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The Synthesis and Structure of Telluranes

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Data concerning the methods for the synthesis of organic derivatives of tellurium—σ- and π-telluranes—are surveyed and described systematically. Problems of the electronic and steric structures of their molecules, the results of structural determinations, quantum-chemical calculations, and experiments by spectroscopic and other physical research methods are examined. The bibliography includes 214 references.

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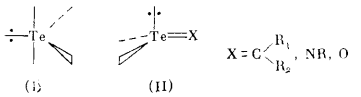
I. INTRODUCTION

The chemistry of organotellurium compounds has been investigated in considerably less detail than the chemistry of organic compounds of higher neighbours of tellurium in the Periodic Table—sulphur and selenium. The studies by Lederer and Morgan in the 1920s (see the relevant reviews[1,2]) made an important contribution to the field of organotellurium chemistry and in essence established it as a separate branch of the chemistry of organoelemental compounds. However, subsequently there was a decrease of activity in research on the methods of synthesis and reactions of organic compounds of tellurium. In the last 10–15 years there has been a renewal of interest in the organic chemistry of tellurium and there has been a sharp increase of the number of publications in this field. Most of them are described systematically in a review[2] and also in periodic collections[3,4]. Finally, a separate monograph devoted to the organic chemistry of tellurium has been published recently[5].

The study of the synthesis, reactions, and structures of various organotellurium compounds is being prosecuted on an increasing scale. It is now necessary to examine in detail data for organotellurium chemistry differentiated into individual classes rather than surveying the results for the entire field of such chemistry.

This review is devoted to tetra- and tri-coordinate organic derivatives of tellurium–telluranes. In tellurane structures the tellurium atom expands its electronic valence shell to ten electrons (or five electron pairs). The ability to form stable compounds in this hypervalent state is also manifested by sulphur and selenium, but there is no doubt that it is shown most strikingly by tellurium. The latter not only gives rise to stable π-telluranes (π-sulphuranes and π-selenuranes are as a rule also entirely stable) but also σ-telluranes. In contrast to their tellurium analogues, σ-type sulphuranes are usually stable only in cyclic structures[6-8].

The difference between σ- and π-telluranes is that in the former all five valence electron pairs occupy localised σ orbitals (I), while in π-telluranes one electron pair of tellurium forms a π bond with a neighbouring element in the Second Period (II).



(I) (II)

In agreement with predictions of valence shell electron pair repulsion theory[9], σ- and π-telluranes have different bond configurations at the central tellurium atoms, which is responsible for large differences between their physical properties and reactivities. Nor is there any similarity between the methods of synthesis of these compounds. Because of this, data for σ- and π-telluranes are examined in separate sections of the review. Initially a systematic account is given of the methods of synthesis of different telluranes and then the results of experimental and theoretical studies on their structures and reactivities are discussed.

II. THE SYNTHESIS OF σ-TELLURANES

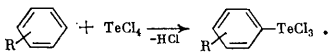
In the series of σ-telluranes (I) we shall examine below only true organotellurium compounds, i.e. those in which at least one of the four σ bonds is linked to a carbon atom. In terms of the number of such bonds, it is convenient to subdivide σ-telluranes into mono-, di-, and tetra-organo-derivatives. Such subdivision is particularly useful, since the synthetic approaches to compounds of these types are significantly different.

1. METHODS OF SYNTHESIS OF MONOORGANO-DERIVATIVES OF TELLURIUM(IV)

The most important monoorgano-derivatives of tellurium(IV) are the trihalides, the methods of synthesis of which are extremely varied.

(a) Telluration of an Aromatic Ring

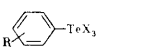
The direct method of synthesis of aryltellurium trichlorides—the telluration reaction (1)—is based on the interaction of $TeCl_4$ with benzene derivatives having fairly powerful electron-donating substituents. This reaction was achieved by Rust[10] as early as 1897 and was later investigated by Rohrbaech[11] and Lederer[12], but a correct interpretation of the structures of the compounds obtained was given only by Morgan[13,14]. When equimolar amounts of tellurium tetrachloride and phenetole were allowed to react in dry chloroform, *p*-ethoxyphenyltellurium trichloride was obtained[13]. Anisole, certain other alkyl aryl ethers, and other compounds also undergo this reaction (Table 1)[15-18]:



(I.1)

On the other hand, *p*-nitroanisole, the aromatic ring of which is highly deactivated by the nitro-group, does not react in this way[14].

Table 1. Mono-organo-derivatives of tellurium(IV) of the type $RTeX_3$.

R	X	M.p., °C	Methods of preparation	Yield, %	Refs.
Compounds of the type 					
H	Cl	215—217	(I.4)—(I.9)	69—98	45, 48, 49, 50, 52
H	Br	228—229	(I.9)	44	54
H	I	190—195	(I.9)	27	54
2-CH_3	Br	165—167	(I.9)	75	182
3-CH_3	Cl	165,5—168	(I.8)	60	50
4-CH_3	Cl	187—188	(I.4), (I.8), (I.9)	70	45, 50, 54
4-CH_3	Br	224—226	(I.9)	33, 86	54, 55
4-CH_3	I	179—180	(I.9)	54, 66	54, 55
4-OCH_3	F	176—178	(I.14)	—	26
4-OCH_3	Cl	191—193	(I.1)	90	14
4-OCH_3	Br	189—190	(I.9)	100	14, 17
4-OCH_3	I	132—133	(I.9)	93	17
4-OC_2H_5	F	204	(I.14)	—	26
4-OC_2H_5	Cl	182—183	(I.1)	92	13
4-OC_2H_5	Br	205—208	(I.9)	100	17
4-OC_2H_5	I	133—134	(I.9)	100	17
4-OC_3H_7	Cl	174	(I.1)	76	18
4-OC_4H_9	Cl	169	(I.1)	85	18
4-OC_6H_5	Cl	160—161	(I.1)	87	16
4-OC_6H_5	Br	206—207	(I.9)	100	17
4-OC_6H_5	I	160—161	(I.9)	100	17
4-$OCOCH_3$	Cl	195	(I.1)	64	18
4-$OCOC_2H_5$	Cl	198	(I.1)	58	18
2-(4′$CH_3C_6H_4O$)	Cl	180—185	(I.4)	80	44
2-(4′-$HOOCC_6H_4O$)	Cl	205—206	(I.4)	—	44
4-OH	Cl	223—225	(I.1)	84	15
4-OH	I	140—150	(I.12)	97	17
4-$NHCOCH_3$	Cl	—	(I.1)	—	15
2-SC_6H_5	Cl	213—215	(I.4)	81	17
4-SCH_3	Cl	188—190	(I.1)	51	18
4-SC_6H_5	Cl	165—166	(I.1)	42	17
4-SC_6H_5	Br	206—207	(I.9)	100	17
4-SC_6H_5	I	180	(I.9)	100	17
3-F	Cl	205—206	(I.4), (I.9)	94, 100	18, 174
3-F	Br	220—222	(I.9)	100	174
4-F	Cl	241—242	(I.9)	100	174
4-F	Br	265—267	(I.9)	100	174
3-Cl	Cl	210—211	(I.4)	95	55
4-Cl	Cl	225	(I.4)	96	18
4-Cl	Br	241	(I.9)	94	55
4-Cl	I	189—190	(I.9)	70	55
3-Br	Cl	193—194	(I.4)	92	55
4-Br	Cl	220	(I.1), (I.4) (I.8)	38, 95, 50	24, 18, 50
4-Br	Br	237	(I.9)	90	55
4-Br	I	176—180	(I.9)	63	55
2-CHO	Cl	195—200	(I.9)	95	182
3-NO_2	Cl	170—172	(I.4)	64	18
4-NO_2	Cl	193—195	(I.4)	56	18
2,3-C_4H_4	Cl	177—181	(I.1), (I.4)	24, 96	18, 17
2,3-C_4H_4	Br	159—160	(I.9)	100	17
2,3-C_4H_4	I	133	(I.9)	100	17
3,4-C_4H_4	Cl	200—202	(I.4)	85	46
3,4-C_4H_4	Br	212—215	(I.9)	100	56
2-Fluorenyltellurium trichloride	Cl	255 (decomp.)	(I.1)	53	18
3-Fluoranthyltellurium trichloride	Cl	241—243	(I.1)	18	18
2,4-$(OCH_3)_2$	Cl	155—156	(I.1)	68	13
3,4-$(OCH_3)_2$	Cl	181	(I.1)	81	13, 18
3-OH, 4-OCH_3	Cl	157—158	(I.1)	—	13
2-CH_3, 4-OCH_3	Cl	154	(I.1)	—	14
3-CH_3, 4-OCH_3	Cl	232—233	(I.1)	—	14
2-OCH_3, 5-CH_3	Cl	135	(I.1)	—	14
2-OCH_3, 5-Br	Cl	184	(I.1)	—	14
2-OCH_3, 5-Br	Br	153	(I.9)	—	14
2,3,4,5,6-F_5	Cl	—	(I.4)	—	47
Aliphatic compounds of the type $RTeX_3$					
CH_3	F	—	(I.12)	—	59
CH_3	Cl	137—139	(I.9)	63	51
CH_3	Br	140	(I.9)	—	52
CH_3	I	175—178	(I.9)	77	53
C_2H_5	Cl	114—115	(I.9)	75	183
C_2H_5	Br	138—140	(I.9)	77	53
C_2H_5	I	178—180	(I.9)	58	53
—$CH(CH_3)$—COOH	Br	139—141	(I.9)	—	14
—$CH_2CHClCH_3$	Cl	—	(I.2)	—	40
—CH_2CH_2Cl	Cl	118	(I.2)	—	41
—$CH_2CHClCH_2CH_3$	Cl	—	(I.2)	—	40
	Cl	111—114	(I.2)	—	37
	I	175—190	(I.11)	88	38
—$CH=C(Cl)C_6H_5$	Cl	205—215	(I.4)	94	43
—$C=C_6H_5=C(Cl)C_6H_5$	Cl	125—128	(I.4)	70	43

The telluration of an aromatic ring by tellurium tetrachloride is a typical electrophilic substitution reaction. It proceeds only when the benzene ring is strongly activated by electron-donating substituents and the electrophile is probably the cation $TeCl_3^+$. The tendency of $TeCl_4$ to undergo ionisation of the type $TeCl_3^+Cl^-$ or $TeCl_3^+TeCl_5^-$ in the crystalline phase and in solution is confirmed by Raman spectroscopic[19,20] and conductimetric[21] data. The stabilisation of the cation $TeCl_3^+$ on formation of tellurium tetrachloride complexes with Lewis acids, particularly with $AlCl_3$ in the form of $TeCl_3^+AlCl_4^-$,[22,23] was used by Bergman[24], who was able to achieve the interaction with tellurium tetrachloride, in the presence of catalytic amounts of $AlCl_3$, of a number of compounds (benzene, toluene) which had previously been believed to be inert in relation to this reagent. This gave small yields of the corresponding aryltellurium trichlorides (see Section 2 for a description of the synthesis of diaryltellurium dichlorides by this method). By carrying the reaction between benzene and tellurium tetrachloride in the presence of a twofold–threefold excess of $AlCl_3$, Günther et al.[25] later obtained phenyltellurium trichloride (isolated as the ditelluride), diphenyltellurium dichloride, and triphenyltelluronium chloride, depending on the reaction time.

In an early study Morgan already showed that the $TeCl_3$ group enters exclusively in the *p*-position (evidently owing to its large size) relative to the electron-donating substituent in the benzene ring, occupying the *o*-position only if the *p*-position is already occupied[13]. This was demonstrated by the fact that, when di-(*p*-ethoxyphenyl) ditelluride—the product of the reduction of the corresponding tellurium trichloride obtained by the reaction of $TeCl_4$ with phenetole—is treated with nitric acid, *p*-nitrophenetole is formed exclusively. The high selectivity of *p*-substitution by the trichlorotelluro-group in reactions of monosubstituted benzenes with tellurium tetrachloride has also been confirmed by infrared and ^1H NMR spectroscopic data[18,26]. The high selectivity of the telluration reaction and the fact that only one $TeCl_3$ group can be introduced into the ring during it constitute an appreciable difference between this process and the mercuration reaction in which the formation of polymercurated products is a normal phenomenon[27].

The study of the telluration reaction, starting with early investigations, involved a gradual expansion of the range of compounds with electron-donating functions which can be made to undergo this reaction—alkyl aryl ethers and then thioethers[17,18], acetanilide[15], etc. As already stated, compounds with a smaller π-electron density in the aromatic ring (benzene, toluene) could be made to react with $TeCl_4$ only by enhancing the electrophilic properties of the latter as a result of the formation of the complex $TeCl_3^+AlCl_4^-$. On the other hand, when the most powerful electron-donating substituent (the dimethylamino-group) is introduced into the aromatic ring, the corresponding telluration product cannot be obtained, since dimethylaniline forms a complex with tellurium tetrachloride (for its composition and reactions, see Section 2). For the same reason, *C*-derivatives are not formed with $TeCl_4$ by other nitrogen-containing bases: aromatic amines[28,29], pyridines[30-32], quinolines[31], acridines[31], and Schiff bases[33]. In contrast to these compounds, certain polycyclic hydrocarbons (naphthalene, fluorene, and fluoranthene) readily interact with tellurium tetrachloride without additional activation of its rings by electron-donating substituents and form respectively 1-naphthyl-, 2-fluorenyl-, and 3-fluoranthyltellurium trichlorides[18].

The synthesis of other aryltellurium trihalides—tribromides, and tri-iodides—by direct telluration is difficult

owing to the lower reactivity of the corresponding tellurium tetrahalides compared with the tetrachloride. The results of a study[34] where it is claimed that in the interaction of tellurium tetrabromide with benzoquinone, naphthoquinone, anthraquinone, and pyrrole the corresponding tellurium tribromides were isolated therefore require additional confirmation.

The possibilities of the telluration reaction are far from exhausted: hitherto, the main tellurating agent has been tellurium tetrachloride, but, by analogy with mercuration and thallation reactions, in which mercury and particularly thallium halide are relatively inactive, the study of the possibility of employing instead of $TeCl_4$ another tellurating agent, for example tellurium tetra-acetate or tetrakistrifluoroacetate, may extend the region where the direct telluration reaction is applicable.

(b) Telluration of Aliphatic Compounds

Organotellurium trichlorides can be synthesised also by the interaction of tellurium tetrachloride with aliphatic compounds containing active methyl and methylene groups[35]:

$$RCOCH_2R' + TeCl_4 \xrightarrow{-HCl} RCOCH(TeCl_3)R' .$$

The early publications by Morgan and coworkers[36] contain interesting but insufficiently firmly demonstrated data concerning the interaction of tellurium tetrachloride with acetic anhydride. One of the possible pathways in this reaction, according to the authors, involves the formation of a mixture of trichlorotelluroacetic acid Cl_3TeCH_2COOH, its anhydride $(Cl_3TeCH_2CO)_2O$, and methylenebis(tellurium trichloride) $CH_2(TeCl_3)_2$. The pathways followed in the formation of the latter are, however, obscure and the reliability of the structure attributed to it is open to doubt.

The ability of tellurium tetrachloride to react with homologues of acetic anhydride diminishes rapidly with increase in the size of the hydrocarbon chain. Whereas trichlorotelluropropionic acid was obtained in the reaction with propionic anhydride and identified as the ditelluride, the reactions with butyric and isovaleric anhydrides involve the reduction of tellurium tetrachloride and the products formed could not be identified[14].

(c) The Addition of $TeCl_4$ to Multiple Bonds

Organotellurium trichlorides can also be obtained by the electrophilic addition of tellurium tetrachloride to a double bond:

$$R{-}CH{=}CH{-}R' + TeCl_4 \rightarrow R{-}\underset{TeCl_3}{CH}{-}CHCl{-}R' \qquad (I.2)$$

Campos and Petragnani[37,38] showed that tellurium tetrachloride reacts with cyclohexene in carbon tetrachloride, yielding 2-chlorocyclohexyltellurium trichloride. On the other hand, styrene, di-isobutene, and 1,4-diphenylbuta-1,3-diene only reduce tellurium tetrachloride to tellurium in carbon tetrachloride[38]. It is of interest to note that $TeCl_4$ is reduced to tellurium also when cyclohexene interacts with tellurium tetrachloride in the absence of a solvent[38,39]. Tellurium tetrachloride can add also to propene[40,41], giving rise to 2-chloropropyltellurium chloride or di-(2-chloropropyl)tellurium dichloride, depending on the reaction conditions. Earlier data for the addition of $TeCl_4$ to butene[42], where the formation of only two isomeric di(chlorobutyl)tellurium dichlorides was postulated and the formation of 2-chlorobutyltellurium trichloride was ruled out, were later revised[40].

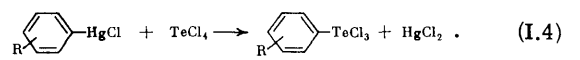
Tellurium tetrachloride adds comparatively readily also to a triple bond, forming substituted 2-chlorovinyltellurium trichlorides[43]:

$$C_6H_5C{\equiv}CR + TeCl_4 \rightarrow C_6H_5\underset{Cl}{C}{=}\underset{R}{C}{-}TeCl_3 . \qquad (I.3)$$

On the whole, one should note that the addition of the tetrahalides and other tellurium compounds to multiple bonds has still been little investigated.

(d) Exchange Reactions of Organoelemental Compounds with $TeCl_4$

In order to obtain organotellurium trichlorides by this method, organic mercury compounds are usually employed. Thus the commonest method for the synthesis of aryltellurium trichlorides[44] is based on the interaction of arylmercury chlorides with tellurium tetrachloride:



(I.4)

The best solvent in this case is dioxan, which forms a complex with mercury(II) chloride, precipitated on cooling the reaction mass. The $ArTeCl_3$ derivatives obtained in this way are usually contaminated by a small amount of mercury(II) chloride, which necessitates their careful purification. In contrast to direct telluration, which leads exclusively to *p*-substituted $ArTeCl_6$ derivatives with electron-donating substituents in the aromatic ring, this method makes it possible to obtain compounds with any relative disposition of substituents, including electron-accepting substituents[17,18,44-47].

Organic compounds of lead[48] and tin[49] have been used recently to synthesise $ArTeCl_3$:

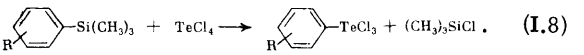
$$(C_6H_5)_3PbCl + TeCl_4 \rightarrow C_6H_5TeCl_3 + (C_6H_5)_2PbCl_2 ; \qquad (I.5)$$

$$(C_6H_5)_3SnCl + TeCl_4 \rightarrow C_6H_5TeCl_3 + (C_6H_5)_2SnCl_2 ; \qquad (I.6)$$

$$(C_6H_5)_4Sn + TeCl_4 \rightarrow C_6H_5TeCl_3 + (C_6H_5)_3SnCl . \qquad (I.7)$$

The reaction of $(C_6H_5)_3PbCl$ with $TeCl_4$ proceeds with virtually quantitative yields. Since $(C_6H_5)_2PbCl_2$ is insoluble in dioxan, this makes it possible to separate it readily from $C_6H_5TeCl_3$. Triphenyltin and tetraphenyllead chlorides also give high yields on reaction with $TeCl_4$. The separation of $C_6H_5TeCl_3$ from organotin compounds presents no difficulties, because they are sparingly soluble in the solvent employed (toluene) and are precipitated.

The recently proposed synthesis of aryltellurium trichlorides from aryltrimethylsilanes is related to these reactions. The compounds $ArTeCl_3$ are obtained in high yields on boiling $ArSi(CH_3)_3$ with $TeCl_4$ in toluene[50]:



(I.8)

(e) Synthesis from Diorganoditellurides

An important method of synthesis of organic tellurium trihalides is based on the interaction of ditellurides with halogens:

$$RTe{-}TeR + 3X_2 \rightarrow 2RTeX_3 ; \qquad (I.9)$$

X=Cl, Br, or I.

Sulphuryl or thionyl chloride is used instead of chlorine in the synthesis of tellurium trichlorides.

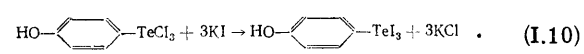
The importance of this method of synthesis consists in the possibility of employing it to obtain aliphatic tellurium trihalides: methyltellurium trichloride[51], tribromide[52], and tri-iodide[53], ethyltellurium tribromide, and tri-iodide[53], and tribromotelluropropionic acid[14]. In the synthesis of aromatic aryltellurium trichlorides this reaction has been used only when the corresponding ditelluride was comparatively readily available. However, the method is perhaps the only convenient procedure for the synthesis of aromatic tellurium tribromides and tri-iodides[14,17,54,55].

In the case of ditellurides the reaction products are as a rule tellurium trihalides, while the reaction of diorganodiselenides with halogens yields mono- and tri-halides depending on the amount of halogen employed. 2-Naphthyltellurium iodide was isolated only in the reaction of di-(2-naphthyl) ditelluride[56]. However, according to some workers[54], aryltellurium monoiodides are obtained together with tri-iodides on treatment of diphenyl and di-*p*-tolyl ditellurides with iodine in solution in carbon tetrachloride at 10–15°C. These relations can apparently be accounted for by the tendency of tri-iodides towards dissociation with liberation of free iodine, which has been noted for arylmethyltellurium di-iodides[55].

The earlier[57] claim that phenyltellurium triacetate can be synthesised by the interaction diphenyl ditelluride with lead tetra-acetate was not confirmed in a more detailed investigation[58].

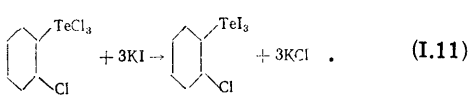
(f) Other Methods of Synthesis

In this section we shall note mainly halogen exchange reactions involving organotellurium trihalides. These reactions have still been comparatively little investigated but nevertheless in certain cases they are of preparative value, particularly when the corresponding ditellurides are not available[57]:



(I.10)

Chlorine is readily exchanged for iodine in 2-chlorocyclohexyltellurium trichloride[38]:



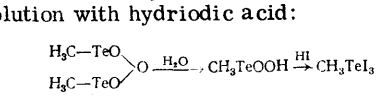
(I.11)

Methyltellurium trifluoride[59] and certain aryltellurium trifluorides[26] have been obtained by the exchange reactions (I.12)–(I.13) with AgF:

$$CH_3TeI_3 + 3AgF \rightarrow CH_3TeF_3 + 3AgI \quad ; \qquad (I.12)$$

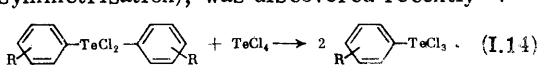
$$ArTeCl_3 + 3AgF \rightarrow ArTeF_3 + 3AgCl \quad . \qquad (I.13)$$

In an early study Drew[60] noted the formation of CH_3TeI_3 from the anhydride of methyltelluric acid on treatment of its aqueous solution with hydriodic acid:



Reactions of this type have been used more frequently to synthesise organoselenium trihalides[61].

The conversion of diaryltellurium dichlorides into aryltellurium trichlorides, based on the reaction of diaryltellurium dichlorides with $TeCl_4$ (a reaction which is the reverse of symmetrisation), was discovered recently[62]:



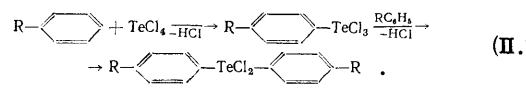
(I.14)

2. METHODS OF SYNTHESIS OF DIORGANO-DERIVATIVES OF TELLURIUM(IV)

(a) Aryltelluration of Aromatic Compounds

If the telluration reaction is carried out in the presence of an excess of an aromatic compound and under conditions more severe than those required to substitute one chlorine atom (a higher temperature), the reaction may proceed further and can lead to diaryltellurium dichlorides.

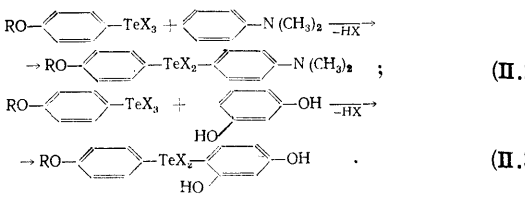
Thus, when $TeCl_4$ is refluxed with a large excess of anisole or phenetole, high yields of di-(*p*-anisyl)tellurium dichloride[13] and di-(*p*-phenetyl)tellurium dichloride[14] are obtained:



(II.1)

The two-stage mechanism of the substitution reaction is demonstrated by the fact that the interaction of *p*-methoxyphenyltellurium trichloride, prepared beforehand, with anisole and of *p*-phenoxyphenyltellurium trichloride with phenyl ether lead to di-(*p*-anisyl) and di-(*p*-phenoxyphenyl)-tellurium dichlorides respectively[16].

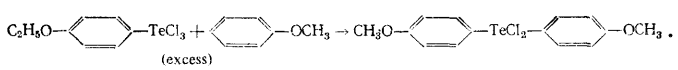
Petragnani[63] used this reaction to synthesise certain asymmetric diaryltellurium dihalides. He established that aryltellurium trichlorides and tribromides (but not tri-iodides) react with dimethylaniline and resorcinol to give aryl-(4-dimethylaminophenyl)- and aryl-(2,4-dihydroxyphenyl)-tellurium dihalides respectively:



(II.2)

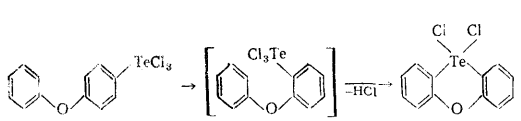
(II.3)

Interesting results were obtained by Bergman[24] in an attempt to reproduce certain earlier studies[13] of the interaction of aryltellurium trichlorides with alkyl aryl ethers. Thus, when *p*-ethoxyphenyltellurium trichloride (1 M) is heated for 6 h with anisole (4 M) at 160°C, only the symmetrical di-(*p*-anisyl)tellurium dichloride is obtained:

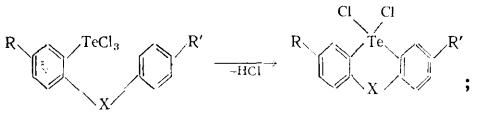


Other compounds of the type $RC_6H_4TeCl_3$ undergo a similar reaction (R = 4-Br or 4-CH_3), but the causes of the exchange of the substituent in the *p*-position relative to the trichlorotelluro-group are still obscure.

If the second aromatic ring attacked by the TeX_3 group is part of the same molecule, intramolecular electrophilic substitution takes place, leading to the formation of heterocyclic tellurium dihalides. Drew[16] observed that heating of *p*-phenoxyphenyltellurium trichloride at a high temperature leads to its conversion into 10,10-dichlorophenoxatellurin, evidently via an intermediate stage in which the *p*-isomer is converted into the *o*-isomer, which could not be isolated:

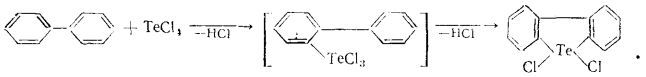


Substituted 10,10-dichlorophenoxatellurins[44,64], and 10,10-dichlorophenothiatellurin[17] were obtained analogously:

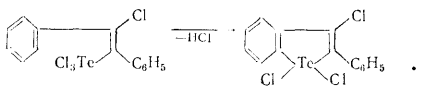


X=O or S.

A similar reaction probably occurs also when tellurium tetrachloride or tetrabromide interacts with biphenyl at a high temperature, the tellurium trichloride formed initially being converted into dichlorodibenzotellurophen[65]:

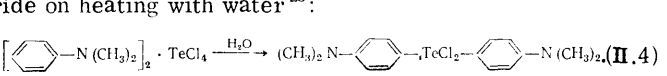


The cyclisation of 2-chloro-1,2-diphenylvinyltellurium trichloride (the product obtained by the addition of $TeCl_4$ to tolan[43]) has been used to synthesise 1,1,3-trichloro-2-phenylbenzotellurophen[66]:



Bergman[24] used the interaction of $TeCl_4$ with an excess of aromatic compounds (benzene, chlorobenzene, and bromobenzene) in the presence of $AlCl_3$ (see Section 1 concerning the role of $AlCl_3$ in the telluration reaction) in order to synthesise certain symmetrical diaryltellurium dichlorides. According to the author, their yields ranged from 30 to 45%.

As stated above, dimethylaniline does not undergo the telluration reaction directly, since its interaction with $TeCl_4$ gives rise to the complex $[PhNMe_2]_2.TeCl_4$, which is converted into di-(*p*-dimethylaminophenyl)tellurium dichloride on heating with water[28]:

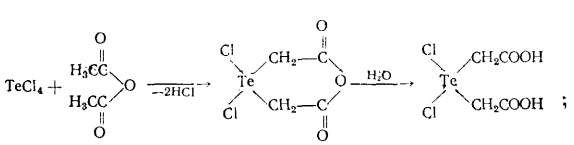


(II.4)

The mechanism of this unexpected reaction has not been studied but the structure of the final product has been clearly demonstrated both by its chemical properties and by ^1H NMR.[67]

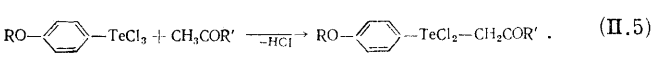
(b) Electrophilic Substitution in Methylenecarbonyl Compounds

If the electrophilic substitution reaction involving aliphatic compounds, considered above, is carried out with compounds containing not one but two activated methyl or methylene groups, then the substitution can occur in both groups. Double substitution is also promoted by an excess of the methyl- or methylene-carbonyl compounds. Thus the interaction of $TeCl_4$ with a large excess of acetic anhydride gives rise to dichlorotellurodiacetic acid (evidently as a result of the hydrolysis of the intermediate anhydride[36]), while the reactions with methyl ketones yield the corresponding diorganotellurium dichlorides[35]:



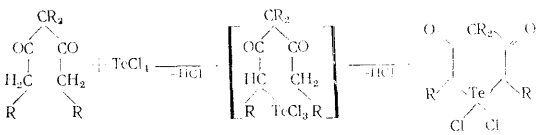
$$TeCl_4 + 2RCOCH_3 \xrightarrow{-2HCl} (RCOCH_2)_2TeCl_2 .$$

In the analogous reactions of aryltellurium trichlorides with acetone and acetophenone the products are respectively acetonyl- and acetophenonyl-aryl tellurium dichlorides[63]:



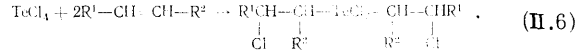
(II.5)

The formation of derivatives of tellurin-3,5-dione by interaction of $TeCl_4$ with β-diketones evidently proceeds via an intermediate organotellurium trichloride, which is converted into a cyclic diorganotellurium dichloride[68-71]:



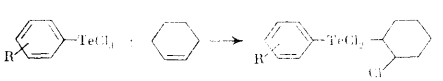
(c) The Addition of $TeCl_4$ and Organotellurium Trichlorides to a Double Bond

The involvement of two olefin molecules in the electrophilic addition of $TeCl_4$ to a double bond leads to diorganotellurium dichlorides. Various workers have shown that, by reacting with an excess of cyclohexene[40,42,72] or ethylene[41,72] in boiling CCl_4, $TeCl_4$ gives rise to addition products:



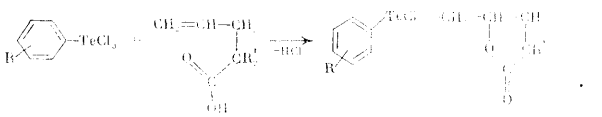
(II.6)

Petragnani[37,38] showed that, like tellurium tetrachloride, certain aryltellurium trichlorides are capable of adding to the double bond of cyclohexene to form aryl-2-chlorocyclohexyltellurium dichlorides:



However, like the reaction of tellurium tetrachloride, this reaction is not general. Unsaturated compounds such as styrene, di-isobutene, and 1,4-diphenylbutadiene are not involved in it and the initial aryltellurium trichlorides are recovered unchanged from the reaction mixture[38].

When aryltellurium trichlorides interact with γ, δ-unsaturated acids, the addition to the double bond is accompanied by cyclisation[37,38,73] with formation of 5-aryldichlorotelluro-2,2-diphenylpentanolactones:



2-Chlorocyclohexyltellurium trichloride undergoes an analogous reaction[38]. The structure of the above dichlorotellurolactone was confirmed by its specific synthesis[38] from an aryltellurium trichloride and 5-chloromercuri-2,2-diphenylpentanolactone, known previously. A study was also made of the interaction of $TeCl_4$ with but-1-ene[40,42], propene[40,41], and butadiene[41], leading to the formation of organotellurium trichlorides and diorganotellurium dichlorides.

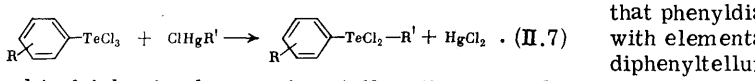
The interaction of 1,1-diarylethylenes with $TeCl_4$ is unusual. The high electrophilicity of the conjugated methylene group in compounds of this type leads to the preferential substitution of a methylene hydrogen atom. When the

reaction was carried out in ether, bis-(1,1-diarylethylene)-tellurium dichlorides were obtained in low yields instead of the products of the addition of $TeCl_4$ to the double bond:

$$(RC_6H_4)_2C{=}CH_2 + TeCl_4 \rightarrow \begin{matrix}(RC_6H_4)_2C{=}CH\\(RC_6H_4)_2C{=}CH\end{matrix}\!\!>TeCl_2 \quad .$$

(d) Exchange Reactions of Aryltellurium Trihalides and $TeCl_4$ with Organoelemental Compounds

The reaction of aryltellurium trichlorides with aryl(alkyl)-mercury chloride is very important preparatively. Depending on the structure of the initial reactants, it leads to symmetrical or asymmetric diaryltellurium dichlorides[46,75] or alkylaryltellurium dichlorides[75]:



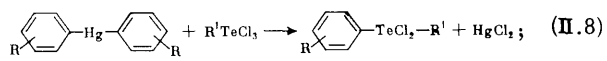
(II.7)

The method is fairly simple experimentally; the best solvent for the reaction is dioxan, which not only dissolves aryltellurium trichlorides effectively but also gives rise to a molecular compound with mercury(II) dichloride, which is precipitated on cooling the reaction mass. The use of aryltellurium tribromides and tri-iodides in this synthesis has not been studied.

In order to obtain symmetrical diaryltellurium dichlorides, it is possible to employ the reaction of arylmercury chlorides with $TeCl_4$ taken in molar proportions of 2 : 1:[2]

$$2ArHgCl + TeCl_4 \rightarrow Ar_2TeCl_2 + 2HgCl_2 \quad .$$

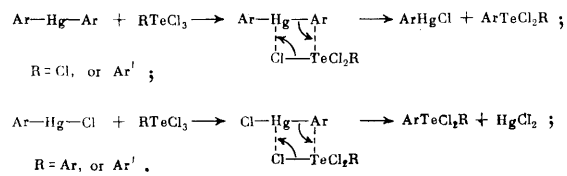
However, in this case diaryltellurium dichlorides are obtained in a less pure form than in the reaction of equivalent amounts of an arylmercury chloride and an aryltellurium trichloride. It has been shown recently that diaryltellurium dichlorides can be obtained in high yields by the reaction of a substituted diarylmercury with tellurium tetrachloride or aryltellurium trichlorides[76]:



(II.8)

R' = Cl, or Ar .

According to the view adopted[77], the mechanism of the above reactions involves the formation of a four-centre transition state:



It is of interest to note that the reaction of di-(*p*-nitrophenyl)mercury stops at the first stage: when $TeCl_4$ was introduced into the reaction, *p*-nitrophenylmercury chloride was obtained in 64% yield. This is probably associated with the reduction of the nucleophilic properties of the Mg–Ar bond in *p*-nitrophenylmercury chloride and with the weakening of the electrophilic properties of the trichlorotelluro-group (particularly in *p*-nitrophenyltellurium trichloride) compared with tellurium tetrachloride.

Organolead[48], organotin[49], and organosilicon[50] compounds have also been used to synthesise both symmetrical and asymmetric diaryltellurium dichlorides:

$$Ar_4Pb + TeCl_4 \rightarrow Ar_2TeCl_2 + Ar_2PbCl_2 \quad ; \qquad (II.9)$$

$$Ar_2Pb(CH_3)_2 + TeCl_4 \rightarrow Ar_2TeCl_2 + (CH_3)_2PbCl_2 \quad ; \qquad (II.10)$$

$$Ar_3PbCl + Ar'TeCl_3 \rightarrow ArTeCl_2Ar' + Ar_2PbCl_2 \quad ; \qquad (II.11)$$

$$Ar_4Sn + TeCl_4 \rightarrow Ar_2TeCl_2 + Ar_2SnCl_2 \quad ; \qquad (II.12)$$

$$Ar_3SnCl + Ar'TeCl_3 \rightarrow ArTeCl_2Ar' + Ar_2SnCl_2 \quad ; \qquad (II.13)$$

$$ArSi(CH_3)_3 + Ar'TeCl_3 \rightarrow ArTeCl_2Ar' + (CH_3)_3SiCl \quad . \qquad (II.14)$$

(e) The Diazo-method

The diazo-reaction for the synthesis of organic derivatives of tellurium(IV) was first used by Waters, who showed that phenyldiazonium chloride in acetone reacts on cooling with elemental tellurium, giving rise to a low yield of diphenyltellurium dichloride[78]:

$$2RC_6H_4N_2Cl + Te \rightarrow (RC_6H_4)_2TeCl_2 + 2N_2 \quad . \qquad (II.15)$$

According to Waters' observation, the yield of diphenyltellurium dichloride can be increased somewhat by employing instead of phenyldiazonium chloride its double salt with zinc chloride. Subsequently Tanijama et al.,[79] who used Waters' method, obtained a series of diaryltellurium dichlorides in low yields.

It has been shown that the principal version of Nesmeyanov's diazo-method[27], based on the decomposition of double salts of an arenediazonium chloride with tellurium tetrachloride, having the formula $(ArN_2)_2TeCl_6$,[80-82] under the influence of powdered copper in acetone[83], can be used to synthesise diaryltellurium dichlorides

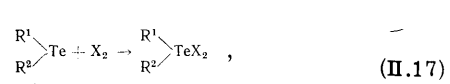
$$(ArN_2)_2TeCl_6 + 4Cu \rightarrow Ar_2TeCl_2 + 2N_2 + 4CuCl \quad . \qquad (II.16)$$

The double salts were obtained in yields of 85–95% on mixing solutions of an arenediazonium chloride and tellurium tetrachloride in concentrated HCl. The yields of diaryltellurium dichlorides are between 20 and 50% depending on the nature of the substituent.

Nesmeyanov et al.[84] proposed another version of the diazo-reaction. Benzenediazonium tetrafluoroborate was treated with zinc dust in acetone solution in the presence of $TeCl_4$. The reaction probably proceeds via diphenyltellurium dichloride and leads directly to diphenyl telluride. The yield of the latter, isolated as diphenyltellurium dibromide, is only 6%.

(f) The Synthesis of Diorganotellurium Dihalides from Other Organotellurium Compounds. The Synthesis from Diorganotellurides and Diorganoditellurides

A widely used method for the synthesis of diorganotellurium dihalides involves the addition of halogens to diorganotellurides:



(II.17)

R¹, R² = Ar or Alk; X = Cl, Br, or I.

The addition of chlorine, bromine, and iodine proceeds readily under the influence of free halogens in an inert solvent (benzene, CCl_4, and, more rarely, chloroform and ethyl ether) with slight cooling. Thionyl or sulphuryl chlorides are also frequently used to synthesise diorganotellurium dichlorides. The above reactions are used particularly frequently in converting diorganotellurides into

diorganotellurium dibromides and di-iodides[85], since direct introduction of these tellurium-containing functional groups into aromatic and aliphatic fragments is difficult.

The considerable affinity of diorganotellurides for halogens can be used in the synthesis of olefins. Like diaryl ditellurides[86], diaryl tellurides debrominate vicinal dibromides, which leads to the formation of olefins in high yields[87]:

$$ArTeAr' + \underset{Br}{\overset{|}{R}}CH-\underset{Br}{\overset{|}{C}}HR' \rightarrow ArTeBr_2Ar' + RCH=CHR' \quad .$$

Even metal salts can serve as donors of halogens. Thus the following reaction takes place on heating di-(*p*-tolyl)-telluride with certain metal chlorides in glacial acetic acid (sealed tube, 100–140°C)[88]:

$$a\,Ar_2Te + b\,MX_n \rightarrow a\,Ar_2TeX_2 + b\,MX_{n-2} \quad ;$$
$$M=Fe^{3+},\ Cu^{2+},\ \text{or}\ Hg^{2+};\ X=Cl.$$

The interaction of diaryl ditellurides with tellurium tetrahalides[86], aryltellurium trichlorides, and diarylselenium dihalides[86] also leads to diaryltellurium dihalides:

$$2Ar_2Te_2 + TeX_4 \rightarrow 2Ar_2TeX_2 + 3Te\ (X=Cl,\ Br,\ I)\ ;$$
$$2ArTeCl_3 + 2Ar_2Te_2 \rightarrow 3Ar_2TeCl_2 + 3Te\ ;$$
$$Ar_2SeBr_2 + Ar'_2Te_2 \rightarrow Ar'_2TeBr_2 + Ar_2Se + Te\ .$$

The study of the kinetics of the exchange of halogen atoms in diaryltelluride–diaryltellurium dihalide systems[89], demonstrated by Nefedov et al.,[90] was begun recently by NMR:

$$Ar_2Te + Ar'_2TeX_2 \rightleftarrows Ar_2TeX_2 + Ar'_2Te\ ;$$
$$X=F,\ \text{or}\ ClBr\ .$$

Di-(*p*-anisyl)- and di-(α-naphthyl)tellurium difluorides have been obtained by treating the corresponding diaryl tellurides with tri-(*p*-tolyl)bismuth difluoride[91,92], but they have been identified only chromatographically.

The conversion of diaryl tellurides into the corresponding difluorides is best achieved by the interaction of diaryl tellurides with SF_4 in boiling benzene[93]:

$$Ar_2Te \xrightarrow{SF_4} Ar_2TeF_2. \qquad (II.18)$$

It is of interest that the same compounds are obtained by the reaction of diaryl ditellurides with SF_4; this involves the elimination of one tellurium atom[93]:

$$Ar_2Te_2 \xrightarrow{SF_4} Ar_2TeF_2 + Te\ . \qquad (II.19)$$

Diorganotellurides can be converted not only into the corresponding dihalides but also into diacyloxy-derivatives with the aid of the addition reaction. Compounds of this type have been obtained by the reaction of dialkyl tellurides with benzoyl peroxide[94,95]:

$$\begin{matrix} R \\ R' \end{matrix}\!\!>\!Te + (C_6H_5COO)_2 \rightarrow \begin{matrix} R \\ R' \end{matrix}\!\!>\!Te\,(OCOC_6H_5)_2 \qquad (II.20)$$

and by the oxidation of diaryl tellurides with lead tetraacetate[57,58,96]:

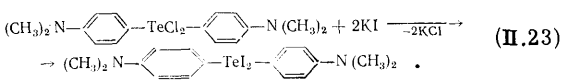
$$Ar_2Te + Pb\,(OCOCH_3)_4 \rightarrow Ar_2Te\,(OCOCH_3)_2 + Pb\,(OCOCH_3)_2\ . \qquad (II.21)$$

The most convenient method for the preparation of aliphatic di-iodides is the interaction of tellurium and alkyl iodides[4,97,98]:

$$2RI + Te \rightarrow R_2TeI_2\ . \qquad (II.22)$$

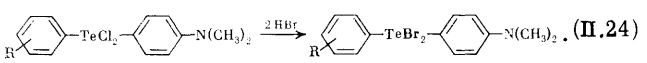
These reactions, which apparently proceed via the dialkyl telluride stage, are carried out over a period of several days on heating in sealed tubes.

Exchange of halogens in diorganotellurium dihalides. Diorganotellurium dibromides and di-iodides can also be obtained by the exchange of chlorine atoms in diorganotellurium dichlorides. For example, di-(*p*-dimethylaminophenyl)tellurium di-iodide can be obtained from the dichloride on treating the latter with an aqueous KI solution[28]:



$$(CH_3)_2N-C_6H_4-TeCl_2-C_6H_4-N(CH_3)_2 + 2KI \xrightarrow{-2KCl} (CH_3)_2N-C_6H_4-TeI_2-C_6H_4-N(CH_3)_2\ . \qquad (II.23)$$

and aryl-(*p*-dimethylaminophenyl)tellurium bromides can be synthesised by the reaction of the corresponding dichlorides with hydrobromic acid[63]:



$$R-C_6H_4-TeCl_2-C_6H_4-N(CH_3)_2 \xrightarrow{2\,HBr} R-C_6H_4-TeBr_2-C_6H_4-N(CH_3)_2\ . \qquad (II.24)$$

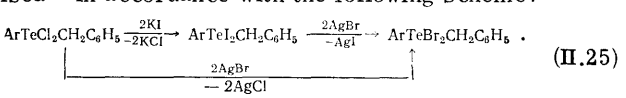
Similarly the chlorine atoms in (di-2,2-diphenylvinyl)tellurium dichlorides can be readily exchanged for bromine or iodine atoms on treatment with KBr or KI solutions[74]; according to the authors, this can involve the exchange of one or both chlorine atoms:

$$(Ph_2C=CH-)_2TeCl_2 + KX \xrightarrow[-KCl]{KX} (Ph_2C=CH-)_2TeClX \xrightarrow[-KCl]{KX} (Ph_2C=CH-)_2TeX_2$$
$$X=Br,\ \text{or}\ I\ .$$

Di-(2-chloro-2-phenylvinyl)tellurium dichloride also readily exchanges the chlorine atoms attached to the tellurium atom in the reaction with potassium iodide[43]:

$$(C_6H_5CCl=CH-)_2TeCl_2 + 2KI \xrightarrow{-2KCl} (C_6H_5CCl=CH-)_2TeI_2\ .$$

The exchange reactions are particularly useful in those cases where the corresponding diorganotellurides are unstable and direct halogenation is therefore impossible. Thus certain arylbenzyltellurium dihalides have been synthesised[75] in accordance with the following scheme:



$$ArTeCl_2CH_2C_6H_5 \xrightarrow[-2KCl]{2KI} ArTeI_2CH_2C_6H_5 \xrightarrow[-AgI]{2AgBr} ArTeBr_2CH_2C_6H_5\ .$$
$$\xrightarrow[-2AgCl]{2AgBr} \qquad (II.25)$$

The same method has been used to synthesise aryl-(2,4-dihydroxyphenyl)tellurium dibromides and di-iodides[63], since aryl-(2,4-dihydroxyphenyl)tellurium dichlorides give rise to the corresponding ditellurides on reduction.

One must also note that diorganotellurium dibromides and di-iodides can be converted into the corresponding dichlorides by treatment with thionyl chloride or chlorine and di-iodides can be converted into dibromides on treatment with bromine or phosphorus tribromide[99].

Halogen atoms are also substituted comparatively readily by fluorine atoms and acyloxy-groups. Thus, treatment of the corresponding dihalides with AgF in a suitable solvent can yield diorganotellurium difluorides[26]:

$$R_2TeX_2 + 2AgF \rightarrow R_2TeF_2 + 2AgX\ ;$$
$$R=Ar,\ \text{or}\ Alk;\ X=Cl,\ \text{or}\ I. \qquad (II.26)$$

On the other hand, when silver salts of carboxylic acids were allowed to react with diaryltellurium dichlorides, the corresponding diaryltellurium diacylates were isolated[88]:

$$Ar_2TeCl_2 + 2AgOCOR \rightarrow Ar_2Te\,(OCOR)_2 + 2AgCl\ . \qquad (II.27)$$

Synthesis from diorganotellurium oxides. The reaction of diorganotellurium oxides with hydrogen halides in an aqueous medium is sometimes also used to

synthesise diorganotellurium dihalides:

$$R_2TeO + 2HX \rightarrow R_2TeX_2 + H_2O \quad ; \qquad \text{(II.28)}$$

R=Ar, or Alk; X=F, Cl, Br, or I.

This reaction is used most frequently in relation to aliphatic compounds, which makes it possible to avoid the synthesis of dialkyl tellurides, which have an extremely unpleasant smell. Thus, when dimethyltellurium di-iodide is acted upon by moist silver oxide, a solution of the hydrated form of dimethyltellurium oxide is formed and its treatment with hydrogen halides results in the formation of dimethyltellurium dihalides [100]. Among aromatic compounds, the interaction of aqueous solutions of diaryltellurium oxides with hydrofluoric acid to form diaryltellurium difluorides is of preparative importance [67].

A general method for the synthesis of diaryltellurium diacylates, based on the interaction of diaryltellurium oxides with carboxylic acid anhydrides was discovered

Table 2. Diorgano-derivatives of tellurium(IV) of the type $R^1R^2TeX_2$.

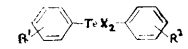
R^1	R^2	X	M.p., °C	Method of preparation	Yield, %	References
Diaryl derivatives of the type 						
H	H	F	154	(II.18), (II.19) (II.26), (II.28)	60—87	93, 59, 67
H	H	Cl	160—161	(II.1), (II.8), (II.13), (II.15)—(II.17)	36, 58, 75—98, 4, 22, 100	24, 25, 76, 48, 49, 78, 83, 132
H	H	Br	198	(II.17)	69	133
H	H	I	235—236	(II.17)	100	132
H	H	CH_3COO	163—164	(II.21), (II.29)	98, 100	57, 102
H	H	$ClCH_2COO$	107—109	(II.29)	100	102
2-CH_3	2-CH_3	Cl	184—185	(II.15), (II.17)	15, 100	79, 132
2-CH_3	2-CH_3	Br	182	(II.17)	100	132
2-CH_3	2-CH_3	I	175	(II.17)	100	132
3-CH_3	3-CH_3	F	118	(II.28)	60	67
3-CH_3	3-CH_3	Cl	128	(II.15), (II.17)	21, 100	79, 2
3-CH_3	3-CH_3	Br	165—166	(II.17)	100	2
3-CH_3	3-CH_3	I	164	(II.17)	100	2
4-CH_3	4-CH_3	F	163	(II.28)	60	67
4-CH_3	4-CH_3	Cl	163	(II.1), (II.8), (II.9) (II.15)—(II.17)	42, 95, 90, 24, 36, 100	24, 76, 48, 79, 83, 132
4-CH_3	4-CH_3	Br	203—204	(II.17)	100	132
4-CH_3	4-CH_3	I	216	(II.17)	100	132
4-CH_3	4-CH_3	CH_3COO	181—182	(II.21), (II.29)	100	57, 102
4-CH_3	4-CH_3	C_3H_7COO	141—142	(II.27), (II.29)	100	88, 102
4-CH_3	4-CH_3	$C_7H_{15}COO$	85—86	(II.27)	—	88
4-CH_3	4-CH_3	$C_{11}H_{23}COO$	66—68	(II.27)	—	88
4-CH_3	4-CH_3	C_6H_5COO	230—231	(II.27), (II.29)	96, 100	88, 102
4-CH_3	4-CH_3	$ClCH_2COO$	163	(II.29)	100	102
2-OCH_3	2-OCH_3	Cl	184—185	(II.15), (II.17)	23, 100	79, 112
2-OCH_3	2-OCH_3	Br	195—196	(II.17)	100	112
2-OCH_3	2-OCH_3	I	199—200	(II.17)	100	112
3-OCH_3	3-OCH_3	Cl	163	(II.15), (II.17)	23, 100	79, 2
3-OCH_3	3-OCH_3	Br	185—186	(II.17)	100	2
3-OCH_3	3-OCH_3	I	167—168	(II.17)	100	2
4-OCH_3	4-OCH_3	F	131	(II.18), (II.19) (II.26), (II.28)	60—92	93, 26, 67
4-OCH_3	4-OCH_3	Cl	182	(II.1), (II.8) (II.15), (II.16)	95, 86 41, 55	14, 76, 79, 83
4-OCH_3	4-OCH_3	Br	198—200	(II.17)	91	79
4-OCH_3	4-OCH_3	CH_3COO	135—136	(II.21), (II.29)	100	57, 102
4-OCH_3	4-OCH_3	C_3H_7COO	128	(II.29)	100	102
4-OCH_3	4-OCH_3	C_6H_5COO	210—211	(II.29)	100	102
4-OCH_3	4-OCH_3	$ClCH_2COO$	160	(II.29)	100	102
4-OCH_3	4-OCH_3	CF_3COO	152	(II.29)	100	102
4-OCH_3	4-OCH_3	CCl_3COO	122—125	(II.29)	100	102
2-OC_2H_5	2-OC_2H_5	Cl	166	(II.15), (II.17)	9, 100	79, 2
2-OC_2H_5	2-OC_2H_5	Br	183—184	(II.17)	100	2
2-OC_2H_5	2-OC_2H_5	I	214—215	(II.17)	100	2
3-OC_2H_5	3-OC_2H_5	Cl	114—115	(II.15)	23	79
4-OC_2H_5	4-OC_2H_5	F	170	(II.26), (II.28)	16, 60	26, 67
4-OC_2H_5	4-OC_2H_5	Cl	110—111	(II.1), (II.15)	88, 15, 100	111
4-OC_2H_5	4-OC_2H_5	Br	127	(II.17)	100	111
4-OC_2H_5	4-OC_2H_5	I	144	(II.17)	100	111
4-OC_2H_5	4-OC_2H_5	CH_3COO	—	(II.21)	100	57
4-OC_2H_5	4-OC_2H_5	Cl	157—158	(II.1)	52	16
4-$N(CH_3)_2$	4-$N(CH_3)_2$	Cl	188—189	(II.4)	33	28
4-$N(CH_3)_2$	4-$N(CH_3)_2$	Br	149—150	(II.23)	91	173
4-$N(CH_3)_2$	4-$N(CH_3)_2$	I	158—159	(II.23)	100	28
4-$N(CH_3)_2$	4-$N(CH_3)_2$	CH_3COO	183—184	(II.29)	100	102
4-$N(CH_3)_2$	4-$N(CH_3)_2$	C_3H_7COO	132—133	(II.29)	100	102
4-$N(CH_3)_2$	4-$N(CH_3)_2$	C_6H_5COO	188,5—189	(II.29)	100	102
4-$N(CH_3)_2$	4-$N(CH_3)_2$	$ClCH_2COO$	167	(II.29)	100	102
3,4-$(OCH_3)_2$	3,4-$(OCH_3)_2$	Cl	155—156	(II.1)	65	24
2,4-$(OCH_3)_2$	2,4-$(OCH_3)_2$	Cl	204—205	(II.1)	63	24
3-CH_3, 4-OCH_3	3-CH_3, 4-OCH_3	Cl	146—147	(II.1)	52	24
2,5-$(CH_3)_2$	2,5-$(CH_3)_2$	Cl	197—198	(II.17)	100	12
2,5-$(CH_3)_2$	2,5-$(CH_3)_2$	Br	189—190	(II.17)	100	12
2,5-$(CH_3)_2$	2,5-$(CH_3)_2$	I	161—162	(II.17)	100	12
2,4-$(CH_3)_2$	2,4-$(CH_3)_2$	Cl	187—188	(II.17)	100	12
2,4-$(CH_3)_2$	2,4-$(CH_3)_2$	I	181—182	(II.17)	100	12
2,4,6-$(CH_3)_3$	2,4,6-$(CH_3)_3$	Cl	178—179	(II.17)	100	109
2,4,6-$(CH_3)_3$	2,4,6-$(CH_3)_3$	Br	205—206	(II.17)	100	109
2,4,6-$(CH_3)_3$	2,4,6-$(CH_3)_3$	I	111	(II.17)	100	109

Table 2 (Cont'd.)

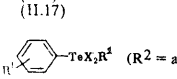
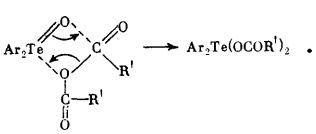
R^1	R^2	X	M.p., °C	Method of preparation	Yield, %	References
2-Cl	2-Cl	Cl	192	(II.15)	33	79
3-Cl	3-Cl	Br	178	(II.17)	95	67
4-Cl	4-Cl	Cl	182—183	(II.15), (II.16)	41, 55	79, 83
4-Cl	4-Cl	Br	184—185	(II.17)	100	2
4-Cl	4-Cl	I	220	(II.17)	100	67
2-Br	2-Br	Cl	244—246	(II.15)	17	79
3-Br	3-Br	Cl	143—144	(II.15)	47	79
3-Br	3-Br	Br	200	(II.17)	95	67
4-Br	4-Br	Cl	190	(II.8), (II.15), (II.1)	90, 40, 44	76, 79, 24
4-Br	4-Br	Br	195—196	(II.17)	90	79
4-Br	4-Br	I	231	(II.17)	90	79
4-F	4-F	Cl	128	(II.17)	95	67
4-F	4-F	Br	171	(II.17)	95	67
2,3,4,5,6-F_5	2,3,4,5,6-F_5	Cl	201	(II.17)	68	132
2,3,4,5,6-F_5	2,3,4,5,6-F_5	Br	210	(II.17)	77	132
2,3-C_4H_4	2,3-C_4H_4	Cl	265	(II.17)	100	108
2,3-C_4H_4	2,3-C_4H_4	Br	244	(II.17)	100	108
2,3-C_4H_4	2,3-C_4H_4	I	184—186	(II.17)	98	2
3,4-C_4H_4	3,4-C_4H_4	Cl	245—246	(II.7), (II.17)	92, 100	46
3,4-C_4H_4	3,4-C_4H_4	Br	253—255	(II.17)	100	46
3,4-C_4H_4	3,4-C_4H_4	I	217—220	(II.17)	94	46
H	4-OCH_3	Cl	114—115	(II.7), (II.8), (II.13), (II.14), (II.17)	87, 97, 80, 30, 100	46, 76, 49, 50, 46
H	4-OCH_3	Br	148.5—149.5	(II.17)	100	46
H	4-OCH_3	I	166—167	(II.17)	100	46
H	4-OC_6H_5	Cl	128.5—129.5	(II.7), (II.17)	70, 100	46
H	4-OC_6H_5	Br	156.5—158	(II.17)	100	46
H	4-OC_6H_5	I	184.5	(II.17)	100	46
H	2,3-C_4H_4	Cl	202.5—203.5	(II.7), (II.17)	80, 100	46
H	2,3-C_4H_4	Br	180.5—182	(II.17)	100	46
H	2,3-C_4H_4	I	212	(II.17)	100	46
H	3,4-C_4H_4	Cl	171.5—172.5	(II.7), (II.17)	76—100	46, 56
H	3,4-C_4H_4	Br	186—187	(II.17)	100	46
H	3,4-C_4H_4	I	182	(II.17)	100	46
4-OCH_3	2,3-C_4H_4	Cl	218—220	(II.7), (II.17)	95, 100	46
4-OCH_3	2,3-C_4H_4	Br	220—222	(II.17)	100	46
4-OCH_3	2,3-C_4H_4	I	189	(II.17)	100	46
4-OCH_3	3,4-C_4H_4	Cl	129.5—130.5	(II.7), (II.17)	84, 100	46
4-OCH_3	3,4-C_4H_4	Br	163—164	(II.17)	100	46
4-OCH_3	3,4-C_4H_4	I	173,5	(II.17)	100	46
4-OC_6H_5	2,3-C_4H_4	Cl	175—176	(II.7), (II.17)	70, 100	46
4-OC_6H_5	2,3-C_4H_4	Br	189—190	(II.17)	100	46
4-OC_6H_5	2,3-C_4H_4	I	184	(II.17)	100	46
4-OC_6H_5	3,4-C_4H_4	Cl	138—139	(II.7), (II.17)	87, 100	46
4-OC_6H_5	3,4-C_4H_4	Br	146—147	(II.17)	100	46
4-OC_6H_5	3,4-C_4H_4	I	206	(II.17)	100	46
2,3-C_4H_4	3,4-C_4H_4	Cl	232—233	(II.7), (II.17)	92, 100	46
2,3-C_4H_4	3,4-C_4H_4	Br	215—217	(II.17)	100	46
2,3-C_4H_4	3,4-C_4H_4	I	205	(II.17)	100	46
4-OC_2H_5	2,3-C_4H_4	Cl	193—194	(II.17)	—	2
4-CH_3	4-CH_3	Cl	158—159	(II.8)	93	76
4-$N(CH_3)_2$	4-CH_3	Cl	170—172	(II.2), (II.24), (II.17)	75—100	63, 173
4-$N(CH_3)_2$	4-CH_3	Br	183—184	(II.2), (II.24), (II.17)	51—100	63, 173
4-$N(CH_3)_2$	4-CH_3	I	130	(II.17)	100, 85	63, 173
4-$N(CH_3)_2$	H	Cl	150—151	(II.17)	95	63, 173
4-$N(CH_3)_2$	H	Br	140	(II.17)	95	63, 173
4-$N(CH_3)_2$	H	I	145—146	(II.17)	95	63, 173
4-$N(CH_3)_2$	4-Br	Cl	151—152	(II.17)	95	63, 173
4-$N(CH_3)_2$	4-Br	Br	168—169	(II.17)	95	63, 173
4-$N(CH_3)_2$	4-Br	I	144—145	(II.17)	95	63, 173
4-$N(CH_3)_2$	4-OC_6H_5	Cl	152—154	(II.2), (II.24), (II.17)	59—100	63, 173
4-$N(CH_3)_2$	4-OC_6H_5	Br	121—123	(II.2), (II.24), (II.17)	49—100	63, 173
4-$N(CH_3)_2$	4-OC_6H_5	I	96—97	(II.17)	100, 94	63, 173
4-$N(CH_3)_2$	4-OC_6H_5	Cl	194—195	(II.2), (II.17)	41, 50	63, 173
4-$N(CH_3)_2$	4-OC_6H_5	Br	188—189	(II.2), (II.24), (II.17)	89—100	63, 173
4-$N(CH_3)_2$	4-OC_6H_5	I	135—136	(II.17)	100, 91	63, 173
4-$N(CH_3)_2$	4-CH_3	Cl	165—166	(II.17)	88	173
4-$N(CH_3)_2$	4-CH_3	I	134	(II.17)	97	173
4-$N(CH_3)_2$	4-Cl	Cl	151—152	(II.17)	86	173
4-$N(CH_3)_2$	4-Cl	Br	146	(II.17)	75	173
4-$N(CH_3)_2$	4-Cl	I	124	(II.17)	82	173
4-$N(CH_3)_2$	3-Br	Cl	149	(II.17)	87	173
4-$N(CH_3)_2$	3-Br	Br	133	(II.17)	84	173
4-$N(CH_3)_2$	3-Br	I	116—118	(II.17)	85	173
4-$N(CH_3)_2$	3-NO_2	Cl	138	(II.7)	50	173
2,4-$(OH)_2$	4-OCH_3	Cl	182—183	(II.3)	70	63
2,4-$(OH)_2$	4-OCH_3	Br	179—180	(II.3), (II.24)	6, 100	63
2,4-$(OH)_2$	4-OCH_3	I	130	(II.24)	100	62
2,4-$(OH)_2$	4-OC_2H_5	Cl	189—190	(II.3)	70	63
2,4-$(OH)_2$	4-OC_2H_5	Br	190—191	(II.3), (II.24)	28, 100	63
2,4-$(OH)_2$	4-OC_2H_5	I	132	(II.24)	100	63
2,4-$(OH)_2$	4-OC_2H_5	Cl	181	(II.3)	61	63
2,4-$(OH)_2$	4-OC_2H_5	Br	181—182	(II.24)	100	63
2,4-$(OH)_2$	4-OC_2H_5	I	122—124	(II.24)	100	63
2,4-$(OCOCH_3)_2$	4-OCH_3	Cl	166—167	(II.3)	88	63
2,4-$(OCOCH_3)_2$	4-OC_2H_5	Cl	162—168	(II.3)	88	63
2,4-$(OCOCH_3)_2$	4-OC_6H_5	Cl	172—173	(II.3)	100	63
4-Br	H	Cl	144	(II.7)	80	67
4-F	H	Cl	132	(II.7)	78	67
4-F	H	Br	177—179	(II.17)	100	67
3-F	H	Cl	150	(II.7)	84	67
3-F	H	Br	184	(II.17)	100	67
			Compounds of the type  (R^2 = alkyl)			
H	CH_3	Cl	157.5—158	(II.17)	86	55
H	CH_3	Br	156.5—157	(II.17)	84	55
H	CH_3	I	146	(II.17)	60—65	55, 85
4-CH_3	CH_3	Cl	150—152	(II.17)	96	55

Table 2 (Cont'd.)

R^1	R^2	X	M.p., °C	Method of preparation	Yield, %	References
4-CH_3	CH_3	Br	163—163.5	(II.17)	75	55
4-CH_3	CH_3	I	135—137	(II.17)	57	55
4-OCH_3	CH_3	Cl	159—160	(II.17)	74	55
4-OCH_3	CH_3	Br	162—163	(II.17)	57	55
4-OCH_3	CH_3	I	115—116	(II.17)	51	55
4-OC_2H_5	CH_3	Cl	142—143.5	(II.17)	81	55
4-Cl	CH_3	Cl	145—146	(II.17)	66	55
4-Cl	CH_3	Br	169—170	(II.17)	80	55
4-Cl	CH_3	I	134—135	(II.17)	72	55
3-Cl	CH_3	Cl	116—117	(II.17)	70	55
4-F	CH_3	Cl	111	(II.17)	100	174
4-F	CH_3	Br	133—134	(II.17)	100	174
4-F	CH_3	I	128	(II.17)	100	174
3-F	CH_3	Cl	94	(II.17)	100	174
3-F	CH_3	Br	137	(II.17)	100	174
3-F	CH_3	I	126	(II.17)	100	174
2-CH_3	CH_3	Cl	95—97	(II.17)	100	182
2-CHO	n-C_4H_9	Cl	105—110	(II.17)	85	182
2-CHO	CH_3	Cl	154—159	(II.17)	100	182
2-$COOC_2H_5$	n-C_4H_9	Cl	135—137	(II.17)	100	182
2-$COOC_2H_5$	CH_3	Br	130—136	(II.17)	100	182
H	C_2H_5	I	96	(II.17)	64	85
H	n-C_3H_7	I	95	(II.17)	62	85
H	iso-C_3H_7	I	97	(II.17)	46	85
H	n-C_4H_9	Br	74—75	(II.17)	95	85
H	n-C_4H_9	I	82—84	(II.17)	84	85
H	n-$C_{14}H_{29}$	I	70	(II.17)	70	85
4-OCH_3	C_2H_5	Cl	80—81	(II.7), (II.17)	30, 100	75
4-OCH_3	C_2H_5	Br	107—108	(II.17)	100	75
4-OCH_3	C_2H_5	I	135	(II.17)	100	75
3,4-C_4H_4	cyclo-C_6H_{11}	Cl	140—141	(II.7), (II.17)	59, 100	75
3,4-C_4H_4	cyclo-C_6H_{11}	Br	157	(II.17)	100	75
3,4-C_4H_4	cyclo-C_6H_{11}	I	139	(II.17)	100	75
4-OCH_3	$C_6H_5CH_2$	Cl	126—127.5	(II.7)	100	75
4-OCH_3	$C_6H_5CH_2$	Br	153	(II.25)	77	75
4-OCH_3	$C_6H_5CH_2$	I	133	(II.25)	75	75
3,4-C_4H_4	$C_6H_5CH_2$	Cl	128.5—130	(II.7)	80	75
3,4-C_4H_4	$C_6H_5CH_2$	Br	149	(II.25)	80	75
3,4-C_4H_4	$C_6H_5CH_2$	I	144	(II.25)	100	75
3,4-C_4H_4	$C_6H_5CH=CH$	I	153—154	(II.17)	59	43
3,4-C_4H_4	C_2H_5	Cl	138—139	(II.17)	100	56
3,4-C_4H_4	C_2H_5	Br	141—142	(II.17)	100	56
3,4-C_4H_4	C_2H_5	I	102	(II.17)	100	56
4-OCH_3	CH_2COCH_3	Cl	137—138	(II.5)	65	63
4-OC_2H_5	CH_2COCH_3	Cl	134—135	(II.5)	75	63
4-OCH_3	$CH_2COC_6H_5$	Cl	136—137	(II.5)	60	63
4-OCH_3	$CH_2COC_6H_5$	Br	151—152	(II.5)	29	63
4-OC_2H_5	$CH_2COC_6H_5$	Cl	141—142	(II.5)	57	63
4-OC_6H_5	$CH_2COC_6H_5$	Cl	146—147	(II.5)	46	63
Compounds of the type $R^1TeX_2R^2$ (R^1 and R^2 = alkyl)						
CH_3	CH_3	F	84	(II.26)	—	59
CH_3	CH_3	Cl	92	(II.28)	—	97
CH_3	CH_3	Br	92	(II.28)	—	97
CH_3	CH_3	I	127	(II.22)	50	97
CH_3	CH_3	C_6H_5COO	154	(II.27)	—	97
C_2H_5	C_2H_5	I	57	(II.22)	20	98
n-C_4H_9	n-C_4H_9	I	61	(II.17)	70	94
CH_2CH_2Cl	CH_2CH_2Cl	Cl	111	(II.6)	—	41
$CH_2CHClCH_3$	$CH_2CHClCH_3$	Cl	100	(II.6)	30	41
		Cl	134—135	(II.6)	80	42
n-C_5H_{11}	$CH_2COOC_2H_5$	C_6H_5COO	77—78	(II.20)	—	95
$C_6H_5CCl=CH$	$C_6H_5CCl=CH$	Cl	205—215	(II.30)	83	43
$C_6H_5CCl=CH$	$C_6H_5CCl=CH$	I	168—169	(II.17)	100	43
$C_6H_5C\equiv C$	$C_6H_5C\equiv C$	I	120—125	(II.17)	33	43

recently [101,102]; the reaction probably involves electron transfer via a four-membered transition state:



(II.29)

Synthesis from aryltellurium trichlorides. Apart from the telluration of aromatic and aliphatic systems leading to diorganotellurium dihalides (see above), an unusual method of synthesis of these compounds, involving the symmetrisation of organotellurium trichlorides, will be described in this Section. In certain cases (2-chloro-2-phenylvinyltellurium trichloride) it proceeds fairly readily under the influence of hydroxylated solvents. However, usually such reactions require the use of a symmetrising agent [62]:

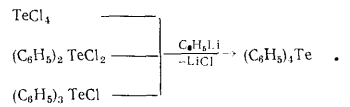
$$2ArTeCl_3 + 4Cu \rightarrow Ar_2TeCl_2 + 4CuCl + Te \ . \qquad \text{(II.30)}$$

Data on diorgano-derivatives of tellurium(IV) are compiled in Table 2.

3. SYNTHESIS OF TETRAORGANOTELLURANES

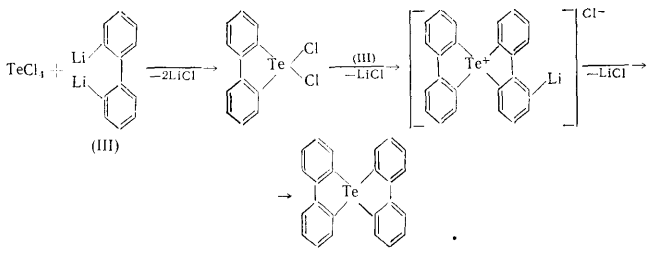
In contrast to tellurium trihalides and dihalides, triorganotellurium halides have an ionic structure in the crystalline state and in solutions [3], i.e. they are telluronium salts and do not therefore belong to telluranes. However, if all four σ bonds are of the Te–C type and are covalent, the corresponding compounds are tetraorganotelluranes.

The synthesis of tetraorganotelluranes is based on the interaction of halogen-containing compounds of tellurium with aryl-lithium derivatives. The first representative of this class (tetraphenyltellurium) has been obtained [103] by the interaction of $TeCl_4$, $(C_6H_5)_2TeCl_2$, or $(C_6H_5)_3TeCl$ with phenyl-lithium:



Tetrakis(pentafluorophenyl)tellurium was obtained similarly [104].

Bis-(2,2-diphenylene)tellurium was synthesised by the reaction of 2,2′-dilithiobiphenyl (III) with $TeCl_4$. [105,106] It is formed via the following mechanism:



This compound was also obtained by the reaction of 2,2′-dilithiobiphenyl with tetra- and hexa-methoxytellurium [105,106].

In order to synthesise tetra-alkyltellurium derivatives, studies were made of the reactions of the corresponding alkyl-lithium derivatives (butyl, methyl) with $TeCl_4$ or trialkyltelluronium iodides [105]. However, tetra-alkyl derivatives of tellurium were never isolated, although their existence in solution as unstable intermediates was postulated on the basis of the study of the composition of the reaction mixture. Other attempts to synthesise tetra-alkyltellurium derivatives [alkyl–aryl exchange between bis(diphenylene)tellurium or triphenyltellurium iodide and butyl-lithium] led to the same results [106].

III. THE SYNTHESIS OF π-TELLURANES

In contrast to σ-telluranes, the methods of synthesis of which have now been developed in fair detail, the synthetic approaches to π-telluranes of different structure have been very little investigated.

1. ATTEMPTS TO PREPARE DIARYLTELLURIUM OXIDES

The commonest method for the synthesis of diaryltellurium oxides is hydrolysis of diaryltellurium dihalides by dilute alkalis or ammonia [107-112]:

$$(RC_6H_4)_2TeX_2 + 2OH^- \rightarrow (RC_6H_4)_2TeO + H_2O + 2X^-;$$

R = H [107-108,110], 4-CH_3 [108], 2,3-C_4H_4 [111], 2,4,6-$(CH_3)_3$ [112], or 4-OC_2H_5 [109].

When dialkyl tellurides are oxidised [95] with hydrogen peroxide in an alkaline medium or with nitric acid, the dihydroxide $R_2Te(OH)_2$ and the basic nitrate $R_2TeOH(NO_3)$ are obtained. Complex compounds, for example $R_2TeO.3RTeOOH$, are formed in air or on interaction with other oxidants. On the other hand, when diaryl tellurides are oxidised by nitric acid, the products are the dinitrates $Ar_2Te(NO_3)_2$, whose hydrolysis by alkalis gives rise to diaryltellurium oxides [113].

2. THE SYNTHESIS OF TELLURIUM IMIDES

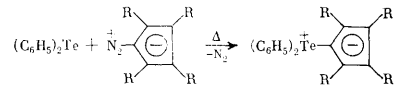
The only method known at the present time for the synthesis of tellurium imides involves the interaction of diaryltellurium oxides with sulphonamides in boiling chloroform [114]:

$$(4\text{-}CH_3OC_6H_4)_2TeO + H_2NSO_2R \rightarrow (4\text{-}CH_3OC_6H_4)_2\overset{+}{T}e-\overline{N}SO_2R;$$

R = 4-$CH_3C_6H_4$, C_6H_5, or $C_6H_5CH_2$.

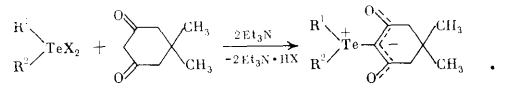
3. THE SYNTHESIS OF TELLURONIUM YLIDS

The methods of synthesis and properties of telluronium ylids have been studied comparatively little. Stable telluronium ylids (cyclopentadienylides) were obtained for the first time [115,116] in the thermal decomposition of the corresponding diazocyclopentadienes in an excess of diphenyl telluride:



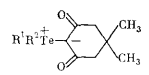
R = H, or C_6H_5.

Later, a large series of dicarbonyl-stabilised telluronium ylids, containing both alkyl and aryl substituents at the tellurium atom, were obtained by a method common to Group VI elements, based on the interaction of diorganotellurium dihalides (chlorides, bromides) with dimedone in the presence of two equivalents of triethylamine [117,118]:



Data for ylids of this type are compiled in Table 3.

Table 3. Diorganotellurium dimedone ylids of the type



R^1	R^2	Yield, %	M.p., °C	μ^*_{exp}, D	μ_{calc}, D	pK_a^{**}
p-$(CH_3)_2NC_6H_4$	*p*-$(CH_3)_2NC_6H_4$	91	149—150	5.49	4.96	11.48
p-$CH_3OC_6H_4$	*p*-$CH_3OC_6H_4$	89	144	4.16	3.95	10.74
p-$C_2H_5OC_6H_4$	*p*-$C_2H_5OC_6H_4$	97	142—143	4.26	4.09	10.86
p-$CH_3C_6H_4$	*p*-$CH_3C_6H_4$	94	136—137	3.58	3.58	10.69
C_6H_5	C_6H_5	100	158—159	3.16	3.16	10.59
p-BrC_6H_4	*p*-BrC_6H_4	95	156—157	1.74	1.68	10.07
p-FC_6H_4	*p*-FC_6H_4	83	127—128	2.06	1.82	10.22
CH_3	C_6H_5	89	147—148	2.90	—	11.22
CH_3	*p*-$CH_3OC_6H_4$	100	155—156	3.28	—	11.40
CH_3	*p*-$C_2H_5OC_6H_4$	92	96—97	3.42	—	11.25
CH_3	C_6H_5	80	97—98	3.18	—	12.07
p-$CH_3OC_6H_4$	*p*-$(CH_3)_2CHC_6H_4$	91	103—104	4.06	—	10.69

*In benzene at 30°C.
**In acetonitrile at 25°C.

IV. THE STRUCTURE OF ORGANIC DERIVATIVES OF TELLURIUM (IV)

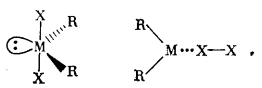
The data accumulated at the present time on the structure of tellurane molecules and their relation with physical and physicochemical properties are at present extremely

limited. In their discussion, it is therefore useful to resort to information about the structure and properties of sulphuranes and selenuranes, which helps to discover certain regularities or tendencies in the structure of tetracoordinate compounds of Group VI elements as a function of the nature of the central atom.

1. THE STERIC STRUCTURE OF σ-TELLURANES

(a) X-Ray Diffraction and Spectroscopic Studies of Molecular Structures

When the halides (X = Cl, Br, or I) react with compounds of the type R_2M (M = S, Se, or Te), there is a possibility, in principle, of the formation of two types of structures: (1) a bisphenoid structure with covalent M–X bonds (IV) and (2) a molecular σ-complex (V):



(IV) (V)

The study of the infrared Raman spectra of the adducts of halogens with R_2M (R = CH_3, M = S, Se, or Te)[119] as well as investigation of the ^1H NMR spectra and electrical conductivities of the products of the interaction of halogens with thiane and selenane[120] led to the conclusion that there is a clear-cut relation between the structure of these adducts and the nature of M and X. Whereas only structure (V) obtains for sulphur derivatives with X = Br or I, for selenium the adducts have structures (IV) with X = Cl or Br and (V) when X = I. For any X, diorganotellurides have the bisphenoid structure (IV) (a trigonal bipyramid) both in the solid phase and in solution, in which the lone electron pair of the tellurium atom plays the role of a third equatorial phantom ligand.

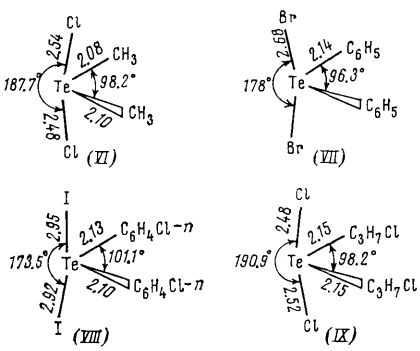


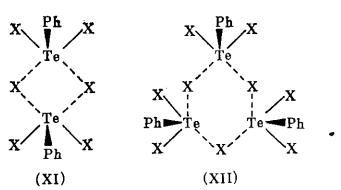
Figure 1. The results of an X-ray diffraction study of dimethyltellurium dichloride (VI)[122], diphenyltellurium dibromide (VII)[123], di-(4-chlorophenyl)tellurium di-iodide (VIII)[124], and di-(2-chloropropyl)tellurium dichloride (IX)[133].

This structure of σ-telluranes with equivalent Te–X bonds (see also data for the NQR spectra of dimethyltellurium dichloride[121] and isotope exchange in the $Ph_2TeCl_2^*$ + Ph_2Te system[90]) has been clearly confirmed by X-ray diffraction studies of dimethyltellurium dichloride (IV)[122], diphenyltellurium dibromide (VII)[123], di-(*p*-chlorophenyl)-tellurium di-iodide (VIII)[124], and di-(2-chloropropyl)tellurium dichloride (IX)[125] (Fig. 1).

Certain data for the Te–C and Te–X bond lengths in the dihalides of a series of tellurium-containing heterocycles have been published[126–131].

On the basis of a comparison of the infrared and Raman spectra of substituted diaryltellurium dihalides of the type R_2TeX_2 (R = *p*-tolyl, *o*-tolyl, *p*-anisyl, or pentafluorophenyl and X = Cl, Br or I) with the spectra of diphenyltellurium dihalides, it has been concluded[132] that in all cases the halogen atoms occupy the axial positions in the trigonal bipyramid.

An X-ray diffraction study has so far been made of only one trihalide—2-chloroethyltellurium trichloride (X)[133,134], obtained by the addition of $TeCl_4$ to ethylene (Fig. 2). Whereas diorganotellurium dihalides are monomeric in the crystal, compound (X) forms in the crystal a polymeric chain with bridge bonds via a chlorine atom. Because of this, the tellurium atom acquires a coordination number of 5 and the chlorine atoms are located at the vertices of a square pyramid. The Te–Cl distance is 2.39 Å and the Te–Cl$_{bridge}$ distance is 2.72 Å. In terms of the Te–Cl bond type, this compound lies between the monomeric dimethyltellurium dichloride[122] and the tetrameric tellurium tetrachloride[135], which is reflected in the average Te–Cl distance (2.39 Å) (2.51 Å in dimethyltellurium dichloride and 2.31 Å in tellurium tetrachloride). Examination of the low-frequency infrared and Raman spectra of various compounds $RTeX_3$ (R = phenyl, *p*-tolyl, *p*-anisyl, *p*-phenetyl, or *p*-phenoxyphenyl; X = Cl, Br, or I) also led to the conclusion that in compounds of this type the tellurium atom is pentacoordinate[54]. According to the authors, the trichlorides and tri-iodides are isomorphous and dimeric in the solid state [structure (XI)], while structure (XII) is quite probable for the tribromides (R = phenyl, *p*-tolyl, or *p*-phenoxyphenyl), which are more associated according to the authors' data. On the other hand, other results[51] showed that the tri-iodide is associated to the greatest extent in the series of methyltellurium trihalides. The structures proposed for the trihalides, based on the donor–acceptor interaction of the $PhTeX_2$ units with bridging halogen atoms, are fairly unstable because aryltellurium trichlorides are monomeric in solution (in dioxan)



(XI) (XII)

The available data suggest that the tendency towards tetracoordination increases appreciably in the sequence S < Se < Te. The influence of the halide ligand on the capacity of the chalcogen for involvement in tetracoordination is appreciable. On passing from F, Cl to Br and I, σ-telluranes are somewhat destabilised. Thus iodotelluranes of the type R_2TeI_2 show a tendency in solutions in polar solvents towards dissociation with a transition from structure (IV) to structure (V).[55] Nevertheless, in the crystalline state the compounds R_2TeI_2 exist as the σ-telluranes (IV). Apart from the X-ray diffraction data for diaryltellurium di-iodides[124], this is indicated by data obtained recently for dimethyltellurium di-iodide[136,137] from ^{125}Te Mössbauer spectra. The parameters of the Mössbauer spectra show clearly that even dimethyltellurium tetrahalides, particularly Me_2TeI_4, are also derivatives of tellurium(IV), i.e. the latter compounds probably have the structure $Me_2TeI_2.I_2$.[137]

(b) The Polarity Rule and the Conformational Effects of Substituents in the Molecules of σ-Telluranes

The above data concerning the molecules of σ-telluranes show that in all the compounds (VI)–(X) the more electronegative substituents occupy the axial positions, which reflects the polarity rule. According to this rule, in polyhedral molecular structures with topologically different bond types, derived from the configuration of a trigonal bipyramid, topomers containing more electronegative substituents in the axial positions exhibit the greatest stability [138-140]. The axial bonds in the corresponding structures are loosened and lengthened by 0.2–0.3 Å compared with the equatorial bonds.

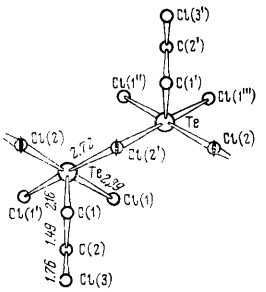


Figure 2. The results of an X-ray diffraction study of 2-chloroethyltellurium trichloride (X) [133].

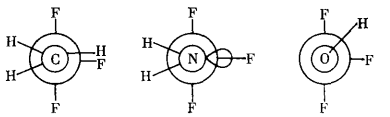
The polarity rule, established initially for phosphoranes, has now received theoretical justification also for tetracoordinate compounds of Group VI elements—sulphuranes and their analogues [141-144]. A clear explanation of the loosening of the diaxial bonds in σ-sulphuranes and their analogues is associated with the structure of the highest occupied molecular orbital, which is regarded, in terms of the perturbation theory, as a combination of a bonding molecular orbital of the angular MR^1R^2 molecule with the antibonding molecular orbital of the extended linear R^3R^4 molecule, where R^3 and R^4 are axial ligands [139,140].

The high stability of configurations in which the most electronegative ligands occupy axial positions is independent of the inclusion in the basis set of the *d* orbitals of the central atom and is determined by the form of the molecular orbital which permits the concentration of electron density at the axial bonds and leads to the accumulation of negative charges at the axial centres.

The fulfillment of the requirements of the polarity rule for σ-telluranes is illustrated, for example, by calculations on the topomers of dibromodichlorotellurium (Fig. 3), which show that tellurane structures with the most electronegative substituents in the axial positions are preferable [144]. In this connection it is interesting to note that, on the basis of Raman spectra, Ozin and Voet [145] initially concluded that $TeCl_2Br_2$ exists in configuration *b* (Fig. 3), but later [146] a more exact calculation led them to attribute conformation *a* to this compound (Fig. 3).

The conformational effects in sulphurane, selenurane, and tellurane molecules, due to the complexity of the dependence of the total energy of the molecule on the rotation of the ligands with lone electron pairs and axial and equatorial π bonds have also been analysed [142,144,147,148]. The general conclusions arising from the theoretical calculations reduce to the following postulates:

1. The introduction of a strong π-acceptor substituent into the molecules of σ-telluranes can stabilise, regardless of the electronegativities of the remaining ligands, its axial conformation in which the axes of the vacant π molecular orbitals of the acceptor and the localised orbital of the lone electron pair are parallel.
2. π-Donor ligands always occupy equatorial positions.
3. In bisphenoid structures of telluranes, as in the systems of analogues located in the highest positions in the Periodic System, the conformational *gauche*-rule holds [149], i.e. the conformation with the greatest number of *gauche*-interactions has the minimum energy. Indeed it follows from calculations [144,147] that the most stable rotational isomeric forms of MF_3R molecules (R = CH_3, NH_2, or OH; M = S, Se or Te) are the conformations (XIII)–(XV).



The above conclusions are so far based exclusively on theoretical calculations and await experimental studies on the new and interesting field of the conformational analysis of tetracoordinate structures of Group VI elements.

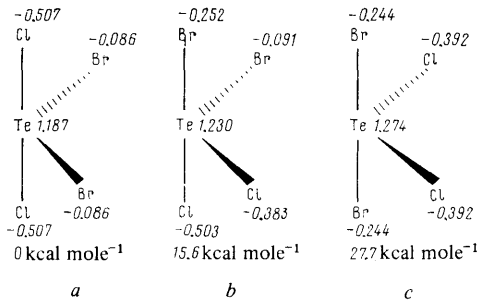
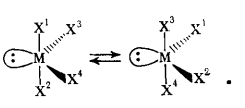


Figure 3. The relative stabilities of various configurations (*a*–*b*) and atomic charges in tellurium dibromide dichloride obtained by the extended Hückel method [144]. (The numerals under the structures indicate their relative energies and those opposite the atoms indicate the atomic charges.)

(c) Polytopic Rearrangements

The stereochemical non-rigidity at the bisphenoid structures of the molecules of σ-sulphuranes and their analogues leads to the possibility of a rapid exchange of the axial (X^1,X^2) and equatorial (X^3,X^4) ligands—topomerisation:



The most convenient method for the investigation of the mechanism and kinetics of such polytopic rearrangements is dynamic NMR. ^{19}F NMR is particularly useful because of the high sensitivity of the ^{19}F nuclei to the characteristics of their chemical environment. The polytopic rearrangements in MF_4 (M = S, Se, or Te) molecules have been investigated [150-154]. It was observed that the topomerisation of SF_4 takes place at a high rate even at room temperature (the separation of the signals of the axial and equatorial fluorine atoms is achieved only at $-98°C$,[150] which corresponds to a barrier of 4.5 ± 0.8 kcal mole^{-1}). For SeF_4, there are only two unresolved peaks even at $-200°C$, which are broadened and merge into a singlet at a temperature $> -190°C$; consequently the exchange in SeF_4 is faster than in SF_4.[150] There is only one sharp peak in the TeF_4 spectrum up to $-100°C$ (the freezing point of the solution). Thus the rate of the axial–equatorial exchange in molecules of the type MF_4 increases in the sequence S < Se < Te.[150]

The rate of ligand exchange is extremely sensitive to the catalytic influence of impurities (H_2O, HF).[154] Indeed, when bis(trimethylsilyl)amine, which binds water, is added to SF_4 solutions, the separation of the signals due to the axial and equatorial fluorine atoms in the ^{19}F NMR spectrum is achieved already at $-60°C$ (this temperature is reproducible, in contrast to earlier studies), which yields an activation energy of 16.3 ± 5 kcal mole^{-1}.

Table 4. The σ constants of tellurium-containing groups.

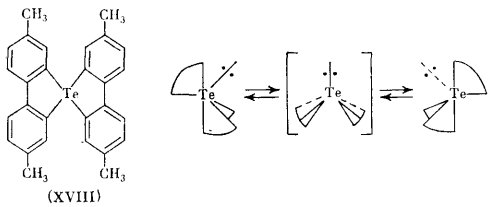
Substituent	δ^F_m, p.p.m.*	δ^F_p, p.p.m.	σ_I	σ_c	σ_n
$Te(CH_3)Cl_2$	−2.93	−4.67	0.50	0.06	0.56
$Te(CH_3)Br_2$	−3.15	−4.86	0.53	0.06	0.59
$Te(CH_3)I_2$	−3.50	−4.79	0.58	0.04	0.62
$Te(C_6H_5)Cl_2$	−3.06	−5.08	0.52	0.07	0.59
$Te(C_6H_5)Br_2$	−3.21	−5.09	0.54	0.06	0.60
$TeCl_3$	−3.28	−6.62	0.55	0.11	0.66
$TeBr_3$	−3.05	−6.43	0.51	0.11	0.62

*The position of the centre of the multiplet relative to the chemical shift of the fluorine signal in fluorobenzene is indicated; the "minus" sign indicates a downfield shift and the "plus" sign indicates an upfield shift relative to δ in C_6H_5F.

The replacement of one of the fluorine atoms by a dialkylamino-group [155,156] or transition to tetra-arylsulphuranes [157] leads to an appreciable decrease of the rate of exchange, which is extremely sensitive to catalytic influences of the impurities. The latter factor indicates a significant role of the intermolecular mechanism of ligand exchange in the polytopic rearrangement (XVI) ⇌ (XVII). Various possibilities of associative, dissociative, and catalytic mechanisms have been examined [158-162]. In dilute solutions and in the gas phase truly intramolecular processes can compete with intermolecular processes [162]. The wide variety of mechanisms of such reactions is still greater than in the series of trigonal bipyramidal structures of Group V elements. Calculations on the pathways followed in the topomerisation of various model sulphuranes, carried out by the CNDO/2 and extended Hückel methods, led to the isolation of two more mechanisms specific to bisphenoid structures: the lever and pyramidal mechanisms, each of which is due to the non-synchronous motion of the ligands involved in the exchange, in contrast to Berry's pseudorotation mechanism [141].

The calculations [141] predict an interesting dependence of the energy to topomerisation in MX_4 molecules via the lever mechanism (the motion of a single axial ligand, while the skeleton made up of the remaining bonds remains stationary). In agreement with experiment, the topomerisation barrier for fluorides decreases on passing from sulphuranes to telluranes. However, for less negative substituents X the situation may be reversed.

In the series of σ-telluranes (except TeF_4) there is yet another experimental indication of a rapid polytopic rearrangement of the type (XVI) ⇌ (XVII). Hellwinkel and Fahrbach [106] explained their observation of the equivalence of all the methyl groups in the spirotellurane (XVIII) as a consequence of Berry's pseudorotation (other mechanisms are hindered by the spiran structure).



(XVIII)

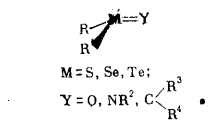
In view of the possible random isochronic nature of the protons of the methyl group (very remote from the chiral centre) the possibility of pseudorotation in structures of type (XVIII) requires further tests.

2. THE STEREOCHEMISTRY OF π-TELLURANES

There are no literature data for the molecular structure of π-telluranes obtained by direct methods. However, it had been concluded earlier on the basis of the results of thermal analysis that the configurations of diaryltellurium and diarylselenium oxides are identical [110].

Like the corresponding sulphonium [163,164] and selenonium ylids [165-167], telluronium ylids should evidently have the structure of a trigonal pyramid with a tellurium atom at the apex. Proof of the high stability of the tellurium pyramid in the dimedone ylids synthesised previously [117] has been obtained [118] by ^1H NMR (using a chiral shift reagent).

Recent theoretical calculations of the inversion and rotational barriers and on the mechanism of the topomerisation of the oxides, ylids, and imides of Group VI elements of type (XIX) [168] revealed definite tendencies in the above series:



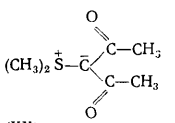
M = S, Se, Te; Y = O, NR^2, $C\langle^{R^3}_{R^4}$

(XIX)

1. The barriers to the pyramidal inversion of the central atom M in all compounds of type (XIX) with identical Y increase in the sequence S < Se < Te. This justifies the assertion that selenium and tellurium oxides can be resolved into highly stable enantiomers of type (XIX) (M = Te, R ≠ R′). The methods of synthesis and reactions of these compounds are being studied in detail at the present time [101,102]. Correspondingly, selenium and tellurium imides and ylids with different substituents at the central atom can also exist as stable optically active compounds.

2. The stability of the pyramid of the central atom M and the barrier to pyramidal inversion depend markedly on the nature of Y. In agreement with experimental data, the barrier to inversion in the oxides is highest.

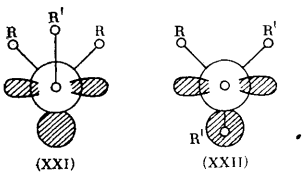
3. On passing from S and Se to Te, the barriers to rotation in the imides and ylids decrease. In the sulphonium ylid of type (XX) (M = S) the barrier to rotation about the C=S bond has been estimated as 12 kcal mole^{-1} [169] on the basis of the broadening of the signals due to the methyl groups in the ^{1}H NMR spectrum on cooling:



(XX)

Such broadening is observed also in the spectra of selenium ylids but at lower temperatures (−60°C),[166] which corresponds to a lowering of the rotation barrier. Presumably in telluronium dimedone ylids the rotation about the Te=C bonds is characterised by particularly high rates.

4. The stable molecular conformation of the imides and ylids of type (XIX) satisfies, according to the calculations, the *gauche*-rule and corresponds to conformation (XXI):



(XXI) (XXII)

This makes it possible to reject conformation (XXII), postulated by Claus and Gycydilik [170] to explain the observed isochronic nature of the signals due to the protons of the methyl groups in aryldimethylsulphimines.

3. THE ELECTRONIC STRUCTURE AND PHYSICAL PROPERTIES OF TELLURANES

(a) The Electronic Effects of Tellurium-Containing Substituents According to Dipole Moment Measurements and ^{19}F NMR

The dipole moments of compounds of the type $RC_6H_4TeX_2C_6H_4R'$ have been determined in a number of studies [67,171-173]. The appreciably higher dipole moments of diphenyltellurium dihalides compared with the corresponding dimethyl derivatives show (taking into account the direction of the C–Te bond moment) that the lone electron pair of the tellurium atom in diphenyltellurium dihalide molecules is not involved in conjugation with the π electrons of the aromatic rings. On the other hand, this difference between the dipole moments can be a consequence of the opposed electronic effect, of which the tellurium atom is capable in principle (d,π conjugation). The inductive and resonance components of the σ constants of the substituents $RTeX_2$ (R = Me or Ph), obtained from the ^{19}F NMR spectra of methyl (and phenyl) derivatives of *p*- (and *m*-)fluorophenyltellurium dihalides [174] with the aid of the Taft equations [175-177] (Table 4), do indeed show that the $RTeX_2$ groups do not exhibit electron-donating mesomeric properties. The σ_C constants of these groups are comparatively small compared with σ_I and, remaining virtually invariant when the halogen is altered, amount to ~ 10% of the overall σ_n constant of the substituent. The σ_I constants increase steadily on passing from chlorine-containing to iodine-containing compounds. Comparison of the values of σ_I and σ_C shows that the above groups interact with the π-electron system of the benzene ring mainly via an inductive mechanism.

When the values of σ_I, σ_C, and σ_n are examined for a series of substituents CH_3TeX_2, it is seen that the increase of the last constant is determined mainly by the increase of the σ_I constant and the values of the σ_n constants of the CH_3TeX_2 groups in the series Cl, Br, I increase on passing from chlorine-containing to iodine-containing compounds. An analogous increase of the σ constants is observed also in the $C_6H_5TeX_2$ series. Here the σ_I constants are greater than for the CH_3TeX_2 groups, evidently owing to the more pronounced inductive properties of the phenyl group compared with the methyl group. Thus one may speak of the preferential inductive mechanism of the interaction of the $RTeX_2$ groups with the π-electron system of the benzene ring. However, as for tellurides [178], when there is an active π-donor substituent (the dimethylamino-group) in the *p*-position relative to the TeX_2 group, there is a possibility of a sharp enhancement of the electron-accepting properties of the tellurium-containing group, probably owing to the population of the vacant *d* orbitals of the Te atom. The experimental dipole moments of aryl(*p*-dimethylaminophenyl)tellurium dihalides greatly exceed the values calculated by the vector scheme [173], the direction of the dipole moment coinciding with the direction expected for d,π conjugation.

In the series of similarly substituted diorganotellurium dihalides the dipole moment increases steadily, like the σ_I and σ_n constants, on passing from the difluorides to the di-iodides. To explain this, it has been suggested [172] that, under the influence of electronegative axial halogen atoms, the lone electron pair of tellurium undergoes contraction to different extents, which leads to a change in the dipole moment and the moment of the molecule as a whole.

A more rigorous explanation in terms of the resolution of the overall moment into the charge and hybridised components [144] was obtained as a result of calculations by the CNDO/2 method with inclusion in the basis set of the *d* orbitals of the central atom of the molecules of dimethylchalcogen dihalides $(CH_3)_2MX_2$. An increase of the dipole moment in the series X = F, Cl, or Br and M = S or Se can be accounted for by the simultaneous increase of the point component and the decrease of the *pd*-hybridised component (the *sp* components remain almost constant).

The problems of the electronic properties of TeX_3 groups have been investigated by ^{1}H and ^{19}F NMR [148,174] and by the dipole moment method [148].

The ^{1}H NMR spectra of *p*-substituted aryltellurium trihalides show that the *o*,*o'*- and *m*,*m'*-protons are isochronous and the barrier to rotation about the Te–Ar bonds is therefore small. The chemical shifts of the *o*-protons of aryltellurium trichlorides, which occur in a very weak field, indicate a strong deshielding effect of the trichlorotelluro-group, whose magnitude ($\delta_0^H = -1.0 \pm 0.1$ p.p.m.) is comparable to the analogous effect of the nitro-group. The value of δ_M^H for the $TeCl_3$ group has been calculated from the chemical shifts of the *m*-protons (satisfactorily correlated with the substituent constants δ_0^H),[148] as −0.23 p.p.m., which almost agrees with the corresponding value for the nitro-group. These data agree with the strong negative inductive effect of the $TeCl_3$ group.

The chemical shifts of the *o*-protons of the tribromides and *p*-substituted trichlorides are almost identical and the chemical shifts of *m*-protons are displaced upfield by

0.15–0.25 p.p.m., which indicates a smaller negative inductive effect of the tribromotelluro-group compared with the trichlorotelluro-group.

The σ_C constants of the TeX_3 groups, determined from ^{19}F NMR data [174], amount to 15% of the overall electronic effect of the substituent, which indicates a predominantly inductive nature of the interaction of these substituents with the π-electron system of the ring. In the Cl, Br series, the σ_n constants of the TeX_3 groups diminish, which is consistent with the overall ^1H NMR spectroscopic data.

The dipole moments of aryltellurium trichlorides calculated by the usual vector scheme agree satisfactorily with the experimental values. The vector of the dipole moment of the $TeCl_3$ group, equal to that of the dipole moment of phenyltellurium dichloride, makes an angle of 115° with the Ph–Te bond, which agrees closely with the direction of the equatorial Te–Cl bond. The absence of the moment of the interaction of the $TeCl_3$ group and the nitro-group in the benzene ring indicates the localisation of the lone electron pair and the similar dipole moments of phenyl- and methyl-tellurium trichlorides confirm the absence of an appreciable mesomeric electron-accepting effect of the $TeCl_3$ group.

The results of the calculation of orbital populations and examination of the nature of the highest bonding and lowest vacant molecular orbitals explain the causes of the observed characteristics of the electronic properties of the trichlorotelluro-group. The π-electron system of the benzene ring is only slightly affected by substituent influences and retains six electrons. The large positive charge on the tellurium atom is due to the merging of its p_Z orbital with a combination of suitable orbital symmetry, of the p_X and p_Z orbitals of the chlorine atoms in the π molecular orbital [148].

(b) The Basicity and Dipole Moments of π-Telluranes

The thermodynamic basicity constants of diorganotelluronium dimedone ylids in anhydrous acetonitrile and the correlation of the pK_a values with the σ constants of the substituents have been investigated [118]. Ylids of this type are fairly strong bases (Table 3), comparable in strength with aromatic amines. In the series of dicarbonyl-stabilised ylids of Group VI elements, having structures of the same type, the basicity increases in the sequence S < Se < Te, i.e. increases with decrease of the electronegativity of the 'onium atom and with increase of its size (an analogous relation obtains also for the ylids of Group V elements [179]). The pK_a values of the ylids investigated are best correlated with the σ^0 constants of the substituents ($r = 0.983$; $\rho = 0.958$), which indicates a predominantly inductive effect of the interaction of the aryl rings with the 'onium tellurium atom.

The ylids examined above have relatively low dipole moments compared with the usual values for ylids (Table 3), lying in the range 2–5 D. Such relatively low dipole moments of the ylids, compared, for example, with the dipole moments of diorganosulphonium dicyanomethylides [180] and the fact that they are comparable to the dipole moments of the structurally related arylmethylsulphonium 1,3-indandion ylids (3–5 D) [181] can be explained by the fact that the $Te^+–C^-$ bond moments in telluronium dimedone ylids and the group moment of the dimedone fragment are directed to opposite sides and to a large extent cancel out. In most cases the dipole moments calculated on the basis of a fragmentary vector scheme and determined experimentally agree fairly satisfactorily. The only exception is the *p*-dimethylamino-derivative, where the effect of the direct polar conjugation of the dimethylamino-group with the vacant *d* orbitals of tellurium is evidently manifested.

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During the period when the review was dealt with by the editors a number of new studies were published.

Methods of synthesis of mono-organo-derivatives of tellurium (IV). The interaction of 4-halogeno-substituted diphenyl ethers with tellurium tetrachloride, which proceeds via a stage involving the formation of 2-trichlorotelluro-derivatives and leading ultimately to 10,10-dichlorophenoxatellurins, has been investigated [184,185]. Berry et al. [186] established that, when acetic anhydride reacts with $TeCl_4$, bis(trichlorotelluro)methane is indeed formed and its reduction by potassium metabisulphite yields cyclo-1,4-dimethylenetetratellurium $\overline{CH_2–Te_4–CH_2}$. It has been shown [187] that organotin compounds of the type R_3SnBr and R_4Sn react with $TeBr_4$ (there is no reaction with TeI_4 or the yields are extremely low) to form organotellurium tribromides or diorganotellurium dibromides. An earlier report [57] of the synthesis of phenyltellurium triacetate on oxidation of diphenyl ditelluride with lead tetra-acetate was not subsequently confirmed. Although the presence of $C_6H_5Te(OCOCH_3)_3$ in solution was demonstrated by NMR, [188,189] attempts to isolate this compound in a pure form yielded only a substance of unknown structure. Aryltellurenyl halides ArTeX (X = Br or I), obtained by the reaction of diaryl ditellurides with one equivalent of a halogen in non-polar solvents [190,191], are unstable compounds, particularly in the case of bromine, which disproportionates to diaryltellurium dihalides and elemental tellurium [192]. Use of these compounds in the synthesis of asymmetric diaryl tellurides and selenotellurides has been described by Petragnani [193].

Methods of synthesis of diorgano-derivatives of tellurium (IV). Diphenacyl- and arylphenacyl-tellurium dichlorides have been obtained by the reaction of the trimethylsilyl ether of the enolic form of acetophenone with $TeCl_4$ and aryltellurium trichlorides [194]. Symmetrical and asymmetric diaryltellurium dichlorides have been obtained by treating sodium (or potassium) tellurophenoxides with arene-diazonium tetrafluoroborates in ethanol with subsequent chlorination [195] or by the arylation of diaryl ditellurides with arenediazonium chlorides in the presence of copper(II) salts [196]. A new class of diorgano-derivatives of tellurium(IV)—diaryltellurium di-isocyanates $Ar_2Te(NCS)_2$—have been synthesised by the oxidation of diaryl tellurides with free thiocyanogen [197,198] or by the interaction of diaryltellurium dichlorides with ammonium thiocyanate in methanol [198]. A series of studies have been devoted to methods of synthesis and the investigation of the properties of diaryltellurium diacylates. Petragnani [199] obtained these compounds by treating diaryltellurium dichlorides with carboxylic acids in the presence of silver oxide and Pant [189] synthesised them by oxidising diaryl tellurides with lead tetra-acetate and by the double decomposition of diaryltellurium dichlorides with silver salts of carboxylic acids. In order to obtain diaryltellurium diacylates, including derivatives of dicarboxylic acids, Tamagaki et al. [200] used the reaction, described previously by the present authors [100,101], of diaryltellurium oxides with carboxylic acid anhydrides and the acids themselves. It is of interest to note that dicarboxylic acid anhydrides, for example, phthalic anhydride, give rise to

monomeric compounds on reaction with diaryltellurium oxides, while, according to the results of Dance and McWhinnie[201], the reaction of diaryltellurium dichlorides with sodium salts of phthalic acids yield dimeric diaryltellurium diacylates. The infrared spectra of diaryltellurium diacylates, investigated by Pant et al.,[188] indicate the non-equivalence of the carboxylate groups in certain diaryltellurium diacylates, although according to ^{1}H NMR data both the arene rings and the carboxylate groups are completely equivalent[101]. The mass spectra of diaryltellurium diacylates and certain diaryltellurium dichlorides have been investigated[202,203]. The synthesis of previously unknown esters derived from diorganotellurium dioxides $R_2Te(OR')_2$, based on the interaction of dialkyl- or diaryltellurium dihalides with sodium alkoxides, as well as some of their properties have been described[204].

The synthesis of π-telluranes. Diaryltelluronium ylids have been obtained by refluxing diaryltellurium oxides with active methylene compounds (dimedone, indandione, and nitroacetic and malonic esters) in benzene with simultaneous distillation of the water formed[205]. When tellurium tetrahalides TeX_4 (X = F or Cl) interact with hexamethyldisilamides of acetic and arenesulphonic acids, the products are *N*-substituted halogeno-derivatives of iminotelluryls and tellurium *N*,*N*'-diacyldi-imides[206].

The structure of organic derivatives of tellurium(IV). Crystallographic data have been obtained recently for the compounds *o*-$HCOC_6H_4TeX$ (X = Cl, Br, or I)[207] and a complete X-ray diffraction analysis of di-(*p*-anisyl)telluronium dimedone ylid was carried out[208]. The electronic effects of the tellurium-containing substituents $-Te(CH_3)F_2$, $-Te(C_6H_5)(NCS)_2$, and $-Te(C_6H_5)F_2$ have been investigated[209] with the aid of ^{19}F NMR. Studies have been made on the Mössbauer[210-213] and ^{125}Te NMR[214] spectra of various organotellurium compounds, including σ-telluranes.

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