TELLURIUM

LITERATURE SURVEY COVERING THE YEARS 1972–1974

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I. Introduction

"The Organic Chemistry of Tellurium", a book in which all aspects of the chemistry of compounds containing at least one tellurium-carbon bond have been reviewed, has been published in 1974[79]. The publications, which have appeared during the time span from 1840, when Wohler reported the preparation of the first organic tellurium compound, through 1971 and papers abstracted in Chemical Abstracts, Volume 76, No. 1 to 11 have been considered in this book.

The survey presented here is based mainly on the literature, which became available since 1971 and has been abstracted in Chemical Abstracts Volume 76, No. 12 through Volume 81, No. 26. A few earlier publications, which had not been incorporated into the book, have also been included. Just as in the above mentione book, the principle to discuss only compounds containing at least one tellurium-carbon bond has not been followed strictly. Thus, triorganylphosphine tellurides compounds with a group IV element-tellurium bond, such as bis(triethylgermyl) telluride, and bis(methylmercuryl) telluride have been included. However, tellurium sulfur compounds, which do not have at least one tellurium-carbon bond, have been excluded. These derivatives are commonly discussed in the context of sulfur compounds.

In this survey the symbol R is used for alkyl as well as aryl groups. The term "organyl" denotes any organic group. When older results are mentioned, the original references are not cited; instead, the reader is referred to ref. 79, which will provide access to the appropriate papers. Results of physicochemical investigations of organic tellurium compounds are treated in section X.

The partial financial support for this endeavor by the Robert A. Welch Foundation of Houston, Texas, is gratefully acknowledged.

II. Reviews

Many of the reviews, which have appeared since 1970, are mainly concerned with sulfur and/or selenium derivatives. Organic tellurium compounds, which are greatly outnumbered by sulfur and selenium derivatives, have generally only few pages devoted to them. However, these reviews are an ideal starting point for comparative studies of the chemical and physical properties of organic compounds of group VI elements.

The Organic Chemistry of Tellurium (K.J. Irgolic, 1974)[79]: A comprehensive coverage of organic tellurium compounds 1840-1971.

Tellurium (C.W. Cooper, 1971)[34]: A book dealing with all aspects of tellurium and its chemistry.

Organic Compounds of Tellurium (R.A. Zingaro and K.J. Irgolic, 1971)[177]: A brief exposition of the chemistry of the various classes of organic tellurium compounds.

Covalent Carbon-Metal(loid) Compounds (J.B. Dence, 1973)[40]: An elementary discussion of organic compounds of groups III, IV, V and VI elements.

Some Developments of Organic Tellurium Chemistry (N. Petragnani, 1972)[128]: Review of the author's work in the area of organic tellurium and selenium chemistry.

Some Donor and Acceptor Complexes of Organoselenium and Organotellurium Halides (K.J. Wynne, 1971)[73]: Preparation and characterization of compounds obtained from organic selenium and tellurium halides and Lewis acids or bases.

The Chemistry of Selenium-Bearing Organometallic Derivatives of Group VA Elements (R.A. Zingaro, 1972)[178]: Discussion of the chemistry of compounds of the type R_3MXR including $R_3P \rightarrow Te$ derivatives.

Some Aspects of Bonding and Structure in Hypervalent Selenium and Tellurium Chemistry (J.I. Musher, 1972)[115]: Discussion of the theory of hypervalent bonding in selenium and tellurium compounds.

Hypervalent Organic Derivatives of Tellurium and Selenium (D. Hellwinkel, 1972)[77]: Preparation and properties of bis(biphenylylene) tellurium and selenium.

Perfluoroorganic Compounds of Tellurium (A. Haas, 1972)[71]: Review of perfluorinated compounds of tellurium.

Fluorine Compounds of Selenium and Tellurium (B. Cohen and R.D. Peacock, 1970)[31]: Discussion of inorganic fluorine compounds of selenium and tellurium and their fluoroorganic derivatives.

Polyfluoroaromatic Derivatives of Metals and Metalloids (S.C. Cohen and A.G. Massey, 1970)[32]: Review of perfluoroaromatic main group and transition element compounds including tellurium derivatives.

Organic Selenium Compounds: Their Chemistry and Biology (D.L. Klayman and W.H.H. Guenther, eds., 1972)[84]: A comprehensive coverage of organic selenium compounds; the few chapters containing also data on organic tellurium compounds are listed below and are marked with an asterisk*.

Organometallic Derivatives of Silicon (H. Buerger, 1972)[20]: Review of organic silicon compounds containing a silicon-group V or group VI element bond.

d_π-p_π Interactions in Organic Compounds of Group IVB Elements (A.N. Egorochkin et al., 1972)[45]: Review of spectroscopic studies on d_π-p_π interactions of Si, Ge, Sn and Pb including tellurium containing compounds.

Organotin Compounds with Sn-S, Sn-Se and Sn-Te Bonds (H. Schumann et al., 1971)[153]: Review of covalent organometallic compounds of tetravalent tin with sulfur, selenium and tellurium.

Tertiary Phosphine Sulfides, Selenides and Tellurides (L. Maier, 1972)[99]: Discussion of the methods of preparation, reactions and physical properties of tertiary phosphine chalcogenides and tabulation of compounds.

Coordination Compounds with Organic Selenium- and Tellurium-Containing Ligands* (K.A. Jensen and C.K. Jorgenson, 1973)[82]: Review of complexes with selenium or tellurium as central atom and of complexes with selenium- or tellurium-containing ligands.

Metal Complexes of Ligands Containing Sulfur, Selenium or Tellurium (S.E. Livingstone, 1965)[90]: Review of complexes with dialkyl chalcogenides and chalcogeno-derivatives of metal carbonyls and cyclopentadienyls.

Thiophens and Their Selenium and Tellurium Analogues (S. Gronowitz, 1973)[68]: This review contains a brief discussion of the chemistry of tellurophene and benzotellurophene.

Infrared Spectra of Organic Selenium Compounds* (K.A. Jensen et al., 1973)[81]: Infrared data on organic tellurium compounds have been included.

Characteristic Vibrational Frequencies of Compounds Containing Main Group Elements (S.R. Stobart, 1973)[162]: Raman and ir data for compounds with a main group element-tellurium bond have been included in this review.

Physicochemical Investigations of Selenium Compounds, X-Ray Diffraction* (I.L. Karle and J. Karle, 1973)[83]: Structural data for organic tellurium compounds are discussed and tabulated.

The following reviews are not concerned with organic tellurium compounds. They treat, however, subjects of interest to the organometallic tellurium chemist.

Inorganic Chemistry of Tellurium (W.A. Dutton, 1971)[43]: A review of all of the major work on inorganic compounds of tellurium.

Analytical Chemistry of Tellurium (C.W. Cooper, 1971)[36]: A reasonably comprehensive treatment of the separation, isolation, detection, identification and determination of tellurium as well as the analysis of tellurium.

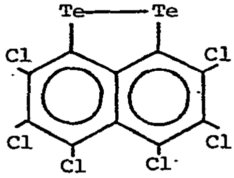
Toxicology of Tellurium and Its Compounds (C.W. Cooper, 1971)[35]: A presentation of data on the toxicity of tellurium and its compounds to serve as a guide for those working with these materials.

III. Methods for the Introduction of Tellurium into Organic Molecules

During the time covered by this survey elemental tellurium, tellurium tetrachloride and tetrabromide, sodium telluride, hydrogen telluride, $Te_4(AsF_6)_2$ and tellurium(IV) tetrakis(diethyldithiocarbamate) have been employed as reagents to introduce tellurium into organic molecules. Generally, methods reported in the older literature have been applied to prepare hitherto unknown organic tellurium compounds. A few novel preparative procedures have, however, also been reported.

Thayer[165] heated tellurium with the alkyl iodides n-RI (R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_5H_{11}) and obtained the dialkyl tellurium diiodides, R_2TeI_2, in yields ranging from 66% (R = CH_3) to 5% (R = C_5H_{11}). Only black intractable mixtures were formed in reactions with iso-propyl or 2-butyl iodide. Iodobenzene did not react with tellurium[166].

Although arenediazonium chlorides and tellurium produced diaryl tellurium dichlorides in low yields[79], benzenediazonium tetrafluoroborate did not react[116]. Octachloronaphthalene and tellurium[P-2] were claimed to yield the ditelluride **1**.



1

Tellurium is known to insert into carbon-lithium, carbon-sodium, and carbon-magnesium bonds. The thus prepared tellurium compounds, R-Te-M (M = Li, Na, MgBr) are used _in situ_. The following derivatives have been prepared: C_6H_5TeLi[151], $2\text{-}[(C_2H_5O)_2C(R)]C_6H_4TeLi$ (R = H, CH_3)[133], _tert_-$C_4H_9C{\equiv}CTeNa$[142], 2- and $4\text{-}\begin{matrix}CH_2-O\\|\\CH_2-O\end{matrix}\!\!>C(CH_3)C_6H_4TeLi$[132], and $4\text{-}RC_6H_4TeMgBr$ (R = H, CH_3)[151].

Tellurium replaced mercury in $[(\underline{i}\text{-}C_3H_7)_3Ge]_2Hg$, when the reactants were heated in tetrahydrofuran[65] at 70°. With ethyldi(ethoxy)phosphine[69] or N-diphenylphosphinotriphenylphosphazene[69] the corresponding phosphine tellurides were obtained.

In the older literature[79] "tellurium dihalides", TeX_2, were described to react with Grignard reagents to produce a variety of organic tellurium compounds. It has been shown, that these dihalides disproportionate in diethyl ether solution. A recent investigation[28] has now shed doubt on the existence of $TeCl_2$ in the solid state.

Futekov[62] claimed to have prepared $(C_6H_5COCH_2)_2TeCl_2$ from acetophenone and tellurium tetrachloride in an aqueous hydrochloric/sulfuric acid medium. The condensation reaction between tellurium tetrachloride and aromatic compounds has been extended (eqn. 1).

(1) $$TeCl_4 \xrightarrow[160°,\ 6\ hrs.]{excess\ RR'C_6H_4} (RR'C_6H_3)_2TeCl_2$$

R, R': H, $4\text{-}CH_3O$; $3\text{-}CH_3O$, $4\text{-}CH_3O$; $2\text{-}CH_3O$, $4\text{-}CH_3O$; $3\text{-}CH_3$, $4\text{-}CH_3O$; $4\text{-}C_2H_5O$, H[10].

An excess of the aromatic compound, high temperatures and long reflux times favor the formation of the diaryl tellurium dihalides. However, bromobenzene gave only 4-bromophenyl tellurium trichloride in 38% yield. Chlorobenzene did not react. Benzonitrile heated with tellurium tetrachloride for 12 hours at 190° produced 2,4,6-triphenyl-sym-triazine[10]. Sadekov[147] prepared para-substituted aryl tellurium trichlorides by refluxing the benzene derivatives, RC_6H_5 (R = C_3H_7O, C_4H_9O, CH_3COO, C_2H_5COO, CH_3S) in toluene for several hours. Naphthalene, fluorene and fluoranthene yielded under similar conditions aryl tellurium trichlorides, whereas anthracene and pyrene gave diaryl tellurium dichlorides[10].

Mononuclear aromatic hydrocarbons, which are not activated, for instance, by an alkoxy group, have been found to condense with tellurium tetrachloride in the presence of aluminum chloride. Thus, the diaryl tellurium dichlorides, $(4\text{-}RC_6H_4)_2TeCl_2$ (R = H, Cl, Br, CH_3) were obtained in yields ranging from 30% to 44%[10]. Guenther[70] showed that the nature of the product of the condensation reaction between benzene and tellurium tetrachloride in the presence of aluminum chloride is dependent on the $TeCl_4:AlCl_3$ ratio and the reflux time. By proper adjustment of these variables phenyl tellurium trichloride, diphenyl tellurium dichloride or triphenyl telluronium chloride were obtained in acceptable yields.

The decomposition of benzene- or 4-methylbenzenediazonium tetrafluoroborate by zinc dust in acetone in the presence of tellurium tetrachloride yielded very small amounts of diaryl tellurides[116].

Tellurium tetrabromide has been shown to react with cyclohexene to form the crystalline compound 1,2-bis(tribromotelluro)cyclohexane[74].

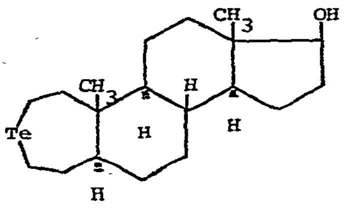
Tellurium-carbon bonds can be formed in reactions between tellurium tetrachloride and organometallic compounds. Perfluorophenyl lithium and tellurium tetrachloride employed in a 2:1 molar ratio gave surprisingly tris(perfluorophenyl) tellurium chloride[32]. With phenyl lithium, triphenyl telluronium salts were obtained[72]. McWhinnie[107] reported that phenylmagnesium bromide and tellurium tetrachloride in a 5:1 molar ratio in diethyl ether/benzene medium at 0° yielded diphenyl telluride without the formation of elemental tellurium, a side product observed by other workers[79] in these reactions. Similarly, were obtained bis(pentafluorophenyl) and dibenzyl telluride[107]. However, tellurium tetrachloride and phenyl magnesium bromide in a 1:5 molar ratio gave a 36% yield of the triphenyl telluronium salt[72].

Organic mercury compounds, which have been one of the earliest reagents employed in the synthesis of organic tellurium compounds[79], have been used by Sadekov[147] to convert tellurium tetrachloride into the aryl tellurium trichlorides, $RC_6H_4TeCl_3$ (R = 3-F, 4-Cl, 4-Br, 3-NO_2, 4-NO_2).

Pant[123] found that tetraaryl lead compounds and tellurium tetrachloride in toluene formed at room temperature the tellurium dichlorides $(4\text{-}RC_6H_4)_2TeCl_2$ (R = H, CH_3). Triphenyl lead chloride in dioxane produced phenyl tellurium trichloride and dimethyl diphenyl lead yielded diphenyl tellurium dichloride. The organic tellurium compounds were obtained in yields higher than 90%.

Tellurium(IV) tetrakis(diethyldithiocarbamate) was quantitatively converted to diphenyl telluride by a large excess of phenylmagnesium bromide in diethyl ether solution[155].

Lithium telluride and silyl bromide[66] or trimethylsilyl chloride[19] gave the respective disilyl tellurides. Sodium telluride has been reacted with butadiyne[54] and 1,4-bis(trimethylsilyl)butadiyne[7,171] in absolute methanol to yield tellurophene. Bis(alkylacetylenyl) sulfides, similarly, produced 3,5-dialkyl-1-thia-4-tellura-2,5-cyclohexadienes[111]. Sodium telluride and 4,8-dibromo-1,5-cyclooctadiene in dimethylformamide gave 9-tellurabicyclo[3,3,1]-nona-2,6-diene and bicyclo[5,1,0]octa-2,5-diene[38]. The heterocyclic ring system **2** was generated[176] when sodium telluride was refluxed in ethanol with the steroid derivative **3**.



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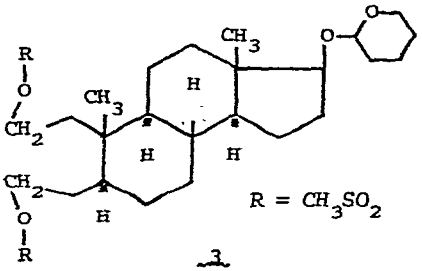


3

Sodium telluride refluxed in benzene with trimethylgermyl, -stannyl and -plumbyl chloride yielded the tellurides $[(CH_3)_3M]_2Te$ (M = Ge, Sn, Pb)[154].

Hydrogen telluride was condensed with methyl mercury bromide[17] to yield $(CH_3Hg)_2Te$. Paige[121] allowed $Te_4(AsF_6)_2$ to interact with tetrafluoroethylene in the presence of SO_2 or SO_2F_2 at 100°. In both cases, $(C_2F_5)_2Te$ and $(C_2F_5)_2Te_2$ were obtained as the major products.

The reactions of organic tellurium compounds which proceed with formation of novel organic tellurium derivatives are summarized in Fig. 1.

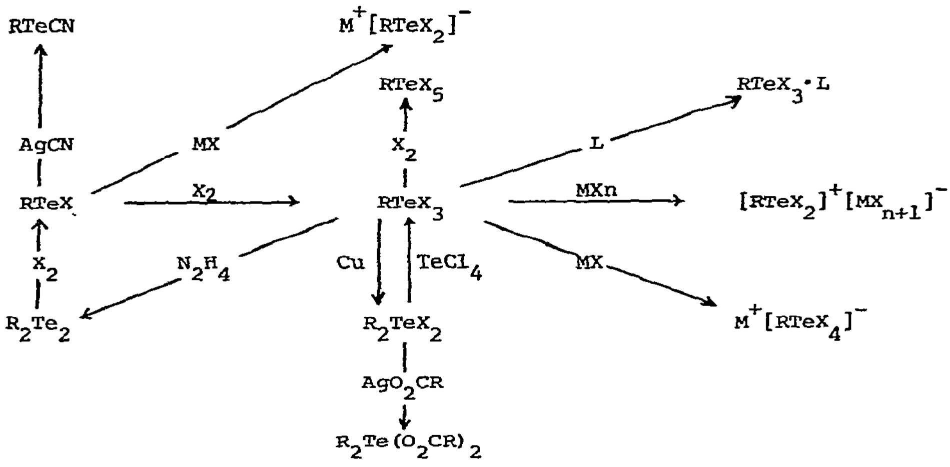


Fig. 1: New Transformations of Organic Tellurium Compounds

All these reactions will be discussed in the sections devoted to the appropriate organic tellurium compounds.

IV. Tellurocyanates and Tellurium Derivatives, X=C=Te

Tellurocyanates, M^+TeCN^-, have been isolated for the first time only a few years ago. In order to stabilize the tellurocyanate anion, large counter ions such as the tetraalkylammonium or tetraphenylarsonium cations were necessary. Austad has recently investigated a few reactions of the tellurocyanate ion employing its tetraphenylarsonium salt. In acetonitrile solution the salt reacted with triphenylphosphine in the presence of lithium perchlorate[3] to produce in 30% yield according to eqn. (2) the zerovalent tellurium complex

$$\text{TeCN}^- + 2(C_6H_5)_3P \rightleftarrows [(C_6H_5)_3P]_2Te + CN^- \quad (2)$$

$[(C_6H_5)_3P]_2Te$, which decomposed at 83-85°. Addition of tetraphenylarsonium cyanide displaced the equilibrium toward the left. When the tellurocyanate in acetonitrile was treated with lithium perchlorate alone, elemental tellurium precipitated[3]. Tetraphenylarsonium tellurocyanate and benzyl bromide in acetonitrile medium combined in a second order reaction. The tetraphenylarsonium benzylbromocyanotellurate(II) was isolated in 73% yield in form of yellowish crystals melting at 118°. Benzyl chloride reacted at least three orders of magnitude slower than the bromide[4].

The ir and Raman spectra of tetramethylammonium and tetraphenylarsonium tellurocyanate have been reported[46]. The N(1s) binding energy in the tetraphenylarsonium salt was determined by electron spectroscopy using X-ray excitation[117].

The second organic tellurocyanate ever prepared, was obtained by heating 2-formylphenyl tellurium bromide with silver cyanide[133]. The remarkable stability of the tellurocyanate, which melted at 104°, is caused by the interaction of the tellurium atom with the carbonyl oxygen atom as discussed in section V-B.

Carbon oxide telluride[163], O=C=Te, was probably formed from carbon monoxide and recoil tellurium atoms produced by fission of ^{235}U.

V. Compounds Containing a Single Carbon-Tellurium Bond

The compounds treated in this section contain only one carbon-tellurium bond and, therefore, comprise tellurols, RTeH, organyl tellurium halides and pseudohalides, RTeX, organyldihalotellurium compounds, $[RTeX_2]^-$ and $[RTeX_2]^+$, organyl tellurium trihalides, organyltetrahalotellurates(IV), organyl tellurium pentahalides, $RTeX_5$, tellurinic acids, RTeOOH, and their derivatives and diorganyl ditellurides, R_2Te_2. Tellurium derivatives, in which the second tellurium valence is satisfied by group I to V element atoms or selenium are discussed in section VIII.

A. Tellurols

The only paper during the survey period concerning tellurols was published by Sink[158]. Methanetellurol and trideuteriomethanetellurol was prepared in greatly varying yields by hydrolysis with dilute sulfuric acid of the residues obtained through reactions of the appropriate dimethyl ditelluride and sodium in liquid ammonia. The hydrogen atom on the tellurium atom was exchanged for deuterium derived from D_2O. These methanetellurols, pale yellow, volatile liquids of obnoxious and persistent odor, were easily oxidized by mild oxidizing agents such as 10% sulfuric acid. At room temperature the tellurols decomposed to the ditellurides, a reaction which seemed to be catalyzed by stopcock grease. On irradiation of samples with 632.8 nm light of a He-Ne laser the decomposition products dimethyl ditelluride, hydrogen, methane, higher organics and tellurium mirrors were observed.

B. Tellurenyl Compounds

With the exception of 2-naphthyl tellurium iodide it has not been possible to isolate other aryl tellurium halides, which do not have in the ring a stabilizing carbonyl group in ortho-position to the tellurium atom. Aliphatic tellurium halides, RTeX, are still unknown. However, aromatic derivatives can be prepared in solution from diaryl ditellurides and an equimolar amount of elementary halogen (eqn. 3).

(3) $$R_2Te_2 + X_2 \longrightarrow 2RTeX$$

R, X: C_6H_5, Cl[73]; C_6H_5, Br[73]; C_6H_5, I; 4-$CH_3C_6H_4$ I; 4-$CH_3OC_6H_4$, Br; 4-$CH_3OC_6H_4$, I; 4-$C_2H_5OC_6H_4$, Br; 4-$C_2H_5OC_6H_4$, I[130].

Petragnani[130] performed the halogenolysis of the ditellurides in benzene at 0° and added to the reaction mixtures phosphonium salts, which produced tetraorganylphosphonium organyldihalotellurates(II). These compounds are treated in section V-C.

Hauge[73] carried out the preparation of the phenyl tellurium halides by adding the required amount of chlorine or bromine dissolved in methanol to an ethanolic or methanolic solution of diphenyl ditelluride containing thiourea, selenourea or a phosphine selenide.

The ligands complexed with the tellurium halides according to eqn. (4).

(4) $$C_6H_5TeX + nL \longrightarrow C_6H_5TeX{\cdot}L_n$$

X, L, n, % yield, mp.°C: Br, thiourea, 1, 90%, –;
Cl, selenourea, 1, 89%, 165° (dec); Cl, selenourea, 2, 70%, 169° (dec)
Br, selenourea, 1, 72%, 195° (dec); Br, $(C_6H_5)_3PSe$, 1, 70%, 127° (dec);
Cl, trimorpholylphosphine selenide, 1, 72%, 137° (dec);
Br, trimorpholylphosphine selenide, 1, 79%, 138° (dec).

When four moles of selenourea per mole of ditelluride were used, the bis(selenourea) complex of phenyl tellurium chloride was isolated. The same compound formed upon mixing aqueous methanolic hydrochloric acid solutions of the monoligated complex with an additional amount of selenourea.

When potassium selenocyanate was present during the halogenolysis of diphenyl ditelluride with bromine, bis(phenyltellurium) selenide instead of the expected phenylbis(selenocyanato)tellurate(II) was obtained. The following reaction sequence (eqn. 5) has been suggested[73]:

(5)

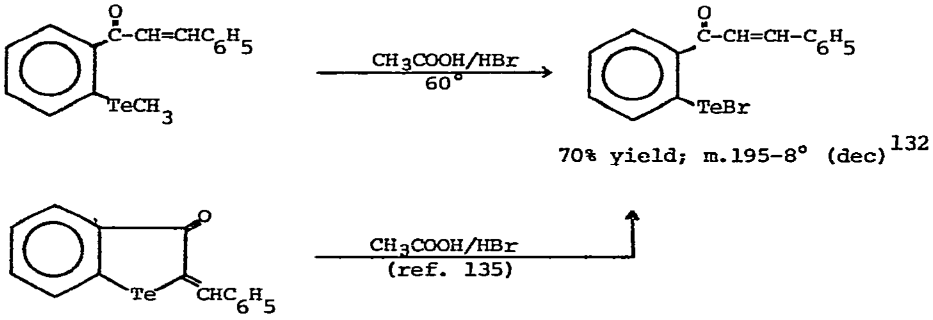
$$\begin{tikzcd}
\mathrm{RTeBr} \arrow[r, "\mathrm{KSeCN}"] & \mathrm{RTeSeCN} \arrow[r, "\mathrm{SeCN}^-"] & \mathrm{RTeSe}^- + \mathrm{Se(CN)}_2 \arrow[dl, "\mathrm{RTeSeCN}"] \\
& \mathrm{RTeSeTeR} + \mathrm{SeCN}^- &
\end{tikzcd}$$

4

The same compound 4 was the product of the reaction of the selenourea complex of phenyl tellurium chloride and potassium selenocyanate. The reactions of phenyl tellurium bromide with tetramethylammonium seleno- or thiocyanate, which led to the phenylbis(chalcogenocyanato)tellurate(II) are discussed in section V-C.

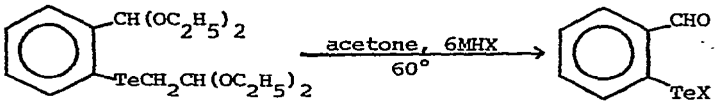
The isolation of aryl tellurium halides becomes possible, when a carbonyl group is present in ortho-position to the tellurium atom. These tellurium monohalides were prepared by Piette and coworkers as described by eqns. (6) - (8).

(6)



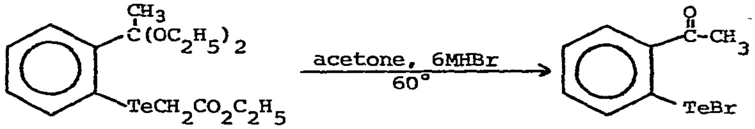
70% yield; m.195-8° (dec)[132]

(7)



X, % yield, mp.°C: Cl, 50, 94°; Br, 50, 119°; I, –, 96°[133].

(8)

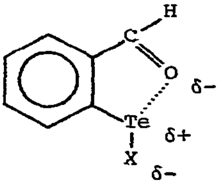


50% yield, m.115°[133].

The formation of these tellurium monohalides seems to be facilitated by the presence of a carbonyl function in the aliphatic group bonded to the tellurium atom. Only the ditelluride was obtained when 4-acetylphenyl carbethoxymethyl telluride was treated as described by eqn. (8). 2-Naphthyl 1,1-diethoxy-2-ethyl telluride furnished only tarry products and elemental tellurium[133].

The successful preparation of 2-formylphenyl tellurium selenocyanate and thiocyanate has also been claimed[5].

An X-ray structural analysis of 2-formylphenyl tellurium bromide[6] and nmr investigations employing carbon disulfide solutions of the 2-formylphenyl tellurium derivatives, RTeX (X = Cl, Br, I, CN, SCN, SeCN)[5], showed, that the molecules exist in the conformation **5**, which permits the tellurium atom to



5

interact with the carbonyl group. This interaction sufficiently stabilizes the tellurium halide, which is now coordinatively less unsaturated, to allow the isolation of these compounds.

In addition to the reactions leading to organyldihalotellurates(II), which have already been mentioned the tellurium halides undergo reactions, in which the halogen atom is replaced by cyanide[133] (section IV) or benzenethiolate or -selenolate[133] (section VIII-D). Dimethylcadmium and 2-formyl[135] or 2-cinnamoylphenyl[135] tellurium bromide produced the corresponding 2-acylphenyl methyl tellurides. Chlorine and 2-formylphenyl tellurium chloride gave the trichloride, $RTeCl_3$[133]. Benzaldehyde and 2-acetylphenyltellurium bromide condensed in the presence of hydrogen chloride to 3-oxo-2-benzylidene-2,3-dihydrobenzotellurophene[135].

C. Organyldihalotellurium Compounds, $[RTeX_2]^-$ and $[RTeX_2]^+$

Salts, in which the $RTeX_2$ moiety serves either as an anion or as a cation have recently been prepared. The anionic aryldihalotellurates(II) were obtained, when aryl tellurium monohalides serving as halide ion acceptors were reacted with ammonium, phosphonium or arsonium halides (eqn. 9).

$$\text{RTeX} + \text{M}^+\text{Y}^- \xrightarrow{C_6H_6,\ CHCl_3} \text{M}^+[\text{RTeXY}]^- \qquad (9)$$

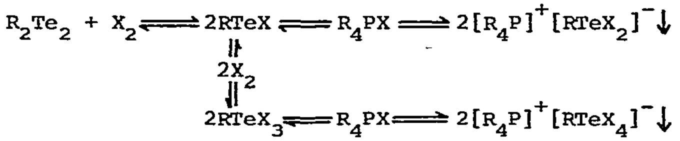
The compounds, which have been isolated and characterized, are listed in Table 1. Dihalo-, mixed dihalo-, bis(thiocyanato)- and bis(selenocyanato)tellurates(II) have been synthesized. The aryl tellurium halides obtained by halogenolysis of diaryl ditellurides (section V-B) were used in situ. When the preparation of triphenylmethylphosphonium 4-ethoxyphenyldibromotellurate(II)[130] or tetramethylammonium phenyldibromotellurate(II)[73] was attempted, only the aryltetrabromotellurate(IV) was isolated. Only intractable oils were obtained from reactions which should have produced triphenylbenzylphosphonium 4-ethoxyphenlchloroiodo-

TABLE 1
ORGANYLDIHALOTELLURATES(II)

$M^+[RTeXY]^-$						Ref.
R	X	Y	M^+	Yield, %	mp. °C	
C_6H_5	SCN	SCN	$(CH_3)_4N$	65	108 (dec)	73
	SeCN	SeCN	$(CH_3)_4N$	78	134 (dec)	73
$4\text{-}CH_3OC_6H_4$	Br	Br	$(C_6H_5)_3PCH_3$	96	145	130
	I	I	$(C_6H_5)_3PCH_3$	85	104-6	130
$4\text{-}C_2H_5OC_6H_4$	Br	I	$(C_6H_5)_3PCH_3$	90	128	130
	I	I	$(C_6H_5)_3PCH_3$	95	143	130
$C_6H_5CH_2$	Br	CN	$(C_6H_5)_4As$	92	118	4
$2\text{-}C_{10}H_7$	I	I	$(C_6H_5)_3PCH_3$	98	160-2	130

tellurate(II) or the methyltriphenylphosphonium salts of $C_6H_5TeI_2^-$, $4\text{-}CH_3C_6H_4TeI_2^-$ and $C_6H_5TeBrI^-$. It has been claimed, that the relative stabilities and solubilities of the tellurium containing species influencing the equilibria represented in eqn. (10) will determine whether a pure product or a mixture of tellurium(II) and tellurium(IV) compounds is obtained[73,130].

(10)



$$\begin{tikzcd}
R_2Te_2 + X_2 \arrow[r, leftrightharpoons] & 2RTeX \arrow[r, leftrightharpoons] \arrow[d, leftrightharpoons, "2X_2"] & R_4PX \arrow[r] & 2[R_4P]^+[RTeX_2]^-\downarrow \\
& 2RTeX_3 \arrow[r, leftrightharpoons] & R_4PX \arrow[r] & 2[R_4P]^+[RTeX_4]^-\downarrow
\end{tikzcd}$$

These dihalotellurate(II) compounds seem to be rather stable. The red 2-naphthyldiiodotellurate(II) is reported to be stable in air[130]. The colorless benzylbromo(cyano)tellurate(II) was only slowly decomposed by water[4].

Raman data[130] suggest a trigonal bipyramidal geometry for these compounds with the halide ions in the apical and the organic group and the two lone electron pairs of the tellurium atom in the equatorial positions.

The cationic tellurium species, $[RTeX_2]^+$ are formed, when an organyl tellurium trihalide acts as a halide ion donor. The only example known[126,173] is methyldichlorotellurium(IV) hexachloroantimonate(V) obtained according to eqn. (11).

(11) $$CH_3TeCl_3 + SbCl_5 \longrightarrow [CH_3TeCl_2]^+SbCl_6^-$$

The compound $C_2F_5TeF_3 \cdot 2SbF_5$ prepared from the components[41] at 50° has perhaps a similar constitution.

D. Organyl Tellurium Compounds, $RTeX_3$

Aryl tellurium trichlorides are monomeric in donor solvents[113,174] and behave as weak electrolytes with a tendency to form weak solvates[9,174]. The aryl tellurium trihalides have much greater thermal stability and give much more stable solutions than the aliphatic derivatives[174]. Raman and ir data suggest that in the solid state the trihalides are dimeric with five-coordinate tellurium atoms. The bromides might be more associated than the chlorides or iodides[108]. Calculations with the extended Hückel method indicated that for phenyl tellurium trichloride the conformation with the phenyl group in the equatorial position is more stable than the axial conformation. The results of dipole moment measurements on a series of aryl tellurium trichlorides indicated that conjugation between the p- or d-orbitals of the tellurium atom and the ring Π-orbitals does not exist. The energy barrier for the rotation of the phenyl group about the phenyl-Te axis was calculated to be 15 to 20 kcal/mole[113].

The organyl tellurium compounds, which have received attention, are the trifluoride, trichlorides, tribromides, triiodides, triacetates and tris(diethyldithiocarbamates). A fair number of new organyl tellurium trihalides have been prepared by established methods such as the halogenolysis of ditellurides in organic medium, the condensation of tellurium tetrachloride with aromatic hydrocarbons containing an activating substituent and reaction of aryl mercury chlorides with tellurium tetrachloride. The products obtained by these methods and by novel approaches to the synthesis of organyl tellurium trihalides are listed in Table 2. The new synthetic methods are discussed below.

Diphenyl ditelluride was converted to phenyl tellurium trichloride by thionyl chloride[148]. Chlorine monofluoride and bis(pentafluoroethyl) ditelluride gave the alkyl tellurium trifluoride[41], the first fluoride prepared by halogenolysis. It should be noted that the preparation of phenyl tellurium triiodide from the ditelluride and iodine must be done at 5°. At higher temperatures intractable mixtures were obtained[108]. The addition of chlorine to 2-formylphenyl tellurium chloride produced the trichloride[133]. This reaction is not of importance for $RTeX_3$ compounds, since the conversion of ditellurides to tellurium trichlorides can be effected in one step. The monohalides, which can be isolated only in special cases, would, however, be useful as starting materials for $RTeXY_2$ derivatives.

The condensation of tellurium tetrachloride with aromatic compounds containing an activating substituent such as an alkoxy group has been known for a long time. This reaction has now been extended to bromobenzene[10], naphthalene, fluorene and fluoranthene[147]. By refluxing these reagents in toluene until the hydrogen chloride evolution had ceased, the aryl tellurium trichlorides were obtained in rather low yields. Chlorobenzene and benzonitrile did not react[10]. Guenther[70], found, that the trichlorotelluro group can be introduced into benzene by refluxing it with a 1:2 molar mixture of tellurium tetrachloride and aluminum chloride until an amount of hydrogen chloride equimolar to the tellurium tetrachloride had been generated. To facilitate the isolation of the organic tellurium compound it was reduced to the ditelluride, which was obtained in a 53% yield. Bergman[10] noted that benzene, chlorobenzene or bromobenzene and tellurium tetrachloride produced upon refluxing for long times a mixture of the organyl tellurium trichloride and the diorganyl tellurium dichloride.

An exchange of organic groups had been observed when the aryl tellurium trichlorides, $4\text{-}RC_6H_4TeCl_3$ ($R = CH_3$, Br, C_2H_5O), were heated with anisole at 110°. Under these conditions the 4-methoxyphenyl tellurium trichloride was

TABLE 2
ORGANYL TELLURIUM TRIHALIDES*

$RTeX_3$	Prepared from	Yield %	mp.°C	Ref.
$C_2F_5TeF_3$*	R_2Te_2 + 6ClF, -78°	72	~95	41
1,2-<u>cyclo</u>-$C_6H_{10}(TeBr_3)_2$*	cyclohexene + $TeBr_4$	-	-	74
$C_6H_5TeCl_3$	$TeCl_4$ + $C_6H_6/AlCl_3$	53**	-	70
	R_2Te_2 + $SOCl_2/CHCl_3$	-	-	148
	R_2TeCl_2 + $TeCl_4$	69	211-4	148
	$TeCl_4$ + $(C_6H_5)_3PbCl$	98	214-6	123
$C_6H_5TeBr_3$*	R_2Te_2 + Br_2/CCl_4, 10°	45	227-9	108
$C_6H_5TeI_3$*	R_2Te_2 + I_2/CCl_4, 5°	27	181	108
4-$CH_3C_6H_4TeBr_3$*	R_2Te_2 + Br_2/CCl_4, 10°	33	216	108
4-$CH_3C_6H_4TeI_3$*	R_2Te_2 + I_2/CCl_4, 5°	54	176	108
3-$FC_6H_4TeCl_3$*	$TeCl_4$ + RHgCl/diox	94	195	147
4-$ClC_6H_4TeCl_3$*	$TeCl_4$ + RHgCl/diox	96	225	147
4-$BrC_6H_4TeCl_3$*	R_2TeCl_2 + $TeCl_4$/toluene	75**	-	148
	$TeCl_4$ + RH reflux	38	210(dec)	10
	$TeCl_4$ + RHgCl/diox	95	199	147
3-$O_2NC_6H_4TeCl_3$*	$TeCl_4$ + RHgCl/diox	64	170-2	147
2-formyl$C_6H_4TeCl_3$	RTeCl + Cl_2	-	-	133
4-$O_2NC_6H_4TeCl_3$*	$TeCl_4$ + RHgCl/diox	56	193-5	147
4-$CH_3OC_6H_4TeCl_3$	R_2TeCl_2 + $TeCl_4$/toluene	93	191	148
	4-$RC_6H_4TeCl_3$† + $CH_3OC_6H_5$	-	-	10

3,4-$(CH_3O)_2C_6H_3TeCl_3$*	$TeCl_4$ + RH/toluene	81	181	147
4-$C_2H_5OC_6H_4TeCl_3$	R_2TeCl_2 + $TeCl_4$/toluene	81	180	148
4-$C_3H_7OC_6H_4TeCl_3$*	$TeCl_4$ + RH/toluene	76	174	147
4-$C_4H_9OC_6H_4TeCl_3$*	$TeCl_4$ + RH/toluene	85	169	147
4-$CH_3SC_6H_4TeCl_3$*	TeCl + RH/$CHCl_3$	51	188-90	147
2-$CH_3COC_6H_4TeCl_3$*	R_2Te_2 + Cl_2	100	130-6	132
4-$CH_3COC_6H_4TeCl_3$*	$TeCl_4$ + RH/toluene	64	195	147
4-$C_2H_5COC_6H_4TeCl_3$*	$TeCl_4$ + RH/toluene	58	198	147
1-$C_{10}H_7TeCl_3$	$TeCl_4$ + RH	24	177-81	147
2-fluorenyl-$TeCl_3$*	$TeCl_4$ + RH	53	255 (dec)	147
3-fluoranthenyl-$TeCl_3$*	$TeCl_4$ + RH	18	241-3	147

*The compounds marked by one asterisk are derivatives reported for the first time during the period covered by the survey.

**The tellurium trichloride was not isolated but reduced to the ditelluride, whose yield is given.

†R = CH_3, Br, C_2H_5O.

formed. These exchange reactions might be useful in organic tellurium chemistry and should be investigated in detail.

Sadekov and coworkers[148] discovered that aryl tellurium trichlorides were formed when diaryl tellurium dichlorides were refluxed in toluene with an equimolar amount or an excess of tellurium tetrachloride (eqn. 12). The yields of these reactions were higher than 80%.

$$(12) \qquad (4\text{-}RC_6H_4)_2TeCl_2 + TeCl_4 \longrightarrow 2(4\text{-}RC_6H_4)TeCl_3$$

$$R = H,\ Br,\ CH_3O,\ C_2H_5O$$

Reaction (12) is reversible. The tellurium dichlorides were obtained when the trichlorides were refluxed in the presence of, for instance, copper powder[148], which removed the tellurium tetrachloride by its reduction to tellurium.

The arylation of tellurium tetrachloride to phenyl tellurium trichloride was carried out in 98% yield with triphenyl lead chloride[123].

In contrast to the addition of tellurium tetrachloride to cyclohexene, which gave 2-chlorocyclohexyl tellurium trichloride[79], tellurium tetrabromide produced 1,2-bis(tribromotelluro)cyclohexane, whose structure has been ascertained by an X-ray single crystal analysis[74].

The attempt to prepare aryl tellurium triacetates, $4\text{-}RC_6H_4Te(O_2CCH_3)_3$ (R = H, C_2H_5O) from the trichlorides and silver acetate in benzene solution or from diaryl ditellurides and lead tetraacetate[124,125] was only partially successful. Although ir and nmr spectroscopic evidence suggested the presence of triacetates in solution, only white crystals of indefinite composition containing hydrolysis products were obtained.

An X-ray structural analysis of phenyl tellurium tris(diethyldithiocarbamate) revealed the molecular shape to be a distorted pentagonal bipyramid with the phenyl group occupying one of the apical positions[48,49].

The reactions of organyl tellurium trihalides will be discussed only in general terms with reference given to those sections in which detailed descriptions can be found. The aryl tellurium trichlorides have been reduced to ditellurides by sodium sulfide nonahydrate[147], sodium disulfite[70] and hydrazine[10]. The reduction of a mixture of two different aryl tellurium trihalides by various reducing agents did not produce asymmetric ditellurides, R-TeTe-R'[109] (section V-H). The exchange of the aryl group for a 4-methylphenyl group[10] upon heating with anisole at 110° has been already mentioned. Aryl tellurium trichlorides were arylated to diaryl tellurium dichlorides by triphenyl lead chloride[123] (section VI-B). Ethoxyphenyl tellurium trichloride and dimethylaniline at room temperature gave the unsymmetric tellurium dichloride; however, with anisole at 160° only bis(4-methoxyphenyl) tellurium dichloride was obtained[10] and not the mixed compound as claimed by Morgan[114a]. Refluxing aryl tellurium trichlorides in benzene in the presence of copper powder yielded diaryl tellurium dichlorides[148] (section VI-B). Pentafluoroethyl tellurium trifluoride combined with chlorine monofluoride to produce $RTeF_4Cl$ and TeF_5Cl (section VI-F) and with cesium fluoride to form a 1:1 adduct[41]. The hydrolysis of aryl tellurium trichlorides[164] will be discussed in section V-G.

Aryl tellurium trichlorides and nickel refluxed in bis(2-methoxyethyl) ether produced biaryl compounds in coupling reactions with elimination of the trichlorotellurium group (eqn. 13). The biaryls were isolated in yields ranging from 50 to 80%[10].

$$(13)\qquad 2(3\text{-R-}4\text{-R}'C_6H_3)TeCl_3 \xrightarrow{Ni} (3\text{-R-}4\text{-R}'C_6H_3)_2$$

$$\text{R, R}'\text{:}\quad H, H;\ H, CH_3;\ H, Br;\ H, CH_3O;\ H, C_2H_5O;\ CH_3, CH_3O.$$

Section V-E is devoted to organyltetrahalotellurates(IV), which are formed from organyl tellurium trihalides and ionic halides. The reactions between organyl tellurium trihalides and antimony halides leading to compounds of the type $[RTeCl_2]^+SbCl_6^-$ are described in section V-C.

Aryl tellurium trihalides formed 1:1 adducts with pyridine, 4-picoline, 4-picoline N-oxide and N,N,N',N'-tetraethyldithiooxamide upon combining equi-

TABLE 3
COMPLEXES OF ARYLTELLURIUM TRICHLORIDES WITH NEUTRAL LIGANDS

$RTeX_3 \cdot L$				Ref.
R	X	L*	mp.°C	
C_6H_5	Cl	pic	211	9, 174
		picO	199	9, 174
$4\text{-}CH_3C_6H_4$	Cl	py	235-7	9, 174
		pic	231	9, 174
		picO	210	9, 174
$4\text{-}CH_3OC_6H_4$	Cl	py	201	9, 174
		pic	197	9, 174
		picO	184	9, 174
	Cl	teto	-	29
	Br	teto	-	29
	I	teto	-	29
$4\text{-}C_2H_5OC_6H_4$	Cl	teto	-	29
	Br	teto	-	29
	I	teto	-	29

*py = pyridine, pic = 4-picoline, picO = 4-picoline N-oxide,

teto = tetraethyldithiooxamide

molar amounts of the reactants in an organic solvent (Table 3). In these adducts, in which the tellurium atom serves as the acceptor, the ligands are coordinated via the nitrogen, oxygen or sulfur atoms. A structure involving a six-coordinate tellurium atom has been suggested for the oxamide complex[29]. The pyridine and picoline complexes are probably five-coordinated in the solid state. They dissociated into $[RTeCl_2 \cdot L]^+$ and chloride ions in solution. The N-oxide complexes seem to be extensively dissociated in solution into their components[174]. These complexes are not appreciably sensitive to atmospheric agents.

E. Organyltetrahalotellurates(IV), $M^+[RTeX_4]^-$

Although inorganic hexa- and pentahalotellurates(IV) are well known[43], only one organyltetrahalotellurate(IV) namely $[(CH_3)_3Te]^+[CH_3TeI_4]^-$, had been reported in the literature[79] prior to 1973. A large number of organyltetrahalotellurates(IV) (Table 4) have now been prepared in yields higher than 85% by refluxing organyl tellurium trihalides with ammonium, phosphonium, arsonium or tropylium halides in chloroform or by addition of an aqueous onium salt solution to a solution of the organyl tellurium trihalides in 3M hydrochloric or 3M hydrobromic acid (eqn. 14)[73,129,164].

(14a)

(14b)

$$\begin{tikzcd} RTeX_3 \arrow[rr, "M^+Y^-"] \arrow[dr, "HX"'] & & M^+[RTeX_3Y]^- \\ & H^+[RTeX_4]^- \arrow[r, "M^+X^-"] & M^+[RTeX_4]^- \end{tikzcd}$$

By employing the appropriate onium halides, tellurates containing two different halogen atoms can be synthesized. When hydrohalic acid solutions were employed, compounds containing only the same halogen atoms as present in the acid were isolated because of rapid halogen exchange.

Such halogen exchange reactions (eqn. 15) have been used to prepare compounds not obtainable through reaction (14). The replacement of a halogen atom by one of its heavier homologs proceeded easily in tetrahydrofuran solutions employing dilute hydrohalic acids. The conversion of tetrabromides to chlorides required refluxing with concentrated hydrochloric acid. The iodo derivatives could not be transformed into the bromo or chloro compounds[129]. The aryltetrahalotellurates(IV) ions were retained by the anion exchange resin IRA·400·BDR

(15)

$$\begin{tikzcd} {[RTeCl_3Br]^-} \arrow[r, "HCl"] \arrow[d, "HBr"] \arrow[rr, bend left, "HI"] & {[RTeCl_4]^-} \arrow[r, "\text{HI or}", "KI/HCl"'] \arrow[dl, "\text{HCl conc.}"'] & {[RTeI_4]^-} \\ {[RTeBr_4]^-} \arrow[urr, bend right, "HI"'] & & \end{tikzcd}$$

and were eluted with solutions of tetraethylammonium bromide in ethanol/tetrahydrofuran[129]. The only alkali metal organyltetrahalotellurate(IV) is $Cs[C_2F_5TeF_4]$ prepared by heating cesium fluoride with the alkyl tellurium trifluoride at 100° for one hour[41].

TABLE 4
ORGANYLTETRAHALOTELLURATES(IV)

$M^+[RTeX_3Y]^-$				mp.°C	Ref.
R	X	Y	M^+		
CH_3	Cl	Cl	$(C_2H_5)_4N$	-	8
C_2F_5	F	F	Cs	-	41
C_6H_5	Cl	Cl	C_7H_7†	223-6	129
			pyridine·H	245-7 (dec)	164
			$(C_2H_5)_4N$	-	129
			$(C_6H_5)_3PCH_3$*	143	129
			$(C_6H_5)_3PCH_2CO_2C_2H_5$*	186-8	129
			$(C_6H_5)_3PCH_2C_6H_5$	187-90	129
			$(C_6H_5)_4P$	220-3	129
			$(C_6H_5)_4As$†	-	164
			$(C_6H_5)_3Te$*	197-9	129
	Cl	Br	C_7H_7	220-3	129
			$(C_6H_5)_3PCH_3$	133-5	129
			$(C_6H_5)_3PCH_2CO_2C_2H_5$	169-72	129
			$(C_6H_5)_3Te$	192-4	129
	Br	Br	C_7H_7	275-7	129
			$(CH_3)_4N$	290 (dec)	73
			$(C_6H_5)_3PCH_3$	166-70	129
			$(C_6H_5)_3PCH_2CO_2C_2H_5$	147-50	129
			$(C_6H_5)_3PCH_2C_6H_5$*	190-2°	129
			$(C_6H_5)_4P$	224-6	129
			$(C_6H_5)_3Te$*	192	129
	I	I	C_7H_7*	169-72	129
			$(C_2H_5)_4N$	176-8	129
			$(C_6H_5)_3PCH_3$*	169-71	129
			$(C_6H_5)_3PCH_2C_6H_5$	141-3	129
	I	Cl	$(C_6H_5)_3PCH_2C_6H_5$	138-41	129
	I	Br	C_7H_7	230-2	129
$4\text{-}C_2H_5OC_6H_4$	Cl	Cl	pyridine·H†	212-4	164
			C_7H_7*†	218-21	129
			$(C_2H_5)_4N$	-	129
			$(C_6H_5)_3PCH_3$*†	157	129
			$(C_6H_5)_3PCH_2CO_2C_2H_5$*	128-31	129

TABLE 4 (continued)

M$^+$[RTeX$_3$Y]$^-$				mp. °C	Ref.
R	X	Y	M$^+$		
4-$C_2H_5OC_6H_4$			$(C_6H_5)_3PCH_2C_6H_5$	177-80	129
			$(C_6H_5)_4P$	210-2	129
			$(C_6H_5)_3Te^{\dagger}$	143	129
	Cl	ClO_4	C_7H_7	213	129
	Cl	Br	C_7H_7	218-21	129
			$(C_6H_5)_3PCH_3$	169-72	129
			$(C_6H_5)_3PCH_2CO_2C_2H_5$	177-81	129
	Br	Br	C_7H_7	205-8	129
			$(C_6H_5)_3PCH_3$	206	129,130
			$(C_6H_5)_3PCH_2CO_2C_2H_5{}^{\dagger}$	113-5	129
			$(C_6H_5)_3PCH_2C_6H_5{}^*$	185-7	129
			$(C_6H_5)_4P$	228-32	129
	Br	Cl	$(C_6H_5)_3PCH_2C_6H_5$	122-4	129
	I	I	$(C_2H_5)_4N$	130-3	129
			$(C_6H_5)_3PCH_2C_6H_5{}^*$	138-41	129
	I	Cl	$(C_6H_5)_3PCH_2C_6H_5$	140-2	129
	I	Br	C_7H_7	142-5	129

*These compounds were prepared through halogen exchange reactions.

†These compounds were prepared according to eqn. (14b). All others were obtained by means of reaction (14a).

The organyltetrahalotellurates(IV), for which a square pyramidal geometry has been proposed on the basis of ir and Raman data[129], are 1:1 electrolytes in nitrobenzene[129] and nitromethane[164]. They are soluble in water. Their aqueous solutions were stable for a few hours but deposited tellurinic acid halides after 16 to 20 hours[129]. Pyridinium phenyl- or 4-ethoxyphenyltetrahalotellurate(IV) condensed with acetone to give aryl acetonyl tellurium dichlorides[164].

F. Organyl Tellurium Pentahalides

The only organyl tellurium pentahalide known is $C_2F_5TeF_4Cl$. It has been prepared from the ditelluride or the telluride and an excess of chlorine monofluoride, and from the alkyl tellurium trifluoride and an equimolar amount of ClF. All these reactions proceeded at room temperature. It has been claimed that the alkyl group is in trans-position to the chlorine atom in the octahedral molecule[41].

G. Tellurinic Acids and Their Derivatives

Thavornyutikarn[164] investigated the hydrolysis of phenyl and 4-ethoxyphenyl tellurium trihalides by water and 10% sodium carbonate solutions. He found in agreement with earlier work[79] that cold water hydrolyzed aryl tellurium trihalides to arenetellurinic acid halides (eqn. 16).

$$\mathrm{RTeX_3} \xrightarrow{\mathrm{H_2O}} \mathrm{RTe(O)X} \tag{16}$$

R, X, % yield, mp. °C: C_6H_5, Cl, 84, 280° (shrank at 226-8°); C_6H_5, Br, 80, 218-22°; 4-$C_2H_5OC_6H_4$, Cl, –, 222-5°; 4-$C_2H_5OC_6H_4$, Br, 84, 210-5; 4-$C_2H_5OC_6H_4$, I, 94, 170°.

The reaction time required for complete hydrolysis to the acid chloride increases from chlorine to iodine. It was necessary to stir the 4-ethoxyphenyl tellurium triiodide for 48 hours with cold water or four hours with boiling water to obtain the acid iodide. Phenyl tellurium triiodide reacted only slightly with cold water and was decomposed by hot water. The rate determining step in these reactions seems to be the dissolution of the rather insoluble organyl tellurium trihalides.

When the 4-ethoxyphenyl tellurium trihalides were treated with a 10% aqueous solution of sodium carbonate at room temperature for two hours, the arenetellurinic acid, RTeOOH, which shrank at 200° and decomposed between 235-40°, precipitated. When dilute acetic acid was added to the tellurinic acid or the hydrolysis mixture, the tellurinic acid anhydride $(RTeO)_2O$, which decomposed at 234-8°, was obtained. Most of the melting or decomposition temperatures reported are at variance with the older literature values. It was not possible to isolate any intermediate hydrolysis products, e.g., $RTe(OH)X_2$ or $(RTeX_2)_2O$. On the basis of ir and Raman spectra a trimeric structure with three four-coordinate tellurium atoms and three oxygen atoms forming a six-membered ring was postulated for the tellurinic acid halides.

H. Diorganyl Ditellurides

The diorganyl ditellurides, which have been prepared during the period covered by this survey, are listed in Table 5 together with the pertinent references. It was not possible to prepare asymmetric diaryl ditellurides by reducing a mixture of two different aryl tellurium trichlorides or irradiating a benzene solution containing diphenyl and bis(4-ethoxyphenyl) ditellurides[109]. The new compounds are marked by an asterisk. The other ditellurides in Table 5 are not new derivatives, but were now obtained by different routes. The reduction of aryl tellurium trichlorides by sodium sulfide has been extensively employed. Bergman[10] found that aryl tellurium trichlorides were reduced to the ditellurides by hydrazine in ethanolic medium. The yields in the hydrazine reactions seem to be lower than with the other reduction methods. Bis(pentafluoroethyl) ditelluride was one of the products of the reaction between $Te_4(AsF_6)_2$ and tetrafluoroethylene at 100°[121].

Piette obtained several diaryl ditellurides with carbonyl or acetal groups in the ortho-positions from aryl alkyl tellurides by cleavage of the alkyl group and air oxidation of the tellurol intermediate in acidic medium[133] (eqn. 17).

(17)

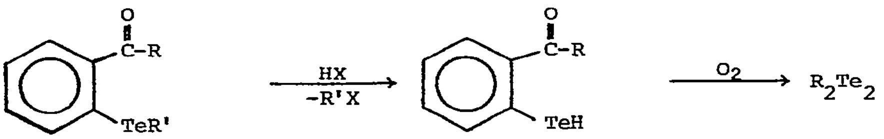
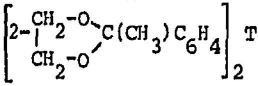
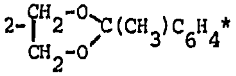


TABLE 5
DIORGANYL DITELLURIDES

R_2Te_2	Method	% Yield	mp.°C	Ref.
R				
C_2F_5*	$Te_4(AsF_6)_2$ + C_2F_4/SO_2 or SO_2F_2/100°	-	-	121
C_6H_5	$Na_2S_2O_5/H_2O$ + $RTeCl_3$	-	66	70
	N_2H_4/C_2H_5OH + $RTeCl_3$	45	67	10
3-FC_6H_4	Na_2S + $RTeCl_3$	-	-	148
	Na_2S + $RTeCl_3$	44	44	147
4-ClC_6H_4	Na_2S + $RTeCl_3$	80	114	147
4-BrC_6H_4	Na_2S + $RTeCl_3$	92	153	147,148
	N_2H_4/C_2H_5OH + $RTeCl_3$	48	154	10
4-$CH_3OC_6H_4$	N_2H_4/C_2H_5OH + $RTeCl_3$	68	58	10
3,4-$(CH_3O)_2C_6H_3$*	Na_2S + $RTeCl_3$	45	130	147
4-$C_2H_5OC_6H_4$	N_2H_4/C_2H_5OH + $RTeCl_3$	84	108	10
4-$C_3H_7OC_6H_4$*	Na_2S + $RTeCl_3$	86	84	147
4-$C_4H_9OC_6H_4$*	Na_2S + $RTeCl_3$	56	40	147
4-$CH_3COOC_6H_4$	Na_2S + $RTeCl_3$	41	49	147

4-$C_2H_5COOC_6H_4$*	Na_2S + $RTeCl_3$	36	45	147
4-$CH_3C_6H_4$	N_2H_4/C_2H_5OH + $RTeCl_3$	44	52	10
3-CH_3-4$CH_3OC_6H_3$	N_2H_4/C_2H_5OH + $RTeCl_3$	57	78	10
2-formylC_6H_4	2-$(C_2H_5O)_2CHC_6H_4TeCH_2CH(OC_2H_5)_2$ + CH_3COOH/H_2SO_4	-	-	133
2-$CH_3COC_6H_4$*	$RTeCH_3$ + HBr/CH_3COOH	-	-	133
	$R(CH_3)TeCl_2$ + pyridine/reflux	20	178-83	132
	 Te_2 on hydrolysis	90	-	132
	RTeLi + HCl	55	165-8	132
4-$CH_3COC_6H_4$*	$RTeCH_2CO_2C_2H_5$ + 6MHX/reflux	-	-	133

*New Compounds

The bis[2-methyl(dioxyethylene)methylphenyl] ditelluride, obtained through hydrolysis of the aryl lithium telluride followed by oxidation of the thus formed tellurol, was hydrolyzed to bis(2-acetylphenyl) ditelluride. This compound was also obtained when 2-acetylphenyl methyl tellurium dichloride was refluxed with pyridine[132].

The orange to red diaryl ditellurides are rather stable compounds, which can be handled in air without difficulties. However, certain ditellurides such as the 4-methoxyphenyl derivative, which must be stored in an ampoule in the dark, the 4-phenoxyphenyl compound, which slowly decomposed in petroleum ether solution, the bis(2-naphthyl) ditelluride, which became yellow on storage[109], and the perfluoroethyl derivative, which decomposed to the telluride and tellurium upon extended exposure to light[121], must be treated with care. UV, ESR, ir and Raman spectra of ditelluride solutions gave no indication that ditellurides dissociate into RTe· radicals[109].

A dihedral angle of 88.5° was found by X-ray structural analysis for diphenyl ditelluride[91]. Results of dipole moment measurements on diaryl ditellurides[80] and on dialkyl ditellurides[112] in benzene solutions suggest that the ditellurides assume a similar conformation in the dissolved state. The total energies and the interaction energies of the Te-Te atoms in dimethyl ditelluride have been calculated as a function of the dihedral angle using the extended Hueckel and the CNDO/2 methods[114]. The free electron model has been used to explain the electronic spectrum of diethyl ditelluride[16]. The long wave length absorption responsible for the color of the ditellurides is caused by excitation of electrons from the lone pairs on the tellurium atoms. In the ground state these pairs participate in the formation of a bond between the tellurium atoms.

The halogenolysis reactions of diaryl ditellurides leading to aryl tellurium monohalides and trihalides, have been discussed in sections V-B and V-D, respectively. Chlorine monofluoride converted bis(pentafluoroethyl) ditelluride at -78° to the alkyl tellurium trifluoride and the tetrafluoride chloride,

$RTeF_4Cl$, and caused some carbon-tellurium bond cleavage[41]. The conversion of diaryl ditellurides to tellurides by copper powder is treated in section VI. Dimethyl and bis(methyl-d_3) ditellurides were converted to RTeNa by sodium in liquid ammonia[158]. Diphenyl ditelluride in benzene solution was oxidized to phenyl tellurium triacetate by lead tetraacetate at room temperature[124,125] (section V-D). Bis(pentafluoroethyl) ditelluride and mercury produced $(RTe)_2Hg$[121] Diethyl ditelluride reacted with bis(triethylgermyl)mercury to form ethyl triethylgermyl telluride[65].

Bergman[10] showed, that treatment of the diaryl ditellurides, $(4\text{-}RC_6H_4)_2Te_2$ (R = H, Br, CH_3, CH_3O, C_2H_5O) and the 3-methyl-4-methoxyphenyl derivative with Raney Nickel in refluxing bis(2-methoxyethyl) ether for eight hours readily afforded the biaryls in high yields.

VI. Compounds Containing a Carbon-Tellurium-Carbon Moiety

In this section diorganyl tellurides, diorganyl tellurium dihalides and dicarboxylates, diorganyltrihalotellurates(IV), diorganylhalotellurium(IV) compounds and diorganyl compounds of the general formula, R_2TeX_4 and $R_2TeX_2Y_2$ (X,Y = halogen) are discussed. Several new methods to prepare such organic tellurium compounds have been developed and a number of new compounds were synthesized using procedures reported earlier.

A. Diorganyl Tellurides

Since the preparative procedures leading to symmetric diorganyl tellurides are quite different from those employed for the synthesis of unsymmetric derivatives, these two classes of compounds will be treated separately.

1. Symmetric diorganyl tellurides

The only new method for the preparation of diorganyl tellurides was reported by Sadekov[149]. He refluxed diaryl ditellurides in dioxane for eight hours in the presence of a three-fold molar excess of activated copper powder and isolated the diaryl tellurides in good yields (eqn. 18).

(18) $$(4\text{-}RC_6H_4)_2Te_2 + Cu \longrightarrow (4\text{-}RC_6H_4)_2Te + CuTe$$

R, % yield, mp.°C: H, –, –; CH_3, 77, 77°; CH_3O, 81, 54 ;
C_2H_5O, 79, 69°; Cl, 83, 98°; Br, 76, 122°.

McWhinnie[107] synthesized diphenyl, dibenzyl and bis(pentafluorophenyl) telluride by reacting tellurium tetrachloride in a diethyl ether/benzene mixture at 0° with a five-fold molar excess of the appropriate Grignard reagent. The yields of the crude diaryl tellurides were higher than 100%. The separation of tellurium reported earlier[79] to occur in these reactions was not observed. Tellurium(IV) diethyldithiocarbamate and a large excess of phenylmagnes bromide gave in quantitative yield diphenyl telluride, which was determined by gas chromatography[155].

Arenediazonium chlorides reacted with tellurium to produce diaryl tellurides[79]. Benzenediazonium tetrafluoroborate was now found to be unreactive toward tellurium. Diphenyl telluride and bis(4-methylphenyl) telluride were, however, formed in 6% yields, when the arenediazonium tetrafluoroborates interacted with a mixture of tellurium tetrachloride and zinc dust[116] in acetone.

When $Te_4(AsF_6)_2$ was heated with C_2F_4/SO_2 or C_2F_4/SO_2F_2 at 100° bis(pentafluoroethyl) telluride was obtained as one of the reaction products.

Bergman[10] has introduced hydrazine as a reducing agent for diaryl tellurium dichlorides. By adding hydrazine dissolved in ethanol to refluxing aqueous ethanol containing the dichloride until nitrogen was no longer evolved the tellurides $(4\text{-}RC_6H_4)_2Te$ (R = H, CH_3, Br, CH_3O, C_2H_5O) were obtained in 80% yields.

The reactions of diorganyl tellurides with elemental halogens and sulfuryl chloride leading to diorganyl tellurium dihalides is presented in section VI-B.

When bis(pentafluorophenyl) telluride and an excess of chlorine monofluoride interacted at room temperature, R_2TeF_4, $RTeF_4Cl$ and $TeClF_5$ were formed, whereas with a two-fold excess at -78° the major product was R_2TeF_2[41].

The formation of triorganyl telluronium salts from diorganyl tellurides and an alkyl halide is discussed in section VII. The conversions of diaryl ditellurides by lead tetraacetate to diaryl tellurium diacetates are treated in section VI-B. The transition metal complexes, in which a diorganyl telluride serves as a ligand, are included in section VIII-F.

The tellurium atom in diorganyl tellurides is capable to form hydrogen bonds with phenol[27,97] and aniline[97], but not with phenylacetylene[97]. These investigations were carried out be means of ir and nmr techniques.

Bergman[10] produced biaryls $(4\text{-}RC_6H_4)_2$ in approximately 80% yield by refluxing the diaryl tellurides, $(4\text{-}RC_6H_4)_2Te$ (R = H, CH_3, Br, CH_3O, C_2H_5O), with Raney Nickel in bis(2-methoxyethyl) ether for eight hours. The flash photolysis of dimethyl telluride generated methyl tellurium radicals, $CH_3Te\cdot$, whose uv spectrum was recorded[175].

The irradiation of diphenyl telluride with neutrons initiates a (n, γ)-process causing tellurium-carbon bond fission[146,168]. The isomeric transition $^{129m}Te \rightarrow {}^{129g}Te$ is also responsible for such a bond cleavage[146]. The ^{60}Co radiolysis of pure diphenyl telluride produced a variety of tellurium containing and tellurium-free compounds[167].

2. Unsymmetric diorganyl tellurides

Methods developed earlier[79] have been extensively applied to synthesize new unsymmetric diorganyl tellurides. These reactions are described by eqns. (19) - (21).

Those diorganyl tellurides, which contain a functional group in the molecule or carbon-carbon multiple bonds in the aliphatic part of the molecule, can be converted to new diorganyl tellurides by modification of the organic moiety. Thus, 2-acetylphenyl alkyl tellurides were quantitatively converted

(19)

R, Y, R', % yield, bp.°C/torr: H, $(OC_2H_5)_2$, $(C_2H_5O)_2CHCH_2$, 50, 175-80°/0.0

CH_3, $(OC_2H_5)_2$, $(C_2H_5O)_2CHCH_2$, –, –;

CH_3, OCH_2CH_2O, C_4H_9, 53, 175-80°/0.3;

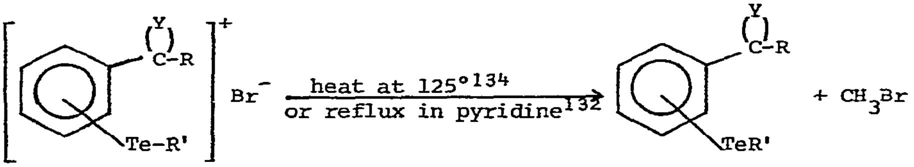
CH_3, O, $CH_2CO_2C_2H_5$, –, –.[133]

(20)

$$(CH_3)_3C\text{-}C{\equiv}C\text{-}TeNa + CH_3I \xrightarrow{NH_3(l)} (CH_3)_3C\text{-}C{\equiv}C\text{-}Te\text{-}CH_3$$

50% yield, bp.61°/5torr[142]

(21)



position of Te, R, Y, R', % yield, mp.°C: 2, H, O, $CH_2CO_2C_2H_5$, –, –;

2, CH_3, O, CH_2COOH, –, 133°;

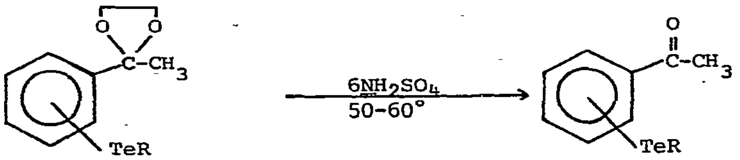
2, CH_3, O, $CH_2CO_2C_2H_5$, –, 59°;[134]

2, CH_3, OCH_2CH_2O, CH_3, 80, 64°;

4, CH_3, OCH_2CH_2O, CH_3, 80, 76°.[132]

to the 2,4-dinitrophenylhydrazone (R = CH_3, m. 191-5°; R = C_4H_9, m. 90-3°)[132]. The hydrolysis of the cyclic acetals **6** of 2-acetylphenyl alkyl tellurides by 6N sulfuric acid at 50-60° regenerated the keto function[132] (eqn. 22). Condensation of 2-acetylphenyl methyl telluride with benzaldehyde in a refluxing mixture of pyridine and acetic acid gave 2-cinnamoylphenyl methyl telluride melting at 102-4° in 20% yield[132]. Heating 2-formylphenyl methyl telluride with the phosphoranes, $(C_6H_5)_3P{=}CHR$ (R = $COCH_3$, C_6H_5, $CO_2C_2H_5$, CN) at 125° in

(22)



6

position of Te, R, % yield, bp.°C/torr, mp.°C: 2, CH_3, 35% (overall from ArI), –, 43°;
4, CH_3, 75, –, 75-7°;
2, C_4H_9, 90, 182°/0.5, 38-40°.

an oil bath gave the styryl derivatives 2-$(RCH{=}CH)C_6H_4TeCH_3$ in yields higher than 90%. These tellurides were not isolated but converted to the dibromides (section VI).

Several attempts to introduce the acyl group into the 2-position of phenyl methyl tellurides or convert substituents already present in the ortho-position have been unsuccessful. Oxidation of 2-(methylhydroxymethyl)phenyl methyl telluride by dimethyl sulfoxide in acetic anhydride yielded only tellurium and tellurium dioxide. The reaction of bis(carbethoxy)methyl magnesium ethoxide with 2-chloroformylphenyl methyl telluride caused decomposition. A Friedel-Crafts acylation of 4-methylphenyl methyl telluride with acetyl chloride gave only the aryl methyl tellurium dichloride[132].

Piette prepared 2-formylphenyl[133] and 2-cinnamoylphenyl methyl tellurides[135] from the respective phenyl tellurium monobromide and dimethyl cadmium. No further data concerning these reactions have been reported. The 2-formylphenyl methyl tellurides assume according to nmr results a conformation which allows the tellurium atom to interact with the carbonyl oxygen atom[5].

Petrov[131] was able to add diethylamine in a copper(I) chloride catalyzed reaction to the unsaturated telluride 7 (eqn. 23). When the amine and telluride

(23) $CH_2{=}CH{-}C{\equiv}C{-}TeCH_3 + (C_2H_5)_2NH \xrightarrow{Cu_2Cl_2} (C_2H_5)_2N{-}CH_2{-}CH{=}C{=}CH{-}TeCH_3$

7

34% yield, b.104-6°/1.5torr

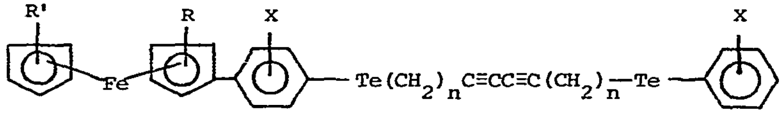
were heated without the catalyst, the telluride was decomposed. Partial decomposition with precipitation of tellurium occurred even in the presence of the catalyst. The reaction of ethyl magnesium bromide prepared in situ with vinylacetylenyl alkyl selenide yielded the allenic selenide, $C_2H_5CH_2$-CH=C=CH-SeR. The corresponding tellurium compound treated similarly experienced tellurium-carbon(acetylenic) bond cleavage forming dialkyl tellurides[141].

The addition of bromine to ethyl vinylacetylenyl telluride in chloroform solution at -60° produced ethyl 3,4-dibromo-1-butynyl tellurium dibromide in 87% yield[144].

The following reactions of unsymmetric diorganyl tellurides are treated in the sections indicated: Conversion to tellurium monohalides by hydrohalic acids (V-B); conversion to diaryl ditellurides by mineral acids (V-H); oxidation to diorganyl tellurium dihalides or diacetates (VI-B); formation of tellurium salts through combination with alkyl halides (VII); and cyclization of 2-formyl- or 2-acylphenyl alkyl tellurides (IX-C, IX-D).

3. Tellurides with two tellurium atoms in the molecules

A Russian patent[P-4] claimed the synthesis of the telluride 7a from a



7a

ferrocene derivative and the telluride $XC_6H_4Te(CH_2)_nC{\equiv}CBr$. The reaction was performed in an organic solvent in the presence of a complex forming compound ($C_4H_9NH_2$), a reducing agent ($NH_2OH{\cdot}HCl$) and a catalyst (Cu_2Cl_2).

B. Diorganyl Tellurium Compounds, R_2TeX_2

To the already long list of known diorganyl tellurium dihalides additional compounds have been added. The new symmetric derivatives have been compiled in

Table 6; the unsymmetric compounds have been collected in Table 7. These tables contain not only the new diorganyl tellurium dihalides, but also those compounds which have been previously reported in the literature, and have now been prepared by a new technique. The diorganyl tellurium dicarboxylates are also included in the tables.

The reaction of diorganyl tellurides with the elemental halogens or sulfuryl chloride, widely used methods for the synthesis of diorganyl tellurium dihalides, was used to prepare a number of new derivatives. Bromine added not only to the tellurium atom in ethyl vinylacetylenyl telluride but also to the carbon-carbon double bond producing ethyl 3,4-dibromo-1-butynyl tellurium dibromide[143]. Chlorine monofluoride and bis(pentafluoroethyl) telluride mixed in a 2:1 molar ratio at -78° yielded the dialkyl tellurium difluoride[41]. Acetyl chloride under the conditions of a Friedel-Crafts reaction converted 4-methylphenyl methyl telluride into its dichloride[132].

The condensation of aryl tellurium trichlorides with appropriate aromatic compounds has been used in the past to prepare unsymmetric diorganyl tellurium dihalides[79]. It has now been established[10], that under more vigorous conditions condensation as well as replacement of the organic group originally bonded to the tellurium atom occurred (eqn. 24).

$$\text{(24)}\quad 4\text{-RC}_6\text{H}_4\text{TeCl}_3 + \text{CH}_3\text{OC}_6\text{H}_4 \xrightarrow{160^\circ} (4\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{TeCl}_2 + 4\text{-RC}_6\text{H}_5$$

$$\text{R} = \text{CH}_3,\ \text{C}_2\text{H}_5\text{O},\ \text{Br}$$

One chlorine atom in 4-ethoxyphenyl tellurium trichloride was replaced at room temperature by a phenyl group in a reaction with triphenyl lead chloride[123] or diphenyl·dimethyl lead. Sadekov[148] established that diaryl tellurium dichlorides were formed when the trichlorides were refluxed in benzene for several hours. The postulated equilibrium (eqn. 25) is displaced toward the

$$\text{(25)}\quad 2(4\text{-ROC}_6\text{H}_4)\text{TeCl}_3 \rightleftharpoons (4\text{-ROC}_6\text{H}_4)_2\text{TeCl}_2 + \text{TeCl}_4$$

TABLE 6
DIORGANYL TELLURIUM DIHALIDES AND DICARBOXYLATES

R_2TeX_2		Method of Preparation	% Yield	mp.°C	Ref.
R	X				
CH_3	Br	$R_2TeCl_2 + BBr_3$/benzene	100	-	26
	I	Te + RI, 63°, 56 hrs.	66	127	166
C_2H_5	I	Te + RI	18	56	166
C_2F_5*	F	R_2Te + 2ClF, -78°	84	4	41
C_3H_7*	I	Te + RI, 85°, 5 days	26	69	166
C_4H_9	I	Te + RI	16	61	166
C_5H_{11}	I	Te + RI	5	oil	166
$C_6H_5CH_2$*	Cl*	$R_2Te + SO_2Cl_2/CCl_4$	-	-	107
	Br*	$R_2Te + Br_2/CCl_4$	-	-	107
$C_6H_5COCH_2$	Cl	$TeCl_4 + C_6H_5COCH_3/HCl,H_2SO_4$	75	-	62
C_6H_5	Cl	$TeCl_4 + C_6H_6/AlCl_3$	58	161	10,70
		$R_2Te(O_2CCH_3)_2 + (CH_3)_3SiCl$	-	160	125
		$TeCl_4 + (C_6H_5)_2(CH_3)_2Pb$	97	159	123
		$TeCl_4 + (C_6H_5)_3PbCl$	96	-	123
		$TeCl_4 + (C_6H_5)_4Pb$/toluene	97	-	123
	I	$R_2Te(O_2CCH_3)_2$ + KI/acetone	-	-	125
C_6F_5	Cl*	$R_2Te + SO_2Cl_2/CCl_4$	88	201	107
	Br*	$R_2Te + Br_2/CCl_4$	77	210	107
$4-CH_3C_6H_4$	Cl	$TeCl_4 + R_4Pb$	90	165-7	123
		$TeCl_4 + RH/AlCl_3$	42	165	10
$3-CH_3-4-CH_3OC_6H_3$*	Cl	$TeCl_4 + RH/(CH_3OCH_2CH_2)_2O$	52	147	10

4-$CH_3OC_6H_4$	Cl	R'$TeCl_3$† + RH, 160°	80	183	10
		$RTeCl_3$ + Cu/benzene	67	181	148
2,4-$(CH_3O)_2C_6H_3$	Cl	$TeCl_4$ + RH	63	204	10
3,4-$(CH_3O)_2C_6H_3$*	Cl	$TeCl_4$ + RH	65	156	10
4-$C_2H_5OC_6H_4$	Cl	$RTeCl_3$ + Cu/benzene	64	108	148
4-ClC_6H_4	Cl	$TeCl_4$ + RH/$AlCl_3$	31	183	10
4-BrC_6H_4	Cl	$TeCl_4$ + RH/$AlCl_3$	44	191	10
9-anthryl*	Cl	$TeCl_4$ + RH	34	211	147
1-pyrenyl*	Cl	$TeCl_4$ + RH	18	236	147
C_6H_5	CH_3COO	R_2TeCl_2 + CH_3COOAg	94	139-41	125
		R_2Te + $Pb(OOCCH_3)_4$	98	-	125
	C_6H_5COO*	R_2TeCl_2 + C_6H_5COOAg	92	159-61	125
4-$CH_3C_6H_4$	CH_3COO*	R_2TeCl_2 + CH_3COOAg	90	178-80	125
4-$CH_3OC_6H_4$	CH_3COO*	R_2Te + $Pb(OOCCH_3)_4$	89	135-7	125
4-$C_2H_5OC_6H_4$	CH_3COO*	R_2TeCl_2 + CH_3COOAg	89	111	125
		R_2Te + $Pb(OOCCH_3)_4$	96	-	125

*New compounds.

†R' = 4-$C_2H_5OC_6H_4$, 4-$CH_3C_6H_4$, 4-BrC_6H_4

TABLE 7
UNSYMMETRIC DIORGANYL TELLURIUM DIHALIDES AND DIACETATES

$RR'TeX_2$			Method of Preparation	% Yield	mp.°C	Ref.
R	R'	X				
$BrCH_2CHBr-C{\equiv}C$*	C_2H_5	Br	$R'TeC{\equiv}CCH{=}CH_2 + Br_2$	87	68-70	144
CH_3COCH_2*	C_6H_5	Cl	$[R'TeCl_4^-]pyridine{\cdot}H^+ + CH_3COCH_3$	-	114	164
$4-C_2H_5OC_6H_4$*	C_6H_5	Cl	$RTeCl_3 + (C_6H_5)_3PbCl$	90	113-5	123
		CH_3COO	$RR'TeCl_2 + CH_3COOAg$	90	114-6	125
		CH_3COO	$RR'Te + Pb(OOCCH_3)_4$	97	-	125
$4-CH_3C_6H_4$	CH_3	Cl	$RR'Te + CH_3COCl$	-	-	132
$2-CH_3COC_6H_4$*	CH_3	Cl	$RR'Te + Cl_2$	100	145-50	132
$4-CH_3COC_6H_4$*	CH_3	Cl	$RR'Te + Cl_2$	-	172-8	132
$2-NCCH{=}CHC_6H_4$*	CH_3	Br	$RR'Te + Br_2/CHCl_3$	100	164	134
$2-CH_3COCH{=}CHC_6H_4$*	CH_3	Br	$RR'Te + Br_2/CHCl_3$	-	150	134
$4-C_2H_5OOCCH{=}CHC_6H_4$*	CH_3	Br	$RR'Te + Br_2/CHCl_3$	-	162	134
$4-C_6H_5COCH{=}CHC_6H_4$*	CH_3	Br	$RR'Te + Br_2/CHCl_3$	100	139	134

*New compounds.

right by removing the tellurium tetrachloride through reduction by copper to elemental tellurium. The yields in these reactions are between 60 to 70%. The preparation of aryl tellurium trichlorides from the dichlorides and tellurium tetrachloride has been discussed in section V-D. A condensation between acetone and pyridinium phenyltetrachlorotellurate(IV) leading to acetonyl phenyl tellurium dichloride has also been observed[164].

The direct condensation of tellurium tetrachloride with aromatic hydrocarbons bearing an activating substituent such as an alkoxy group has long been known and has now been extended to 2,4- and 3,4-dimethoxybenzene, 2-methoxybenzene, 2-methoxytoluene[10], anthracene and pyrene[147]. Whereas the yields of the methoxy derivatives were between 50 and 65%, the yields of the dianthryl and dipyrenyl tellurium trichlorides were 34 and 18%, respectively.

The reaction temperature can be considerably lowered in such reactions, and aromatic compounds without an activating group can be condensed with tellurium tetrachloride when aluminum chloride is added to the reaction mixtures. Whereas Bergman[10] used catalytic amounts of aluminum chloride (0.0075 moles $AlCl_3$ per 0.1 mole $TeCl_4$), Guenther[70] recommended a three-fold molar excess of the aluminum salt and interruption of the reaction, when two moles of hydrogen chloride per mole of tellurium tetrachloride had been evolved. The latter procedure gave a 58% yield of diphenyl tellurium dichloride. Bergman's yield was 36%. Toluene, 4-chlorobenzene and 4-bromobenzene, tellurium tetrachloride and catalytic amounts of aluminum chloride produced bis(4-R-aryl) tellurium dichlorides in yields of 31 to 44%[10]. Futekov[62] has claimed the preparation of bis(benzoylmethyl) tellurium dichloride in 75% yield from acetophenone and tellurium tetrachloride in a hydrochloric/sulfuric acid medium.

Tetraphenyl lead, triphenyl lead chloride, diphenyl dimethyl lead and tetrakis(4-methylphenyl) lead each exchanged two aryl groups for chlorine from tellurium tetrachloride in reactions performed at room temperature in toluene or dioxane medium. The diorganyl lead dichloride precipitated. The diaryl tellurium dichlorides were isolated in almost quantitative yields upon evaporation of the solvent in vacuum[123].

Thayer[166] reinvestigated the reaction between alkyl iodides and elemental tellurium leading to dialkyl tellurium diiodides. The methyl derivative was obtained in 66% yield, whereas the other iodides were produced in yields not higher than 25%. 2-Iodopropane and 2-iodobutane reacted faster with tellurium than the straight chain alkyl iodides. However the expected products were isolated only in trace amounts. Iodobenzene did not react with tellurium.

Diorganyl tellurium diacetates were prepared either from diorganyl tellurium dichlorides and silver acetate or by oxidation of diorganyl tellurides with lead tetraacetate (Table 6). Diphenyl tellurium dibenzoate and 4-ethoxyphenyl phenyl tellurium diacetate were prepared from the dichlorides and the silver carboxylate. The yields in all these reactions was 90% or higher. These dicarboxylates are colorless, crystalline materials, which can be stored over long periods without hydrolysis or decomposition[125]. They are non-electrolytes in nitromethane, possess trigonal bipyramidal shape with four coordinate tellurium atoms. The acetate groups act as unidentate ligands. Infrared data suggest non-equivalence of the two acetate groups in the molecule[124]. Diphenyl tellurium dinitrate is also a non-electrolyte in nitromethane. The measurement of its ir absorption was complicated by the reactions of this compound with the supporting materials. The spectra obtained with silver chloride support favor a monomeric structure with unidentate or very unsymmetric bidentate nitrato groups[124].

Only a few reactions, in which the electronegative groups in R_2TeX_2 are exchanged, have been reported. Dimethyl tellurium dichloride and an equimolar amount of BBr_3 in benzene solution gave dimethyl tellurium dibromide. The complex $[(CH_3)_2TeBr_2]_2 \cdot BBr_3$ was obtained when an excess of boron tribromide was employed[26]. Diphenyl tellurium diacetate refluxed with trimethylchlorosilane yielded the tellurium dichloride and trimethylsilyl acetate. With potassium iodide the tellurium diiodide was formed. Potassium hydroxide in aqueous ethanol produced the telluroxide[125].

Bergman[10] prepared biaryls in good yields by refluxing the diaryl tellurium dichlorides, $(4\text{-RC}_6H_4)_2TeCl_2$ (R = H, CH_3, CH_3O, C_2H_5O, $(CH_3)_2N$, Br), $(4\text{-CH}_3O\text{-R-C}_6H_3)_2TeCl_2$ (R = 2-CH_3O, 3-CH_3O, 3-CH_3), and bis(2-naphthyl) tellurium dichloride with Raney Nickel in bis(2-methoxyethyl) ether for eight hours.

The following reactions of diorganyl tellurium dihalides are described in the sections indicated: reduction to diorganyl tellurides by hydrazine (VI-A); reaction with tellurium tetrachloride to give aryl tellurium trichlorides (V-D); reaction with elemental halogen to produce $R_2TeX_2Y_2$ (VI-D); and cyclization of 2-(2-R-vinyl)phenyl methyl tellurium dibromides to benzotellurophene derivatives (IX-D).

Beattie[8] concluded on the basis of the similarity of the Raman spectra of dimethyl tellurium dichloride in pyridine and non-donor solvents, that this compound has weak acceptor properties. Bis(pentafluoroethyl) tellurium difluoride formed 1:1 adducts with cesium fluoride and antimony pentachloride (section VI-C).

C. Diorganyltrihalotellurates(IV) and Diorganylhalotellurium(IV) Compounds

When bis(pentafluoroethyl) tellurium difluoride was reacted with cesium fluoride a 1:1 adduct was obtained, which in analogy to organyltetrahalotellurates (section V-E) must be formulated as cesium dialkyltrifluorotellurate(IV). The reaction of the difluoride with antimony pentafluoride produced $R_2TeF_2 \cdot SbF_5$, which probably has the constitution of a dialkylfluorotellurium(IV) hexafluoroantimonate(V)[41]. Perhaps the complex $(R_2TeBr_2)_2 \cdot BBr_3$[24] should be written as $[R_2TeBr]^+BBr_4^- \cdot [R_2TeBr_2]$. No other derivatives of this type have been reported.

D. Diorganyl Tellurium Compounds, R_2TeX_4 and $R_2TeX_2Y_2$

The dimethyl and diethyl derivatives of R_2TeI_4 have been reported previously[79].

Thayer and coworkers[159,166] have now prepared the propyl and the butyl compounds from the dialkyl tellurium diiodides and iodine in organic solvents (eqn. 26) in quantitative yields[166].

(26) $$R_2TeI_2 + I_2 \longrightarrow R_2TeI_4$$

R, mp. °C: CH_3, 99°; C_2H_5, 97°; C_3H_7, 100°; C_4H_9, —

The longer chain compounds are unstable. The dibutyl derivative decomposed on standing at room temperature[166]. The dipentyl and diphenyl compounds could not be prepared[159,166]. Dimethyl tellurium diiodide and bromine did not form $R_2TeI_2Br_2$[159].

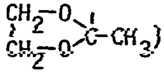
Dialkyl tellurium tetraiodides dissociate when dissolved in organic solvents. In vacuum iodine vapors were evolved. Infrared and mass spectral studies discount the presence of triiodide ions. The tetraiodides are, therefore, probably solid state adducts of the diiodides with iodine[159].

Desjardins[41] detected trans-$(C_2F_5)_2TeF_4$ by ^{19}F nmr spectroscopy as a product of the reaction between bis(pentafluoroethyl) telluride and chlorine monofluoride at room temperature. This molecule has octahedral shape with all six groups bonded directly to the tellurium atom in contrast to the suggested structure of the dialkyl tellurium tetraiodides.

VII. Triorganyl Telluronium Compounds, $[R_3Te]^+X^-$

Table 8 lists the telluronium compounds, which have not been reported previously, and also all those, for which pertinent data have not been available in the older literature. Almost without exception standard methods such as the reaction of a diorganyl telluride with an alkyl halide, interaction of tellurium tetrachloride with a Grignard or an organic lithium reagent, and exchange of the halide ions for other anions have been employed. Pertinent details can be found in Table 8.

Günther showed, that tellurium tetrachloride in the presence of a threefold molar excess of aluminum trichloride reacted with refluxing benzene and produced triphenyl telluronium chloride in 60% yield, when the reaction was stopped after three moles of hydrogen chloride per mole of tellurium trichloride had been evolved[70]. This reaction should be capable of extension to the synthesis of other telluronium salts.

It is not necessary to isolate the tellurides required for the preparation of telluronium salts in reactions with alkyl halides. For instance, the aryl lithium telluride, n-RC_6H_4TeLi (n = 2 or 4, R =  $\begin{matrix}CH_2-O\\CH_2-O\end{matrix}\!\!>C-CH_3$) yielded the dimethyl aryl telluronium iodides when treated with an excess of methyl iodide. Acid hydrolysis of acetal functions generated the acetylphenyl dimethyl telluronium iodides[132].

When telluronium salts are to be prepared from aliphatic low molecular mass tellurides, the odor problem created by these compounds can perhaps be minimized by generating the telluride through reduction of the corresponding dialkyl tellurium dihalide in the presence of an alkyl halide. This method first used by Scott[79] in 1904 was used by Thayer to prepare several trialkyl telluronium iodides, $[R_3Te]^+I^-$ and $[R_2R'Te]^+I^-$ (Table 8). It should be noted that iodobenzene and dimethyl telluride combined under those conditions to give dimethyl phenyl telluronium iodide in 50% yield[166].

Hashimoto[72] treated triphenyl telluronium halides in chloroform solutions with elemental halogens. The triphenyl telluronium salts, $[(C_6H_5)_3Te]^+Y^-$ ($Y = ClBr_2, ClI_2, Br_3, BrI_2, IBr_2, I_3$) were isolated.

In new anion exchange reactions iodide ion in trimethyl and triphenyl telluronium iodide was exchanged for tetrafluoroborate ion. The triphenyl telluronium tetrafluoroborate and potassium bromide gave the telluronium bromide[72]. Thayer[166] noted that trialkyl telluronium picrates in contrast to the aromatic derivatives were rather soluble in water and were obtained in very low yields.

Three telluronium salts of the type $[RR'R''Te]^+Br^-$ were synthesized at room temperature from 2-$RCOC_6H_4-Te-CH_3$ and $BrCH_2COOR'$ in chloroform. These compounds

TABLE 8
TRIORGANYL TELLURONIUM COMPOUNDS, $[R_2R'Te]^+X^-$

$[R_2R'Te]^+X^-$			Method of Preparation	Yield, %	mp.°C	Ref.
R	R'	X.				
CH_3	CH_3	Cl	R_3TeBF_4 + KCl/C_2H_5OH	80	225	72
		Br	R_3TeBF_4 + KBr/C_2H_5OH	83	320	72
		I	R_2Te + RI	82	247 (dec)	72
		I	R_2TeI_2 + RI/K_2SO_3, Na_2CO_3, H_2O	45	244-6	166
		BF_4*	R_3TeI + $AgBF_4/ClCH_2CH_2Cl$	87	230 (dec)	72
		picrate*	R_3TeI + picric acid	20	127 (dec)	72
	C_2H_5	I*	R_2TeI_2 + $R'I/K_2SO_3$, Na_2CO_3, H_2O	40	145	166
		picrate*	$R_2R'TeI$ + picric acid	5	126 (dec)	166
	C_6H_5	I	R_2TeI_2 + $R'I/K_2SO_3$, Na_2CO_3, H_2O	50	171-4	166
	CH_2=CH-C≡C	I*	RR'Te + RI	100	76-8 (dec)	142
	$(CH_3)_3$C-C≡C	I*	RR'Te + RI	100	107-9 (dec)	142
	C_6H_5C≡C	I*	RR'Te + RI	100	104-6 (dec)	142
	2-$CH_3COC_6H_4$	I*	acid hydrolysis of ortho-**8****	90	145-50	132
	4-$CH_3COC_6H_4$	I*	acid hydrolysis of para-**8****	80	151-4	132
	ortho-**9**††	I*	ortho-**9**-Li + CH_3I	57	165 (dec)	132
	para-**9**††	I*	para-**9**-Li + CH_3I	67	151-3	132
C_3H_7	CH_3	I*	R_2TeI_2 + $R'I/K_2SO_3$, Na_2CO_3, H_2O	49	-	166
	C_3H_7	I*	R_2TeI_2 + RI/K_2SO_3, Na_2CO_3, H_2O	41	111-4	166
C_4H_9	CH_3	I	R_2TeI_2 + $R'I/K_2SO_3$, Na_2CO_3, H_2O	62	155-7	166
C_6H_5	C_6H_5	Cl†	$TeCl_4$ + C_6H_5Li	60		72

C_6H_5	C_6H_5	Cl	$TeCl_4/3AlCl_3/C_6H_6$	60	250	70
		Br	R_3TeBF_4 + KBr	86	261 (dec)	72
		I	$TeCl_4$ + C_6H_5MgBr, then KI	36	255	72
		$ClBr_2$*	R_3TeCl + $Br_2/CHCl_3$	-	123	72
		ClI_2*	R_3TeCl + $I_2/CHCl_3$	-	141	72
		Br_3*	R_3TeBr + $Br_2/CHCl_3$	-	118	76
		BrI_2*	R_3TeBr + $I_2/CHCl_3$	-	118	72
		IBr_2*	R_3TeI +$Br_2/CHCl_3$	-	156	72
		I_3*	R_3TeI + $I_2/CHCl_3$	-	164	72
		BF_4*	R_3TeI + $AgBF_4$	70	206 (dec)	72

*New compounds.

†Isolated as the tetrafluoroborate.

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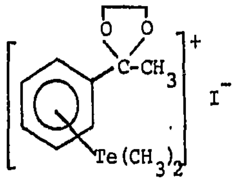

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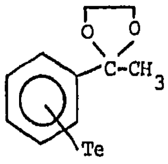
††.



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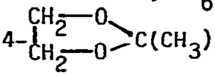
melted at 122° (R = H, R' = C_2H_5), 100° (R = CH_3, R' = H) and 151° (R = CH_3, R' = C_2H_5)[134]. No data were reported for the telluronium salt with R = H and R' = CH_3[134].

The cleavage of methyl iodide from aryl dimethyl or aryl methyl carboxymethyl telluronium iodides upon heating has been described in section V-A2. The formation of triphenyl telluronium aryltetrahalotellurates(IV) from triphenyl telluronium salts has been treated in section V-E. Calculations have been carried out employing ASMO-SCFMO and EHMO methods to correlate the catalytic properties of trimethyl telluronium chloride in the liquid phase oxidation of hydrocarbons with its electronic properties[120].

VIII. Organic Tellurium Compounds Containing a Tellurium-Metal or a Tellurium-Metalloid Bond

During the period covered by this survey new organic tellurium compounds have been synthesized which contain a tellurium atom bonded to lithium, sodium, magnesium, aluminum, silicon, germanium, tin, lead, phosphorus, sulfur, selenium, titanium, zirconium, tantalum, chromium, molybdenum, tungsten, iron, iridium, nickel, palladium, platinum, copper, cadmium or mercury.

A. Organic Compounds of Tellurium with Metals of Group I, II or III.

Tellurium inserted into carbon-lithium bonds, when the element was reacted with the appropriate aryl lithium derivative in diethyl ether medium. The aryl lithium tellurides, RC_6H_4TeLi (R = H[151], 2-$(C_2H_5O)_2CH$, 2-$(C_2H_5O)_2C(CH_3)$[133], 2- and 4-  [132]) were prepared in this manner. These compounds were not isolated but reacted with organic halides to produce tellurides (section VI-A2) or telluronium compounds (section VIII).

Sato[150] obtained the aryl sodium tellurides, RC_6H_4TeNa (R = H, 4-CH_3, 3-CF_3, 4-Cl, 4-CH_3O) employing Giua's method[79]. First the aryl bromomagnesium tellurides were prepared from aryl magnesium bromide and elemental tellurium. The ethereal reaction mixtures were hydrolyzed with hydrochloric acid. The ether layer containing the arenetellurols were then probably treated with aqueous sodium hydroxide solutions to produce the aryl sodium tellurides.

Phenyl and 4-methylphenyl bromomagnesium telluride were prepared from the Grignard reagents and elemental tellurium in tetrahydrofuran medium[151]. Organyl halomangesium telluride solutions were contacted with a ceramic support. Then air was blown through. The material obtained in this manner was claimed to catalyze the polymerization of alkyl vinyl ethers[P-5].

The first compound containing a covalent tellurium-aluminum bond was prepared by Vyazankin[170] and Bochkarev[11] from triethylsilanetellurol and triethyl aluminum (eqn. 27).

$$(27)\quad (C_2H_5)_3Si\text{-}TeH + (C_2H_5)_3Al \xrightarrow{\text{hexane}} (C_2H_5)_3Si\text{-}Te\text{-}Al(C_2H_5)_2 + C_2H_6$$

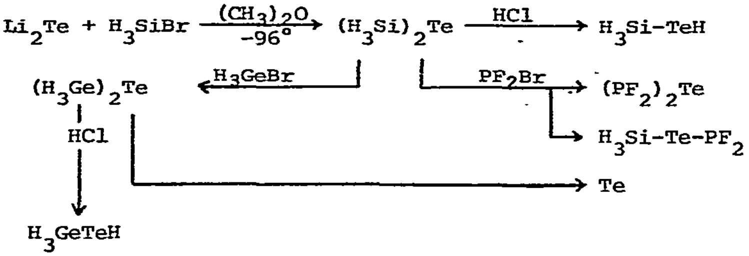
Ethane was liberated in quantitative yield. The product, however, was obtained in only 35% yield, because large losses of this very oxygen and water sensitive compound, which decomposed at 34°, occurred during isolation and purification. The telluride underwent disproportionation in hexane solution with formation of triethyl aluminum, bis(trimethylsilyl) telluride and (ethyl aluminum) telluride, $C_2H_5As{=}Te$. This compound was instantly oxidized in air to elemental tellurium. Its high decomposition temperature of 352° is indicative of its polymeric nature.

The reactions of aryl sodium tellurides and aryl bromomagnesium tellurides with transition metal complexes are treated in section VIII-F.

B. Organic Compounds of Tellurium Containing a Tellurium-Group IV Element Bond

Arnold[2] and Glidewell[66] prepared silyl and germyl tellurium compounds according to eqn. (28). The presence of bis(difluorophosphine) telluride and

(28)

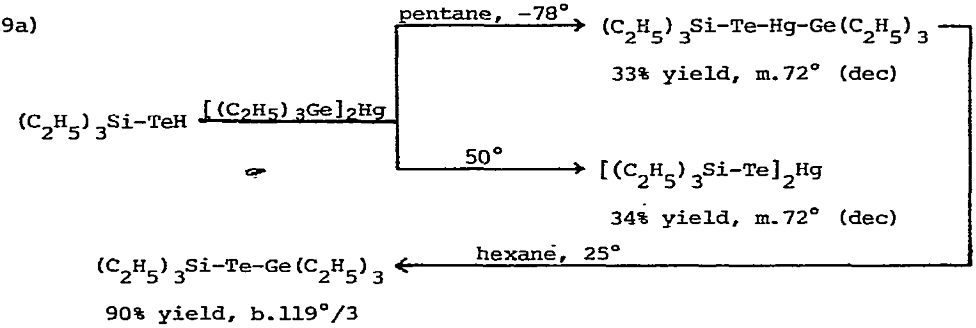


difluorophosphine was ascertained by nmr techniques[2]. The existence of silanetellurol in mixtures containing the appropriate telluride, $(H_3M)_2Te$, hydrogen chloride and hydrogen telluride was similarly proven. Equilibrium constants for the reaction (29) were found to be approximately 0.9[66].

(29) $$(H_3M)_2Te + H_2Te \rightleftharpoons 2H_3M\text{-}TeH$$

Triethylsilanetellurol cleaved at low temperatures one, at higher temperatures both triethylgermyl groups from bis(triethylgermyl) mercury (eqn. 29a)[13].

(29a)



When triethylsilanetellurol was treated with ethyl lithium in hexane triethylsilyl lithium telluride was isolated in 22% yield as a colorless crystalline substance. This compound, which was tetrameric in benzene solution decomposed at 122°. Heating triethylsilyl lithium telluride with butyl chloride at 60° gave triethylsilyl butyl telluride, boiling at 108-110°/6 torr, in 79% yield[25].

Bis(tri-i-propylgermyl) telluride, which melted at 23°, was isolated in 78% yield, when tellurium and digermyl mercury were heated at 70°. Diethyl ditelluride and bis(triethylgermyl) mercury kept at 20° produced ethyl triethylgermyl telluride in 73% yield. The compound boiled at 59-61°/1 torr[65].

Bis[tris(pentafluorophenyl)stannyl] telluride which melted at 119° was prepared in 50% yield from the triarylstannyl bromide and bis(triethylsilyl) or bis(triethylgermyl) telluride. A four centered intermediate has been proposed for this reaction, which proceeded at 100° with the silyl telluride and at 70° with the germyl compound[12].

The tellurides, $[(CH_3)_3M]_2Te$, were prepared from lithium or sodium telluride and the appropriate trimethyl group IV element chlorides in benzene (eqn. 30).

$$(30) \qquad 2(CH_3)_3MCl + M'_2Te \longrightarrow [(CH_3)_3M]_2Te + 2M'Cl$$

M, M', % yield, bp.°C/torr: Si, Li, 40, 74°/11 (m.13.5°)[19]; Ge, Na, 32, 51°/0.5; Sn, Na, 60, 70-2/0.5; Pb, Na, 16, 51-4°/0.2[154].

Bis(triethylsilyl), germyl and stannyl tellurides formed at room temperature in toluene solution adducts with bis[tris(pentafluorophenyl)germyl]-cadmium[14] The transition metal carbonyl complexes with $[(CH_3)_3M]_2Te$ as ligands[154] are discussed in section VIII-F. The reactions of triethylsilanetellurol with triethyl aluminum has been treated in section VIII-B. Bis(triethylgermyl) telluride and mercury(II) chloride in tetrahydrofuran gave mercury telluride and triethylgermyl chloride[13].

C. Organic Compounds of Tellurium Containing a Tellurium-Phosphorus Bond

All of the organic tellurium-phosphorus compounds, which have been investigated during the survey period, are represented by the general formula R_3PTe. They are: $[(C_2H_5)_2N]_3PTe$, $(C_2H_5)_2NP(Te)(C_2H_5)_2$[157], $C_2H_5OP(Te)[N(C_2H_5)_2]_2$, $C_2H_5OP(Te)(C_2H_5)_2$, $[(CH_3)_2N]_2P(Te)CH_3$[118], $(C_6H_5)_3P{=}N{-}P(Te)(C_6H_5)_2$[104] (87% yield, m.150°, dec.), $(C_2H_5O)_2P(Te)C_2H_5$ (100% yield)[69]. These compounds were prepared from the appropriate phosphines and elemental tellurium.

Austad[3] isolated $[(C_6H_5)_3P]_2Te$ in 30% yield when tetraphenylarsonium tellurocyanate in acetonitrile was treated with triphenylphosphine in the presence of lithium perchlorate. The compound, which is stable in the solid state in sun light and moist air, decomposed on heating at 83-85°. It decomposed, however, upon dissolution in acetonitrile, benzene, acetone or diethyl ether unless excess triphenylphosphine was present. This zerovalent tellurium compound contains a linear P-Te-P group with P-Te bond lengths of 2.4 and 3.5Å.

Shagidullin[157] investigated the ability of the phosphine tellurides R_3PTe $[R = (CH_3)_2N, (C_2H_5)_2N]$ and $(C_2H_5)_2(C_2H_5)_2NPTe$ to form hydrogen bonds with phenol in chloroform medium. The shifts in the infrared OH frequencies indicated that such an interaction occurred. The enthalpies of formation were found to be approximately 5.4 kcal/mole. The electron donating capacity of the PX group decreases substantially from the phosphoryl (X = O) to the thiophosphoryl (X = S) group but changes little in the sequence S, Se, Te[157].

The results of nmr investigations[94,118] concerning $^{31}P-^{125}Te$ spin-spin coupling are discussed in section X-C. The difluorophosphine tellurides, $(F_2P)_2Te$ and $F_2P\text{-}Te\text{-}SiH_3$, were generated in reactions involving difluorobromophosphine and disilyl telluride in a solvent mixture of trichlorofluoromethane and cyclohexane. The phosphine tellurides were detected by means of their nmr spectra. They have, however, not been isolated[2].

D. Organic Compounds of Tellurium Containing a Tellurium-Sulfur or a Tellurium-Selenium Bond

The 2-formylphenyl phenylchalcogeno tellurides were obtained by refluxing the aryl tellurium bromide with benzenethiol or -selenol[133] (eqn. 31).

(31) $$2\text{-}H(O)CC_6H_4TeBr + C_6H_5XH \xrightarrow{\text{pyridine}} 2\text{-}H(O)CC_6H_4TeXC_6H_5$$

X, % yield, mp.°C: S, 50, 73°; Se, 40, 70°.

Se-Methyl Te-i-propyl selenide telluride was made by equilibrating dimethyl diselenide and bis(i-propyl) ditelluride. The compound was not isolated[106].

Hauge[73] obtained the blue-violet bis(phenyltelluro) selenide, which melted at 65°, in 97% yield from phenyl tellurium bromide or from the thiourea adduct of phenyl tellurium chloride and potassium selenocyanate in methanol. The following mechanism (eqn. 32) has been suggested for the formation of the selenide:

(32)

$$\begin{tikzcd} \mathrm{RTeBr} \arrow[r, "\mathrm{SeCN}^-"] & \mathrm{RTeSeCN} \arrow[r, "\mathrm{SeCN}^-"] \arrow[d] & \mathrm{RTeSe}^- + \mathrm{Se(CN)}_2 \arrow[dl] \\ R = C_6H_5 & \mathrm{RTe{-}Se{-}TeR} + \mathrm{SeCN}^- & \end{tikzcd}$$

The preparation of 2-formylphenyl tellurium thiocyanate and selenocyanate has also been claimed[5].

E. Organic Compounds of Tellurium Containing a Tellurium-Mercury Bond

Bis(methylmercury) telluride, a substance, which easily decomposed, was prepared from methyl mercury bromide and hydrogen telluride in methanol solution in 20% yield. When bis(pentafluoroethyl) ditelluride was shaken with mercury for eleven days, the yellow product $(C_2F_5Te)_2Hg$ precipitated, which was insensitive to water and could be recrystallized from acetone[121]. Bis(phenyltelluro) mercury has been reported earlier[79].

F. Organic Tellurium Compounds as Ligands in Transition Metal Complexes

To the list of known complexes of Cr, Mo, W, Mn, Re, Fe, Ru, Rh, Pd, Pt, Ag, Au, Cd, Hg, and U containing an organic tellurium compound as a ligand[79], Ti, Zr, Ta, Ir, Ni and Cu complexes have been added. Diaryl tellurides, dialkyl tellurides, $(R_3M')_2Te$ (M' = Si, Ge, Sn, Pb), tellurophene and tetrachlorotellurophene have been used as ligands. Complexes of Ti, Zr and Ni were prepared, which had an aryltelluro group covalently bonded to the metal atom.

Sato[151] prepared bis(cyclopentadienyl) complexes of titanium(IV) and zirconium(IV) from the bis(cyclopentadienyl)metal(IV) dichlorides and aryl bromomagnesium telluride or phenyl lithium telluride (eqn. 33).

$$(33)\qquad (\pi\text{-cp})_2MCl_2 + 2RC_6H_4TeM' \xrightarrow[-MgBrCl]{THF} (\pi\text{-cp})_2M(TeC_6H_4R)_2$$

M, M', R, % yield, mp.°C: Ti, MgBr, H, 80, 123-6°; Ti, MgBr, 4-CH_3, 78, 165-7°;
Zr, Li, H, 77, 118-20°.

The brown titanium complexes were rather unstable. Phenyl lithium telluride had to be used to prepare the red zirconium complex. With phenyl bromomagnesium telluride a red insoluble product was obtained.

The nickel complexes $(\pi\text{-cp})(C_4H_9)_3PNi\text{-}TeC_6H_4R$ were obtained as fairly air stable compounds according to eqn. (34)[150].

$$(34)\qquad \{(\pi\text{-cp})[(C_4H_9)_3P]_2Ni\}^+Cl^- + RC_6H_4TeNa \xrightarrow{H_2O} (\pi\text{-cp})(C_4H_9)_3PNi\text{-}TeC_6H_4R$$

R, % yield, mp.°C: H, 81, 50°; 4-CH_3, 80, 39°; 3-CF_3, 88, 44°; 4-Cl, 76, 48°;
4-CH_3O, 83, 54°.

The tantalum pentahalides, TaX_5 (X = Cl, Br) reacted in methylene chloride with an excess of dimethyl telluride to yield the complexes $TaX_5 \cdot Te(CH_3)_2$. These brown to black tantalum telluride complexes are more stable than the selenide or sulfide adducts[67].

The iridium complex $[(CO)_2ClIr \cdot Te(C_2H_5)_2]_n$ was prepared from $[Ir(CO)_3Cl]_n$ and diethyl telluride[137]. Pitombo[137a] used diphenyl telluride to extract palladium chloride as $PdCl_2 \cdot 2R_2Te$ into benzene and determine palladium in the organic phase spectrophotometrically at the absorption maximum of 400 nm.

When sulfur dioxide was condensed onto trans-$C_6H_5(Cl)Pt[Te(C_2H_5)_2]_2$ at -60°, sulfur dioxide insertion into the carbon-platinum bond occurred. The sulfinate complex, trans-$(C_6H_5SO_2)ClPd[Te(C_2H_5)_2]_2$, was isolated[52].

McWhinnie[110] obtained Cu(I) diaryl telluride complexes from the copper(I) halides and the diaryl tellurides in aqueous ethanol containing the appropriate hydrohalic acid. Although the metal/ligand ratio was varied from 1:1 to 1:4 only the following derivatives were isolated: $[(4\text{-}RC_6H_4)_2Te]_4Cu_2X_2$ (R, X : H, Br; H, I; CH_3, Cl; CH_3, Br; C_2H_5O, Cl; C_2H_5O, Br; C_2H_5O, I), $[(C_6H_5)_2Te]_3CuCl$ and $[(4\text{-}CH_3C_6H_4)_2Te]_2CuI$.

Chromium, molybdenum and tungsten complexes of the formula $(CO)_5M{\cdot}Te[M'(CH_3)_3]_2$ (H' = Ge, Sn, Pd) were obtained according to eqn. (35), as yellow solids[154], which rapidly decomposed below 0°.

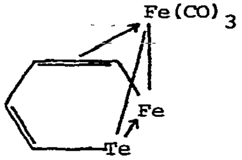
(35) $$(CO)_5M{\cdot}THF + Te[M'(CH_3)_3]_2 \xrightarrow{THF,\ 0^\circ} (CO)_5M{\cdot}Te[M'(CH_3)_3]_2$$

M, M', % yield, dec. °C: Cr, Ge, 36, 91°; Mo, Ge, 20, 83°; W, Ge, 41, 95°;
Cr, Sn, 44, 85°; Mo, Sn, 29, 93°; W, Sn, 39, 101°;
Cr, Pb, 42, 52°; Mo, Pb, 17, 53°; W, Pb, 45, 56°.

Bochkarev[14] obtained from the components in toluene the following complexes: $[(C_6F_5)_3Ge]_2Cd{\cdot}\{Te[M'(C_2H_5)_3]_2\}_x$ [M', x, % yield, mp.°C (dec)]: Si, 1, 59, 122-5°; Ge, 1, 67, 104-6°; Sn, 1, 73 , 85°; Sn, 2, 47, 80°.

Oefele[119] synthesized a number of tellurophene-transition metal complexes. Tellurophene and $(CH_3CN)_3Cr(CO)_3$ in dibutyl ether formed in 80% yield a purple, air stable compound, which decomposed without melting at 145°. Tellurophene acts as a tridentate ligand involving the tellurium atom. The reaction of tellurophene with sodium tetrachloropalladate(II) in methanol at 25° produced cis-bis(tellurophene)dichloropalladium in 27% yield and the dinuclear complex $L_2Pd_2Cl_4$ in 70% yield with the two tellurophene molecules in trans-position to each other. Treatment of the dinuclear compound with excess tellurophene gave the mononuclear derivative. In both of these air stable compounds, which decomposed at 130°, the tellurophene is bonded to the palladium atom via the tellurium atom. Tetrachlorotellurophene produced similarly trans-L_2PdCl_2 in 61% yield.

When, however, tellurophene was refluxed in benzene with $Fe_3(CO)_{12}$, black $Te_2Fe_3(CO)_9$, yellow $C_4H_4Fe_2(CO)_6$ and an air sensitive, red compound $C_{10}H_4Fe_2O_6Te$ which melted at 50° was obtained. This complex, which was isolated in 18% yield, was converted above its melting point to $C_4H_4Fe_2(CO)_6$. On the basis of ir, nmr and mass spectral data, the structure **10** was suggested for the complex.



10

IX. Heterocyclic Tellurium Compounds

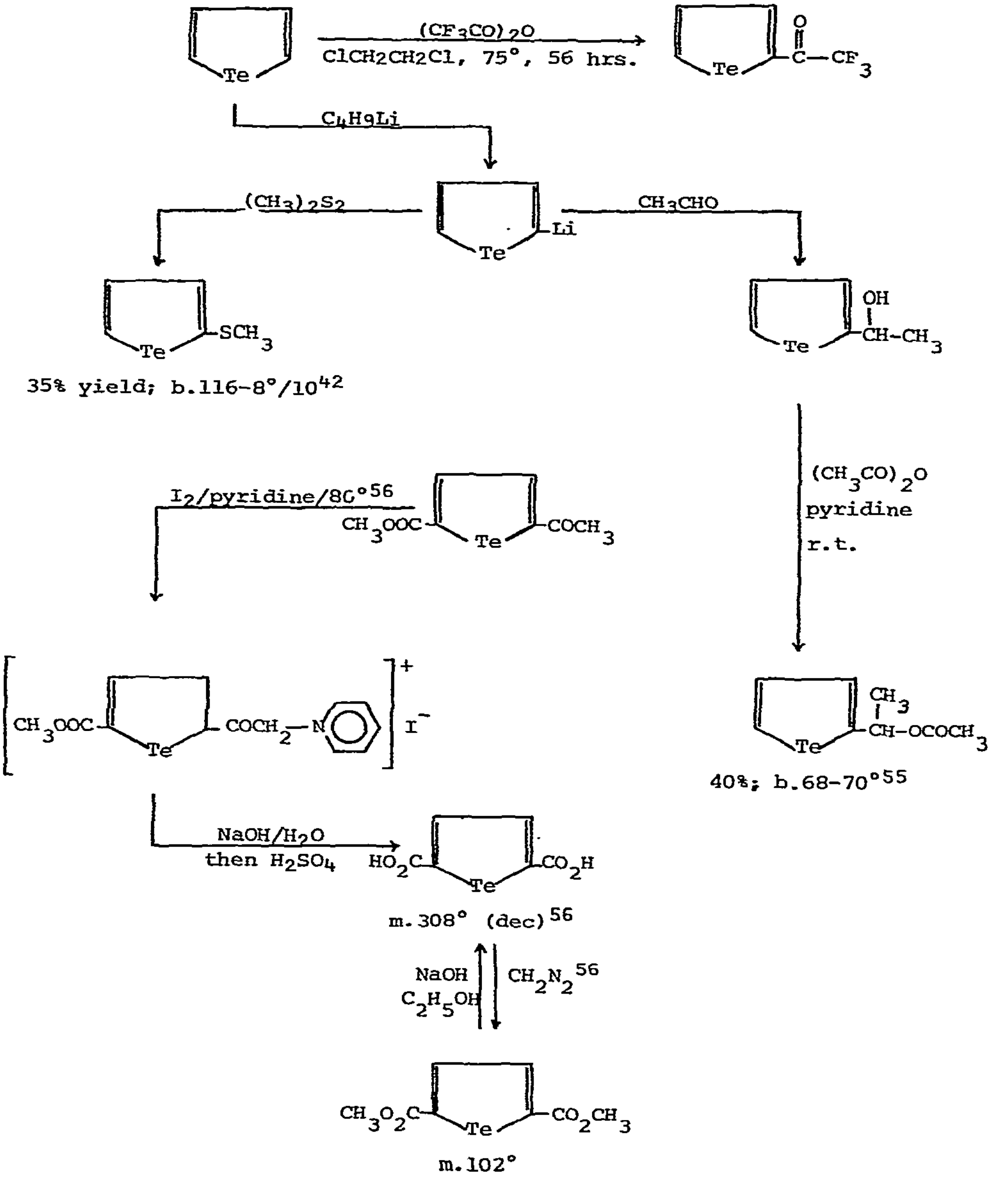
A number of new heterocyclic, tellurium containing compounds have been prepared. The main thrust of activities was concerned with tellurophene and its derivatives and with phenoxtellurine. Tellurophenes received special attention with physicochemical methods having been employed to solve structural problems and to determine the aromaticity of these compounds.

A. Tellurophene

Tellurophene, a light yellow, bad smelling liquid, which is rather stable to air, but should be stored in the dark at 0°, has received considerable attention. Improved methods for its synthesis from sodium telluride and butadiyne[54] or 1,4-bis(trimethylsilyl)butadiyne[7,171] in methanol solution have been reported. Tellurophene was obtained in these reactions in yields varying between 37 and 50%. The reactions of tellurophene leading to substituted derivatives are summarized in eqn. (36). The following pK_a values for 2-carboxy-5-R-tellurophene at 25° were determined (R, pK_a): H, 3.97 ± 0.01 (in water)[56]; H, 5.48 (in C_2H_5OH/H_2O 1:1 v/v)[59]; CH_3, 4.16 ± 0.01[56]; CH_3CO, 3.36 ± 0.02[56]; COOH, 3.11 ± 0.02, 4.24 ± 0.02[56]. These pK_a values were linearly related to the σ_p constants. The reaction constant ρ for the ionization of the carboxyl group is equal to those for thiophene and selenophene. This fact indicates that the electronic effects of substituents are transmitted in the same manner in the three heteroaromatic ring systems.[56]

The formylation of tellurophene, selenophene, thiophene and furan by the dimethylformamide-phosgene complex in chloroform is enthalpy controlled. Studies of the rate constants and activation parameters indicated that differences in the ground state energy of these heterocycles are important in deter-

(36)



mining the relative reactivities of the α-positions. The activity decreases in the sequence furan>tellurophene>selenophene>thiophene[30].

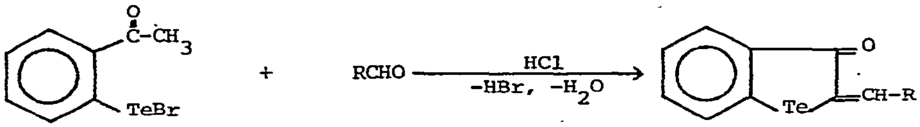
The substituent constant σ^+ relative to the perturbation produced by replacing a CH=CH group in benzene by a tellurium atom has been calculated from rate data for the hydrolysis of 2-(1'-acetoxyethyl)tellurophene, and the acetylation and formylation of tellurophene. The σ^+ constants for the heteroatoms O, S, Se and Te appear to vary in inverse order to that of the ground state aromaticity of these rings[55]. The ground state aromaticity has been found to decreas in the order benzene>thiophene>selenophene>tellurophene>furan based on results of nmr dilution shift experiments, observations of the effect of a 2-methyl substituent on the aromatic proton nmr shifts[58,61], the difference in chemical shifts of the β- and α-protons, the diamagnetic susceptibility exaltation, the sum of the bond orders, the Julg parameter and the mesomeric dipole moments[61].

A patent[P-3] claims that tellurophene or its derivatives added to aircraft hydraulic fluids increases their fire resistance. Tetrachlorotellurophene mixed with blends of phosphate esters, amides of a phosphorus acid, tricarbocylic acid esters or C_{10}-C_{24} hydrocarbons causes higher autoignition temperatures[P-1]. The metal complexes containing tellurophene as ligands have been discussed in section VIII-F.

B. 2,3-Dihydrobenzotellurophene

Piette[135] developed a method for the synthesis of 2-benzylidene-3-oxo-2,3-dihydrobenzotellurophene starting with 2-acetylphenyl tellurium bromide (eqn. 37) The yields in these reactions were 80%. The 2-cinnamoylphenyl tellurium bromides are intermediates, which on treatment with hydrochloric acid produced the benzotellurophene derivatives 10a. Hydrobromic acid (48%) in glacial acetic acid cleaved the ring system 10a($R = C_6H_5$) to the cinnamoylphenyl tellurium bromide.

(37)



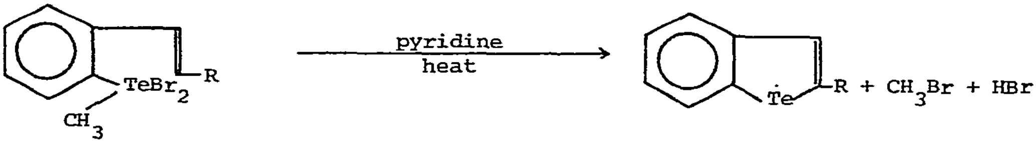
10a

R, mp.°C: C_6H_5, 142; 4-$CH_3C_6H_4$, 125; 4-$CH_3OC_6H_4$, 137; 2-ClC_6H_4, 185; 4-ClC_6H_4, 193; 4-IC_6H_4, 208; 4-$(CH_3)_2NC_6H_4$, 243; 1-$C_{10}H_7$, 184.

C. Benzotellurophene

Benzotellurophene derivatives with substituents in the 2-position were obtained by heating 2-R-vinylphenyl methyl tellurium dibromide in pyridine[134] (eqn. 38). 2-Acetylbenzotellurophene was also prepared, but in a small yield, by heating 2-formylphenyl acetonyl methyl telluronium bromide in pyridine[134]. The corresponding 2-acetylphenyl alkyl methyl telluronium bromides were not cyclized under these conditions. This method is, therefore, not suitable for the synthesis of 3-methyl-2-R-benzotellurophenes.

(38)

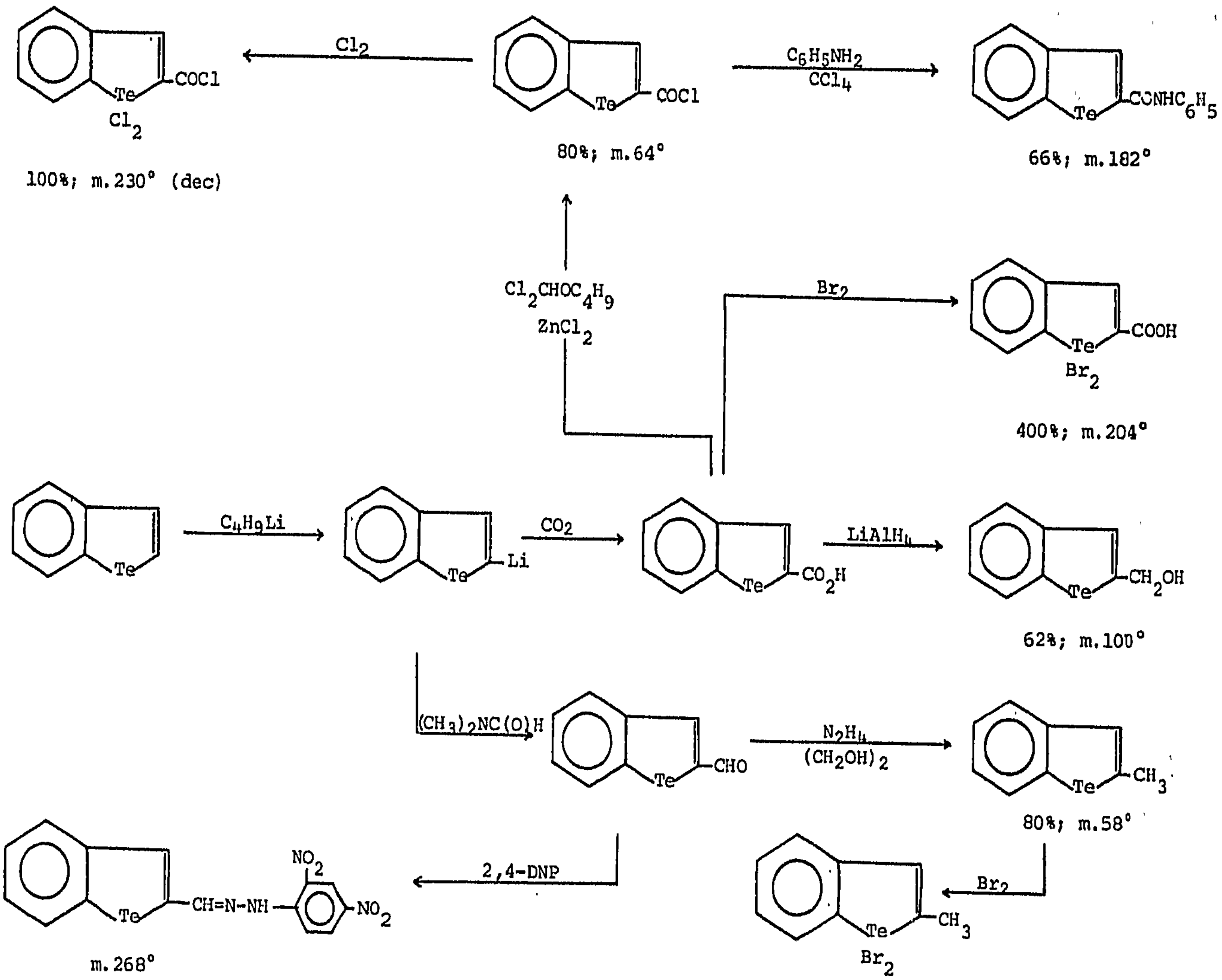


R, % yield, mp.°C: CN, 70, 106°; CH_3CO, 90, 99°; $CO_2C_2H_5$, 70, 57°; C_6H_5CO, 90, 97°.

The reactions of benzotellurophene leading to 2-substituted products and those modifying the substituents are summarized in eqn. (39). The pK_a value of 2-carboxybenzotellurophene in aqueous ethanol (1:1 v/v) at 25° is 5.13[59].

(39)

(39)


Cl2
COCl
Te
Cl2
100%; m.230° (dec)
COCl
Te
80%; m.64°
C6H5NH2
CCl4
CONHC6H5
Te
66%; m.182°
Cl2CHOC4H9
ZnCl2
Br2
COOH
Te
Br2
400%; m.204°
Te
C4H9Li
Li
CO2
CO2H
LiAlH4
CH2OH
62%; m.100°
(CH3)2NC(O)H
CHO
N2H4
(CH2OH)2
CH3
80%; m.58°
Br2
CH3
Br2
2,4-DNP
CH=N-NH
NO2
NO2
m.268°

D. Dibenzotellurophene

Dibenzotellurophene has received almost no attention during the survey period. The mass spectrum of octafluorodibenzotellurophene was analyzed[33]. The compound reacted with sulfur at 330° to produce octafluorodibenzothiophene[32].

E. 1,2-Ditelluracenaphthene

The synthesis of 1,2-ditelluraoctachloroacenaphthene has been claimed by an U.S. patent[P-2].

F. Telluracyclohexane

The free energy of activation to ring reversal for 3,3,5,5-telluracyclohexane-d_4 was determined by nmr techniques to be 7.3 kcal/mole[89]. Through analysis of nmr coupling constant ratios for the 2,3 and 3,4 segments of the tellurophene ring in tellurophene dibromide a trigonal bipyramidal geometry was deduced for the molecule[88].

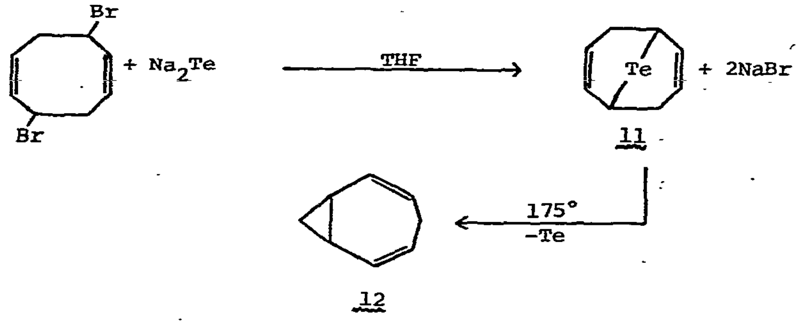
G. 1-Tellura-1,2,3,4-tetrahydronaphthalene

2-Phenyl-4-oxo-1-tellura-1,2,3,4-tetrahydronaphthalene was prepared in 20% yield by heating 2-cinnamoylphenyl methyl telluride at 60° in glacial acetic acid, which had been saturated with hydrogen bromide[132]. The main product of this reaction was 2-cinnamoylphenyl tellurium bromide.

H. 9-Tellurabicyclo[3,3,1]nona-2,6-diene

This bicyclic system 11 was prepared in 18% yield according to eqn. (40)[38]. The tellurium heterocycle was stable in the dark at room temperature under nitrogen. At 175° tellurium was expelled with formation of the bicyclic hydrocarbon 12.

(40)



I. 1-Oxa-4-telluracyclohexane

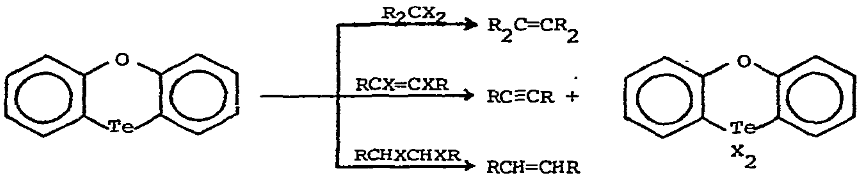
An X-ray structural investigation of 1-oxa-4-telluracyclohexane 4,4-diiodide showed that in the free molecule the tellurium atom is at the center of a trigonal bipyramid with two carbon atoms and an unshared electron pair in the equatorial positions. In the solid, the tellurium atom is surrounded octahedrally by two carbon atoms and four iodine atoms. Two of the iodine atoms form a bridge to the neighboring tellurium atoms[78].

J. Phenoxtellurine

A few new compounds of phenoxtellurine were prepared. The 2,8-dimethylphenoxtellurine 10,10-dibromide and diiodide were obtained in 73% and 93% yield, respectively, from the heterocycle and the appropriate halogen in chloroform or carbon tetrachloride. The dibromide decomposed at 296°, the diiodide at 292°[63a].

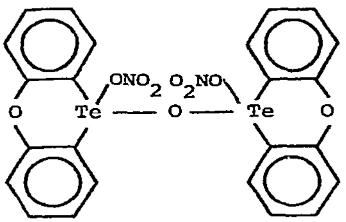
Phenoxtellurine was found to be capable of dehalogenating geminal[63b] and vicinal[63c] dihalides (eqn. 41). These reactions were carried out at about 100°

(41)



with or without solvent. The unsaturated compounds were isolated in good yields. The following organic halides were dehalogenated: 1,2-dibromoethane, trans-1,2-dibromocyclopentane and -cyclohexane, 1-phenyl-1,2-dibromoethane, 1,2-dibromoacenaphthene, 2,3-dibromobutyric acid, 2,3-dibromo-3-phenylpropionic acid and its ethyl ester, 1,2-diiodo-1-phenylethene, 2,3-diiodocinnamic acid, phenothiine 10,10-dichloride and dibromide[63c], phenoxselenine 10,10-dibromide, diphenyldichloromethane, $C_6H_5(ICl_2)$, diethyl dibromomalonate, 9,9-dichlorofluorene[63b]. Some of these dehalogenation reactions were completed in a few minutes. Benzylidene chloride and bromide produced only traces of stilbene[63b]. 1,2-Diiodobenzene[63b], 1,2-diphenyl-1,2-dibromoethane and 1,2-dichlorocyclohexane did not react. The 2,8-dimethyl-, difluoro- and dichlorophenoxtellurine derivatives dehalogenated phenoxathiine 10,10-dibromide[63c].

Phenoxtellurine produced upon dissolution in trifluoroacetic acid a deep purple solution, which deposited after several hours a green, unstable solid. On further standing the green substance redissolved. The white precipitate, which was finally deposited, was phenoxtellurine 10,10-bis(trifluoroacetate)[101]. It is conceivable that this compound was formed from the telluroxide and the acidic acid. Oxidation of phenoxtellurine by air probably produced the oxide. When solutions of phenoxtellurine 10,10-dinitrate were dissolved in acetone and the solutions evaporated the acetonyl phenoxtelluronium nitrate was obtained[161] When equimolar amounts of phenoxtellurine and its 10,10-dinitrate were dissolved in dichloromethane, the solid 13 precipitated[103].



13

The electrochemical oxidation of phenoxtellurine (POT) in acetonitrile produced a radical cation. The solutions turned first violet and then red. In the presence of lithium perchlorate the complex $[(POT^{\cdot+})_2POT]^{++}(ClO_4^-)_2$ was formed[22].

Gioaba[63] and Heller[76] investigated the tetracyanoethylene complex of phenoxtellurine. The thermodynamic properties for this 1:1 complex at 20° are $K = 1.0 \pm 0.3$ $lmol^{-1}$, $\Delta G = 0.00 \pm 0.02$ $kcalmol^{-1}$, $\Delta H = -2.0 \pm 0.4$ $kcalmol^{-1}$ and $\Delta S = 6.8 \pm 1.3$ $caldeg^{-1}mol^{-1}$. Similar results were obtained for the chloranil complex[76]. No significant trends of the thermodynamic values for the interactions of phenoxachalcogenines with these acceptors were observed when the chalcogen atom was changed from Te to Se to S to O. These interactions are probably of the π-π molecular complex type[76]. Gioaba[63] studied the spectral characteristics of the tetracyanoethylene complexes of phenoxtellurine and its 2,8-dimethyl, dichloro and difluoro derivatives. From the charge-transfer band the ionization potential of the donors were obtained and correlated with Hückel MO calculations.

The reaction of phenoxtellurine and its 10,10-dinitrate, which produced a violet complex when the solids were rubbed together, yielded in dichloromethane solution at -90° a violet compound containing two molecules of the dinitrate and one of phenoxtellurine. This complex converted to the 1:1 adduct at higher temperatures[75].

The X-ray structural studies on phenoxtellurine and its derivatives are described in section X-G.

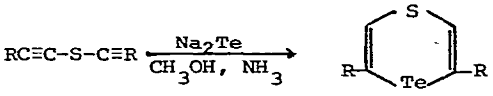
K. Thiophenoxtellurine

Thiophenoxtellurine 10,10-dichloride was obtained as a yellow solid, melting at 264-6° with decomposition, in 6% yield by heating tellurium tetrachloride and diphenyl sulfide at 200°. The dichloride was reduced to the thiophenoxtellurine by an aqueous solution of potassium disulfite. The thiophenoxtellurine 10,10-dibromide was prepared in 80% yield from the heterocycle and bromine in carbon tetrachloride solution. The dibromide melted at 271°. Thiophenoxtellurine was not as effective as phenoxtellurine as dehalogenating agent. These reactions show that thiophenoxtellurine is a weaker dehalogenation agent than phenoxtellurine but better than phenoxaselenine[63b].

L. 1-Thia-4-tellura-2,5-cyclohexadiene

This heterocyclic compound was prepared from diacetylenyl sulfides and sodium telluride in methanol/ammonia medium (eqn. 42)[111].

(42)



R, % yield, bp.°C/torr: H, 70, 110°/12; CH_3, 78, 70°/0.001; *tert*-C_4H_9, 82, 92°/0.001.

M. Telluracycloheptane

The only known telluracycloheptane compound is the steroid derivative **2** (section III), which was prepared from the steroid methanesulfonate **3** and sodium telluride. The compound melted at 100-103°. It decomposed on standing for several weeks.

X. Physicochemical Investigations of Organic Tellurium Compounds

Infrared, Raman, uv-visible, nmr, electron and mass spectroscopy, X-ray structural analysis and dipole moment measurements have been employed to characterize organic tellurium compounds and solve special problems posed by these derivatives. By far the most popular tools were infrared and nmr spectroscopy.

A. Infrared and Raman Spectroscopy

A large number of organic tellurium compounds were investigated during the survey period with infrared and Raman techniques. Some of these studies were concerned only with small frequency regions, in which vibrations of special importance occurred, others covered the entire accessible infrared region. A summary of all these investigations is presented in this section. Normal coordinate analyses were performed on methanetellurol and its deuterated derivatives[158], tellurophene[171] and 1-oxa-4-telluracyclohexane[47]. The microwave spectrum of tellurophene[18] and centrifugal stretching constants for dimethyl telluride[169] were also reported. The tellurium-carbon(alkyl) stretching frequencies were located in the region 530-450 cm^{-1} [46,158,159,164]. The corresponding tellurium-carbon(phenyl) modes[108,109] occur between 200-260 cm^{-1} and not in the region 555-487 cm^{-1} as suggested by Keller[79].

A region of 700-300 cm^{-1} has been suggested for Te-O vibrations in tellurinic acid halides[164], whereas in diaryl tellurium diacetates a band at 280 cm^{-1} was assigned to this mode[124]. In the complexes $RTeX_3$·tetraethyldithiooxamide ν(TeS) occurred in the region 262-215 cm^{-1} [29]. Tellurium-halogen modes were extensively investigated. The tellurium-halogen stretching vibrations were found in the regions 287-247 cm^{-1} (Cl), 193-157 (Br)[29,107,129,164] and 153-109 cm^{-1} (I)[29,107,130,164]. The antisymmetric $\nu(TeCl_2)$ occurred at lower energies than the symmetric vibration[107]. The skeletal vibrations for $[(CH_3)_3M]_2Te$ (M = Ge, Sn, Pb) were found in the region 236-48 cm^{-1} [154]. The corresponding Te-Hg modes of $(CH_3Hg)_2Te$ were located between 165 and 57 cm^{-1} [17].

Two reviews, which contain some data concerning infrared spectroscopy of organic tellurium compounds have appeared[81,162]. In the compilation of infrared and Raman data the following abbreviations have been used:

ir	infrared
l	liquid
n	neat
N	Nujol
s	solid
sl	solution
v	vapor

The frequency ranges used in the investigations are also given in the tables. If these ranges were not reported, the frequency spans tabulated or discussed ~~in the paper were included.~~

$(CH_3)_4N^+TeCN^-$: ir-N, R-s[46], 4000-200;

$(C_6H_5)_4As^+TeCN^-$: ir-N, R-s[46], 4000-200;

The fundamental frequencies for the $TeCN^-$ ion are 2073-2081 cm^{-1} (CN stretch), 450-466 cm^{-1} (TeC stretch) and 359-366 cm^{-1} (TeCN bend) in the solid ir and Raman spectra and ir solution spectra[46].

CH_3TeH: R-l 3100-100; ir-v, 4000-200; ir-matrix[158];

CH_3TeD: R-l 3100-100;

CD_3TeH: R-l 3100-100;

CD_3TeD: R-l 3100-100;

Normal coordinate calculations were performed. The force constants for methanetellurol are tabulated. It was not possible to observe the torsional fundamental[158].

2-formylbenzenetellurol: ir, $\nu(CO)$[5].

2-formylphenyl tellurium chloride: ir, $\nu(CO)$[133];

$2\text{-}H(O)CC_6H_4TeX$ (X = Cl, Br, I, CN, SCN, SeCN): ir, $\nu(CO)$[5];

2-cinnamoylphenyl tellurium bromide: ir, $\nu(CO)$[132];

$[(C_6H_5)_3PCH_3]^+[4\text{-}CH_3OC_6H_4TeI_2]^-$: R-sl ($CH_3CN$), 200-40[130];

$[(C_6H_5)_3PCH_3]^+[4\text{-}C_2H_5OC_6H_4TeI_2]^-$: R-sl ($CH_3CN$), 200-40[130];

$[(C_6H_5)_3PCH_3]^+[C_2H_5OC_6H_4TeIBr]^-$: R-sl ($CH_3CN$), 200-40[130];

$[(C_6H_5)_3PCH_3]^+[2\text{-}C_{10}H_7TeI_2]^-$: R-sl, ($CH_3CN$), 200-40[130];

The X-Te-X' stretching modes were assigned to bands in the region 96-149 cm^{-1}.

$[C_6H_5]_4As^+[C_6H_5CH_2TeBr(CN)]^-$: ir, peak at 2162 cm^{-1} [4];

$[CH_3TeCl_2]^+SbCl_6^-$: far ir-s[126];

CH_3TeCl_3: R-s, sl (benzene), 540-220, Te-Cl modes[8];
ir-s 550-50, Te-Cl modes[173];

$CH_3TeCl_3\cdot$tetramethylthiourea: ir-s, 550-50, Te-Cl modes[173];

4-$RC_6H_4TeCl_3$ (R = H, CH_3): ir, 580-130[174];

4-$RC_6H_4TeX_3$ (R = H, CH_3, CH_3O, C_2H_5O, C_6H_5O; X = Cl, Br, I): far ir-N or KBr, R[10

The Te-halogen bands were used to suggest structures for the aryl tellurium trihalides[108].

4-$RC_6H_4TeCl_3\cdot$pyridine (R = CH_3, CH_3O): ir, 600-150[174];

4-$RC_6H_4TeCl_3\cdot$4-methylpyridine (R = H, CH_3, CH_3O): ir, 600-150[174];

4-$RC_6H_4TeCl_3\cdot$4-methylpyridine N-oxide (R = H, CH_3, CH_3O): ir, 600-150[174];

The Te-Cl stretching modes shifted toward lower frequency upon complexation[17

4-$ROC_6H_4TeX_3\cdot$tetraethyldithiooxamide (R = CH_3, C_2H_5; X = Cl, Br, I): ir-N or KBr, R-s, 4000-80[29];

Absorptions between 262-215 cm^{-1} can be assigned to ν(TeS), those at 285-256 189-158 cm^{-1} and 153-128 cm^{-1} to ν(TeCl), ν(TeBr) and ν(TeI), respectively[29].

$[(C_2H_5)_4N]^+[CH_3TeCl_4]^-$: ir-s ($CH_3NO_2$), R-s, sl ($CH_3NO_2$), TeCl modes[8];

$[(C_6H_5)_4As]^+[C_6H_5TeCl_4]^-$: far ir, R, 400-220[164];

$[C_5H_5NH]^+[4\text{-}RC_6H_4TeCl_4{}^-]$ (R = H, C_2H_5O): far ir, R, 300-150[164];

$[(C_6H_5)_3PCH_3]^+[C_6H_5TeX_4]^-$ (X = Cl, Br): ir-N, R-s, N, sl (CH_3CN)[129];

$[(C_6H_5)_3PCH_2C_6H_5]^+[4\text{-}C_2H_5OC_6H_4TeX_4]^-$ (X = Cl, Br): R-N[129];

Tellurium-halogen modes were assigned to the region 160-250 cm^{-1} [129].

<u>trans</u>-$C_2F_5TeF_4Cl$: ir-v, 1325-610[41];

4-$C_2H_5OC_6H_4TeOOH$: ir-N, R-s, 4000-200[164];

$[4\text{-}C_2H_5OC_6H_4Te(O)]_2O$: ir-N, R-s, 4000-200[164];

$C_6H_5Te(O)X$ (X = Cl, Br): ir-N, R-s, 4000-200[164];

4-$C_2H_5OC_6H_4Te(O)X$ (X = Cl, Br, I): ir-N, R-s, 4000-200[164];

Bands in the region 300-700 cm^{-1} have been assigned to Te-O modes. The

TeX stretch occurred at 248 (X = Cl), 187 (X = Br) and 115 cm^{-1} (X = I)[164].

$(C_2F_5)_2Te_2$: ir-v, 1315-530[121];

$(4\text{-}RC_6H_4)_2Te_2$ (R = H, CH_3, CH_3O, C_2H_5O, C_6H_5O): ir-N, R-s, 4000-40[109];

$(2\text{-}C_{10}H_7)_2Te_2$: ir-N, R-s, 4000-40[109];

Detailed assignments of the spectra below 400 cm^{-1} are offered. The Te-Te stretching mode was found in the range 187-167 cm^{-1} [109].

$(CH_3)_2Te$: A force field for dimethyl telluride was deduced from correlations between the force constants of the other dimethyl chalcogenides and the electronegativity of the chalcogen atoms[87]. The centrifugal stretching constants for dimethyl telluride were calculated from the force constants[169].

$(C_2F_5)_2Te$: ir-v, 1315-530[121];

R_2Te: ir investigation of H-bonding with phenol[27];

$(4\text{-}RC_6H_4)_2Te$ (R = H, CH_3, CH_3O): ir-N, R-s, 4000-60[107];

$(C_6F_5)_2Te$: ir-N, R-s, 4000-60[107];

The data for these compounds are compiled in the Supplementary Publication No. SUP20252. Only the frequencies for diphenyl telluride below 400 cm^{-1} are given in the paper[107].

$C_6H_5Te\text{-}C(O)R$ (R = CH_3, C_2H_5): ir, $\nu(CO)$[136];

$C_6H_5Te\text{-}C(O)C_6H_4R$ (R = H, 2-F, 2-Cl, 2-Br, 2-I, 2-CH_3, 2-CH_3O, 4-CH_3O, 2-CH_3S, 2-CH_3Se): ir, $\nu(CO)$[136];

$2\text{-}CH_3C_6H_4Te\text{-}C(O)R$ (R = CH_3, C_6H_5, 2-$CH_3C_6H_4$, 2-BrC_6H_4, 2-$CH_3OC_6H_4$): ir, $\nu(CO)$[136];

The carbonyl frequency has been studied in various solvents and at different temperatures. The splitting of the carbonyl band was attributed to Fermi resonance[136].

2-formylphenyl methyl telluride: ir, $\nu(CO)$[5];

$CH_3TeC{\equiv}C\text{-}C(CH_3)_3$: ir-KBr, 3000-700[142];

$CH_3TeCH{=}C{=}CH\text{-}CH_2N(C_2H_5)_2$: ir-n, $\nu(C{=}C{=}C)$[131];

$(CH_3)_2TeCl_2$: R-s, sl (benzene), TeCl modes[8];

$(CH_3)_2TeI_2$: ir-s, 4000-100[159];

$(2\text{-}C_4H_9)_2TeI_2$: ir[166];

$(C_6H_5COCH_2)TeCl_2$: ir-N, 2000-400[62];

$(C_6H_5)_2TeX_2$ (X = Cl, Br, I): ir-N, R-s, 4000-60[107];

Detailed assignments are made for bands below 400 cm^{-1}. The tellurium-phenyl stretching mode was assigned to bands between 272 and 256 cm^{-1} and not as suggested by Keller[79] to the region 487-555 cm^{-1} [107].

$(C_6H_5)_2TeBr_2$: ir-N, s $(CHCl_3)$, 4000-200[124];

$(2\text{-}CH_3C_6H_4)_2TeX_2$ (X = Cl, Br, I): ir-N, R-s, 4000-60[107];

$(4\text{-}CH_3C_6H_4)_2TeX_2$ (X = Cl, Br, I): ir-N, R-s, 4000-60[107];

$(C_6F_5)_2TeX_2$ (X = Cl, Br): ir-N, R-s, 4000-60[107];

The symmetric tellurium-halogen stretching modes occur in the region 287-269 cm^{-1} (Cl), 168-157 cm^{-1} (Br) and 116-109 cm^{-1} (I). The antisymmetric modes span the regions 264-247 cm^{-1}, 193-173 cm^{-1} and 148-129 cm^{-1}. Bands for the dichlorides between 140 and 120 cm^{-1} were assigned to $\delta(TeCl_2)$[107].

$C_6H_5(CH_2COCH_3)TeCl_2$: ir, R, 4000-200; (TeC alkyl) 530 cm^{-1}, ν(TeCl) 250, 260 cm^{-1} [164].

$(C_6H_5)_2Te(NO_3)_2$: ir, nitrate bands[124]; $Na_2Te(CF_3COO)_6$: ir-KBr, 1700-900[145];

$(C_6H_5)_2Te(OOCCH_3)_2$: ir-N, sl (CCl_4), 4000-200[122,124,125];

$(C_6H_5)_2Te(OOCC_6H_5)_2$: ir-N, sl (CCl_4), 4000-200[124];

$(4\text{-}CH_3C_6H_5)_2Te(OOCCH_3)_2$: ir-N[125];

$(4\text{-}CH_3OC_6H_4)_2Te(OOCH_3)_2$: ir-N[125];

$(4\text{-}C_2H_5OC_6H_4)_2Te(OOCH_3)_2$: ir-N, sl (CCl_4), 4000-200[124,125];

$C_6H_5(4\text{-}C_2H_5OC_6H_4)Te(OOCCH_3)_2$: ir-N[125];

The acetate modes have been assigned[122,124,125]. Tellurium-oxygen modes were located at 280 cm^{-1} [124].

$(CH_3)_2TeI_4$: ir, 3000-100[159];

The ν_s and ν_{as}(TeI) occurred at the same frequencies found for $(CH_3)_2TeI_2$[159].

$[RC{\equiv}C\text{-}Te(CH_3)_2]^+I^-$ ($R = CH_2{=}CH$, <u>tert-</u>C_4H_9, C_6H_5): ir-KBr, 3000-600, carbon modes[142];

$(R_3Si)_2Te$ ($R = H$, CH_3): ir-v, l; R-l 4000-33[19];

Force constant calculations suggest that the bond order in Si-Te-Si is not enhanced. The spectra are in accord with a Si-Te-Si bond angle of 90°[19].

$[(C_2H_5)_3M]_2Te$ (M = Si, Ge): ir-n, R-n, 4000-33[154]; γ(C-M)[44];

$[(CH_3)_3M]_2Te$ (M = Ge, Sn, Pb): ir-n, 4000-33[154];

The following Te-M modes (in the order Ge, Sn, Pb) were assigned: $\nu_s(M_2Te)$ 236s, 191s, 161 cm^{-1}s (Raman); $\nu_{as}(M_2Te)$ 222s, 182s, 160 cm^{-1}s (ir); $\delta(M_2Te)$ 65w, 60w, 48 cm^{-1} [154].

$[(C_6H_5)_3P]Te$: ir-KBr, R, 4000-250[3]; $[(CH_3)_2NC(O)H]_{2.5}\cdot TeX_4$: ir-N[127].

Peaks at 528, 318 and 226 cm^{-1} arise from the P-Te-P group[3].

2-formylphenyl phenylthio telluride: ir, ν(CO)[133];

$(CH_3Hg)_2Te$: far ir-s; ν_{as}(TeHg) 165 cm_{-1}; ν_s(TeHg) 156 cm^{-1}; $\delta(Hg_2Te)$ 57 cm^{-1} [17];

$(C_2F_5Te)_2Hg$: ir-KBr, C_2F_5 modes[121];

$[(C_6H_5)_2Te]_4Cu_2X_2$ (X = Br, I): ir-N, KBr, 4000-40[110];

$[(C_6H_5)_2Te]CuCl$: ir-N, KBr, 4000-40[110];

$[(4\text{-}CH_3C_6H_4)_2Te]_4Cu_2X_2$ (X = Cl, Br): ir-N, KBr, 4000-40[110];

$[(4\text{-}CH_3C_6H_4)_2Te]_2CuI$: ir-N, KBr, 4000-40[110];

$[(4\text{-}C_2H_5OC_6H_4)_2Te]_4Cu_2X_2$ (X = Cl, Br, I): ir-N, KBr, 4000-40[110];

The low frequency ir bands are listed with special consideration of the copper-halogen stretching modes[110].

<u>trans-</u>$[(C_2H_5)_2Te]_2PtCl(O_2SC_6H_5)$: ir, $\nu_{s,as}(SO_2)$, ν(PtCl)[52];

$[(CH_3)_3M]_2Te\cdot M'(CO)_5$ (M = Ge, Sn, Pb; M' = Cr, Mo, W): ir-N, or sl(pentane), R-s, 4000-50[154];

The vibrations of the M_2Te skeleton have been assigned. It was not possible to unequivocally locate the M'-Te bands[154].

$(CO)_3Cr$·tellurophene: ir-sl (benzene), ν(CO)[119];

$(CO)_6Fe_2TeC_4H_4$: ir, ν(CO), tellurophene bands region[119];

cis-(tellurophene)$_2$PdCl$_2$: ir, 4000-600, ν(PdCl)[119];

trans-(tellurophene)$_2$Pd$_2$Cl$_4$: ir, 4000-600, ν(PdCl)[119];

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tellurophene: ir-sl(CCl_4), Ar matrix ir, R, normal coordinate analysis[171];
microwave spectrum, rotational constants[18];
ir-l, 4000-600[54];

2-trifluoroacetyltellurophene: ir-l, ν(CO)[30];

2-carboxytellurophene: ir-sl(CCl_4) ν(CO)[59];

2-(1'-acetoxyethyl)tellurophene: ir-l, ν(CO)[55];

2,5-bis(carbomethoxy)tellurophene: ir-sl(CCl_4), 4000-600[56];

2-benzylidene-3-oxo-2,3-dihydrobenzotellurophene: ir-KBr, 2000-400[135];

2-carboxybenzotellurophene: ir-sl(CCl_4), ν(CO)[59];

2-R-benzotellurophene (R = COCl, $CO_2C_2H_5$, COOH, $CONH_2$, CHO, $COCH_3$, CN, $CONHC_6H_5$, COC_6H_5): ir-KBr, ν(CO)[134];

1-oxa-4-telluracyclohexane: ir-v, l, s, sl(CS_2), R-l, s, 4000-50[47];

A normal coordinate analysis was carried out with bands at 497 and 518 cm^{-1} assigned to C-Te stretching vibrations[47].

B. Ultraviolet-Visible Spectroscopy

The ultraviolet-visible spectral data for organic tellurium compounds, which became available during the survey period, are summarized in Table 9. The only compound, whose vacuum ultraviolet spectrum in the region 40,000 to 80,000 cm^{-1} was investigated, is dimethyl telluride[156]. Three Rydberg series were assigned, which converged on the ionization potential of 7.926 eV. This ionization potential and the corresponding Rydberg series originate from the central atom valence p orbital. Higher energy absorptions were assigned to arise from a nonbonding orbital of a_1 symmetry localized on the tellurium atom[156]. Assignments for the ultraviolet absorption bands were made by Cradock[37].

Ionization potentials in eV for 2,8-R_2-phenoxtellurines were calculated from the charge-transfer band frequency of the complexes POT·tetracyanoethylene or POT·chloranil according to the empirical equation 0.87IP = $h\nu$ + 4.86. The values are (R, IP in ev, acceptor): H, 7.60, TCNE[63]; H, 7.71, TCNE[75]; CH_3, 7.54, TCNE; Cl, 7.74, TCNE; F, 7.81, TCNE[63].

Free electron model calculations on diethyl ditelluride showed that the long wave length bands are caused by excitation of the lone electrons of the tellurium atom. The results also point out the possibility that there may exist a barrier to internal rotation around the tellurium-tellurium bond[16].

Diffuse reflectance spectra for diphenyl ditelluride[109], bis(4-phenoxyphenyl) ditelluride[109] and diphenyl tellurium dibromide and diiodide have been published.

C. Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy has been extensively employed to characterize organic tellurium compounds and solve special problems concerning the structure and conformation of molecules in solution. The most frequently used tool was ^{1}H nmr spectroscopy. However, data from ^{13}C, ^{19}F, ^{31}P and ^{125}Te nmr investigations on organic tellurium compounds became available also during the survey period.

^{1}H NMR Spectroscopy

As can be judged from Table 10 ^{1}H nmr spectroscopy has been routinely used for the characterization of organic tellurium compounds. In addition to the ^{1}H chemical shifts, H-H, H-^{125}Te, H-Si, H-Ge, H-Sn and H-Pb coupling constants in

TABLE 9
ULTRAVIOLET AND VISIBLE ABSORPTION SPECTRA OF ORGANIC TELLURIUM COMPOUNDS

Compound	λ_{max} x 10^9m (log E)	Solvent	Ref.
$CH_3Te\cdot$	243.5, 237.2, 231.1, 225.3	gas phase	75
$(CH_3)_2Te$	201, 222, 258, 294, 370	gas phase	37
$(C_2H_5)_2Te_2$	395 (2.38)	hexane	16
$(C_6H_5)_2Te_2$	407 (2.97)	ethanol	109
$(CH_3)_2Te$	vacuum uv	gas phase	156
$(C_2H_5)_2Te$	234 (3.845), 290 (1.380), 360 (1.255)	hexane	16
$CH_3TeC{\equiv}C\text{-}CH{=}CH_2$	220-225, 248-270, 261-284, 286-350	water, ethanol or heptane	143
$(C_3H_7)_2TeI_2$	272 (4.55); 336 (4.30)	$CHCl_3$	159
$(C_4H_9)_2TeI_2$	273 (4.58); 335 (4.32)	$CHCl_3$	159
$(CH_3)_2TeI_4$	274 (4.49); 336 (4.29); 510 (3.0); 555 sh	$CHCl_3$	159
$(C_2H_5)_2TeI_4$	268 (4.75); 335 (4.32); 510 (3.0); 555 sh	cyclohexane	159
$(C_3H_7)_2TeI_4$	270 (4.70); 336 (4.40); 510 (3.0)	$CHCl_3$	159
phenoxtellurine (POT)	257.5; 359	heptane	63a
2,8-dichloro-POT	262; 302; 357	heptane	63a
2,8-dimethyl-POT	260; 358	heptane	63a
POT 10,10-dichloride	279; 299	methanol	63a
POT 10,10-dibromide	280; 299	methanol	63a
POT 10,10-diiodide	298; 338	methanol	63a
2,8-dichloro-POT 10,10-dichloride	307	methanol	63a
10,10-dibromide	308		63a
10,10-diiodide	352		63a

2,8-dimethyl-POT 10,10-dichloride	290; 308	methanol	63a
10,10-dibromide	289; 309	methanol	63a
10,10-diiodide	249; 370 (inflections)	methanol	63a
POT•chloranil	590-610 (2.30)	CH_2Cl_2	76
POT•tetracyanoethylene	700-720 (3.04)	CH_2Cl_2	76
	700	CCl_4	63
	665	CH_3NO_2	63
2,8-dimethyl-POT•tetracyanoethylene	717, 730, 700	CCl_4, CH_2Cl_2, CH_3NO_2	63
2,8-dichloro-POT•tetracyanoethylene	655, 660, 610	CCl_4, CH_2Cl_2, CH_3NO_2	63
2,8-difluoro-POT•tetracyanoethylene	620, 640, 610	CCl_4, CH_2Cl_2, CH_3NO_2	63
POT•2 POT 10,10-dinitrate	500 (3.95)	CH_2Cl_2	75
$(POT^{\bullet *})_2 \cdot POT$	525	CH_3CN	22
$(POT^{\bullet *})_2$	445	CH_3CN	22

TABLE 10

^{1}HNMR SPECTRAL DATA FOR ORGANIC TELLURIUM COMPOUNDS

Compound	Solvent	Chemical Shift, ppm††† TMS = 0 ppm	Coupling Constants Hz	Ref.
2-H(O)CC$_6$H$_4$TeCl	CS$_2$	CHO 10.56, H3 8.37, H4 7.67, H5,7.51, H6 8.18	J_{13} 0.76-0.88, J_{34} 8.09-8.30,	5
2-H(O)CC$_6$H$_4$TeBr	CS$_2$	CHO 10.50, H3 8.36, H4 7.64, H5 7.52, H6 8.14	J_{35} 0.88-1.16, J_{36} 0.43-0.54	5
2-H(O)CC$_6$H$_4$TeI	CS$_2$	CHO 10.26, H3 8.28, H4 7.56, H5 7.54, H6 8.02	J_{45} 7.05-7.30, J_{46} 1.49-1.51 J_{56} 7.65-7.90	5
2-H(O)CC$_6$H$_4$TeCN	CS$_2$	CHO 10.22	-	5
2-H(O)CC$_6$H$_4$TeSCN	CS$_2$	CHO 10.42	-	5
2-H(O)CC$_6$H$_4$TeSeCN	CS$_2$	CHO 10.5	-	5
2-cinnamoylphenyl-TeBr	CDCl$_3$	7.60 (2H), 7.5 (m,8H) 8.4 (m,1H)	-	132
C$_6$H$_5$TeCl$_3$	CD$_3$CN	8.50 (m,2H), 7.67 (m,3H)	-	174
4-CH$_3$C$_6$H$_4$TeCl$_3$	CD$_3$CN	CH$_3$ 2.47, 8.35 (d, ortho H); 7.48 (d, meta H)	-	174
	dioxane	8.32 (d, ortho H); 7.40 (d, meta H)	-	113

4-$ClC_6H_4TeCl_3$	dioxane	8.43 (d, ortho H); 7.61 (d, meta H)		113
4-$BrC_6H_4TeCl_3$	dioxane	8.38 (d, ortho H); 7.77 (d, meta H)		113
4-$HOC_6H_4TeCl_3$	dioxane	8.32 (d, ortho H); 6.94 (d, meta H)		113
4-$CH_3OC_6H_4TeCl_3$	CD_3CN	CH_3 3.90, 8.34 (d, ortho H); 7.22 (d, meta H)	J_{23} 9.0	174
	dioxane	8.41 (d, ortho H); 7.11 (d, meta H)		113
4-$C_2H_5OC_6H_4TeCl_3$	dioxane	8.39 (d, ortho H); 7.09 (d, meta H)	J(HH) 9	113
4-$C_3H_7OC_6H_4TeCl_3$	dioxane	8.40 (d, ortho H); 7.08 (d, meta H)		113
4-$C_4H_9OC_6H_4TeCl_3$	-	8.39 (d, ortho H); 7.11 (d, meta H)		147

TABLE 10 (continued)

Compound	Solvent	Chemical Shift, ppm††† TMS = 0 ppm		Coupling Constants Hz	Ref.
4-$C_6H_5OC_6H_4TeCl_3$	dioxane	8.42 (d, ortho H); 7.14 (d, meta H)		-	113
4-$CH_3SC_6H_4TeCl_3$	dioxane	8.25 (d, ortho H); 6.93 (d, meta H)		-	113
4-$C_2H_5COOC_6H_4TeCl_2$	dioxane	8.33 (d, ortho H); 7.43 (d, meta H)		-	113
4-$O_2NC_6H_4TeCl_3$	dioxane	8.61 (d, ortho H); 8.38 (d, meta H)		-	113
$C_6H_5TeCl_3$·picoline	CD_3CN	pic CH_3 2.63	uncomplexed, pic CH_3 2.17	-	174
4-$CH_3C_6H_4TeCl_3$·picoline	CD_3CN	pic CH_3 2.67		-	174
4-$CH_3OC_6H_4TeCl_3$·picoline	CD_3CN	pic CH_3 2.65		-	174
($\underline{i}$-C_3H_7)$_2Te_2$	CH_2Cl_2	CH 3.40, CH_3 1.60		-	106
(4-$CH_3C_6H_4$)$_2Te_2$	-	CH_3 2.34s, CH 6.90 (meta), CH 7.65 (ortho)		J(HH) 9	10
$(CH_3)_2Te$	neat	4.14		-	106
$(C_2H_5)_2Te$	benzene	CH_2 2.57, CH_3 1.59		-	106
($\underline{i}$-C_3H_7)$_2$Te	CH_2Cl_2	CH 3.32, CH_3 1.55		-	106

$(C_2H_5)_2NCH_2CH=C=CH-TeCH_3$	-	NCH_2 3.98-3.79, TeCH=C 6.89-6.57, CCH=C 5.90-5.42		131
$2-H(O)CC_6H_4TeCH_3$	CS_2	CHO 10.07, H3 7.53, H4 7.36, H5 7.32, H6 7.74	J_{13} 0.75, J_{34} 7.64, J_{35} 1.20, J_{36} 0.44, J_{45} 7.43, J_{46} 1.62, J_{56} 7.56	5
$2-(C_2H_5O)_2CHC_6H_4TeCH_2CH(OC_2H_5)_2$	$CDCl_3$	7.6 (m,2H), 7.2 (m,2H), 5.5 (s,1H), 4.84 (t,1H), 3.57 (2q,8H), 3.1 (d,2H), 1.20-1.24 (2t,12H)	-	133
$(C_6H_5)_2Te$	CH_2Cl_2	7.3-8.1	-	106
$(4-CH_3OC_6H_4)_2Te$	-	CH_3 3.11, 6.77 (d, meta H), 7.66 (d, ortho H)	J(HH) 9	10
$(CH_3)_2TeCl_2$	CH_2Cl_2	3.13	-	106
$CH_3)_2TeBr_2$	CH_2Cl_2	3.19	-	106
$(CH_3)_2TeI_2$	CCl_4	3.37	$J(H^{125}Te)$ 26	159
$(C_2H_5)_2TeBr_2$	benzene	CH_2 3.50, CH_3 1.70	-	106
$(C_2H_5)_2TeI_2$	CCl_4	CH_2 3.57, CH_3 1.77	$J(H^{125}Te)$ 22	159
$(C_3H_7)_2TeI_2$	CCl_4	CH_2Te 3.55, CH_2 2.25, CH_3 1.20	$J(H^{125}Te)$ 22	159
$(C_4H_9)_2TeI_2$	CCl_4	CH_2Te 3.53, CH_2 2.16, 1.50, CH_3 1.06	$J(H^{125}Te)$ 25	159

TABLE 10 (continued)

Compound	Solvent	Chemical Shift, ppm††† TMS = 0 ppm	Coupling Constants Hz	Ref.
$(\underline{i}\text{-}C_3H_7)_2TeBr_2$	CH_2Cl_2	CH 3.92, CH_3 1.78	-	106
$(4\text{-}CH_3OC_6H_4)_2TeCl_2$	-	CH_3 3.81, 7.08 (d, meta H), 7.93 (d, ortho H)	J(HH) 9	10
$[3,4\text{-}(CH_3O)_2C_6H_3]_2TeCl_2$	-	CH_3 3.84, 3.89; 7.17 (d, meta H), 7.59-7.75 (ortho H)	J_{56} 9, J_{26} 2.5	10
$[3\text{-}CH_3\text{-}4\text{-}CH_3OC_6H_4]_2TeCl_2$	-	CH_3 2.18, CH_3O 3.85	J_{56} 9, J_{26} 2.5	10
$[4\text{-}(CH_3)_2NC_6H_4]_2TeCl_2$	-	*	-	10
$(4\text{-}C_2H_5OC_6H_4)[4\text{-}(CH_3)_2NC_6H_4]TeCl_2$	-	$\underline{CH_3}CH_2$ 1.37, CH_3N 3.01, $\underline{CH_2}CH_3$ 5.87 *	-	10
$(C_6H_5)_2Te(OOCCH_3)_2$	CCl_4	CH_3 1.90, C_6H_5 8.00-7.30	-	122,125
$(4\text{-}CH_3C_6H_4)_2Te(OOCCH_3)_2$	C_6D_6	CH_3COO 1.80, CH_3 2.00, C_6H_5 6.93, 7.85	-	125
$(4\text{-}CH_3OC_6H_4)_2Te(OOCCH_3)_2$	$CDCl_3$	CH_3COO 1.90, CH_3O 3.75, C_6H_5 6.90, 7.68	-	125
$(4\text{-}C_2H_5OC_6H_4)_2Te(OOCCH_3)_2$	CCl_4	CH_3COO 1.90, CH_3 1.45, CH_2 4.08, C_6H_5 6.98, 7.80	-	125
$(4\text{-}C_2H_5OC_6H_4)C_6H_5Te(OOCCH_3)_2$	CCl_4	CH_3COO 1.85, CH_3 1.43, CH_2 4.05, C_6H_5 7.80-6.80	-	125

$(CH_3)_2TeI_4$	CCl_4	3.35	$J(H^{125}Te)$ 26	159
$(C_2H_5)_2TeI_4$	CCl_4	CH_2 3.56, CH_3 1.77	$J(H^{125}Te)$ 22	159
$(C_3H_7)_2TeI_4$	CCl_4	CH_2Te 3.55, CH_2 2.25, CH_3 1.19	$J(H^{125}Te)$ 22	159
$(C_4H_9)_2TeI_4$	CCl_4	CH_2Te 3.54, CH_2 2.18, 1.50, CH_3 1.06	$J(H^{125}Te)$ 25	159
$(CH_3)_3TeI$	$(CH_3)_2SO$-d_6	2.18	-	106
$C_2H_5(CH_3)_2TeBr$	D_2O	CH_3 2.31, C_2H_5 2.99	-	106
$(C_2H_5)_3TeBr$	D_2O	CH_2 3.00, CH_3 1.51	-	106
$(CH_3)(\underline{i}$-$C_3H_7)_2TeI$	D_2O	**	-	106
$(H_3Si)_2Te$	$CHCl_3$	3.67, 3.59	$J(SiH)$ 224, $^2J(TeH)$ 27.4	2,66
H_3Si-TeH	$CHCl_3$	3.77, TeH -7.46	$J(SiH)$ 224, $J(TeH)$ 57.6, $^2J(TeH)$ 32.4	66
$(H_3Ge)_2Te$	$CHCl_3$	3.66, 3.52	$^3J(HH)$ 4.8	2,66
H_3Ge-TeH	$CHCl_3$	3.62, TeH -7.44	$^2J(TeH)$ 19.4	66
$H_3SiTePF_2$	-	3.94	-	2
$[(CH_3)_3Ge]_2Te$	benzene	$+390.3^{\dagger}$	$J(HCGe^{125}Te)$ 5.5	154
$[(CH_3)_3Sn]_2Te$	benzene	$+400.1^{\dagger}$	$J(HC^{117}Sn)$ 52.5, $J(HC^{119}Sn)$ 54.8	154
	CH_2Cl_2	0.53	-	106
$[(CH_3)_3Pb]_2Te$	benzene	$+386.6^{\dagger}$	$J(HC^{207}Pb)$ 61.4	106
CH_3SeTe-$\underline{i}$-C_3H_7	CH_2Cl_2	CH_3Se 2.60, RTe 3.29	-	106

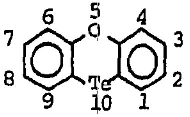
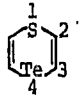
TABLE 10 (continued)

Compound	Solvent	Chemical Shift, ppm††† TMS = 0 ppm	Coupling Constants Hz	Ref.
$(OC)_5Cr\cdot Te[Ge(CH_3)_3]_2$	benzene	+401.6†	$J(HCGe^{125}Te)$ 8.5	154
$(OC)_5Mo\cdot Te[Ge(CH_3)_3]_2$	benzene	+398.9†	$J(HCGe^{125}Te)$ 8.6	154
$(OC)_5W\cdot Te[Ge(CH_3)_3]_2$	benzene	+402.0†	$J(HCGe^{125}To)$ 9.2	154
$(OC)_5Cr\cdot Te[Sn(CH_3)_3]_2$	benzene	+407.2†	$J(HC^{117}Sn)$ 52.5, $J(HC^{119}Sn)$ 54.5	154
$(OC)_5Mo\cdot Te[Sn(CH_3)_3]_2$	benzene	+403.3†	$J(HC^{117}Sn)$ 52.6, $J(HC^{119}Sn)$ 54.7	154
$(OC)_5W\cdot Te[Sn(CH_3)_3]_2$	benzene	+404.4†	$J(HC^{117}Sn)$ 52.2, $J(NC^{119}Sn)$ 54.5	154
$(OC)_5Cr\cdot Te[Pb(CH_3)_3]_2$	benzene	+370†	$J(HC^{207}Pb)$ 57.8	154
$(OC)_5Mo\cdot Te[Pb(CH_3)_3]_2$	benzene	+357.6†	$J(HC^{207}Pb)$ 57.2	154
$(OC)_5W\cdot Te[Pb(CH_3)_3]_2$	benzene	+367.7†	$J(HC^{207}Pb)$ 57.9	154
$TaCl_5\cdot(CH_3)_2Te$	CH_2Cl_2	2.54	-	67
$TaBr_5\cdot(CH_3)_2Te$	CH_2Cl_2	2.58	-	67
$(\pi\text{-}C_5H_5)_2Ti(TeC_6H_5)_2$	CS_2	C_5H_5 5.85s, C_6H_5 7.74-7.50, 7.28-7.02	-	151
$(\pi\text{-}C_5H_5)_2Ti(TeC_6H_4\text{-}4CH_3)_2$	CS_2	C_5H_5 5,82s, C_6H_4 7.52, 7.02, CH_3 2.41	J(HH) 8.0	151
$(\pi\text{-}C_5H_5)_2Zr(TeC_6H_5)_2$	CS_2	C_5H_5 5.82s, C_6H_5 7.70-7.62, 7.30-7.08	-	151
$(\pi\text{-}C_5H_5)LNi(TeC_6H_5)^{\dagger\dagger}$	CS_2	C_5H_5 5.07s, C_6H_5 7.60-7.53, 7.00-6.68	-	150
$(\pi\text{-}C_5H_5)LNi(TeC_6H_4\text{-}4\text{-}CH_3)^{\dagger\dagger}$	CS_2	C_5H_5 5.05s, C_6H_5 7.46, 6.63	J_{23} 7.5	150

$(\pi\text{-}C_5H_5)LNi(TeC_6H_4\text{-}3\text{-}CF_3)^{\dagger\dagger}$	CS_2	C_5H_5 5.16s, C_6H_5 7.99s, 7.82d, 7.21-6.89m	J(HH) 7.5	150
$(\pi\text{-}C_5H_5)LNi(TeC_6H_4\text{-}4\text{-}Cl)^{\dagger\dagger}$	CS_2	C_5H_5 5.11s, C_6H_5 7.58, 6.75	J_{23} 9.0	150
$(\pi\text{-}C_5H_5)LNi(TeC_6H_4\text{-}4\text{-}CH_3O)^{\dagger\dagger}$	CS_2	C_5H_5 5.02s, C_6H_5 7.46, 6.38	J_{23} 8.0	150
$(OC)_3Cr\cdot$tellurophene	acetone-d_6	6.5, 6.0m	-	119
$(OC)_6Fe_2\cdot TeC_4H_4$	acetone-d_6	9.31d, 7.19(2d), 5.73d, 5.23(2d)	J 9.2, 5.6, 7.5, 7.5, 5.6, 9.2	119
<u>trans</u>-$\{Pt(C_6H_5SO_2)[Te(C_2H_5)_2]\}$	-	CH_2 2.92, CH_3 1.54, C_6H_5 8.10-7.35	J 7.8	52
tellurophene	-	-	J_{23} 6.58, J_{24} 1.12, J_{25} 1.82, J_{34} 3.76	39,57
2-hydroxymethyltellurophene	acetone-d_6	H3 7.41, H4 7.64, H5 8.77	J_{34} 3.88, J_{35} 1.25, J_{45} 6.83***	60
2-formyltellurophene	acetone-d_6	H3 8.62, H4 8.05, H5 9.56	J_{34} 4.10, J_{35} 1.32, J_{45} 6.77***	60
2-carboxytellurophene	acetone-d_6	H3 8.53, H4 7.93, H5 9.40	J_{34} 4.20, J_{35} 1.34, J_{45} 6.76***	60
2-carbomethoxytellurophene	acetone-d_6	H3 8.49, H4 7.92, H5 9.38	J_{34} 4.11, J_{35} 1.33, J_{45} 6.79***	60
2-acetyltellurophene	acetone-d_6	H3 8.44, H4 8.00, H5 9.41	J_{34} 4.22, J_{35} 1.16, J_{45} 6.78***	60

TABLE 10 (continued)

Compound	Solvent	Chemical Shift, ppm††† TMS = 0 ppm	Coupling Constants Hz	Ref.
2-methylthiotellurophene	acetone-d_6	H3 7.42, H4 7.55, H5 8.81	J_{34} 4.03, J_{35} 1.28, J_{45} 6.93***	60
2-methyltellurophene		H3 7.20, H4 7.46, H5 8.56, CH_3 2.58	$J(CH_3-H_3)$ 1.0, J_{43} 4.01, J_{45} 7.0, J_{54} 7.0, J_{53} 1.2	61
2-trifluoroacetyltellurophene	CCl_4	H3 8.06, H4 8.65, H5 9.60	J_{45} 6.6, J_{43} 4.5, J_{45} 6.8, J_{35} 1.4	30
2-(1'-acetyloxyethyl)tellurophene	$CDCl_3$	H3 7.50, H4 7.62, H5 8.72, CH_3CO 2.02, CH_3 1.58, CH 6.00	$J(CH_3-CH)$ 6.2, J_{34} 3.9, J_{54} 6.6, J_{53} 1.5, $J(CH-H_3)$ 1.0	55
bis(2-carboxymethyl)tellurophene	-	CH_3 3.85, H3, H4 8.53	-	56
benzotellurophene	CCl_4	H2 8.55, H3 7.84	-	134
	-	H2 8.55, H3 7.84, H4 7.71, H5 7.26, H6 7.03, H7 7.82	J_{23} 6.95, J_{37} 0.43, J_{45} 7.97, J_{46} 1.07, J_{47} 0.51, J_{56} 7.24, J_{57} 1.08, J_{67} 8.00	50,92
2-methylbenzotellurophene	CCl_4	H3 7.26, CH_3 2.58	-	134
2-hydroxymethyl-	CCl_4	H3 7.63, CH_2 4.90, HO 2.30	-	134
2-formyl-	CCl_4	H3 8.47, CHO 9.63	-	134
2-carboxy-	CCl_4	H3 8.50	-	134
2-carboxyethyl-	CCl_4	H3 8.50, CH_3 1.23, CH_2 4.21	-	134
2-chloroformyl-	CCl_4	H3 8.75	-	134
2-acetylbenzotellurophene	CCl_4	H3 8.45, CH_3 2.63	-	134
2-phenacyl-	CCl_4	H3 8.27	-	134

2-amidocarbonyl-	CCl_4	H3 8.47, NH_2 7.90	-	134
2-anilidocarbonyl-	CCl_4	H3 8.30, NH 9.80	-	134
2-cyano-	$CDCl_3$	H3 8.32	-	134
	acetone-d_6	H1 7.64, H2 7.07, H3 7.30, H4 7.26	J_{12} 7.62, J_{13} 1.57, J_{14} 0.41, J_{23} 7.54, J_{24} 1.17, J_{34} 8.20	64
10,10-dichloride	$(CD_3)_2SO$	H1 8.14	-	64
10,10-diiodide	$(CD_3)_2SO$	H1 8.03, H2 7.19, H3 7.43, H4 7.36	J_{12} 7.60, J_{13} 1.50, J_{14} 0.40, J_{23} 7.50, J_{24} 1.50, J_{34} 8.20	64
2,8-difluorophenoxtellurine	$CDCl_3$	H1 7.48, H3 5.05, H4 7.18	J_{12} 7.6, J_{13} 2.5, J_{14} 0.6, J_{23} 7.5, J_{24} 2.4, J_{34} 8.5	64
10,10-dichloride	$CDCl_3$	H1 7.89, H3 7.38, H4 7.50	J_{12} 7.5, J_{13} 2.3, J_{14} 0.6, J_{23} 7.5 J_{24} 2.4, J_{34} 8.5	64
10,10-diiodide	$CDCl_3$	H1 7.75	-	64
	CCl_4	H3 7.14	-	111
3,5-dimethyl	CCl_4	H3 2.38, H2 6.25	-	111
3,5-di(tert-butyl)	CCl_4	H3 1.28, H2 6.76	-	111
	$CDCl_3$	6.1-5.5m (olefinic H), 4.0-3.6 (bridgehead H), 2.9-1.6(CH_2)	-	38

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*Aromatic proton region reproduced in the paper.

**i-Propyl protons are magnetically non-equivalent, no details given.

****The heteroatom-hydrogen coupling constant ranges are: J(TeH3) 9.5-15.2, J(TeH4) 13.0-1.67, J(TeH5) 91.7-97.6 Hz.

†Relative to benzene. ††L = $(C_4H_3)P$. †††s = singlet, d = doublet, m = multiplet

organic tellurium compounds have been determined. A detailed analysis of the nmr spectra of heterocyclic tellurium compounds has been undertaken to determine short and long range coupling constants. All these investigations are summarized in Table 10.

The investigation of the ^1H spectra of a number of substituted aryl tellurium trichlorides made possible the evaluation of the constant δ_m^H for the $TeCl_3$ group affecting the protons in meta-position to the tellurium atom. The low value of -1.0 ± 0.1 ppm indicates that the descreening effect of the $TeCl_3$ group is comparable to that of the nitro group[113].

^{13}C NMR Spectroscopy

The ^{13}C nmr spectra of tellurophene and its 2-hydroxymethyl, 2-formyl, 2-carboxy, 2-carbomethoxy, 2-acetyl and 2-methylthio derivatives were recorded in 20% solutions of acetone-d_6[60]. The shifts ranging from 124.9 to 155.3 ppm relative to TMS were determined from the hydrogen-decoupled spectra. The relative order of the carbon chemical shifts is opposite to those of the hydrogen atoms. The ^{13}C-H coupling constants are tabulated. Linear relationships between the electronegativity of the heteroatoms in the chalcogenophenes and several nmr parameters as well as between nmr parameters have been obtained.

The ^{13}C chemical shifts for 1-thia-4-tellura-2,5-cyclohexadiene were 106.9 (CS) and 127.2 ppm (CTe) with a value of 306.0 Hz for $^1J(CTe)$. The various ^{13}C-H coupling constants are tabulated[111].

^{19}F NMR Spectroscopy

The ^{19}F nmr spectrum of pentafluoroethyl tellurium trifluoride in toluene gave 105.87(CF_2), 77.86(CF_3) and 51.36(TeF_3) as chemical shifts in ppm relative to CCl_3F. For trans-$C_2F_5TeF_4Cl$ the shifts were 80.58(CF_3), 96.18(CF_2) and 11.86 ppm (TeF_4). The fluorine atoms in $(C_2F_5)_2TeF_4$ resonated at 80.38((CF_3), 96.69 (CF_2) and 67.2 ppm (TeF_4)[41].

The ^{19}F shifts in ppm upfield from CCl_3F for $H_3Si-Te-PF_2$ and $(F_2P)_2Te$ are +68.5 and +72.6 ppm, respectively. FF and FY coupling constants for $(F_2P)_2Te$ were not observed. A value of 3.0 Hz was reported for $^4J(FH)$ in $H_3SiTePF_2$[2].

^{31}P NMR Spectroscopy

Spin-spin coupling between ^{31}P and ^{125}Te nuclei was first observed in phospine tellurides, $R_2R'PTe$[94,118]. The ^{31}P chemical shifts and the $^{31}P-^{125}Te$ coupling constants were reported[118] (R, R', chem. shift ppm relative to 85% H_3PO_4, coupling constant Hz): C_4H_9, C_4H_9, -11, 1720; $(CH_3)_2N$, CH_3, -51.8, 1950; C_2H_5, C_2H_5O, -83, 1964; $(C_2H_5)_2N$, $(C_2H_5)_2N$, -48, 2037; $(C_2H_5)_2N$, C_2H_5O, -6.0, 2290.

For $H_3SiTePF_2$ a ^{31}P resonance was found at -297.0 ppm and a $^3J(PH)$ of 11.4 Hz. The ^{31}P chemical shift for $(F_2P)_2Te$ occurred at -295.8 ppm[2].

^{125}Te NMR Spectroscopy

Tellurium-125 chemical shifts relative to dimethyl telluride were determined by the heteronuclear double resonance technique and were found to parallel closely the ^{77}Se shifts in analogous compounds[106]. The following derivatives were investigated [^{125}Te shift ppm, $^2J(^{125}TeH)$ Hz, $^3J(^{125}TeH)$ Hz given]: $(CH_3)_2Te$ (0, 21.6, -); $(CH_3)_2TeCl_2$ (749, 25.7, -); $(CH_3)_2TeBr_2$ (669. 25.8, -); $(CH_3)_3TeI$ (443, 24.4, -); $C_2H_5(CH_3)_2TeBr$ (470, 24.0, -); $(CH_3)_2Te_2$ (63, 23.5, -); $(C_2H_5)_2Te$ (380, -, 22.7); $(C_2H_5)_2Te_2$ (188, -, 34.5); $(C_2H_5)_3TeBr$ (573, -, 32.7); $(C_2H_5)_2TeBr_2$ (879, -, 32.8); $(\underline{i}-C_3H_7)_2Te$ (707, -26.4); $(\underline{i}-C_3H_7)_2Te_2$ (303, -, 22.2); $(\underline{i}-C_3H_7)_2TeBr_2$ (1105, -, 32.8); $CH_3(\underline{i}-C_3H_7)_2TeI$ (630, -, -); $(C_6H_5)_2Te$ (688, -, -); $[(CH_3)_3Sn]_2Te$ (-124, -, 2.9); $CH_3SeTeCH_3$ (512, 23.9, 2.0); $CH_3SeTe-\underline{i}-C_3H_7$ (860, -, 1.7). The ^{125}Te chemical shifts are downfield from $(CH_3)_2Te$ with exception of bis(trimethylsilyl) telluride. The tellurium shielding decreases as the electronegativity of the substituents increases.

D. Nuclear Quadrupole and Nuclear Gamma Resonance Spectroscopy

The nuclear quadrupole and nuclear gamma resonance spectra of iodobenzoic acids and B-iodocarboranes labelled with ^{125}I were studied[15,83a]. The ^{125}I decay produced organic tellurium compounds, which are isoelectronic to the iodine derivatives. A considerable quadrupole splitting was observed in the nuclear gamma resonance spectra of the organic tellurium compounds[15].

E. Electron Spectroscopy

Electron spectroscopic measurements by X-ray excitation have been carried out on the chalcogeno cyanates, XCN^-. The N(1s), C(1s) and appropriate X binding energies in the series $(C_6H_5)_4As^+ XCN^-$ have been determined. The N(1s) energy of 396.8 eV in the tellurocyanate ion is almost equal to the values for the O,S and Se containing ion. The C(1s) in $TeCN^-$ was too weak to be measured. For the Te(3d 5/2) and (3d 3/2) levels binding energies of 573.3 eV and 583.6 eV were found, respectively[117].

Cradock[37] investigated the photoelectron spectra of dimethyl, disilyl and digermyl tellurides employing HeI excitation. The expected bands due to valence-shell molecular energy levels were found. The tellurium lone pair ionization potentials and the shapes of the corresponding bands are consistent with (p-d) π-bonding between silicon or germanium and tellurium.

It was shown by photoelectron spectroscopy, that the sequence of two highest occupied molecular orbitals in tellurophene is $\pi(2b_1) > \pi(1a_2)$[42,152]. In selenophene these levels are almost degenerate and in thiophene the sequence is reversed[152].

F. Mass Spectrometry

A few mass spectroscopic investigations of organic tellurium compounds have been carried out. Dimethyl telluride[1,53] gave major peaks corresponding to the molecular ion, to CH_3Te and Te fragment ions. The mass spectra of $(CH_3)_2TeI_2$ and $(CH_3)_2TeI_4$ contained the following fragment ions (formula, relative intensity for diiodide, relative intensity for tetraiodide)[159]: $(CH_3)_2TeI$, 81, 28; CH_3TeI, 43, 24; TeI, 28, 13; I_2, 100, 100; $(CH_3)_2Te$, 87, 70; CH_3Te, 85, 70; CH_3I, 87, 74; Te, 39, 20; I, 78, 66.

Calder[21] reported the mass spectra of phenoxtellurine (POT) and its 10,10-dibromide, POT•Br_2. Phenoxtellurine produces intense molecular ion peaks (m/e 298-288, 100%), which through loss of tellurium generate an ion at m/e 169 (80.6%) The spectrum contains in addition to a number of tellurium-free fragment ions the doubly (8.1%) and triply charged (0.03%) phenoxtellurine ions. The molecular ion in the spectrum of phenoxtellurine 10,10-dibromide is of low intensity (5.0%). The base peak in the spectrum is the phenoxtellurine ion (100%). Additional tellurium containing ions are $POT{\cdot}Br^+$ (11.2%) and $POT{\cdot}Br^{++}$ (0.8%). The ion formed through loss of $TeBr_2$ from POT•Br_2 is again very intense (86.6%).

Distefano[42] determined the ionization potentials of tellurophene and some of its 2-substituted derivatives by the electron impact technique. The following values were obtained (2-substituent, IP in eV): SCH_3, 8.15; CH_3, 8.25; H, 8.60; CO_2CH_3, 8.64; CO_2H, 8.80; CHO, 8.88; $COCH_3$, 8.60. The ionization potential of tellurophene is significantly lower than those of its congeners and its sensitivity to substituent effects is much smaller. The ionization of tellurophene must, therefore, occur from a different molecular orbital than that used in its congeners.

G. X-Ray Structure Analyses

Unit cell dimensions and symmetries have been reported for the following organic tellurium compounds: $C_6H_5TeCl{\cdot}$thiourea, $C_6H_5TeCl{\cdot}$(thiourea)$_2$, $C_6H_5TeCl{\cdot}$SeP(morpholyl)$_3$, $C_6H_5TeBr{\cdot}$thiourea, $C_6H_5TeBr{\cdot}$selenourea, $C_6H_5TeBr{\cdot}SeP(C_6H_5)_3$, $C_6H_5TeBr{\cdot}$SeP(morpholyl)$_3$, $[(CH_3)_4N]^+[C_6H_5Te(SCN)_2]^-$, $[(CH_3)_4N]^+ [C_6H_5TeBr_4]^-$ [73], $[(C_6H_5)_4As]^+[C_6H_5TeBr(CN)]^-$ [4], $[(CH_3)_4N]^+[C_6H_5TeBr_4]^-$ [73], and $(4\text{-}RC_6H_4)_2Te_2$ (R = H, 4-CH_3, 4-Cl, 4-Br)[93].

Single crystal X-ray structural analyses were carried out for 2-formylphenyl tellurium bromide[6], phenyl tellurium tris(diethyldithiocarbamate)[48,49], 1,2-bis(tribromotelluro)cyclohexane[74]; diphenyl ditelluride[91], dimethyl tellurium diiodide[23,24], bis(2-chloropropyl) tellurium dichloride[86], 2-carboxytellurophene[51] 1-oxa-4-telluracyclohexane 4,4-diiodide[78], 1-thia-4-telluracyclohexane 4,4-dibromide[85], phenoxtellurine (POT)[100,160], POT·I_2[105], POT·$(NO_3)_2$[102], $(POT)_2O(NO_3)_2$[103], POT$(CH_2COCH_3)(NO_3)$[161], and POT·$(O_2CCF_3)_2$[101]. A preliminary report concerning the structure of bis(triphenylphosphine) tellurium stated that the P-Te-P group is linear with Te-P bond lengths of 2.38 and 3.41 Å [3].

The 2-formylphenyl tellurium bromide, the tellurium atom has as its closest neighbors a carbon atom, a bromine atom and the oxygen atom of the formyl group. The coordination sphere of tellurium is completed by a bromine atom from another molecule at a distance of 3.92 Å from the tellurium atom[6].

The molecular shape of phenyl tellurium tris(diethyldithiocarbamate) is a pentagonal bipyramid with the phenyl group in one of the apical positions. All six sulfur atoms of the three dithiocarbamate groups are ligated to the tellurium atom. The five sulfur atoms occupying the equatorial positions form angles between 64 and 79° with one another. The apical tellurium-sulfur bond is approximately 0.5 Å longer than the value of 2.7 Å for the equatorial distances[48,49]

The two tribromotelluro groups in 1,2-bis(tribromotelluro)cyclohexane are bridged by two bromine atoms. The tellurium atoms can be considered to occupy the centers of the base of two square pyramids with bromine atoms in the equatorial planes and carbon atoms of the cyclohexane ring at the two apical positions. The bases share one side. The two basal planes form a dihedral angle of 132° creating a roof over the cyclohexane ring. The Br-Te-Br and the C-Te-Br bond angles are all close to 90°[74].

Diphenyl ditelluride assumes in the solid state a hydrogen peroxide-like conformation with a dihedral angle of 88.5°. The normals to the phenyl rings are parallel to the lone pair containing p-orbitals of the tellurium atom to which the phenyl group is bonded. The C-Te-Te bond angles are 97.4 and 100.3°[91].

The molecular structure of dimethyl tellurium diiodide can be described as a trigonal bipyramid with axial iodine atoms. The two methyl groups and the lone electron pair occupy the equatorial positions. In the solid, the tellurium atom is, however, in a distorted octahedral environment with two iodine atoms from two different molecules completing the coordination octahedron. The Te-I bond lengths for the equatorial iodine atoms are 3.66 and 4.03 Å, whereas the axial Te-I distance is 2.96 Å[24]. Bis(2-chloropropyl) tellurium trichloride assumes the shape of a trigonal bipyramid with the chlorine atom in the axial positions being bent towards the alkyl group[86].

Crystalline 2-carboxytellurophene consists of hydrogen bonded dimers, which are slightly twisted. The dihedral angle between the ring planes is 166°. The carbon-carbon bond opposite the tellurium atom in the probably planar ring measures 1.41 Å, whereas the other two carbon-carbon bond lengths are 1.36 and 1.38 Å. The ring angles are 111.7° at the carbon atoms in the 2- and 5-positions, 81.5° at the tellurium atom and 108.8° and 116.3° at the 4- and 3-carbon atom, respectively. The hydroxy group is on the same side as the tellurium atom[51].

The tellurium atom in 1-oxa-4-telluracyclohexane 10,10-diiodide is surrounded in the equatorial plane by two carbon atoms and two iodine atoms from two other molecules. The equatorial Te-I distances are 3.69 and 3.81 Å. The iodine atoms in the two apical positions are at a distance of 2.88 and 2.93 Å from the tellurium atom. The heterocyclic ring is in the chain conformation[78]. In 1-thia-4-telluracyclohexane 4,4-dibromide the tellurium is also in a distorted octahedral environment. In this case the octahedron is, however, completed by a bromine atom and a sulfur atom from two different molecules.

The interesting features in phenoxtellurine (POT) and its derivatives are the dihedral angle formed by the two phenyl groups and the angle of fold along the Te-O axis. An angle of fold of 135-145° was predicted by Wood[172] for POT. By X-ray crystallography[160] an angle of 138° was found. Al the other POT derivatives are also folded with the exception of POT dinitrate, which possesses a planar ring system. These angles of fold are listed in Table 11. It should be noted that the dihedral angles formed by the phenyl rings in POT and POT•$(OOCCF_3)_2$ are a few degrees larger than the angles of fold. All these POT derivatives with the exception of POT•I_2 provide for the tellurium atom a distorted trigonal bipyramidal environment. The tellurium atom in the diiodide derivative achieves an octahedral environment by coordinating to two additional iodine atoms from two different molecules[105]. In the $(POT)_2O(NO_3)_2$ molecule the two tellurium atoms are linked by an oxygen bridge. This bridging oxygen atom serves as the apical ligand in the two trigonal bipyramids, whose axes connecting the apical positions form an angle of 125°. The remaining two apical positions are occupied by a nitrate group each[103]. The planar or folded structures of these ring systems have been explained using MO arguments developed for the phenothiazine and acridine systems[102,160].

Bond lengths and bond angles involving the tellurium atom have been summarized in Table 11, where pertinent references can also be found.

H. Dipole Moment Measurements

Quite a large number of dipole moments of organic tellurium compounds have been determined. Table 12 summarizes the results. Minkin[113] compared the calculated dipole moments of organyl tellurium trichlorides with experimental values and concluded that the d-orbitals of tellurium are not conjugated with the aromatic π-system. Mesomeric and interaction moments are absent. The powerful electron donor effect shown by the $TeCl_3$ group is, therefore, of an inductive nature.

Mingaleva[112] found that the dipole moments of dimethyl and diethyl ditellurides calculated under the assumption of free rotation about the Te-Te bond are much smaller than the experimental values. This discrepancy was explained by invoking in addition to the Te-Te sigma bond an axially unsymmetric π-bond,

TABLE 11

BOND LENGTHS AND BOND ANGLES IN ORGANIC TELLURIUM COMPOUNDS

Compound	Te-C,Å	Te-X,Å	Te-O,Å	Te-Te,Å	dihedral angle	C-Te-C(or X) angles	X-Te-X angles	Ref.
2-H(O)CC_6H_4TeBr	2.081	2.618	2.31	-	-	94.2	-	6
$C_6H_5Te[S_2CN(C_2H_5)_2]_3$	2.124	2.606-2.816*	-	-	-	84-91	64-69	48,49
1,2-c-$C_6H_{10}(TeBr_3)_2$	2.19,2.25	2.54,2.88†	-	-	-	82-94	86-94	74
$(C_6H_5)_2Te_2$	2.08,2.15	-	-	2.712	88.5	97.4,100.3	-	91
$(CH_3)_2TeI_2$	2.10,2.16	2.91	-	-	-	95	177.3,92††	23,24
$(CH_3CHClCH_2)_2TeCl_2$	2.148	2.52,2.47	-	-	-	98.2	169.1	86
2-carboxytellurophene	2.06	-	-	-	-	81.5	-	51
	2.15,2.17	2.938,2.886	-	-	-	94.1	177,72††	78
	2.14,2.16	2.67	-	-	-	99.4	176.6,102.4††	85
phenoxtellurine (POT)	2.098	-	-	-	145,138***	93	-	160
POT·I_2	2.09,2.11	2.94	-	-	163.9	91.5	176.4,77.7††	105
POT 10,10-dinitrate	2.068	-	2.201	-	180	93	168	102
POT 10-acetonyl-10-nitrate	2.10,2.129**	-	2.775	-	135	88.9	167.4 (O-Te-CH_2)	161
$(POT)_2O(NO_3)_2$	2.09	1.96,2.00†††	2.485,2.392	-	147,163	90.2	168.6,171.8	103
$POT(OOCCF_3)_2$	2.06	-	2.16,2.20	-	156,152***	91.5	167.5	101

* Te-S bond lengths in the equatorial plane of the pentagonal bipyramid. The apical Te-S bond length is 3.228Å.

**Te-C(CH_2COCH_3) bond length.

***Angle of fold along Te-O

† Te-Br (bridging) bond length.

††† Te-O (bridging) bond lengths.

†† Equatorial X-Te-X.

TABLE 12
DIPOLE MOMENTS OF ORGANIC TELLURIUM

Compounds	μ, D	Ref.
$(CH_3)_2Te$	1.52	112
$(C_2H_5)_2Te_2$	1.54	112
$(C_6H_5)_2Te_2$	1.49-1.62*	80†
$(4\text{-}CH_3C_6H_4)_2Te_2$	1.98-2.09*	80
$(4\text{-}ClC_6H_4)_2Te_2$	1.14-1.32*	80
$(4\text{-}BrC_6H_4)_2Te_2$	1.00-1.21*	80
CH_3TeCl_3	3.79**	113
$C_6H_5TeCl_3$	3.66**	113
	2.90*	79
$4\text{-}CH_3C_6H_4TeCl_3$	3.94**	113
$3,4\text{-}(CH_3)_2C_6H_3TeCl_3$	4.01**	113
$3\text{-}FC_6H_4TeCl_3$	3.76**	113
$4\text{-}ClC_6H_4TeCl_3$	3.33**	113
$4\text{-}BrC_6H_4TeCl_3$	3.20**	113
$4\text{-}HOC_6H_4TeCl_3$	4.30**	113
$4\text{-}CH_3OC_6H_4TeCl_3$	4.61**	113
$3,4\text{-}(CH_3O)_2C_6H_3TeCl_3$	4.36**	113
$4\text{-}C_2H_5OC_6H_4TeCl_3$	4.60**	113
$4\text{-}C_3H_7OC_6H_4TeCl_3$	4.39**	113
$4\text{-}C_4H_9OC_6H_4TeCl_3$	4.18**	113
$4\text{-}C_6H_5OC_6H_4TeCl_3$	4.09**	113
$4\text{-}CH_3SC_6H_4TeCl_3$	4.23**	113
$4\text{-}CH_3COOC_6H_4TeCl_3$	4.81**	113
$4\text{-}C_2H_5COOC_6H_4TeCl_3$	5.16**	113
$3\text{-}NO_2C_6H_4TeCl_3$	5.16**	115
$4\text{-}NO_2C_6H_4TeCl_3$	4.13**	113
$(C_4H_9)_2Te$	1.31*	98
$C_6H_5TeCOC_6H_5$	1.03-1.84*	80
$C_6H_5TeCOC_6H_4\text{-}4\text{-}Cl$	1.62-1.74*	80
$(CH_3)_2TeI_2$	2.26	79
$(C_6H_5)_2TeF_2$	1.56*	138
$(C_6H_5)_2TeCl_2$	2.48*	79,138
$(C_6H_5)_2TeBr_2$	2.63*	79,138
$(C_6H_5)_2TeI_2$	3.84*	79,138
$(4\text{-}CH_3C_6H_4)_2TeCl_2$	2.98*	79
$(4\text{-}CH_3C_6H_4)_2TeBr_2$	3.21*	79
$(4\text{-}CH_3C_6H_4)_2TeO$	3.93**	79
$(C_6H_5)_3TeF$	8.77	79
$(C_6H_5)_3TeCl$	5.18	138
$(C_6H_5)_3TeI$	4.69	138
telluracyclohexane	1.63*	96
tellurophene (TP)	0.46*	95,96
	0.36††	95
$1\text{-}CH_3\text{-}TP$	0.64*	95,96
$1\text{-}HOCH_2\text{-}TP$	1.75*	95,96
1-H(O)C-TP	3.18*	95,96
$1\text{-}CH_3CO\text{-}TP$	2.97*	95,96
$1\text{-}CH_3OOC\text{-}TP$	1.95*	95,96
$2\text{-}CH_3CO\text{-}5\text{-}CH_3OOC\text{-}TP$	2.44*	95
$[(4\text{-}CH_3C_6H_4)_2TeCl]_2O$	6.1	79
$(C_8H_7)_3PTe$ (neat)	5.95	79

* in benzene solution

** in dioxane solution

† these values depend on the correction used for the atomic polarization.

†† in CCl_4 solution

which holds the molecule in a conformation close to the cis-arrangements of the alkyl groups.

The bond moment of the carbon-tellurium bond in diphenyl tellurium dihalides was calculated by the method of localized molecular orbitals to be 0.56 D[139,140]. A value of 0.7 D was suggested earlier for this moment[79]. The moment is directed from the tellurium to the carbon atom. Using this value and the experimental moments of the dihalides the moment arising from the tellurium lone electron pair was estimated to be 1.73, 2.39, 2.54 and 3.74 D for F, Cl, Br and I, respectively[140]. A value of 4.5 D has been suggested for the P-Te moment in triorganylphosphine tellurides[79]. Okhubo[120] obtained a value of 12.41 D for the dipole moment of trimethyl telluronium chloride through ASMO-SCFMO and EHMO calculations.

Dipole moment analysis of tellurophene derivatives showed that the dipole moment of the parent heterocyclic is directed from the ring toward the tellurium atom. The mesomeric moment for tellurophene was calculated to be 1.17 D using telluracyclohexane as a comparison compound[96]. The dipole moments of 2-RCO-tellurophene (R = H, CH_3, CH_3O) indicated that these compounds exist in solution as a mixture of conformers with the carbonyl group close to or pointing away from the tellurium atom[95].

The dipole moments of diaryl ditellurides (Table 12) are consistent with their non-planar conformations. A conformation with the phenyl groups in trans-position to each other has been suggested on the basis of the results of dipole moment measurements for benzoyl phenyl tellurides[80].

XI. Analytical Techniques

Thavornyutikarn described a method for the quantitative determination of tellurium in its organic compounds. After the organic compound had been mineralized by heating with a mixture of concentrated nitric and perchloric acid for two hours, the residue obtained by evaporation of the acid mixture was dissolved in water acidified with hydrochloric acid. Tellurium was determined in these aqueous solutions of telluric acid by atomic absorption techniques. The amount of sample required for such a determination is 25-50 mg[165].

XII. Biology of Organic Tellurium Compounds

A strain of Penicillium isolated from raw sewage produced dimethyl telluride from tellurium tetrachloride, H_2TeO_3 or H_6TeO_6. The telluride was formed only in media which also contained a selenium compound[1,53].

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