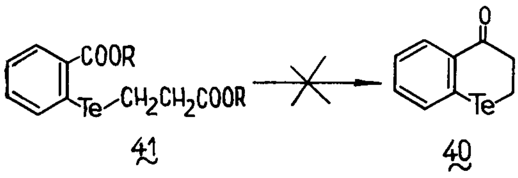
$R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$; $R^1 = CH_3$ (here and further all other $R = H$); $R^2 = CH_3$; $R^5 = CH_3$; $R^6 = CH_3$

Tellurochromenes when oxidized with chromic anhydride are converted to 2-acylbenzotellurophenes.[65]



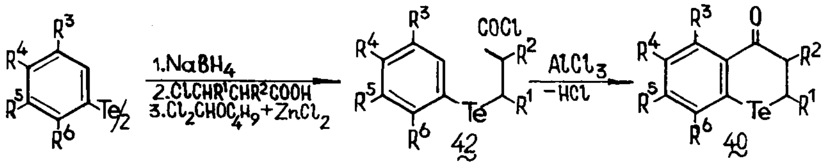
3.2. Tellurochromanones and Tellurochromones

Cleavage of the Te-$C_{aliph.}$ bond and the formation of ditellurosalicylic acid[64] was observed during unsuccessful attempts to synthesize tellurochromanone **40** via pyrolysis of β-(o-carboxyphenyltelluro) propionic acid **41** ($R = H$) or by Dieckmann condensation of the ester of this acid **41** ($R = C_2H_5$), methods frequently utilized for the preparation of oxygen, sulfur, and selenium analogs of **40**. Cyclization of the phenyl-β-telluropropionic acid or its esters catalyzed by polyphosphoric acid under conditions similar to those used to obtain selenochromanones[66] is not an effective route to tellurochromanone. The reaction leads to decomposition of the starting acid with extrusion of tellurium.



$R = H, C_2H_5$

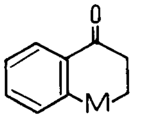
A series of tellurochromanones **40** was prepared via cyclization of aryl (2-chlorocarbonyl) ethyl tellurides **42** under the action of aluminum chloride in methylene chloride at −70 °C and subsequent warming of the reaction mixture to −5 °C.[64] Due to the characteristic propensity of dicoordinated tellurium to add halogens the acyl chlorides **42** cannot be prepared by interaction of the corresponding acids with PCl_5 or $SOCl_2$. Therefore, the compounds **42** were prepared by treating the corresponding acids with dichloromethyl butyl ether in the presence of zinc chloride.[64]



$R^1 = R^2 = R^3 = R^4 = R^5 = R^6 = H$; (below only $R \neq H$ are indicated): $R^2 = CH_3$, $R^3 = CH_3$, $R^5 = CH_3$, $R^6 = CH_3$, $R^4 = R^5 = CH_3$

The reaction, though not as general as one would like, was successfully employed for the preparation of naphtho[1,2-b]tellurochromanone.[64]

It is interesting to compare some spectral characteristics of the chromanones **43** (M = O, S, Se, Te). In the IR spectra of these compounds the bond stretch wave numbers of the carbonyl group decrease in the following order: M = S (1687 cm^{-1}), M = Se (1685 cm^{-1}) M = Te (1679 cm^{-1}). In the UV spectra, a significant bathochromic shift of the long-wave bands is observed in the same order from chromanone to tellurochromanone: λ_{max} is 319 nm (M = O), 346 nm (M = S), 355 nm (M = Se), and 375 nm (M = Te).[64]



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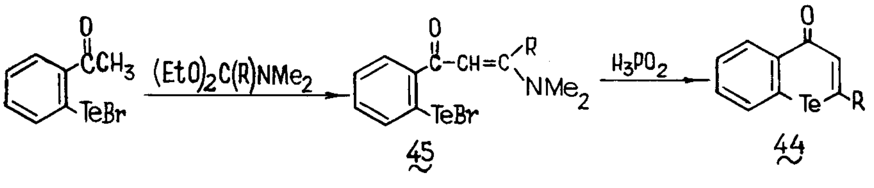
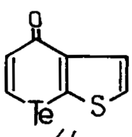
The reactivity of the tellurochromanones has practically not been investigated. The unsubstituted tellurochromanone forms a 2,4-dinitrophenylhydrazone. Upon treatment with methyl iodide it forms the corresponding telluronium salt.[64] Reaction of tellurochromanones with sodium borohydride in ethanol leads to the corresponding tellurochromanols.

According to[67,68] the tellurochromones **44** could not be obtained by methods suitable for the synthesis of their sulfur or selenium analogs. These include the oxidation of chromanones with chloranil, trityl perchlorate or some other standard routes.[68] The preparation of these compounds was achieved *via* the cyclization (under the action of H_3PO_2) of β-(*o*-bromotelluroaroyl) enamines **45**, the condensation products of *o*-bromotelluroacetophenone and the diethyl acetal of *N*,*N*-dimethylformamide or *N*,*N*-dimethylacetamide.



It is interesting to note that when two equivalents of H_3PO_2 were used for the cyclization the tellurochromanones were formed. The above reaction was successfully utilized for the synthesis of the thieno analogs **44** (**46–48**). This reaction may also be employed for the preparation of selenochromones. Although the yield of enamines in this case is rather small, their cyclization to chromones occurs in almost quantitative yield.[68]



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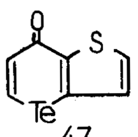

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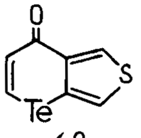
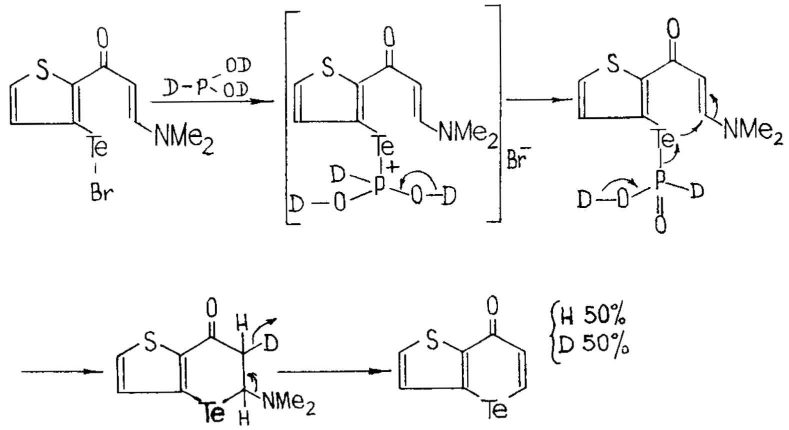


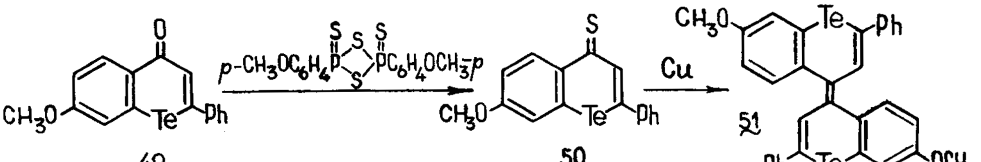
48

Dereu *et al.*[68] proposed the following reaction scheme (see Scheme IV).



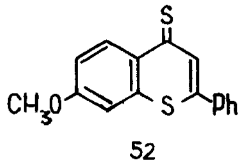
SCHEME IV. The mechanism of tellurochromone formation

The study of the reactivity of tellurochromones and their analogs is only beginning. By interaction of 2-phenyl-7-methoxy-4*H*-benzo[b]telluropyran-4-one **49** with Lawesson's reagent the thione **50** has been obtained and then converted to $\Delta^{4,4'}$-7,7′-dimethoxy-2,2′-diphenyl-4-(benzo[b]telluropyranyl)-4*H*-benzo[b]telluropyran **51** by treatment with copper powder in hot xylene. This compound is considered as a promising donor for charge-transfer complexes.[38]

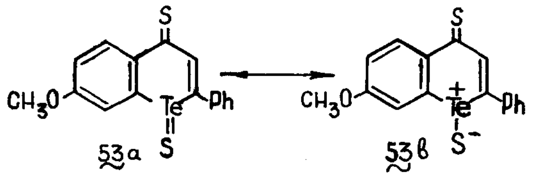


49 **50**

Compound **51** possesses somewhat different properties compared to the monocyclic analog **16**a. Thus, on refluxing it with 5 equivalents of sulfur, several products were isolated the major one being the thione **52**. When compound **51** is interacting in benzene with 2 equivalents of Lawesson's reagent a poorly soluble, deeply colored compound is formed. The spectral characteristics and elemental analysis of this compound agree with the structure of tellurosulfide **53** which is the first stable representative of this class.

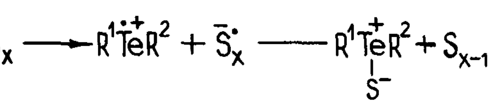


52



53a 53b

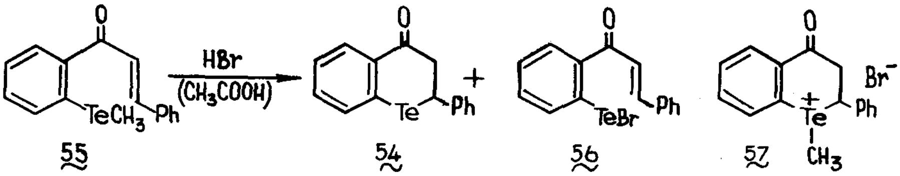
Detty *et al.*[38] suggested that the tellurosulfide is formed via an ion-radical pair according to the following scheme:



$$R^1TeR^2 + S_x \longrightarrow R^1\overset{\bullet+}{Te}R^2 + \bar{S}_x^{\bullet} \longrightarrow R^1\underset{\underset{S^-}{|}}{\overset{+}{Te}}R^2 + S_{x-1}$$

3.3. *Telluroflavanone*

Telluroflavanone **54** could not be prepared by cyclization of 3-phenyltelluropropanoic acid or its acyl chloride.[69] However, the method employed earlier to obtain a selenium analog of **54**[70] proved suitable for the preparation of telluroflavanone in 20 % yield under sufficiently mild conditions, *i.e.* upon heating 2-cinnamoylphenyl methyl telluride **55** at 60 °C in 100 % acetic acid saturated with hydrogen bromide.[69] The major reaction product was 2-cinnamoylphenyl tellurium bromide **56**. It should be noted that the reaction with the selenium analog of **55** does not proceed that way at all.[70]

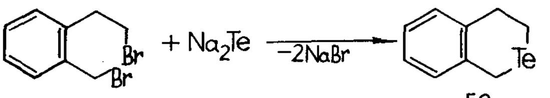


55 54 56 57

Piette *et al.*[69] suggest that the reaction occurs through addition of HBr to the carbon-carbon double bond of compound **55** followed by intramolecular cyclization resulting in the telluronium salt **57**. The latter compound loses CH_3Br on heating and is converted to telluroflavanone.

3.4. *Bicyclic Six-Membered Compounds with the Tellurium Atom in Position 2*

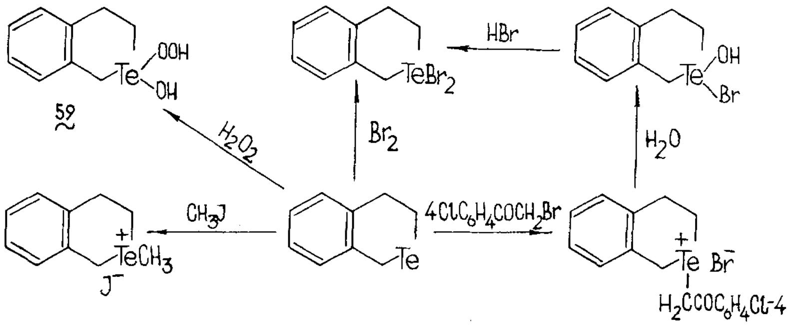
The first representative of bicyclic six-membered systems containing a tellurium atom in position 2, telluroisochroman **58**, was obtained through the reaction of 2-(2-bromoethyl)benzyl bromide with sodium telluride.[71,72]



58

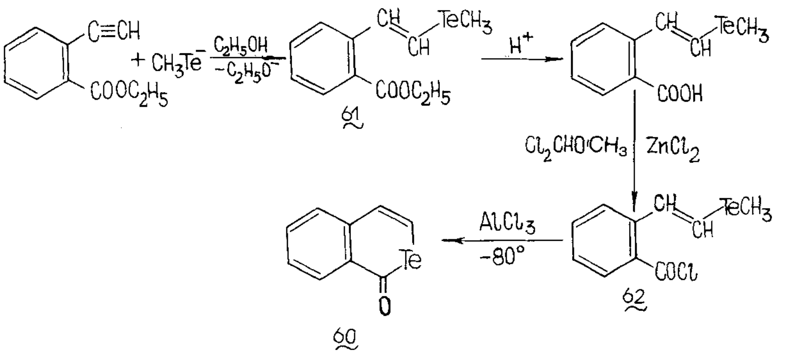
Starting from compound **58**, optically active telluronium salts have been prepared. Interaction of telluroisochroman with 4-chlorophenacyl bromide affords the corresponding racemic telluronium salt which can be separated into two diastereomers by treatment with silver (d)-bromocamphorsulfonate. The (l)-(d)-salt precipitates from the hot alcohol solution whereas the (d)-(d)-salt remains in the solution. Treatment of the optically active sulfonates with sodium picrate gives the optically active picrates: l-d's M_D is −632° and d-d's +575°. The (l)-(d)-picrate slowly racemizes in acetone at room temperature. The racemization, promoted by traces of water in the solution, is complete in approximately 20 days.[72]

Telluroisochroman exhibits properties typical of dicoordinated tellurium derivatives. It interacts with bromine forming tellurium dibromide and produces telluronium salts in the reaction with methyl iodide or 4-chlorophenacyl bromide. The latter salt can be easily hydrolyzed to 4-chloroacetophenone and telluroisochroman hydroxybromide which under the action of HBr is converted to telluroisochroman dibromide. Oxidation of telluroisochroman by hydrogen peroxide leads to compound **59** which is analogous to the products of dialkyl telluride oxidation by hydrogen peroxide.[73] The reactions of telluroisochroman are listed in Scheme V.



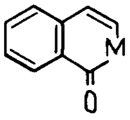
SCHEME V. Reactions of telluroisochroman

Another representative of bicyclic six-membered compounds containing a tellurium atom in position 2, telluroisocoumarine **60**, was obtained by way of a four-step synthesis starting from ethyl *o*-ethynylbenzoate[74] (Scheme VI). Addition of methanetellurolate anion leads to ester **61** as a mixture of Z- and E-isomers in the



SCHEME VI. Synthesis of telluroisocoumarine ratio 9:1. Hydrolysis of this ester and treatment of the acid formed with dichloromethyl methyl ether in the presence of zinc chloride leads to the acyl chloride **62** which under the action of aluminum chloride at low temperatures loses methyl chloride and is converted to telluroisocoumarine **60**.[74]

The IR absorption wave number of the carbonyl group in isocoumarines **63** (as well as in xanthones, see below) decreases in the following order: M = O (1745 cm^{-1}) > M = S (1640 cm^{-1}) ≃ M = Se (1643 cm^{-1}) > M = Te (1628 cm^{-1}).



63

IV. TRICYCLIC TELLURIUM-CONTAINING HETEROCYCLES

The tricyclic compounds are the least studied group of the six-membered tellurium heterocycles. Of six tricyclic tellurium-containing systems known to date, the first representatives of four of them were synthesized during the last five years.

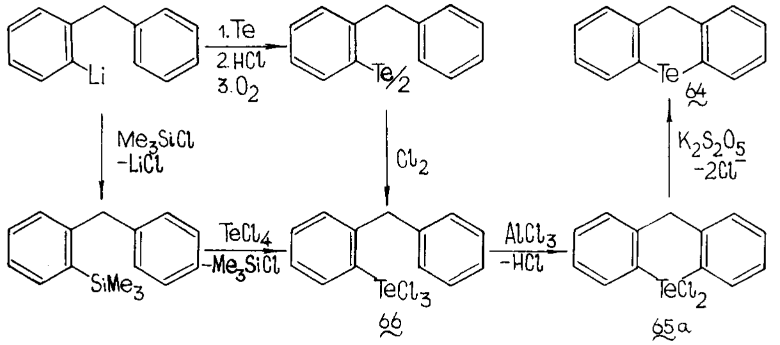
4.1. Telluroxanthene and Its Derivatives

The simplest representative of the tricyclic systems containing a tellurium atom, telluroxanthene **64**, has been prepared by two methods. First, the synthesis of this compound was accomplished by the method used earlier for the preparation of phenoxatellurine[75] and thiophenoxatellurine.[76] The cyclization of 2-benzylphenyltellurium trichloride by heating of its *o*-dichlorobenzene (or 1,2,4-trichlorobenzene) solution in the presence of one equivalent of anhydrous aluminum chloride leads to telluroxanthene 10,10-dichloride **65a** in high yield.[77,78]

2-Benzylphenyltellurium trichloride **66**, which is the starting material for telluroxanthene, was obtained by addition of chlorine to di(2-benzylphenyl) ditelluride. The latter is the product of a reaction between 2-benzylphenyllithium (from 2-benzylphenyl bromide (iodide) and lithium in ether) and tellurium.[77,78] An alternative route to compound **66** is the reaction of 2-(trimethylsilyl)-diphenylmethane with tellurium tetrachloride.[78] The yields in the latter reaction are somewhat lower than those in the former one.

The synthesis of telluroxanthene is shown in Scheme VII.

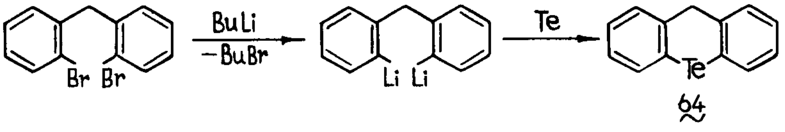
The cyclization of 2-benzylphenyltellurium trichloride, unlike that of 2-phenoxyphenyltellurium trichloride[75] or 2-thiophenoxyphenyltellurium trichloride,[76] occurs only in the presence of the anhydrous aluminum chloride. In its absence, the reaction proceeds only at high temperatures giving rise to telluroxanthene, 10,10-dichloride in very low and difficultly reproducible yields.[78] This is, probably, due to the much weaker electron donor properties of the methylene group in comparison with the oxygen and sulfur atom in diphenyl ether and sulfide, respectively. Aluminum chloride apparently enhances the electrophilicity of the $TeCl_3$ group by coordination. The adduct may be assigned the structure $[RTeCl_2]^+$ $[AlCl_4]^-$ [78] (by analogy with the product of the interaction between tellurium tetrachloride and aluminum chloride



SCHEME VII. Synthesis of telluroxanthene

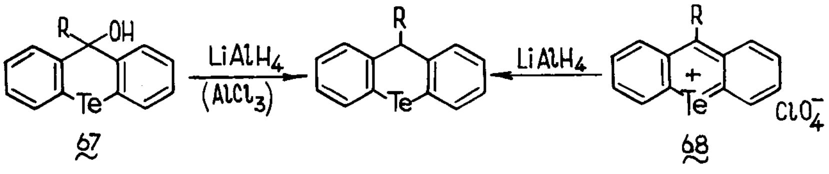
$[TeCl_3]^+ [AlCl_4]^-$ [79]). It should be noted that under analogous conditions, 2-benzylphenyltellurium tribromide does not undergo cyclization, which is due to a considerable decrease in the electrophilicity of $TeHal_3$ groups on passing from chlorine to bromine. The same trend was observed for the reactivities of aryltellurium trihalides.[80]

The second method employed for the synthesis of telluroxanthene is similar to that widely used for the preparation of various tricyclic systems containing heteroatoms in positions 5,10 (9,10). It is based on the interaction of 2,2′-dilithodiphenylmethane (from 2,2′-dibromodiphenylmethane and butyllithium) with powdered tellurium.[81]



Although the first method is a five-step sequence of reactions and the second only a two-step one, the yields of telluroxanthene are approximately equal, but 2-bromodiphenylmethane (the starting material for the first synthesis) is more accessible than 2,2′-dibromodiphenylmethane.

9-Substituted telluroxanthenes have been synthesized by two methods. One is the reduction of 9-telluroxanthenols **67** with lithium aluminum hydride in the presence of anhydrous aluminum chloride[82] and the other is the reduction of 10-telluroniaanthracene perchlorates **68** with lithium aluminum hydride.[82]

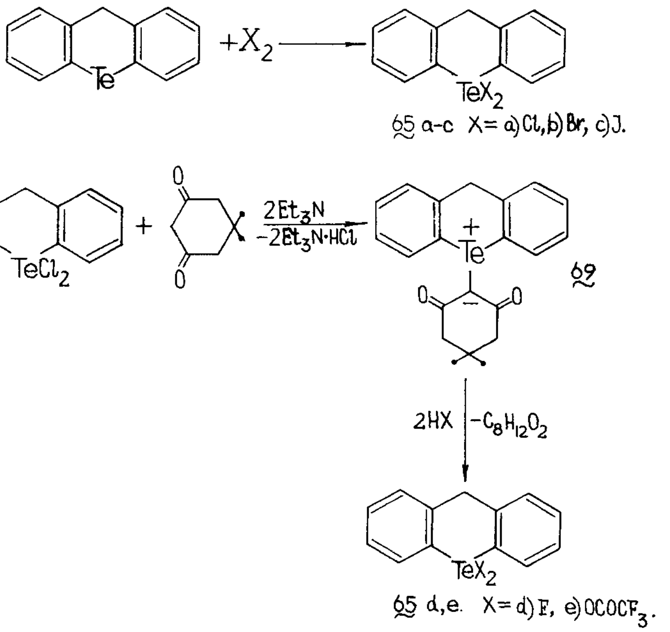


$R = H, p\text{-}CH_3C_6H_4$

The chemical properties of telluroxanthene resemble those of acyclic diaryl tellurides. Its special properties are the greater stability of a number of derivatives as compared to the analogous derivatives of diaryl tellurides.[78] Telluroxanthene is easily converted to derivatives of tetra- and tricoordinated tellurium and it forms complexes with inorganic salts and rhodium (I) carbonyls.[83]

Telluroxanthene adds chlorine, bromine, and iodine forming the corresponding telluroxanthene 10,10-dihalides **65a–c** in practically quantitative yields.[78] Other σ-telluranes, *viz.*, telluroxanthene 10,10-difluoride and telluroxanthene 10,10-di (trifluoroacetate) **65e** were prepared using a reaction developed earlier with the aim of preparing acyclic σ-telluranes.[84] This is a reaction between ylide **69** (formed from telluroxanthene 10,10-dibromide and dimedone in the presence of triethylamine) and HF or CF_3COOH.[78]

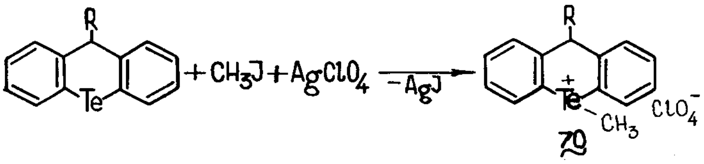
The corresponding reactions of telluroxanthene are shown in Scheme VIII.



SCHEME VIII. Synthetic routes to 10,10-disubstituted telluroxanthenes

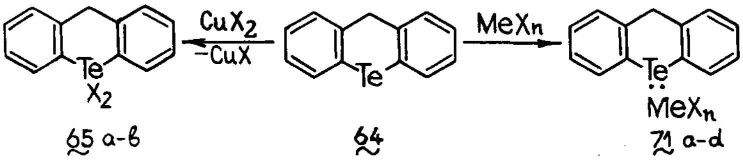
The telluronium ylide **69** possesses a higher thermal stability than corresponding diaryltellurium ylides.[85] The latter decompose after short-time boiling in *o*-xylene (140–150 °C[85]) whereas ylide **69** is stable up to 180 °C.[78]

Unlike arylalkyl(dialkyl)tellurides with a highly nucleophilic tellurium atom[1], telluroxanthene cannot be alkylated with methyl iodide[78] or with butyl bromide.[81] However, when methyl iodide reacts with telluroxanthenes in the presence of an equivalent amount of silver perchlorate the telluronium salts **70** are produced in high yields.[78]



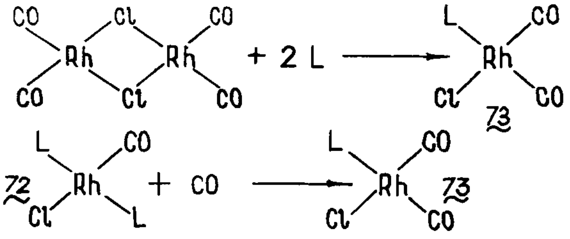
R=H, p-$CH_3C_6H_4$

Telluroxanthene easily forms with mercury and silver salts molecular complexes **71a–d** having the composition of 1 : 1. The last two complexes are unstable and readily decompose under illumination. On the other hand, copper dihalides do not form molecular complexes with telluroxanthene, but rather oxidize it to telluroxanthene 10, 10-dihalides.[78]



a) Me = Hg, X = Cl; b) Me = Hg, X = Br; c) Me = Ag, X = NO_3; d) Me = Ag, X = ClO_4

When telluroxanthene interacts with rhodium *M*, *M*-dichlorotetra-carbonyl the complex RhL_2COCl, where L is telluroxanthene, (**72**) can be isolated.[83] In the IR spectrum of the solution there are seen along with the 1967 cm^{-1} band which is specific for the monocarbonyl complex **72**, bands at 2080 and 2003 cm^{-1} relating to the dicarbonyl complex RhL $(CO)_2Cl$ (**73**), a product of chloride bridge cleavage in rhodium carbonyl chloride by telluroxanthene, or to the product where one of the ligands L in **72** has been replaced by CO.

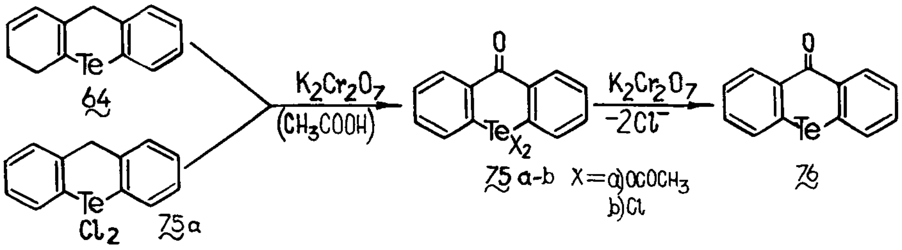


When $RhOxq(C_8H_{14})CO$ (C_8H_{14} is cyclooctene, Oxq is 8-hydroxyquinoline) is allowed to react with telluroxanthene under mild conditions the complex RhOxqLCO (**74**) is formed. The structure of the initial compound warrants the conclusion that telluroxanthene in this complex occupies a position trans to the nitrogen atom.[83]

The phosphines PPh_3 and PBu_3 readily displace telluroxanthene in the complexes **72** and **74** and the respective phosphorus-containing complexes can then be isolated.

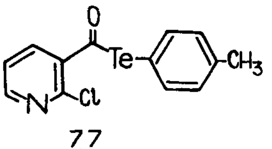
The methylene group of telluroxanthene can be oxidized to a carbonyl group with potassium dichromate in acetic acid.[78,82,86] The reaction product is telluroxanthone 10,10-diacetate **75a**. Apparently, under the action of a strong oxidant such as potassium dichromate telluroxanthene is oxidized to the corresponding oxide. It interacts, like similar acyclic diaryl telluroxides,[87] with the excess acetic acid and is converted to telluroxanthene 10,10-diacetate the methylene group of which is oxidized to a carbonyl group.

The diacetate **70a** can, like other σ-telluranes, easily be reduced to telluroxanthone **76**. Telluroxanthene 10,10-dichloride is oxidized to telluroxanthone 10,10-dichloride **75b** by potassium dichromate in acetic acid[78,82,86] or by chromic acid anhydride.[81]



The preparation of telluroxanthone from 2,2'-bisdiazoniabenzophenone and sodium telluride[88] (in 2% yield) is, apparently, ambiguous, since the melting point of the product obtained (202 °C) and assigned to **76** differs sharply from the accepted melting point of telluroxanthone (115 °C).

Attempts to synthesize substituted telluroxanthones via photocyclization of **77**–**78** failed,[81] although the selenium[89] and sulfur analogs[90] of these compounds are converted to chalcogenoxanthones under identical conditions. Equally unsuccessful was the attempt to effect high-temperature cyclization of 2-(halotelluro)-benzophenones **79**, even in the presence of anhydrous aluminum chloride.



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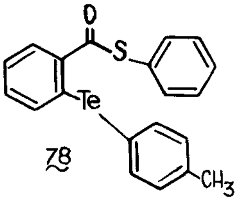
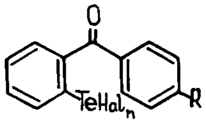


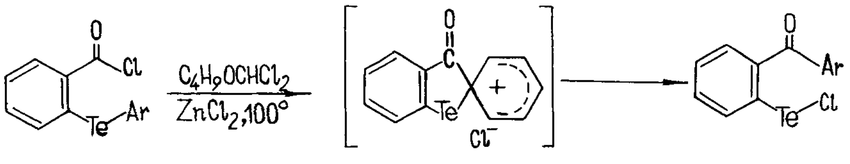
78



79

Hal = Cl, Br; R = H, CH_3; *n* = 1, 3

It is noteworthy that the attempt to prepare telluroxanthone by the standard route employed for the synthesis of xanthones, *viz*. by the cyclization of **80** at 100 °C led not to telluroxanthones but to rearrangement products, **81**, probably via intermediate **82**[91,92]

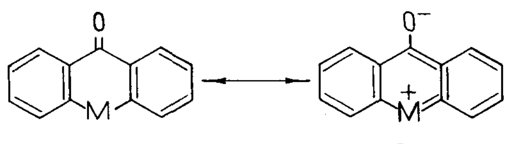


80 82 81

Ar = C_6H_5, p-$CH_3C_6H_4$, 2-C_4H_3S

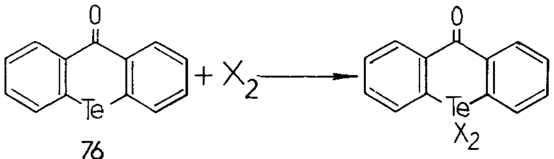
An analogous reaction occurs with selenium derivatives, but not with those of sulfur.[92]

The trend in the bond stretch wave numbers of the carbonyl groups in xanthone (1660 cm^{-1}),[93] thioxanthone (1645 cm^{-1}),[93] selenoxanthone (1620 cm^{-1}),[94] and telluroxanthone (1590 cm^{-1})[78] serves as evidence for the growing contribution of polar resonance structures like **83a** as compared to **83b** when one goes from xanthone to its tellurium analog.[78]



83b M=O,S,Se,Te. 83a

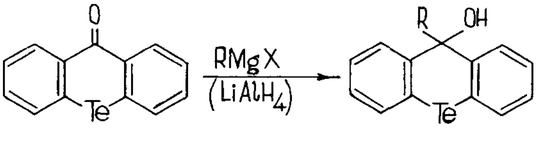
Like telluroxanthene, telluroxanthone adds chlorine, bromine, and iodine to form telluroxanthone 10,10-dihalides **75b,c**[78]



76

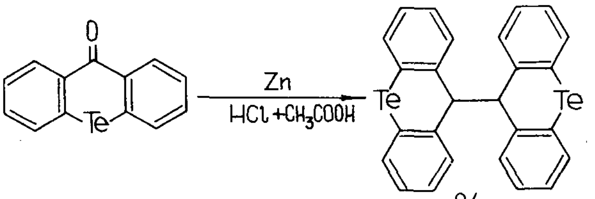
75 b-c X= b)Cl; c)Br.

Through interaction with $LiAlH_4$ or Grignard reagents telluroxanthone can be transformed to the respective 9-telluroxanthenols.[82,86]



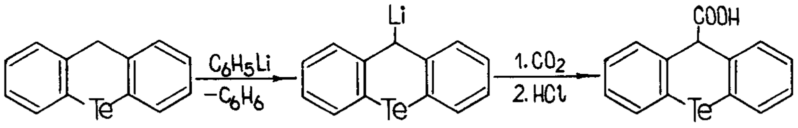
76 67

Telluroxanthone behaves differently from xanthone when it is reduced with the zinc powder in a mixture of acetic acid and hydrochloric acid.[95] When xanthone is reduced under the above conditions, dixanthylene is formed in which two xanthene fragments are bound by a C=C double bond.[96] In contrast to this, telluroxanthone produces 9,9′-bis(telluroxanthenyl) **84** with a C—C single bond between the two tricyclic moieties. This structure has been confirmed by X-ray analysis.[95]



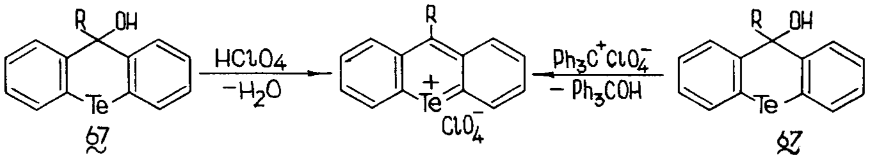
84

The hydrogen atoms in the methylene group of both telluroxanthene and xanthene[97] can be replaced by a lithium atom under the action of phenyllithium[78] resulting in 9-lithotelluroxanthene in more than 65% yield, judging by its convertion to 9-telluroxanthene carboxylic acid.



4.2. *10-Telluroniaanthracene Perchlorates*

The first representatives of the 10-telluroniaanthracene perchlorates 73, were obtained from telluroxanthenols **67** or telluroxanthenes.[82,86] Like 10-thionia-[98,99] and 10-selenoniaanthracene perchlorates,[94,100] the salts **68** were isolated in excellent yields when treating 9-telluroxanthenols in ether solution with perchloric acid or with trityl perchlorate in trifluoroacetic acid.

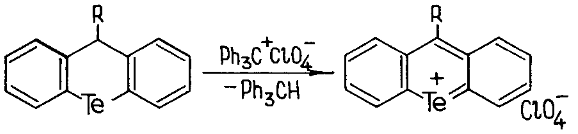


67 68 67

R = H, 4-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3OC_6H_4$, 4-BrC_6H_4, 4-FC_6H_4, 1-$C_{10}H_7$, $C_6H_5CH_2$

R = H, C_6H_5, 4-$CH_3C_6H_4$

Peculiar is the course of the reaction aimed at obtaining 10-telluroniaanthracene perchlorates from telluroxanthenes **64**. While 10-oxonia-[101] and 10-thioniaanthracene perchlorates[102] are easily accessible via the reaction of xanthenes with trityl perchlorate in 100% acetic acid, the perchlorates **68** can be prepared only when trifluoroacetic acid is used as a solvent.[78]



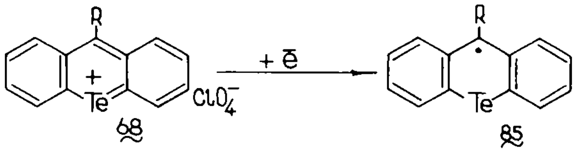
R = H, 4-$CH_3C_6H_4$

68

10-Telluroniaanthracene perchlorates are dark violet, crystalline compounds poorly soluble in trifluoroacetic acid. Due to their extremely strong electrophilic properties, **68** interact readily with acetic acid, nitromethane, and acetone, forming easily soluble and difficultly isolable products of the CH-acid addition to the C9-atom of the heterocycle.

The most typical reaction of the 10-telluroniaanthracene perchlorates as well as of other cations of 10-chalcogenoniaanhtracenes is the addition of nucleophiles to the 9-position of the heterocycle. The reactivity of **68** was studied with 10-telluroniaanthracene (**68a**) and 9-(*p*-tolyl)-10-telluroniaanthracene perchlorate (**68b**).[103] Reduction of the latter compound with $LiAlH_4$ leads to 9-(*p*-tolyl)telluroxanthene in 75–85% yield whereas reduction of the unsubstituted perchlorate **68a** gives a mixture of two substances: telluroxanthene **64** and 9,9′-bis(telluroxanthenyl) **84**.[103] The formation of **84** could indicate that the reduction of the perchlorates **68** proceeds via intermediate telluroxanthyl radicals **85**. The more stable 9-aryltelluroxanthyl radicals exist in solution in reversible equilibrium with their dimers. The radicals are reduced to the corresponding telluroxanthenes. In the case of the more reactive 9*H*-telluroxanthyl radical, the equilibrium is almost totally shifted towards the dimer.[103]

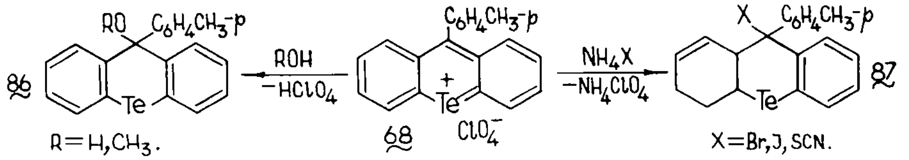
9-Aryltelluroxanthyl radicals **85**, the first representatives of stable tellurium-containing radicals, were obtained by treatment of 9-aryl-10-telluroniaanthracene perchlorates with zinc powder in tetrahydrofuran at room temperature.[104]



R = C_6H_5, 4-$CH_3C_6H_4$, 4-FC_6H_4

The ESR spectra of the radicals **85** consist of five main lines caused, as is also the case with 9-arylxanthyl,[105] thio-[106] and selenoxanthyl radicals,[107] by hyperfine interaction with the protons in positions 1, 3, 6, 8. On lowering the temperature to −40 °C the radicals **85** are reversibly dimerized; this is evidenced by the change in the color of the solution and the vanishing of the ESR signal.[104]

The reactions of 9-(*p*-tolyl)-10-telluroniaanthracene perchlorate with water and methanol lead to 9-oxy(methoxy)-9-(*p*-tolyl)telluroxanthene **86** in high yields as is also the case for other chalcogenium cations.[108] By interaction with salts containing sufficiently nucleophilic anions (Br^-, I^-, SCN^-)9-X-9-(*p*-tolyl)telluroxanthenes **87**[103] are obtained.

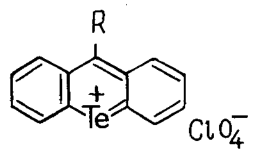


These last reactions, similar to reactions of other heteroaromatic cations with nucleophiles,[109] occur via the respective telluroxanthyl radicals, which were discovered by means of ESR spectroscopy in the reaction between **68b** and tetrabutylammonium bromide in 1,2-dimethoxyethane at room temperature.[103] Unlike 9-aryl-10-telluroniaanthracene perchlorates, the unsubstituted perchlorate **68a**, when treated with the above-mentioned nucleophiles forms 9,9′-bis(telluroxanthenyl) **84** as the major product.[103]

Table VII contains some IR and UV spectra of **68**. Electron absorption spectra of 10-telluroniaanthracene perchlorates are characterized by four absorption bands with maxima at 294–299, 400–410, 590–597, and 633–653 nm.[82] A comparison of the absorption spectrum of 10-telluroniaanthracene perchlorate with that of 10-thioniaanthracene perchlorate (CH_3COOH, λ_{max} at 276, 377, 480 and 506 nm[98]) reveals a considerable bathochromic shift for the tellurium derivatives.

TABLE VII

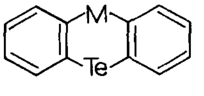
10-Telluroniaanthracene perchlorates



R	IR spectrum, cm^{-1}	UV spectrum (λ_{max}, nm; (log ϵ)) (CF_3COOH)
H	1590, 1525, 1265, 1240, 1070, 760, 710	298(4.50), 403(4.25), 595(3.58), 647(3.52)
4-$CH_3C_6H_4$	1580, 1520, 1270, 1210, 1160, 1070, 720	298(4.82), 403(4.56), 590(3.91), 633(3.88)
3-$CH_3C_6H_4$	1620, 1588, 1270, 1105, 790, 740, 720	296(4.72), 409(4.11), 595(3.98), 653(3.88)
4-$CH_3OC_6H_4$	1610, 1580, 1520, 1280, 1100, 800, 720	299(4.73), 406(4.38), 596(4.00), 651(3.98)
4-FC_6H_4	1680, 1530, 1500, 1300, 1220, 1090	299(4.85), 410(4.49), 590(4.08), 639(4.04)
4-BrC_6H_4	1590, 1540, 1290, 1090, 1000, 800, 720	295(4.75), 409(4.37), 595(3.98), 647(3.93)
1-$C_{10}H_7$	1590, 1540, 1290, 1100, 800, 720	296(4.53), 400(4.00), 597(3.74), 648(3.70)
$C_6H_5CH_2$	1590, 1530, 1260, 1100, 790, 720	294(4.38), 401(3.58), 592(3.31), 639(3.19)

4.3. Tricyclic Systems with Two Heteroatoms

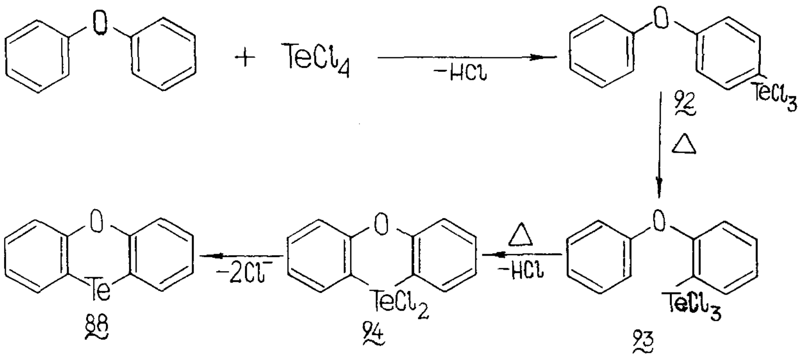
Four tricyclic systems containing, beside one tellurium atom, another heteroatom have been described. These are phenoxatellurine **88**(M = O), thiophenoxatellurine **89**(M = S), telluranthrene **90**(M = Te), and phenotellurazine **91**(M = NAlk).



88, M=O; 89, M=S; 90, M=Te; 91, M=NAlk.

This synthesis of **88**–**91** can be accomplished by various methods some of which (interaction of 2,2′-dilitho derivatives with tellurium or tellurium diiodide, intermolecular electrophilic cyclization of corresponding tellurium trichlorides, see below) can find a more general synthetic application.

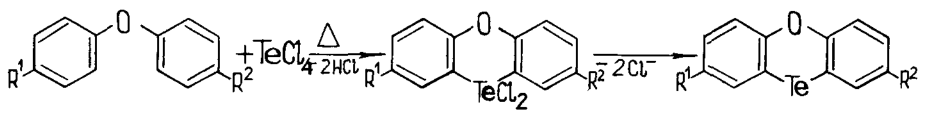
The main approach to the synthesis of phenoxatellurine **88** and its 2,8-disubstituted derivatives, is the reaction of diphenyl ether or its 4,4′-R_2 derivatives with tellurium tetrachloride at high temperatures followed by reduction of the phenoxatellurine 10, 10-dichlorides formed in the cyclization. Reducing agents common in tellurium organic chemistry can be used, such as potassium metabisulfite,[110–113] potassium bisulfite,[114–116] and sodium sulfide.[117] Phenoxatellurine was first isolated by Drew by heating *p*-phenoxyphenyltellurium trichloride **92** above 200 °C.[110] The trichloride **92** is the product of the reaction of tellurium tetrachloride with diphenyl ether because the electron-donating group OC_6H_5[118] directs the group $TeCl_3$ into the *p*-position. The structure of this compound as well as of other aryltellurium trichlorides obtained by means of the tellurium trichloration reaction was established first by chemical[110] and then by spectral methods.[119,120] Evidently, the group $TeCl_3$ migrates at elevated temperatures from the *p*- into the *o*-position and the resulting *o*-phenoxyphenyltellurium trichloride **93** is cyclized to phenoxatellurine 10,10-dichloride.[110] This migration is corroborated by the fact that when *p*-phenoxyphenyltellurium trichloride is heated above its melting point (156 °C) in a nitrogen atmosphere there is formed a trichloride with a m.p. of 125 °C (apparently the *o*-isomer, not isolated, however, in analytically pure form) which, upon further heating (at 150–210 °C), is converted to compound **94**. (Scheme IX).



SCHEME IX. Synthesis of phenoxatellurine

The most convenient method of obtaining phenoxatellurine 10,10-dichlorides is the heating of equimolar amounts of tellurium tetrachloride and diphenyl ether without isolation of the intermediate trichloride.

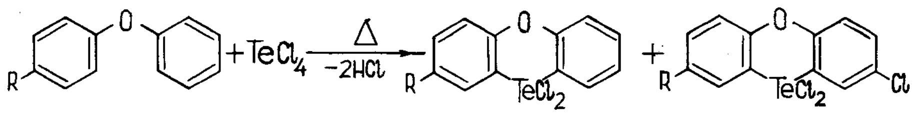
Similarly to this, when tellurium terachloride interacts with 4,4'-disubstituted diphenyl ethers: 4,4'-dimethyl-,[114] 4,4'-dichloro-,[111] 4,4'-difluoro-,[112] 4-fluoro-4'-methyl-,[115] and 4-fluoro-4'-chloro-[116] the corresponding 2,8-disubstituted phenoxathellurine 10,10-dichlorides are obtained.



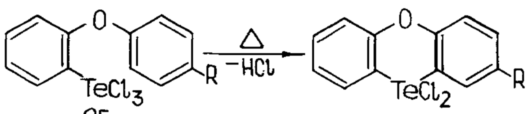
However, a number of other diphenyl ethers: 4-chloro-4'-bromo-,[115] 4-chloro-4'-nitro-,[115] 4-bromo-,[116] 4-iodo-,[116] 4-nitro-[121] when reacting with tellurium tetrachloride produce complex mixtures of poorly separable products or decompose in the course of the reaction. This method is hardly applicable for the preparation of 2(8)-monosubstituted phenoxatellurine 10,10-dichlorides. Thus, when 4-methyl-,[110,122]

Note. The numbering of the atoms in the heterocycles **88–90** is identical to that used in phenoxathiin, according to IUPAC rules, and that in phenotellurazine **91** to that in phenothiazine.

4-fluoro-,[116] 4-chlorodiphenyl ethers[116] are used, then, along with the expected 2-R-phenoxatellurine 10,10-dichlorides, considerable amounts of 2-R-phenoxatellurine 8,10,10-trichlorides are formed owing to the introduction of chlorine into the nucleus, which, in the opinion of the authors of[116] occurs after the cyclization. This substitution is probably due to the partial decomposition of tellurium tetrachloride into tellurium and chlorine and the presence in the reaction mixtures of tellurium tetrachloride which may act as a catalyst in the electrophilic substitution of benzene ring hydrogen atoms by chlorine atoms.[123]

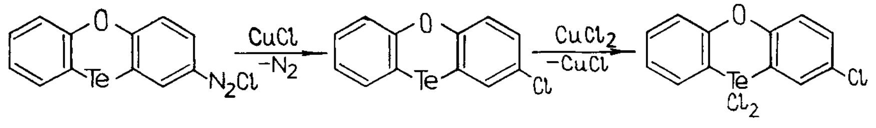


A more general method of preparation of various phenoxatellurine 10,10-dichlorides comprises also intramolecular electrophilic cyclization of 2-phenoxyphenyltellurium trichlorides **95**.[75] These compounds are readily accessible from the corresponding arylmercury chlorides[75,76] or aryltrimethylsilanes[124] as suitable precursors. The principal advantage of this method over those described above is that electron-accepting groups R can be tolerated in the precursor **95**.


95

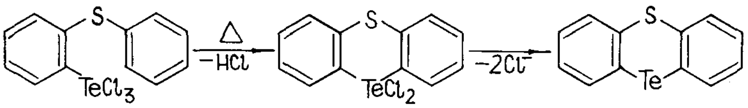
It is, apparently, expedient to utilize this reaction for the preparation of 2, 8-disubstituted and monosubstituted phenoxatellurine 10,10-dichlorides containing substituents in the $TeCl_3$-substituted nucleus or in the *p*-position (with respect to oxygen) of another nucleus. If, however, the substituents in the second nucleus are in *o*- or *m*-positions, then there is, apparently, a possibility for the forming of a mixture of isomeric phenoxatellurine 10,10-dichlorides although the cyclization of compounds with this structure has not been studied yet.

Of limited value is the preparation of various 2- and 2,8-disubstituted derivatives of phenoxatellurine 10,10-dichlorides by Sandmeier reaction of 2-diazo- and 2,8-bis(diazo)phenoxatellurines obtained when the corresponding amines are diazotized.[116,121] Only one example of this reaction has been described so far.[116] It is interesting to note that the final product of the reaction of 2-diazophenoxatellurine chloride with copper (I) chloride is 2,10,10-trichlorophenoxatellurine. It is formed through the oxidation of the initially obtained 2-chlorophenoxatellurine by copper (II) chloride.



Information on the preparation of the thiophenoxatellurine **89** by interaction of diphenyl sulfide with tellurium tetrachloride is contradictory. According to

Petragnani[76] this reaction does not lead to thiophenoxatellurine 10,10-dichloride, but stops at the stage of *p*-thiophenoxyphenyltellurium trichloride. On the other hand, Gioaba[125] when heating diphenyl sulfide with tellurium tetrachloride at 190–200 °C during 12 hours succeeded in obtaining thiophenoxatellurine 10,10-dichloride in low yield (6 %). In a higher yield (40 %), thiophenoxatellurine 10,10-dichloride was obtained when 2-thiophenoxyphenyltellurium trichloride (from 2-thiophenoxyphenylmercury chloride and tellurium tetrachloride) was heated at 200–250 °C. The dichloride obtained is reduced with sodium sulfide to thiophenoxatellurine **89** in excellent yield.[76]

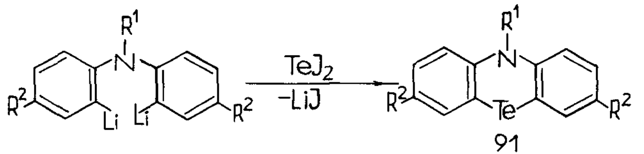


89

The methods useful in the synthesis of phenoxa- and thiophenoxatellurines cannot be applied to the preparation of telluranthrene **90**, since the interaction of diphenyl telluride with tellurium tetrachloride should, apparently, (by analogy with the reaction of diaryl ditellurides with tellurium tetrachloride[126]) result in the formation of diphenyl tellurium dichloride only. The synthesis of telluranthrene was achieved by reaction of tin tetraphenyl with tellurium at 310 °C.[127] Zingaro, however, did not succeed in reproducing this synthesis. Telluranthrene **90** was obtained in over 70 % yield by interaction of powdered tellurium with hexameric *o*-phenylenemercury.[128] A radical mechanism was proposed for this reaction.

The structure of telluranthrene was confirmed by elemental analysis, mass spectroscopy and ^{13}C and ^{125}Te NMR spectroscopy.[128]

A number of 10-alkylphenotellurazines **91** has been synthesized in over 50% yield by reaction of 2,2′-dilitho-*N*-alkyl-diarylamines (from 2,2′-dibromo-*N*-alkyl-diarylamines and butyllithium in ether) with tellurium diiodide[129–131]

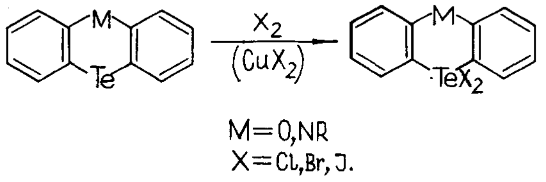


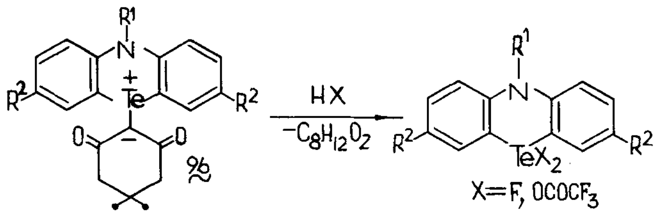
91

$R^1 = CH_3$, $R^2 = Br$; $R^1 = C_2H_5$, $R^2 = H, CH_3, Br$

The reactivity of phenoxatellurine **88** and phenotellurazine derivatives **91** has been studied thoroughly. Data on the reactivity of other tricyclic systems, thiophenoxatellurine and telluranthrene, are practically non-existing. The chemical properties of phenoxatellurine and phenotellurazine are determined by the presence in these systems of two main centers of reactivity, a tellurium atom and benzene rings activated by electron-donating oxygen and nitrogen atoms, and being, therefore, susceptible to electrophilic substitution reactions.

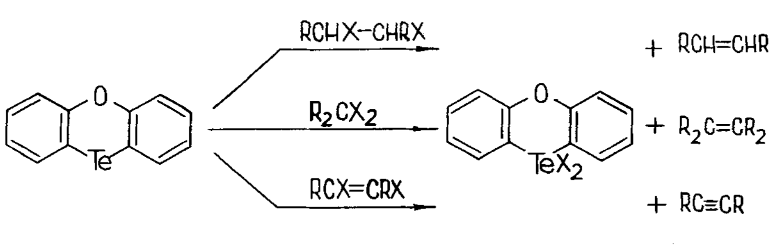
Owing to the presence of a tellurium atom, **88** and **91**, like diaryl tellurides,[1] are easily converted to derivatives of tetracoordinated (σ-telluranes) and tricoordinated (ylides, oxides, telluronium salts) tellurium, they form molecular complexes and eliminate tellurium. Phenoxatellurines[110–112,115,122,132,133] and 10-alkylphenotellurazines[129–131] can be oxidized with chlorine, bromine, and iodine, and also sulfuryl chloride and copper (II) halides to phenoxatellurine 10,10-dihalides or 10-alkylphenotellurazine 5,5-dihalides. A number of other σ-telluranes derived from 10-alkylphenotellurazines has been prepared via interaction of ylide **96** (formed from 10-ethylphenotellurazine 5,5-dibromide, dimedone, and two equivalents of triethylamine) with hydrofluoric or trifluoroacetic acid[130,131]





Phenoxatellurine 10,10-dibromides (diiodides) are converted to dichlorides when acted upon by chlorine or thionyl chloride, and diiodides to dibromides when treated with bromine or PBr_3. Dichlorides can be easily converted to dibromides or diiodides when their methanol solutions interact with potassium bromide or iodide[113].

The ease with which phenoxatellurine is converted to phenoxatellurine 10,10-dihalides allows this compound to be used for the dehalogenation of vicinal[134] and geminal dihalides[125] in order to prepare alkenes and alkynes in high yields. The following compounds have been shown to undergo this reaction: 1,2-dibromoethane, *trans*-1,2-dibromocyclohexane and -pentane, 1-phenyl-1,2-dibromoethane, 2,3-dibromo-3-phenylpropanoic acid and its ethyl ester, 2,3-dibromobutanoic acid, 1,2-diiodo-1-phenylethene, 2,2,-diiodocinnamic acid, diphenyldichloromethane, diethyl dibromomalonate, 9,9-dichlorofluorene, phenothiine 10,10-dichloride and -dibromide and phenoxaselenine 10,10-dibromide. This reaction is, however, not completely general. Thus, only trace amounts of stilbene were obtained from benzylidene chloride and bromide. 1,2-Diphenyl-1,2-dibromoethane and 1,2-dichlorocyclohexane do not undergo this reaction at all.

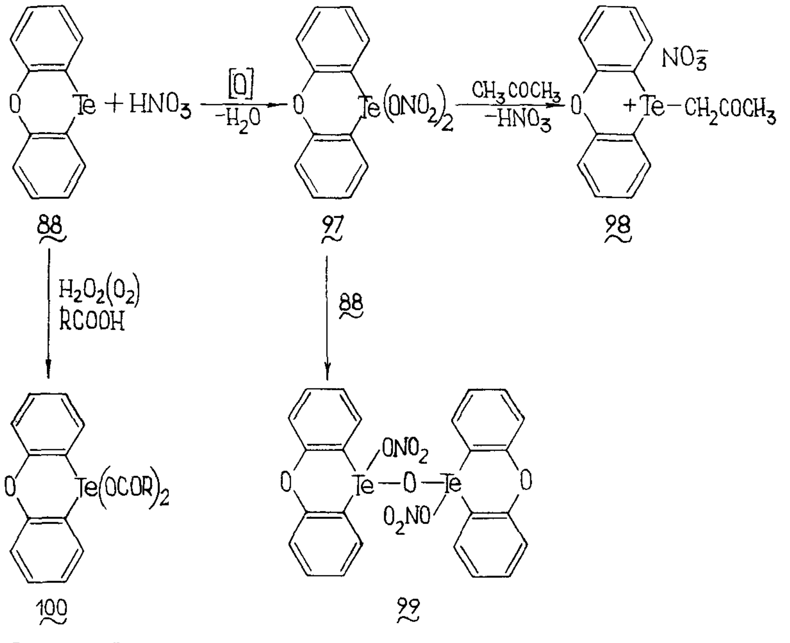


In its dehalogenating ability, phenoxatellurine surpasses diaryl tellurides[135] and diaryl ditellurides[126] as well as thiophenoxatellurine.[125]

Phenoxatellurine and its derivatives can be easily oxidized with dilute nitric acid whereby the corresponding 10,10-dinitrates **97** are formed.[110,121,136] Interestingly, phenoxatellurine 10,10-dinitrate **97** upon evaporation of its acetone solution produces unexpectedly acetonylphenoxatelluronium nitrate **98**,[137] whereas mixing of equimolar amounts of phenoxatellurine **88** and phenoxatellurine 10,10-dinitrate in dichloromethane produces compound **99**.[138] X-Ray structure analyses have been undertaken in order to establish the structure of **99**. One should note that at low temperatures (−90 °C) phenoxatellurine forms with phenoxatellurine 10,10-dinitrate in methylene chloride a violet-colored 1:2 adduct which, at higher temperatures, transforms into the 1:1 adduct.[139]

Treatment of phenoxatellurine with hydrogen peroxide in acetic acid leads to phenoxatellurine 10,10-diacetate **100** (R = CH_3), undoubtedly via intermediate formation of the corresponding phenoxatellurine oxide, which then reacts with the excess acid.[136,140] Analogous diacyl derivatives are formed when a phenoxatellurine solution is left in trifluoroacetic acid with the access of air. This produces phenoxatellurine 10,10-di(trifluoroacetate) **100** (R = CF_3).[141]

The reactions described above are listed in Scheme X.



SCHEME X. Some reactions of phenoxatellurine

Phenoxatellurine oxide[140] and 10-ethyl-3,7-dimethylphenotellurazine oxide[131] (which reacts readily with nitric acid and acetic acid forming dinitrates (diacetates)) were obtained from Te, Te-dichlorides (dibromides) by treating them with wet silver oxide or KOH in water solution.[140,131] Another type of tricoordinated derivatives of

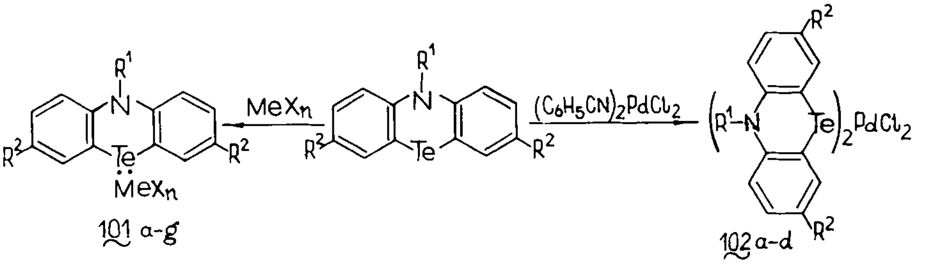
91, 10-alkylphenotellurazine perchlorates, were obtained, as was also the case with telluroxanthene,[78] via interaction of 10-alkylphenotellurazines with methyl iodide in the presence of an equimolar amount of silver perchlorate.[131]

Phenoxatellurine and 10-alkylphenotellurazines form molecular complexes of two different types in which either a tellurium atom or the π-system of benzene rings act as n- or π-electron-donating moieties, respectively. Charge-transfer complexes of phenoxatellurines with the following acceptors have been studied: 1,3,5-trinitrobenzene (TNB),[142–144] picric acid (PA),[142] picryl chloride (PC),[142] tetracyanoethylene (TCNE),[145,146] chloranil (CA),[146] tetracyanoquinodimethane (TCNQ).[147] Molecular complexes formed by compounds **88** and **91** and inorganic acceptors such as mercury,[131] silver,[131] and palladium salts[131] as well as complexes with rhodium(I)[83] and manganese carbonyls[148,149] have also been studied.

Charge-transfer complexes of 1 : 1 composition were mostly isolated in the crystalline state. In all cases, broad absorption maxima were observed in the UV spectra, typical of weakly bound CT-adducts.[146] Data on equilibrium constants, extinction coefficients, and thermodynamic parameters for charge-transfer complexes of phenoxachalcogenines are given in Table VIII.

There exist contradictory suggestions concerning the structures of these complexes (of n- or π-type). The following facts favor the conclusion as to the n-σ type of the complexes considered: 1) dimethyl telluride as well as phenoxatellurine do form complexes with TNB whereas diethyl ether and other dialkyl ethers do not;[143] 2) TNB complexes with diphenyl ether as well as with dibenzo-p-dioxine absorb in the same region;[143,144] 3) TNB complexes with diethyl sulfide and phenoxathiin have nearly identical absorption maxima.[143,144] A different view is held by the authors of.[146,147] Lack of correlation between the electronegativities of the chalcogen atoms and the absorption band maxima and small variations in the absorbance and thermodynamic parameters on passing from dibenzo-p-dioxin to phenoxatellurine led them to assume delocalized π-orbitals of all the phenoxachalcogenines as the source of binding them to the electron acceptors.

10-Alkylphenotellurazines, like diorganyl tellurides,[148] easily form molecular complexes with salts of various metals.[131] With mercury and silver salts, 10-alkylphenotellurazines form the 1 : 1 complexes **101a–g**, whereas with the benzonitrile complex of palladium chloride, **91** produce the 2 : 1 complexes **102a–d**.[131] The



101 a-g

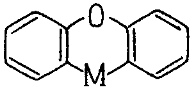
102 a-d

$R^1 = C_2H_5$, $R^2 = H$, MeX_n = a) $HgCl_2$, b) $HgBr_2$;
$R^1 = C_2H_5$, $R^2 = CH_3$, MeX_n = c) $HgCl_2$, d) $HgBr_2$;
e) $AgNO_3$, f) $AgClO_4$; $R^1 = C_2H_5$, $R^2 = Br$,
MeX_n = g) $HgCl_2$

a) $R^1 = C_2H_5$, $R^2 = H$;
b) $R^1 = C_2H_5$, $R^2 = CH_3$;
c) $R^1 = CH_3$, $R^2 = Br$;
d) $R^1 = R^2 = CH_3$

TABLE VIII

Thermodynamic parameters for the formation of charge-transfer complexes of phenoxachalcogenines



with acceptors

M	Acceptor	λ_{max}, nm	ϵ	$K_{(20°)}$ 1/mol	ΔH kcal/mol	ΔG kcal/mol	ΔS e.u.	I_D (eV)	Reference
O	TNB	410–415	—	12.2 ± 0.3	—	—	—	—	143, 144
	TCNE	640–650	200 ± 100	1.6 ± 0.5	−1.95 ± 0.2	−0.00 ± 0.02	−6.7 ± 0.7	7.79[a]	146
	TCNQ	650–670	117[b]	5.29[c]	−3.12	—	−7.35	—	147
S	TNB	420	—	12.8 ± 1.5	−3.2 ± 1.3	—	—	—	143, 144
	TCNE	670–680	400 ± 100	2.0 ± 0.5	−2.1 ± 0.3	−0.04 ± 0.02	−7.2 ± 1.0	7.79	146
	TCNQ	695–715	233[b]	3.75[c]	−2.41	—	−5.58	—	147
Se	TNB	415–420	725	11.2 ± 1.7	—	—	—	—	143, 144
	TCNE	660–680	485 ± 100	1.5 ± 0.5	−2.1 ± 0.2	−0.02 ± 0.02	−7.2 ± 0.7	7.71	146
	TCNQ	670–690	189[b]	6.02[c]	−1.36	—	−1.02	—	147
Te	TNB	440	1020	13.2 ± 2.0	−1.9 ± 0.8	−1.52 ± 0.09	—	—	142–144
	PA	420	900	8.4 ± 1.8	−1.9 ± 0.8	−1.52 ± 0.09	—	—	142–144
	PC	420	820	8.0 ± 2.1	—	—	—	—	142
	TCNE	707±3	—	—	—	—	—	7.60[d]	145
	TCNE	700–720	1100 ± 100	−1.0 ± 0.3	−2.0 ± 0.4	0.00 ± 0.02	−6.8 ± 1.3	7.59	146
	TCNQ	735–775	135[b]	11.8[d]	−4.93	—	−3.49	—	147

[a] Donor ionization potentials were calculated with the aid of the equation $0.87\ I_D = h\nu + 4.86$;

[b] Mean values of • are given obtained for different temperatures (10–30 °C);

[c] Value of ϵ at 20 °C;

[d] The ionization potentials of 2,8-dimethyl-, 2,8-dichloro- and 2,8-difluorophenoxatellurine are 7.54, 7.74 and 7.81 eV, resp.[145]

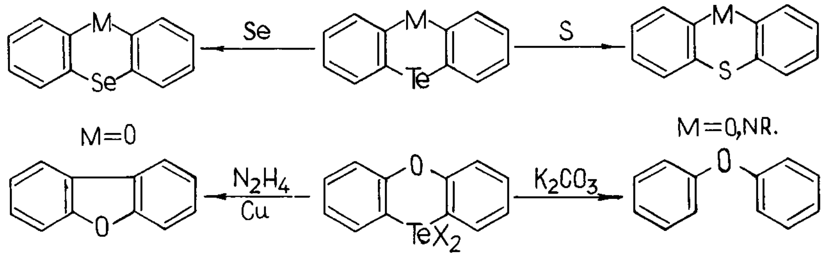
complexes with mercury and palladium salts are stable crystalline compounds, while the complexes with silver salts are unstable and decompose soon after their isolation. Attempts to isolate analogous copper complexes failed as was also the case with telluroxanthene,[78] on account of the oxidation of the 10-alkylphenotellurazines to the corresponding tellurium dihalides[131] upon treatment with CuX_2.

Phenoxatellurine (POT) reacting with pentacarbonylmanganese chloride[149] forms a complex $[(POT)_2Mn(CO)_3]Cl$ and 10-alkylphenotellurazines (PTA) (10-ethyl-3.7-dimethylphenotellurazine, among others) in reaction with $[Rh(CO)_2Cl]_2$ and $RhOxq(C_8H_{14})CO$ behave similarly to telluroxanthene forming the complexes $Rh(PTA)_2COCl$ and Rh(PTA)OxqCO. In the former complex ν_{CO} is observed at 1962 cm^{-1} (suspension) and at 1971 cm^{-1} (solution in $CHCl_3$) and in the latter at 1940, 1939 cm^{-1} (suspension) and at 1964 cm^{-1} (solution in $CHCl_3$). As in complexs with telluroxanthene, 10-ethyl-3,7-dimethylphenotellurazine can be displaced in these complexes by phosphines.[83]

One should also note that phenoxatellurine forms colored complexes with phenoxatellurines having substituents in the ring: 2-chloro-8-methyl-,[121,122] 2-nitro-[121] (composition 1:1) and 2,8-dinitrophenoxatellurine (composition 1:2).[121]

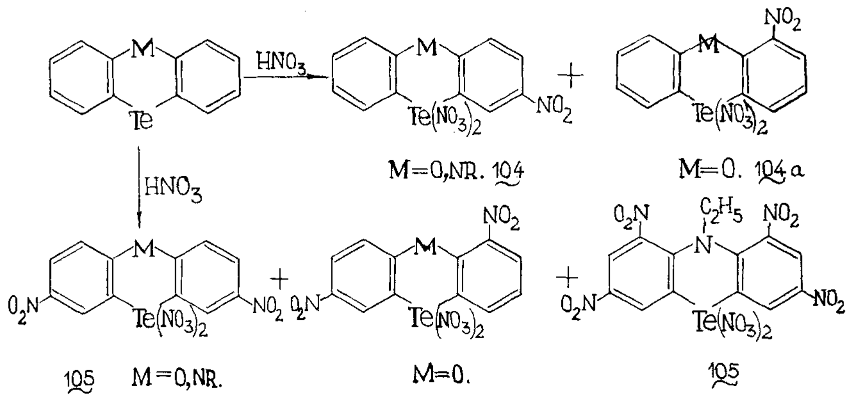
POT when oxidized at the rotating platinum electrode in acetonitrile solution containing $LiClO_4$ is converted to the corresponding cation-radical (absorption maximum 525 nm) which after a fast dimerization forms an associate with one molecule of POT $[(POT^{+\cdot})_2POT](ClO_4^-)_2$ **103** (λ_{max} 425 nm).[150] It has also been isolated in the crystalline state. These data allowed one to interprete the observations of Drew[136] who noted the formation of bluish-violet intermediates when POT was oxidized with nitric acid or when POT 10,10-dinitrate was reduced with sulfur dioxide. Dark-colored compounds were also formed when solid phenoxatellurines were ground together with their dinitrates. The coloration disappeared, however, upon treatment of these compounds with water, ethanol, etc.[136] When POT was dissolved in concentrated sulfuric acid, it was oxidized to the 10,10-di(bisulfate).[122,136] The formation of an intermediate complex salt with the proposed structure $[(POT^{\cdot+})_2POT](HSO_4^-)_2$ by analogy with **103** has been suggested.[150]

A number of reactions of phenoxatellurines and 10-alkylphenotellurazines proceed with the extrusion of the tellurium atom. Thus, heating phenoxatellurines[111,112,114–116] and 10-ethylphenotellurazines[131] with sulfur gives the corresponding phenothiins or phenothiazines, respectively. Elemental selenium acts in analogous reactions similarly to sulfur.[151] When phenoxatellurine was fused with selenium, phenoxaselenine was produced which was separated from unreacted phenoxatellurine by treatment with bromine. Boiling the mixture of phenoxaselenine 10,10-dibromide and phenox-



atellurine 10,10-dibromide with acetone leads to their separation. Phenoxaselenine dibromide reacts with acetone to form bromoacetone and phenoxaselenine whereas phenoxatellurine 10,10-dibromide remains unchanged. In this way, the first synthesis of phenoxaselenine was accomplished. Treatment of phenoxatellurine 10,10-dihalides with boiling aqueous K_2CO_3 gives diaryl ethers.[121,133] Hydrazine in the presence of copper powder reacts with phenoxatellurines to give various dibenzofurans.[152]

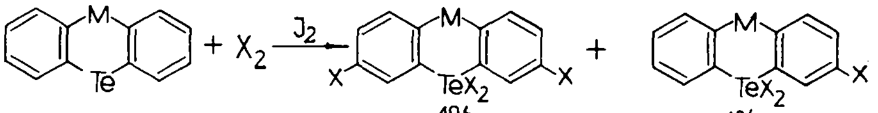
Typical of compounds **88** and **91** is also the possibility of nitration and halogenation. As strong oxidizing agents, nitric acid and halogens first convert **88** and **91** to Te, Te-dinitrates (dihalides). Treatment of phenoxatellurine with concentrated nitric acid (d = 1.42) gives, mainly, 2 nitrophenoxatellurine 10,10-dinitrate **104** (M = O) along with a small amount of the 4-isomer.[121] In the case of 10-ethylphenotellurazine the only product isolated was 3-nitro-10-ethylphenotellurazine 5,5-dinitrate **104** (M = NC_2H_5).[131] When phenoxatellurine and 10-ethylphenotellurazine interacted with concentrated nitric acid (d = 1.51), the major reaction products are 2,8-dinitrophenoxatellurine **105** (M = O)[121] and 3,7-dinitro-10-ethylphenotellurazine dinitrate **105** (M =NC_2H_5),[131] respectively. In the case of phenoxatellurine, some 4,8-dinitrophenoxatellurine 10,10-dinitrate **104a** is also formed, and in the case of 10-ethylphenotellurazine, when the reaction time is long enough (2 hours) 1,3,7,9-tetranitro-10-ethylphenotellurazine 5,5-dinitrate **105** is produced.[131] The data on the nitration of phenoxatellurine and 10-ethylphenotellurazine are presented in Scheme XI.



SCHEME XI. The products of nitration of phenoxatellurine and 10-ethylphenotellurazine

Nitrophenoxatellurines[121] and nitrophenotellurazines[131] are transformed to amines under the action of tin and hydrochloric acid. The amines can then be converted to mono- and bis(diazo) compounds.[121] Electro chemical reduction of 2-nitro- and 2,8-dinitrophenoxatellurines in *N*, *N*-dimethylformamide containing tetrabutylammonium perchlorate produces the corresponding anion-radicals.[153]

The halogens can be easily introduced into the benzene rings of phenoxatellurine via its 10,10-dihalides. For instance, the bromination of phenoxatellurine 10,10-dihalides with bromine in the presence of catalytic amounts of iodine or iron gives mainly 2,8-dibromo phenoxatellurine 10,10-dibromide (**106**, M = O, X = Br) and also 2-bromophenoxatellurine 10,10-dibromide **106a**.[133] The best yields of the former compound are achieved when phenoxatellurine 10,10-diiodide is used as the starting material. The more active bromine replaces iodine at the tellurium atom[133] in the course of the reaction. In a similar way, phenoxatellurine 10,10-diiodide reacts with chlorine producing 2,8-dichlorophenoxatellurine 10,10-dichloride (**106**, M = O, X = Cl).[113] Treatment of 10-ethylphenotellurazine 5,5-diiodide with bromine leads to 10-ethyl-3,7-dibromophenotellurazine 5,5-dibromide (**106**, M = NC_2H_5, X = Br).[131]



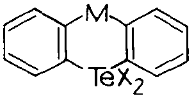
106 106a

M=O, X=Cl,Br. M=NC_2H_5,X=Br. M=O, X=Br.

Phenoxatellurine and its derivatives,[114,154] phenotellurazine derivatives, and 10-telluroniaanthracene perchlorates[155] possess antimicrobial properties which are strongest in tetracoordinated derivatives of phenoxatellurine and phenotellurazine.

4.4. Structural Peculiarities of Tricyclic Tellurium-Containing Heterocycles

The structure of the following type **107** compounds has been investigated by X-ray analysis: telluroxanthene,[95] 9,9'-bis(telluroxanthenyl),[95] 10-ethyl-3,7-dimethylphenotellurazine,[156] phenoxatellurine,[56] telluranthrene,[157] and phenoxatellurine 10,10-dichloride,[150] 10,10-di(trifluoroacetate),[141] 10,10-diiodide,[58] and 10,10-dinitrate.[159] Data on bond lengths and valency angles for these compounds are given in Table IX.



107

These tricyclic systems have a butterfly conformation. In contrast to the corresponding monocyclic compounds their central rings possess the boat conformation. The dihedral angles of bending along the Te-M bonds in compounds **107** depend on the nature of the heteroactoms M as well as on the electronegativity of the substituents at the tellurium atom (see Table IX). Thus, while the dihedral angle for telluranthrene[157] is 124°, for phenoxatellurine it is 145°.[56] For 10,10-disubstituted phenoxatellurines, the dihedral angles decrease in the order: Cl > $OCOCF_3$ > I > ONO_2 which has been interpreted in terms of the electronegativity of the substituents at the tellurium atom.[158,159]

The valency angles C-Te-C, unlike the dihedral ones, vary comparatively little when the nature of M and X is changed; they lie in the range of 90–95°. The angles between electronegative axial substituents in 10,10-disubstituted phenoxatellurines exceed, as is also the case for acyclic σ-telluranes,[57] 180°, in other words, the electronegative substituents suffer the greatest repulsion from the lone electron pair of the tellurium atom.

TABLE IX

Bond lengths (Å) and valency angles in compounds 107

M	X	Te-C	Te-X	Angle C-Te-C	Angle X-Te-X	Dihedral angle
CH_2	—	2.10[a]	—	89.7	—	129.6
$CHC_{13}H_9Te$[b]	—	2.10	—	91.4	—	139.6
NC_2H_5[c]	—	2.11	—	89.8	—	137.7
O	—	2.10	—	89.4	—	145.0
Te	—	2.11	—	95.6	—	124.0
O	Cl	2.09	2.53	90.7	183.2	151.0
O	$OCOCF_3$	2.07	2.20	91.5	192.5	156.0
O	I	2.10	2.95	91.5	183.6	163.9
O	ONO_2	2.07	2.20	93.5	192.0	175.0

[a] Mean values of bond lengths for Te-C and Te-X are given.

[b] Data are given on the structure of 9,9'-bis(telluroxanthenyl); mean values of valency and dihedral angles for both telluroxanthene fragments are presented.

[c] Data are given on the structure of 3,7-dimethyl-10-ethylphenotellurazine.

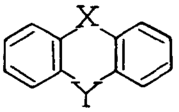
Special attention has been paid to the structures and spectral characteristics of tricyclic tellurium-containing systems in solution.[128,132,160–162] The conformations of the tellurium and related systems **108** in solution have been studied by the determination of dipole moments[160] (Table X).

The conformation of the tricyclic compounds of type **108** is determined by two opposing factors: the π-conjugation between aromatic nuclei and heteroatom lone pair orbitals favoring planarization and steric constraint leading to heterocyclic puckering.

In solution the compounds in question have the butterfly conformation[160] although the dihedral angles as determined by dipole moment measurements are greater in the

TABLE X

Dipole moments (D) of (benzene, 25 °C)



(108)

X	Y	μ	Dihedral angle[a]
O	0	0.55	163.8 (180[163])
S	0	1.18	163.4 (141[164])
Se	0	0.73	162.6
Te	0	0.38	172.2 (145[56])

[a] Values of dihedral angles are given at which the calculated dipole moments coincide with the experimental values. Within parentheses, dihedral angles are given, determined by X-ray structure analyses.

crystalline state. An exception to this is dibenzo-*p*-dioxin which is planar in the crystalline state[163] whereas, according to the dipole moment data, it should have a bent structure. This may be due to an incorrect evaluation of the atomic polarization because the correct estimation of the latter value is especially important with respect to molecules with small dipole moments.

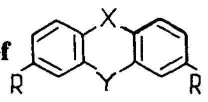
The nonplanar structure of the tricyclic compounds **108** has also been confirmed by photoelectron spectroscopy (PES).[160] The orbital ionization potentials and the UV spectra[132,160] are presented in Table XI.

The energies of the first two MO's in the PES of phenoxachalcogenines depend little on the nature of the chalcogen, although in the case of planar conformations their magnitude should have decreased on passing from dibenzo-*p*-dioxin to phenoxatellurine. But the deviation from planarity reduces both the π-interaction between the chalcogen atom and the benzene nuclei and the ring strain which leads to an approximate constancy in the energies of the first two MO's.[160] At the same time, the results of semiempirical EHMO calculations indicate a predominantly planar conformation of **108**[160] in disagreement with the results of dipole moment and PES studies. The ^{13}C and ^{1}H NMR spectra were studied in.[128,161,162] Data on ^{13}C NMR spectra of **108** are given in Table XII.

Noteworthy is the significant difference of the chemical shifts of the phenoxachalcogenine C-6 atom directly bound to the chalcogen atom. The replacement of oxygen atom in dibenzo-*p*-dioxin by S, Se, and Te results in upfield shifts by 22.2, 26.0, and 40.1 ppm as compared to dibenzo-*p*-dioxin. This may be explained by the inductive effect of the chalcogens corresponding to their electronegativity as well as by the anisotropic effect of the chalcogen atoms which is largest with tellurium.[162] The chemical shifts of the C-5 atom in phenoxachalcogenines, unlike those of the C-6 atom, exhibit downfield shifts increasing in the order: S, Se, Te. This is probably caused by the fact that the σ-electron attraction of the oxygen atom exceeds the

TABLE XI

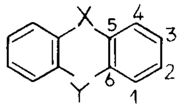
Ionization energies and UV spectra (heptane) of



R	X	Y	I(eV)	λ_{max} (log ϵ)
H	O	O	7.78, 8.76, 9.5, 9.7, 11.24, 11.5, 12.2	300(sh.[a]), 289(3.87), 228(4.73) 222(4.64), 203(w.[a])
H	O	S	7.72, 8.71, 9.4, 9.6, 10.63, 11.13, 11.7	295(3.60), 241(4.50), 238 (4.50), 220(w.)
H	O	Se	7.74, 8.67, 9.33, 9.5, 10.33, 10.9, 11.5	294(3.54), 241(4.30), 238 (4.31), 218(4.13), 202(4.34)
H	O	Te	7.61, 8.66, 9.24, 9.4, 9.94, 10.45, 11.3, 11.4	356(2.55), 290(3.62), 257 (3.91), 230(4.07), 202(4.57)
CH_3	O	Te	—	358, 298, 260, 240
Cl	O	Te	—	357, 302, 262, 244

[a] Sh.—shoulder; w.—weak

TABLE XII

^{13}C Chemical shifts of  **($CDCL_3$, 28 °C)**

X	Y	Chemical shifts, δ, pm					
		C-1	**C-2**	**C-3**	**C-4**	**C-5**	**C-6**
O	O	116.2	123.6	123.6	116.2	142.1	142.1
O	S	127.4	124.3	126.5	117.5	151.9	119.9
O	Se	129.2	124.8	128.0	118.5	152.8	116.1
O	Te	134.8	125.4	128.9	119.5	155.6	102.0
Te	Te	136.9	128.3	128.3	136.9	130.6	130.6

π-electron donation from the chalcogen atoms which decreases in the following order: S,Se,Te. The chemical shifts of the C-1, C-2, C-3, and C-4 atoms also move downfield as compared to dibenzo-*p*-dioxin and the largest difference of chemical shifts is seen for the C-1 atoms.[161]

The downfield shifts of the atoms C-1 to C-4 in **108** observed when passing from dibenzo-*p*-dioxin to phenoxatellurine fit well both with the trend noted in the ^{1}H NMR spectra[162] and the +M-effect variation in the atoms of the VIa group elements decreasing in the following order: O > S > Se > Te.[161]

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