TELLURIUM
LITERATURE SURVEY COVERING THE YEAR 1975

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Table of Contents

Tellurium, Literature Survey covering the years 1972-1974 see J. Organometal. Chem., 103 (1975) 91-196.

I. Introduction

This annual survey of the organic chemistry of tellurium, a sequel to the tellurium review which last year has appeared for the first time in this journal,[1] covers the literature abstracted in Chemical Abstract Volume 82, No. 1 through Volume 84, No. 9. A few older publications, which have not been covered earlier, are also discussed. Generally, only those compounds have been included which contain at least one tellurium-carbon bond. However, this selection criterium has not been strictly applied. Thus, triorganylphosphine tellurides and similar tellurium compounds are described in these surveys. 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 reference is made to older results, the original paper is generally not cited; instead the reader is referred to ref. 1 or 2, which will provide excess to the appropriate literature.

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

II. Reviews

The following reviews were published during the survey period.

Tellurium (K. J. Irgolic, 1975)[1]: A literature survey of organic tellurium chemistry covering the years 1972-1974.

X-Ray Diffraction of Oxygen, Sulfur, Selenium and Tellurium Compounds (M. B. Hursthouse, 1974)[3]: A review of the molecular structures of inorganic and organic compounds of group VI elements published during the period 1972-1973.

Reactions of Atoms in Ground and Electronically Excited States (R. J. Donovan and H. M. Gillespie, 1975)[4]: A review of reactions of atoms in the ground and electronically excited states. Included are reactions of tellurium atoms with olefins.

Formation of Organometallic Compounds in Organisms (N. Imura, 1975)[5]: Review of the reactions which occur in living organisms and lead to the formation of carbon-arsenic, carbon-selenium, carbon-tellurium or carbon-mercury bonds.

Organic Compounds of Sulphur, Selenium, and Tellurium, Volume 3 (The Chemical Society, Specialist Periodical Reports, 1975)[6]: Review of the organic chalcogen chemistry covering the period April 1972 to March 1974. The following tellurium compounds are discussed: Tellurium Ylides (A. W. Johnson); Tellurophens (S. Gronowitz); Aliphatic Tellurium Compounds (G. C. Barrett).

Organophosphorus Tellurium Compounds (I. A. Nuretdinov, et al. 1972)[7]: A lecture presented in 1972 reviewing organophosphorus tellurium compounds (14 references).

Role of Partially Occupied d-Orbitals of Onium-Type Compounds in the Catalytic Activation of Molecular Oxygen (K. Ohkubo, 1974)[8]: A review relating the catalytic influence of onium compounds, among them $(CH_3)_3Te^+$, on the autoxidation of cumene to the d-orbital participation in the formation of O_2-onium complexes.

The following reviews are not devoted to organic compounds of tellurium.

They might, however, be of interest to organometallic tellurium chemists.

Inorganic Chemistry of Tellurium (A. Engelbrecht and F. Seadky, 1975)[9].

Chemistry and Technology of Selenium and Tellurium (A. A. Kudryavtsev, 1974)[10].

Analytical Chemistry of Selenium and Tellurium (I. I. Nazarenko and A. N. Ermakov, 1973)[11].

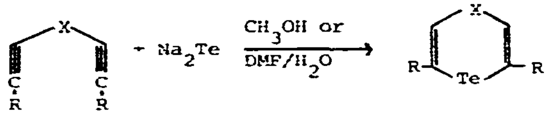
The Chemistry of Sulfur, Selenium, Tellurium and Polonium (M. Schmidt, W. Siebert and K. W. Bagnall, 1975)[12].

III. Methods for the Introduction of Tellurium into Organic Molecules

During the time covered by this survey hydrogen telluride, sodium telluride, tellurium tetrachloride, tellurium tetrabromide, $Te_4(AsF_6)_2$, $Te_6(AsF_6)_2$, $[(C_6H_5)_4As]_2TeS_4O_6$ and elemental tellurium were employed as reagents to introduce tellurium into organic molecules. Most of these reactions are extensions or modifications of previously reported preparative methods.

Hydrogen telluride passed into vinyl cyanide containing sodium methoxide produced bis(2-cyanoethyl) telluride[13], a compound first prepared by Kaabak[2] in 1964. Sodium telluride in methanolic[14,15] or aqueous dimethylformamide medium[15] interacted with the acetylenes 1 to form the heterocyclic tellurium derivatives 2 (eqn. 1).

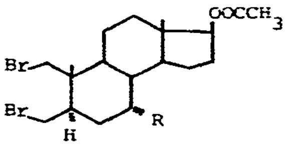
(1)



1 2

X = S[14]; X = R'P(O)[13]; R,R' = H, organic group

Zanati[16] converted the dibromide 3 by means of sodium telluride to the tetrahydrotellurophene derivative 4.



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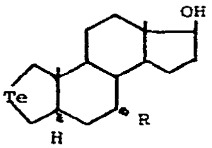


4

R = H, CH_3

Sodium telluride treated with β-chlorovinylaldehydes followed by ethyl chloroacetate, chloroacetaldehyde, chloroacetone or chloronitromethane yielded tellurophenes with the substituent $-COOC_2H_5$, $-CHO$, $-COCH_3$ or NO_2 in the 2-position[17].

Tellurium tetrachloride and tetrabromide combined with trifluoromethyl radicals generated from hexafluoroethane in a glow discharge to give bis(trifluoromethyl) telluride and bis(trifluoromethyl) ditelluride in low yields[18]. Condensation reactions between tellurium tetrachloride and acetic anhydride[13] yielded bis(carboxymethyl) tellurium dichloride. 2-Biphenylyl mercuric chloride or 2-lithiobiphenyl and tellurium tetrachloride gave 2-biphenylyl tellurium trichloride[18]. Attempts to prepare organic tellurium compounds on a milligram scale employing phenyl magnesium bromide and ^{126}Te- or ^{130}Te-$TeCl_4$ failed in the hydrolysis step when too much elemental tellurium precipitated[20]. The desired diaryl tellurium dihalides were obtained when tellurium tetrachloride or tetrabromide were treated with tetraaryl lead compounds[20]. Tellurium tetrachloride accepted one phenyl group from tetraphenyl tin or triphenyl tin chloride in toluene at room temperature to form phenyl tellurium trichloride. In refluxing toluene diphenyl tellurium dichloride was obtained[21].

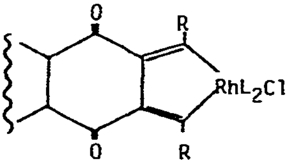
Albeck[22], investigated the reaction of tellurium tetrahalides with anthracene and its 9- and 9,10-chloro or bromo derivatives. Only 9- or 9,10-halogenated anthracenes or products of halogen exchange reactions between tellurium tetrachloride or tetrabromide and haloanthracenes were isolated. The product distribution was found to be solvent and temperature dependent. The halogenation reactions were accelerated by aluminum trichloride. Tellurium tetraiodide did not react with anthracene. Sadekov[23], however, had reported the preparation of bis(5-anthryl) tellurium dichloride from anthracene and tellurium tetrachloride in refluxing toluene under the same conditions, which had been employed by Albeck. Benzene, tellurium tetrachloride and aluminum chloride produced diphenyl tellurium dichloride[22] as reported earlier[1].

Tellurium tetrachloride yielded transient, colored complexes with anthracene, triphenyl phosphine, 1,1-diphenylethylene and many other olefins in toluene, p-xylene, CH_2Cl_2, $CHCl_3$ or CCl_4 but not in dioxane or diethyl ether solution[22]. 1,1-Diphenylethylene in diethyl ether yielded bis(1,1-diphenylethenyl) tellurium dichloride[22]. A U.S.S.R. patent[P-1] claims the preparation of dihalides of the heterocyclic tellurium compounds **2** (X = O, NH, C_6H_5N) from diolefins and tellurium tetrachloride or bromide.

Elemental tellurium did not react with tetraphenyl tellurium[20]. Milligram-scale reactions of tellurium with phenyl lithium or diphenyl iodonium iodide produced too much diphenyl to be of much utility[20].

The well known insertion of tellurium into carbon-lithium, carbon-sodium or carbon-magnesium bonds was used to prepare phenyl lithium telluride[24,25], ethyldiacetylenyl sodium telluride[26], 4-methylphenyl bromomagnesium telluride[24] and 2-biphenylyl iodomagnesium telluride[27]. These moisture and air sensitive compounds were not isolated but used in-situ.

Freshly precipitated tellurium replaced the $Rh[(C_6H_5)_3P]_2Cl$-group in the heterocyclic compounds **5** upon heating in absolute xylene yielding tellurophene derivatives[28,29].



$L = (C_6H_5)_3P$

5

In continuation of an earlier investigation[1], $Te_4(AsF_6)_2$ and $Te_6(AsF_6)_2$ and tetrafluoroethylene were kept under 15 atm. pressure at 100° for approximately ten days. The tellurium containing products $(C_2F_5)_2Te_n$, $C_4F_9Te_nC_2F_5$ $(n = 1, 2)$ and $(C_4F_9)_2Te$ were obtained. When sulfur dioxide was present in the mixture C_2F_5-Te-C_3F_6COF was also observed[30].

The reactions of organic tellurium compounds which have been used to produce new organic tellurium derivatives are summarized in Fig. 1. All these reactions are discussed in the sections devoted to the appropriate tellurium compounds.

IV. Tellurocyanates and Tellurium Derivatives X=C=Te

Austad[31] investigated the kinetics of the reaction between telluropenta-

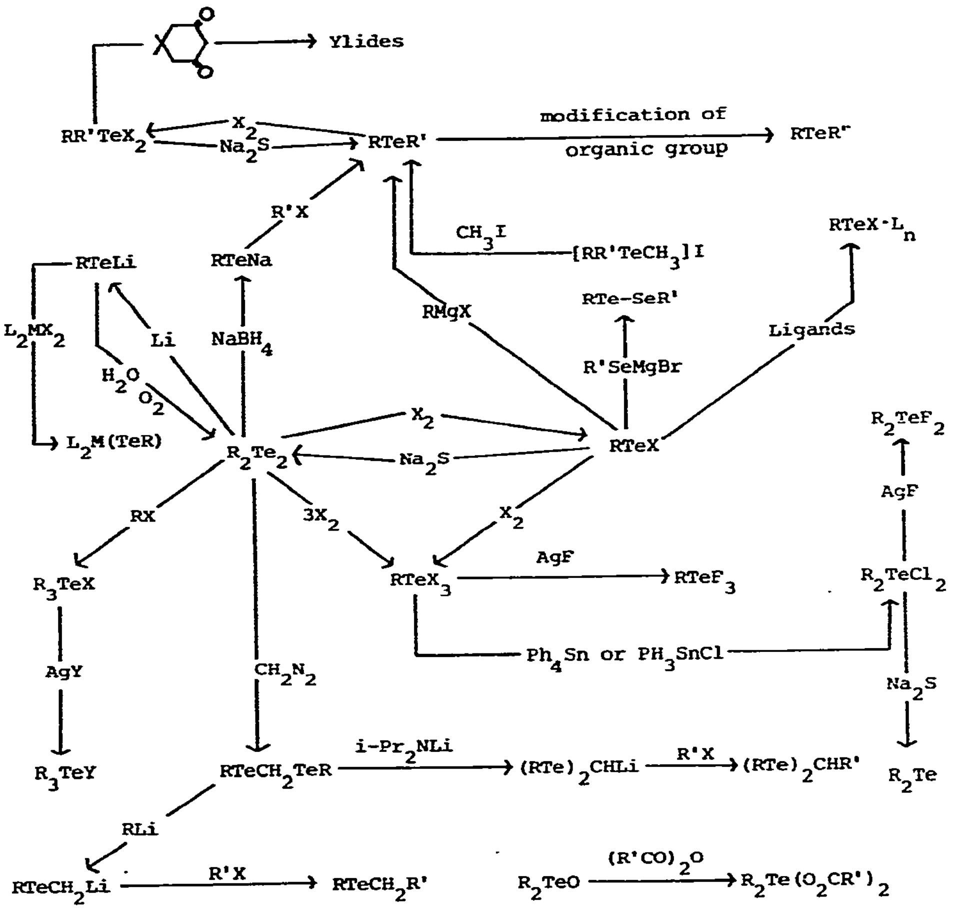


Fig. 1: Transformations of Organic Tellurium Compounds

thionate, $TeS_4O_6^{--}$, and tetraphenyl phosphonium cyanide in acetonitrile medium. The reaction was found to be second order and generated tellurocyanate ion but not elemental tellurium (eqn. 2). Thermodynamic data for this reaction

$$(2) \qquad TeS_4O_6^{--} + 6CN^- \longrightarrow TeCN^- + SCN^- + S_2O_3^{--} + (CN)_4^{--}$$

are reported[31].

Tellurium dicyanide was converted to tellurocyanate by cyanide ion in acetonitrile medium. The CN group in $TeCN^-$ exchanged rapidly with ionic cyanide[32].

V. Compounds Containing a Single Carbon-Tellurium Bond

The compounds treated in this section contain only one carbon-tellurium bond. During the survey period organyl tellurium halides and pseudohalides, RTeX, organyl tellurium trihalides, $RTeX_3$, methyl tellurium pentafluoride, 2-biphenyltellurinic acid and diorganyl ditellurides received attention. No new results were reported for tellurols, RTeH, organyldihalotellurium compounds, $[RTeX_2]^-$ or $[RTeX_2]^+$, and organyltetrahalotellurates(IV), $[RTeX_4]^-$.

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. Tellurenyl Compounds

Aryl tellurium halides[1] with a stabilizing carbonyl group in *ortho*-position to the tellurium atom, and 2-naphthyl tellurium iodide[2] are the only tellurenyl derivatives, which have been isolated without a ligand in the molecule. Not ligated organyl tellurium halides were generated from ditellurides and halogens and used *in-situ*[1]. Schulz and Klar[27,33] have now shown that aryl tellurium bromides and iodides can be isolated when equimolar amounts of halogen and ditelluride are combined in a solvent in which the starting materials are soluble and the tellurenyl compound is insoluble (eqn. 3). Such solvents are

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

benzene, toluene, hexane, petroleum ether, carbon tetrachloride or glacial acetic acid depending on the nature of the compound. The compounds prepared in this manner are listed in Table 1. The aryl tellurium iodides are blue-violet to black, probably polymeric materials, which are rather insoluble in common organic solvent. The solid iodides are stable for weeks in dry air. The red-brown to black bromide derivatives are not very stable even in the solid state and become discolored after one day. Sodium sulfide reduces these halides to the ditellurides, element halogen converts them to aryl tellurium trihalides and base hydrolysis produces a mixture of ditellurides and tellurinic acid derivatives[33].

TABLE 1
ORGANYL TELLURIUM HALIDES, RTeX

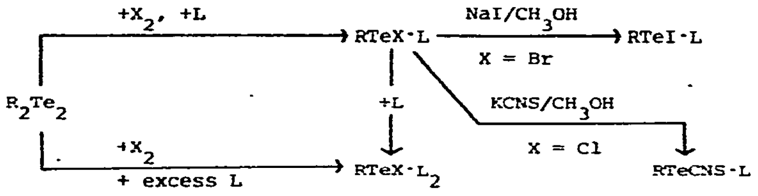
R	X	% yield	dec., °C	Ref.
C_6H_5	Br	45	70-75	33
	I	70-80	120-5	33
$4\text{-}CH_3OC_6H_4$	Br	90	~70	33
	I	70-80	145-150	33
$3,4\text{-}(CH_3O)_2C_6H_3$	I	50	~95	33
$4\text{-}C_6H_5C_6H_4$	Br	55	~250	33
	I	75	~180	33
$2\text{-}C_6H_5C_6H_4$	Br	44	110-5	27
	I	6	115-6	27

A number of phenyl tellurium halide compounds, RTeX·L, stabilized by thiourea and selenourea ligands were prepared by the previously developed method[1,2] of halogenolysis of ditellurides in the presence of the appropriate ligand. Variation of the stoichiometry produced in a few cases adducts of the type $RTeX\cdot L_2$. Several complexes were obtained through halogen exchange. These reactions are summarized in eqn. 4.

The compounds prepared according to eqn. 4 are listed in Table 2.

Petragnani[37] reacted tetrahydrofuran solutions of aryl tellurium bromides with organyl magnesium halides and obtained unsymmetric diorganyl tellurides,

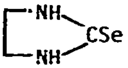
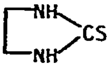
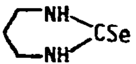
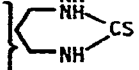
(4)



R = C_6H_5

TABLE 2

PHENYL TELLURIUM HALIDE ADDUCTS, $C_6H_5TeX·L_n$

X	L	n	yield %	mp. °C	Ref.
Cl	$[(CH_3)_2N]_2CSe$	1	73	151-2	34
Br		1	80	162-3	34
Cl	$[(CH_3)_2N]_2CS$	1	63	111-3	35
Br		1	82	115-6	35
Cl		2	68	190-1*	34
Br		1	80	163-4	34
I		1	95	137-9*	36
Cl		1	79	133-6	35
		2	80	166-7	35
Br†		1	83	142-3	35
I		1	94	116-8*	36
SCN		1	70	111-3	35
Br		1	74	152-3	34
Cl		1	71	165-6	35
Br		1	86	159-60	35

*dec.

†This compound exists in two crystalline modifications.

R-Te-R'. Phenyl bromomagnesium selenide and the tellurenyl compounds yielded diorganyl selenide tellurides, RTe-SeR.

B. Organyl Tellurium Compounds, $RTeX_3$

Several new aryl tellurium trihalides were synthesized. Treatment of the appropriate aryl tellurium trichloride in refluxing toluene with silver fluoride produced 4-methoxyphenyl tellurium trifluoride (mp. 176-8°) and 4-ethoxyphenyl tellurium trifluoride (mp. 204°). Yields were not reported[38].

2-Biphenylyl tellurium triodide (dec. 164-5°) was obtained from the ditelluride and iodine in boiling chloroform[27]. The corresponding trichloride (dec. 157°) was formed in 16% yield from tellurium tetrachloride and 2-lithiobiphenyl, and in 76% yield when 2-biphenylyl mercury chloride was employed[19].

The known compound phenyl tellurium trichloride was prepared in 95% yield from triphenyl tin chloride and tellurium tetrachloride at room temperature in toluene medium[21]. Phenyl tellurium tribromide was formed in almost quantitative yield when diphenyl selenide telluride[37] was treated with 2 moles bromine in carbon tetrachloride at 0°.

Aryl tellurium trichlorides behave as Lewis bases in the presence of $AlCl_3$, AsF_5 or $SbCl_5$, but as Lewis acids in the presence of pyridine, ethylenediamine, thiourea or halide ions[22].

The reaction of 4-methoxyphenyl tellurium trichloride with anthracene yielded 9-chloro- and 9,10-dichloroanthracenes, elemental tellurium and bis(4-methoxyphenyl) tellurium dichloride. It was suggested that the tellurium dichloride was formed by disproportionation of the trihalide, $RTeCl_3$, to R_2TeCl_2 and $TeCl_4$[22]. Such a disproportionation reaction was first reported in 1972 by Sadekov[1].

The aryl tellurium trichlorides, $4\text{-}RC_6H_4TeCl_3$ (R = H, CH_3O) produced upon refluxing with triphenyl tin chloride or tetraphenyl tin in toluene the diaryl tellurium dichlorides[21]. When 2-biphenylyl tellurium trichloride was heated in refluxing nitrobenzene dibenzotellurophene dichloride was formed[19].

C. Organyl Tellurium Pentahalides

A study of the cis-influence in tellurium compounds $XTeF_5$ by molecular orbital calculations confirmed the experimental observations that the fluorine atoms in cis-position to the ligand are more labile. Methyl tellurium pentafluoride was included in this investigation. The following order of increasing cis-influence was found[39]: $H < OH < NH_2 < Cl < CH_3 < Br < SH \sim PH_2 < SiH_3$.

D. Tellurinic Acids and Their Derivatives

When the compound $R_2Te_2 \cdot I_4$ (R = 2-biphenylyl) was treated with an aqueous sodium acetate solution at 90° for 9 hrs., kept for an additional 12 hrs. at room temperature and then acidified, 2-biphenyltellurinic acid was isolated in 77% yield[27].

E. Diorganyl Ditellurides

The first unsymmetric diorganyl ditelluride and several hitherto unknown diaryl ditellurides were reported during this survey period.

Perfluorobutyl pentafluoroethyl ditelluride was formed in trace amounts in reactions between tetrafluoroethylene and $Te_4(AsF_6)_2$ or $Te_6(AsF_6)_2$. The compound was identified by mass spectroscopy[30]. A major product of this reaction was the previously reported bis(pentafluoroethyl) ditelluride[30]. The reaction of tellurium tetrachloride or bromide with trifluoromethyl radicals generated from C_2F_6 in a glow discharge gave the known bis(trifluoromethyl) ditelluride in 33% yield[18].

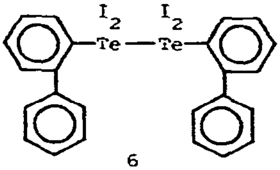
The reaction of 2-biphenylyl magnesium iodide with tellurium in tetrahydrofuran, followed by oxidation of the reaction mixture with air produced the new compound bis(2-biphenylyl) ditelluride (mp. 112-3°) in 28% yield[27]. The 4-biphenylyl derivative was similarly synthesized and obtained for the first time in a pure state by extracting the crude product in a Soxhlet under a nitrogen atmosphere, and re-extracting the collected crystals with absolute acetone[33]. An impure product had been synthesized earlier by Haller[1].

Seebach[25] developed the reaction of phenyl lithium with tellurium in tetrahydrofuran and the subsequent hydrolysis and oxidation of the reaction mixture into a useful method for the preparation of ditellurides. Diphenyl ditelluride was obtained in quantitative yield. Dereu[40] using the procedure of Piette[41], which consists of treating the aryl lithium compound in diethyl ether with tellurium, hydrolyzing the reaction mixture with 6N HCl and oxidizing it with air, prepared the following diaryl ditellurides, R_2Te_2, in moderate yields (R, % yield): C_6H_5, 43%; $2\text{-}CH_3C_6H_4$, 50%; $3\text{-}CH_3C_6H_4^*$, 62% (mp. 32°); $4\text{-}CH_3C_6H_4$, 58%; $2,5\text{-}(CH_3)_2C_6H_3^*$,-; $3,4\text{-}(CH_3)_2C_6H_3^*$,-; $2\text{-}CH_3OC_6H_4^*$, 45% (mp. 82-3°); $1\text{-}C_{10}H_7$, 66% and $2\text{-}C_{10}H_7$, 25%. The compounds marked by an asterisk are new derivatives.

The formation of the known bis(2-carboxyphenyl) ditelluride was observed when 2-carboxyphenyl 2-carboxyethyl telluride was heated[40].

Ditellurides are cleaved by lithium in tetrahydrofuran forming phenyl lithium telluride, which was reacted in-situ with alkyl halides to produce phenyl alkyl tellurides[42]. The reduction of diaryl ditellurides with sodium borohydride in ethanol/benzene medium and the subsequent reaction of the intermediate aryl sodium tellurides with 3-chloropropionic acids yielded aryl 2-carboxyethyl tellurides[40]. Reactions of diaryl ditellurides with elemental halogens generated aryl tellurium monohalides[27,33,34,35,37] and aryl tellurium trihalides[27].

Schulz and Klar[27] isolated a compound of the formula $R_2Te_2I_4$ (R = 2-biphenylyl) as a lilac-brown diamagnetic powder which decomposed at 145-150°. Its molecular mass determined in benzene solution is in agreement with the proposed formula 6.



6

This substance was obtained in 30% yield as the precipitate when the concentrated reaction mixture with benzene, toluene or CCl_4 as solvent containing equimolar amounts of the ditelluride and iodine was diluted with petroleum ether and cooled. From the reaction between 2 moles of iodine and 1 mole of ditelluride in CCl_4, R_2TeI_4 was isolated from the mother liquor after the insoluble aryl tellurium triodide was removed by filtration. Reduction of $R_2Te_2I_4$ with sodium sulfide yielded the ditelluride. Hydrolysis lead to a mixture of ditelluride and tellurinic acid[27].

Diphenyl ditelluride and diazomethane formed in quantitative yield methylene bis(phenyl telluride)[25]. Excess methyl iodide converted the ditellurides $(4\text{-}RC_6H_4)_2Te_2$ (R = H, CH_3, C_2H_5O) into dimethyl aryl telluronium iodides and aryl methyl tellurium diiodides[38]. Morgan[2] had claimed in 1925, that methyl iodide decomposed the bis(4-ethoxyphenyl) ditelluride.

VI. Compounds Containing a Carbon-Tellurium-Carbon Moiety

In this section diorganyl tellurides, diorganyl tellurium dihalides and dicarboxylates and diorganyl telluroxides are discussed. Several new methods for the preparation of some of these compounds were reported and a number of new derivatives were synthesized using procedures developed earlier[1,2]. No work was done during this survey period with diorganyl tellurones, R_2TeO_2, and derivatives of the type $[R_2TeX]^+$, $[R_2TeX_3]^-$, R_2TeX_4 and $R_2TeX_2Y_2$ (X,Y = halogen)

A. Diorganyl Tellurides

The discussion of diorganyl tellurides is divided into three parts: symmetric diorganyl tellurides, R_2Te, unsymmetric diorganyl tellurides, R-Te-R', and tellurides with two tellurium atoms in the molecule.

1. Symmetric diorganyl tellurides

Bis(trifluoromethyl) telluride, a yellow-green liquid with a boiling point of -98° and a melting point below -160°, was obtained in 20% yield from tellurium tetrabromide and CF_3 radicals generated from C_2F_6 in a glow discharge[18]. This telluride contaminated with CF_3-Te-CH_3 was also isolated when dimethyl telluride and trifluoromethyl iodide were irradiated with 3100 Å light quanta for 20 hours. Similarly, bis(pentafluoroethyl) telluride was prepared using pentafluoroethyl iodide[43]. There is considerable disagreement about the properties of these fluorinated tellurides. Lagow[18] reported the trifluoromethyl derivative to be extremely air sensitive, whereas Denniston[43] claimed it to be odorless and stable in air.

A more detailed investigation of the reaction between $Te_4(AsF_6)_2$ or $Te_6(AsF_6)_2$ and tetrafluoroethylene[30] at 100° and 15 atm. pressure showed that bis(pentafluoroethyl) telluride was formed in approximately 15% yield in addition to several unsymmetric tellurides. Traces of bis(perfluorobutyl) telluride were also detected. The pentafluoroethyl compound has an extrapolated boiling point of 64°.

Anthracene dehalogenated the diaryl tellurium dichlorides, $(4\text{-}RC_6H_4)_2TeCl_2$. (R = H, CH_3O), to the diaryl tellurides in refluxing ethyl methyl ketone in the presence of silver nitrate. 9,10-Chloroanthracenes were formed. The chlorinating action of the tellurium dihalides has been attributed to the formation of the $[R_2TeCl]^+$ ions[22].

Attempts to repeat the preparation of $Te(CH_2COOH)_2$ according to Morgan and Drew [J. Chem. Soc., (1925) 531] failed. The reduction of $(HOOCCH_2)_2TeCl_2$

always produced an impure product and caused the precipitation of tellurium[13].

Bis(2-cyanoethyl) telluride (mp. 60°) was synthesized in 22% yield by passing hydrogen telluride into vinyl cyanide containing some sodium methoxide Kaabak's[2] synthesis of this telluride, which employed electrolysis of telluriu in vinyl cyanide, could not be reproduced[13]. Bis(2-cyanoethyl) telluride was hydrolyzed by refluxing 6M HCl. Bis(2-carboxyethyl) telluride (mp. 160°) was isolated in 87% yield. Alkaline hydrolysis gave polytellurides[13].

The vapor pressure of dimethyl telluride is expressed by the equation $\log p_{torr} = (7.98 \pm 0.26) - (1865 \pm 86)/T$ (°K) in the temperature range 25 to 92°C. The Trouton constant, and the enthalpy and entropy of evaporation have values of 23.2, 8.54 ± 0.04 kcal mol^{-1} and 36 ± 1 cal mol^{-1} deg^{-1}, respectively[44]. The thermodynamic functions of dimethyl telluride were calculated using the rigid rotor-harmonic oscillator approximation in the range 273.15 to 1500°K[45]. The orthobaric density and viscosity of dimethyl telluride were determined as a function of temperature[46]. The enthalpy and entropy of hydrogen bonding of dibutyl telluride with benzenethiol and 2,6-di(*tert*-butyl)phenol were determined by nmr techniques[48].

The consecutive ionization constants of bis(carboxyalkyl) tellurides were determined[13]: $Te(CH_2COOH)_2$, $pK_1^{25°} = 3.26$, $pK_2^{25°} = 4.77$; $Te(CH_2CH_2COOH)_2$, $pK_1^{25°} = 3.924(2)$, $pK_2^{25°} = 4.767(2)$.

The following reactions of diorganyl tellurides were reported: alkaline (5M KOH) hydrolysis[43] of pentafluoroethyl and trifluoromethyl tellurides to $C_nF_{2n+1}H$; reaction of bis(trifluoromethyl) telluride with benzyl chloride[43] at 215° for 44 hrs. to produce a small amount of $C_6H_5CH_2CF_3$; the photolytic reaction of dimethyl telluride with CF_3I and C_2F_5I resulting in replacement of methyl by perfluoroalkyl groups[43]; the gas phase bromination of $(CF_3)_2Te$ to $(CF_3)_2TeBr_2$[18]; the formation of the complex $AuBr(CH_3)_2Te$[47] and of silver complexes with $Te(CH_2CH_2COOH)$[13].

2. Unsymmetric diorganyl tellurides

A large number of hitherto unknown unsymmetric diorganyl tellurides were prepared. Petragnani[37] reacted aryl tellurium bromides-generated in tetrahydrofuran solution from ditellurides and bromine-with Grignard reagents (eqn. 5). The unsymmetric tellurides listed in Table 3

$$(5) \quad \mathrm{RTeBr} \xrightarrow{\mathrm{R'MgX}} \mathrm{R{-}Te{-}R'}$$

were obtained in yields higher than 90%. Phenyl lithium telluride, prepared either from diphenyl ditelluride and lithium[42] or from phenyl lithium and tellurium[25], was found to be a convenient staring material for the preparation of phenyl alkyl tellurides. The products of these reactions (eqn. 6) are

TABLE 3

DIORGANYL TELLURIDES*, R-Te-R', FROM TELLURENYL COMPOUNDS AND GRIGNARD REAGENTS, R'MgBr[37]

R	R'	bp. °C/torr, mp. °C
C_6H_5	C_4H_9	71-2°/0.01
	$\underline{c}$-C_6H_{11}	93-4°/0.01
	$C_6H_5C{\equiv}C$	115-6°/0.005
4-$CH_3C_6H_4$	C_4H_9	75-6°/0.1
	$\underline{c}$-C_6H_{11}	100-1°/0.005
	$C_6H_5C{\equiv}C$	74-6°
	C_6H_5	88-90°/0.1
4-$CH_3OC_6H_4$	C_6H_5	60-1°
4-$C_2H_5OC_6H_4$	C_4H_9	90-2°/0.01
	$\underline{c}$-C_6H_{11}	110-1°/0.01
	$C_6H_5C{\equiv}C$	67-8°
	C_6H_5	113-5°/ 0.1

*The yields were reported to be higher than 90%.

TABLE 4

UNSYMMETRIC DIORGANYL TELLURIDES, R-Te-R', FROM ORGANYL ALKALI METAL TELLURIDES, R-Te-M, and ALKYL HALIDES, R'X.

R	M	R'X	R-Te-R'		Ref.
			yield %	bp. °C/torr; mp. °C	
$C_2H_5C{\equiv}C\text{-}C{\equiv}C$	Na	CH_3I	54	101-2°/3	26
C_6H_5	Li	CH_3I	62	64°/ 1.1	42
		CH_3I	43	57-8°/0.7	25
		C_2H_5Br	67	94°/4	42
		C_3H_7Br	81	88°/1.5	42
		$i\text{-}C_3H_7Br$	71	78°/1.3	42
		$CH_2{=}CHCH_2Br$	45	62-3°/0.3	25
	Na	$HOOCCH_2CH_2Cl$	80	65-7°	40
	Li	C_4H_9Br	79	108°/2	42
	Na	$HOOCCH_2CH(CH_3)Cl$	75	liquid	40
		$HOOCCH(CH_3)CH_2Cl$	94	liquid	40
	Li	$C_{10}H_{21}Br$	29	oil*	25
		$C_{14}H_{29}Br$	-	oil†	42
$2\text{-}CH_3C_6H_4$	Na	$HOOCCH_2CH_2Cl$	76	77-8°	40
$3\text{-}CH_3C_6H_4$	Na	$HOOCCH_2CH_2Cl$	56	31°	40
$4\text{-}CH_3C_6H_4$	Na	$HOOCCH_2CH_2Cl$	76	66-8°	40
$3,4\text{-}(CH_3)_2C_6H_3$	Na	$HOOCCH_2CH_2Cl$	78	88-90°	40
$2,4\text{-}(CH_3)_2C_6H_3$	Na	$HOOCCH_2CH_2Cl$	35	85-7°	40
$2,5\text{-}(CH_3)_2C_6H_3$	Na	$HOOCCH_2CH_2Cl$	40	78-80°	40
$2\text{-}CH_3OC_6H_4$	Na	$HOOCCH_2CH_2Cl$	85	104-5°	40
$2\text{-}HOOCC_6H_4$	Na	$HOOCCH_2CH_2Cl$	-	178-82°(dec)	40
$1\text{-}C_{10}H_7$	Na	$HOOCCH_2CH_2Cl$	20	107-8°	40
$2\text{-}C_{10}H_7$	Na	$HOOCCH_2CH_2Cl$	67	109-13°	40

*Purified by chromatography on silicagel with cyclohexane as eluent.

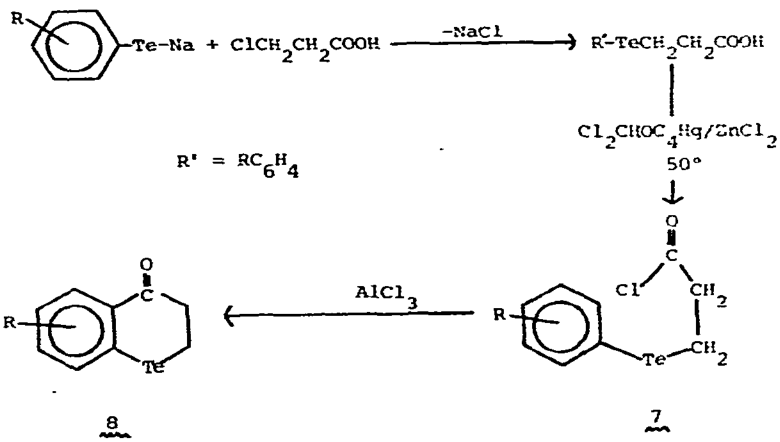
†This dark colored oil could not be distilled. The telluride was converted to the tellurium diiodide, which was obtained in 70% yield.

(6) $$C_6H_5\text{-Te-Li} + RX \xrightarrow[-LiX]{THF} C_6H_5\text{-Te-R}$$

listed in Table 4 together with pertinent data.

The phenyl alkyl tellurides, $C_6H_5\text{-Te-}C_nH_{2n+1}$, are yellowish oils[25], which are stable when stored in the dark, but decompose in light probably to diphenyl ditelluride[42]. Oxidation of phenyl decyl telluride with oxygen or hydrogen peroxide in alkaline or acidic medium yielded a mixture of compounds, which was not further investigated[25]. Similarly, aryl sodium tellurides, obtained by reduction of diaryl ditellurides with sodium borohydride in an ethanol/benzene medium, combined with β-chloropropionic acids to yield aryl 2-carboxyethyl tellurides[40] (eqn. 7). These compounds are also listed in Table 4.

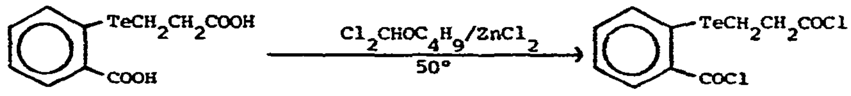
(7)



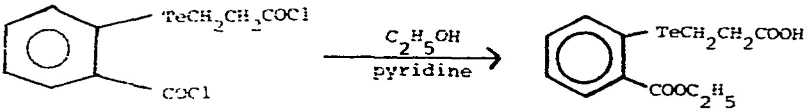
Treatment of the 2-carboxyethyl tellurides with dichloromethyl butyl ether and anhydrous zinc chloride produced the acid chlorides **7**, which were not characterized but converted to the heterocycle **8**[40].

2-Carboxyethyl 2-carboxyphenyl telluride[40] was converted to the acid chloride and ethyl ester as shown in eqn. 8.

(8)



80% yield; mp. 80-5°

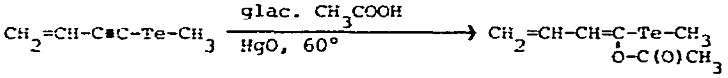


86% yield; bp. 170-5°/2 torr

9

When the 2-carboxyethyl 2-carboxyphenyl telluride was heated cylization did not occur. Only bis(2-carboxyphenyl) ditelluride was obtained. Treatment with polyphosphoric acid precipitated elemental tellurium. The Dieckman condensation attempted with the diester 9 to prepare the heterocycle 8 was unsuccessful[40].

Vinylacetylenyl methyl telluride added to acetic acid across the triple bond[49] (eqn. 9), formed an adduct RR'Te·2HgCl$_2$, an unstable crystalline compound with mercury(II) acetate and $C\equiv C$-, $C=C$- and Te- hydrogen-bonded species with phenol, 4-chlorophenol and diphenylamine[49].

(9) 

$$CH_2=CH-C\equiv C-Te-CH_3 \xrightarrow[HgO,\ 60^\circ]{glac.\ CH_3COOH} CH_2=CH-CH=\underset{O-C(O)CH_3}{C}-Te-CH_3$$

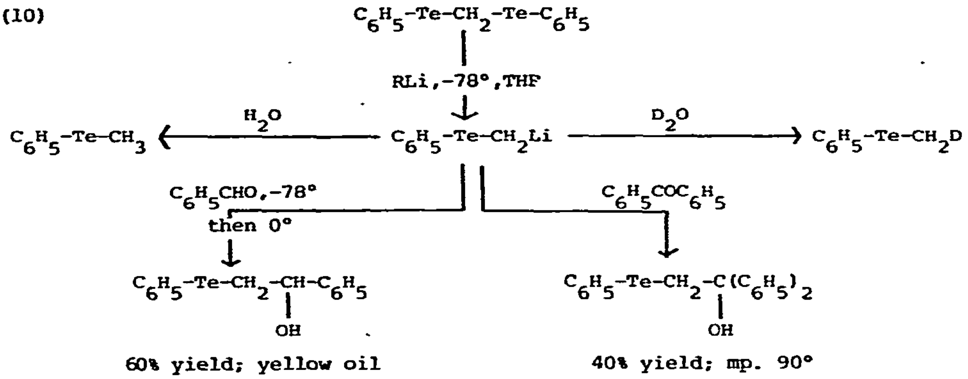
27% yield; bp. 82-3°/5-torr

Boiling glacial acetic acid decomposed the vinylacetylenyl methyl telluride to vinylacetylene, methane and carbon dioxide[49]. Methanethiol in a sealed tube at 100° did not add to the triple bond but caused Te-C bond cleavage. *tert*-Butyl peroxide oxidized the telluride at room temperature[50].

Boiling 10% sulfuric acid decomposed 1-acetoxybuta-1,3-dien-1-yl methyl telluride to α-$CH_3CH=CHCOOH$[49].

Seebach and Beck[25] investigated the reactions of phenyl lithiomethyl telluride, which was prepared by the interaction between $(C_6H_5Te)_2CH_2$ and lithioalkanes. The new compounds synthesized from phenyl lithiomethyl telluride are summarized in eqn. 10.

(10)



R = CH_3, C_4H_9, tert-C_4H_9

The phenyl alkly tellurides formed as co-products in addition to the lithiomethyl telluride (eqn. 10) were detected and identified by nmr techniques but not isolated.

Phenyl lithiomethyl telluride[25] forms a yellow green tetrahydrofuran/ diethyl ether solution. The solutions were kept at 0° under an inert atmosphere for 24 hrs. without decomposition. The solutions were even stable at 20°.

The following diorganyl tellurides were identified in reaction mixtures obtained from $Te_4(AsF_6)_2$ or $Te_6(AsF_6)_2$ and tetrafluoroethylene at 100° and 15 atm[30]: C_2F_5-Te-C_3F_7; C_2F_5-Te-C_4H_9; C_2F_5-Te-$CF_2CF_2CF_2COF$.

The photochemical reaction (3100Å) between dimethyl telluride and CF_3I and C_2F_5I produced CF_3-Te-CH_3 (11% yield) and C_2F_5-Te-CH_3 (40% yield), respectively. These new tellurides were reported to be odorless, yellow liquids, which are stable in air, and liberate $C_nF_{2n+1}H$ (n=1,2) on treatment with 5 M KOH[43].

Petragnani[37] obtained the tellurides c-C_6H_{11}-Te-R (R = C_6H_5, 4-$CH_3C_6H_4$, 4-$C_2H_5OC_6H_4$) by reduction of their dichlorides with sodium sulfide, and, similarly, th compounds 4-RC_6H_4-Te-C_6H_5 (R = CH_3, C_2H_5O) from the dibromides. The dihalides used in these reactions were prepared from the tellurides and sulfuryl chloride or bromine[37].

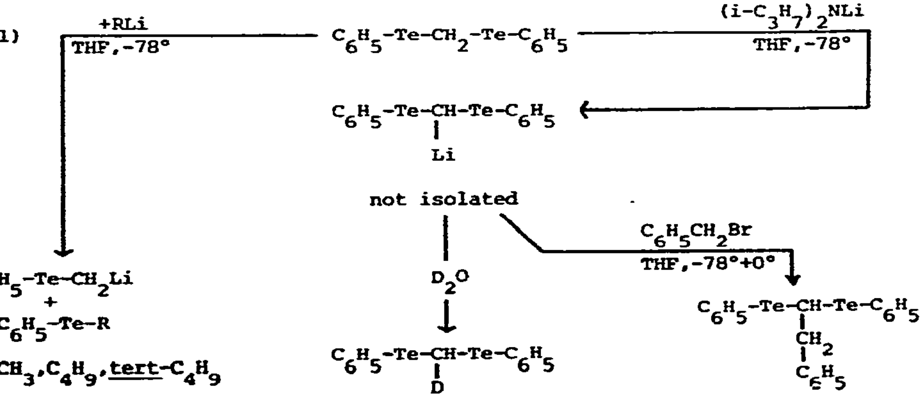
A German patent[P-2] reported the preparation of glycerin triether derivatives useful as indicators in the determination of fat absorption containing oxygen, ^{75}Se and/or ^{123m}Te.

Phenyl methyl telluride formed a charge-transfer complex with tetracyanoethylene in methylene chloride with λ_{max} = 6500Å, from which an ionization potential of 7.82 eV was calculated for the telluride[51]. The following reactions of diorganyl tellurides, R-Te-R', in addition to the ones already discussed in this section, were investigated: conversion to diorganyl tellurium dichlorides by SO_2Cl_2[37], to dibromides[37,42] and diiodides[42] by elemental halogens; reaction of $C_2H_5C{\equiv}C\text{-}C{\equiv}C\text{-}Te\text{-}CH_3$ with methyl iodide to give $[R(CH_3)_2Te]\ I$[26]; and cleavage of the CF_3-Te bond in $CF_3\text{-}Te\text{-}CH_3$ upon heating with $C_6H_5CH_2Cl$ at 215° for 44 hrs. to give $C_6H_5CH_2CF_3$[43].

3. Tellurides with two tellurium atoms in the molecules

Seebach and Beck[25] prepared methylene bis(phenyl telluride) in 6% yield by refluxing phenyl lithium telluride and methylene iodide, and in 70% yield from diphenyl ditelluride and diazomethane using Petragnani and Schill's method reported in 1970[2]. The yellow compound melted at 35-6°. The following reactions (eqn. 11) were carried out with this telluride.

(11)



(Continued on p. 436)

TABlE 5

DIORGANYL TELLURIUM DIHALIDES AND DICARBOXYLATES

$RR'TeX_2$			Method of Preparation	Yield %	m.p. °C	Ref.
R	R'	X				
C_6H_5	CH_3^*	I	$RR'Te + I_2$	65	$146^†$	42
			$R_2Te_2 + CH_3I$	-	145	38
	$C_2H_5^*$	I	$RR'Te + I_2$	64	$96^†$	42
	$C_3H_7^*$	I	$RR'Te + I_2$	62	$95^†$	42
	$\underline{i}$-$C_3H_7^*$	I	$RR'Te + I_2$	46	$96^†$	42
	$C_4H_9^*$	Br	$RR'Te + Br_2$	95	$70^†$	42
		I	$RR'Te + I_2$	84	$79^†$	42
	$\underline{c}$-$C_6H_{11}^*$	Cl	$RR'Te + SO_2Cl_2$	-	61	37
	$C_{14}H_{29}$	I	$RR'Te + I_2$	70	$70^†$	42
4-$CH_3C_6H_4$	CH_3^*	I	$R_2Te_2 + CH_3I$	-	127	38
	$\underline{c}$-$C_6H_{11}^*$	Cl	$RR'Te + SO_2Cl_2$	>90	85	37
	C_6H_5	Br	$RR'Te + Br_2$	>90	181	37
4-$CH_3OC_6H_4$	C_6H_5	Cl	$RTeCl_3 + (C_6H_5)_3SnCl$	80	113	21
4-$C_2H_5OC_6H_4$	CH_3^*	I	$R_2Te_2 + CH_3I$	34	108	38

	$\underline{c}$-C_6H_{11}*	Cl	$RR'Te + SO_2Cl_2$	34	113	37
	C_6H_5*	Br	$RR'Te + Br_2$	-	148-51	37
C_6H_5	C_6H_5	Cl	$C_6H_6 + TeCl_4/AlCl_3$	-	-	22
		Cl	$TeCl_4 + (C_6H_5)_4Sn$ or $(C_6H_5)_3SnCl$	75	159	21
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	F	$R_2TeCl_2 + AgF$	-	121	38
4-$C_2H_5OC_6H_4$	4-$C_2H_5OC_6H_4$*	F	$R_2TeCl_2 + AgF$	7	170	38
$(C_6H_5)_2C{=}CH$	$(C_6H_5)_2C{=}CH$*	Cl	$TeCl_4 + (C_6H_5)_2C{=}CH_2$	--	242	22
4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	CH_3COO	$R_2TeO + (CH_3CO)_2O$	73	139	52
		CF_3COO*	$R_2TeO + (CF_3CO)_2O$	82	152	52
		C_3H_7COO*	$R_2TeO + (C_3H_7CO)_2O$	78	129	52
		C_6H_5COO*	$R_2TeO + (C_6H_5CO)_2O$	69	212	52

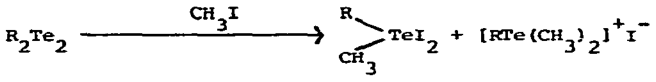
*New compounds

†The melting points given in Ref. 2 are not correct. This table contains the corrected values.

B. Diorganyl Tellurium Compounds, R_2TeX_2

A fair number of new diorganyl tellurium dihalides and dicarboxylates were prepared using mainly well established methods such as the reactions between diorganyl tellurides and sulfuryl chloride[37], elemental bromine[37,42] or elemental iodine[42], or the cleavage of diaryl ditellurides with excess methyl iodide[38] (eqn. 12).

(12)



$$R_2Te_2 \xrightarrow{CH_3I} \overset{R}{\underset{CH_3}{>}}TeI_2 + [RTe(CH_3)_2]^+I^-$$

The new compounds and previously prepared compounds, which now have been synthesized by new methods, are listed in Table 5. These new methods are discussed below.

Tetraphenyl tin or triphenyl tin chloride converted tellurium tetrachloride or aryl tellurium trichlorides to diaryl tellurium dichlorides. Further arylation to triorganyl telluronium chlorides was not possible. Diphenyl tin dichloride was the co-product in these reactions[21].

Refluxing bis(4-alkoxyphenyl) tellurium dichlorides in dry toluene with silver fluoride yielded diaryl tellurium difluorides[38].

The reaction of tetraphenyl or tetrakis(4-methylphenyl) lead with ^{126}Te- or ^{130}Te-$TeCl_4$ or $TeBr_4$ was found to proceed satisfactorily on a milligram scale to yield diaryl tellurium dihalides[20].

Bis(4-methoxyphenyl) tellurium dicarboxylates were prepared in good yields by heating the diaryl telluroxide with a carboxylic acid anhydride[52].

The pertinent data for all these compounds are summarized in Table 5.

Bis(carboxymethyl) tellurium dichloride was synthesized from tellurium tetrachloride and acetic anhydride in chloroform. The dichloride decomposed to tellurium on attempted reduction to the telluride[13]. Attempts to reproduce Morgan and Drew's procedure for the preparation of bis(carboxymethyl) tellurium dichloride were unsuccessful[13].

The following reactions in addition to the ones already discussed in this section have been carried out with diorganyl tellurium dihalides: reduction to diorganyl tellurides by $Na_2S\cdot 9H_2O$[37]; reaction of $(4\text{-}RC_6H_4)_2TeCl_2$ (R=H,CH_3) with anthracene in the presence of silver nitrate to produce diaryl tellurides and 9- or 9,10-chloroanthracenes (no reaction occurred in the absence of $AgNO_3$)[22]; reaction of diaryl tellurium dibromides with 1,1-dimethyl-3,5-cyclohexanedione to yield tellurium ylides[53] (see section VII).

The use of $(CH_3)_2TeI_2$ as a catalyst for the preparation of $RNHCO_2CH_3$ compounds from nitrobenzenes, methanol and carbon monoxide or from nitrosobenzene and azoxybenzene has been claimed[P-3]. Bis(benzoylmethyl) tellurium dichloride has been suggested as an imaging material for photomasks and in microphotography.[P-4]

C. Diorganyl Telluroxides

The reactions of bis(4-methoxyphenyl) telluroxide with carboxylic acid anhydrides to yield diaryl tellurium dicarboxylates[52] has been discussed in section VI-B. No additional work with telluroxides has been done during the survey period.

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

Several new telluronium iodides and nitrosylates were prepared. Methyl iodide and ethyldiacetylenyl methyl telluride kept at 30° gave dimethyl ethyldiacetylenyl telluronium iodide (mp. 89-90°) in 95% yield[26]. Diaryl ditellurides refluxed with excess methyl iodide produced aryl dimethyl telluronium iodides (eqn. 13)[38].

$$(13) \qquad (4\text{-}RC_6H_4)_2Te_2 \xrightarrow{CH_3I} [4\text{-}RC_6H_4Te(CH_3)_2]^+I^- + 4\text{-}RC_6H_4(CH_3)TeI_2$$

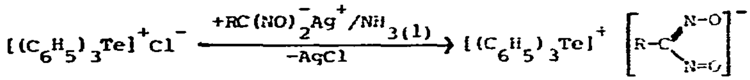
R = H, mp. 168°

R = CH_3, mp. 154°

R = C_2H_5O, mp. 163°

An anion exchange reaction between triphenyl telluronium chloride and silver nitrosylates yielded telluronium nitrosylates[54] (eqn. 14).

(14)



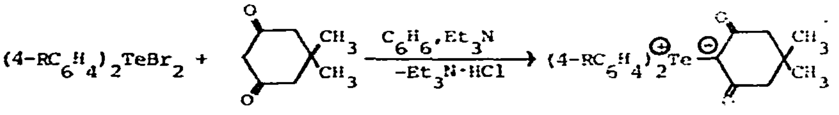
$R=CH_3$: 65% yield, mp. 139° (dec)

$R=C_6H_5$: 25% yield, mp. 57° (dec)

These telluronium compounds are ionic in methanol but covalent in benzene. The telluronium iodide synthesized from tellurochromanone[40] is described in section IX-J.

Sadekov[53] prepared the tellurium ylides 10 from diaryl tellurium dibromides and 1,1-dimethyl-3,5-cyclohexanedione in boiling benzene containing triethylamine (eqn. 15).

(15)



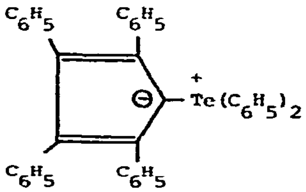
10

R=H, 100% yield, mp. 156-7°

$R=CH_3$, 75% yield, mp. 136-7°

$R=CH_3O$, 88% yield, mp. 143-4°

Compound 11, synthesized by Freeman in 1970[2], is the only other tellurium ylide known. It decomposes slowly in the solid state and more rapidly in solution. Addition of benzaldehyde or nitrosobenzene to a solution of 11 in carbon tetrachloride caused also decomposition. The ylide is unstable in basic medium[55].



11

VIII. Organic 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 sodium, selenium, titanium, niobium, molybdenum, tungsten or silver.

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

Phenyl lithium telluride was prepared from diphenyl ditelluride and lithium[42] and from phenyl lithium and tellurium[24,25]. Reaction of this telluride with alkyl halides yielded phenyl alkyl tellurides[25,42]. It combined with $(\pi\text{-}C_5H_5)_2NbCl_2$ to form $(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2$[24].

The reduction of the diaryl ditellurides, R_2Te_2 ($R=C_6H_5$, $2\text{-}CH_3C_6H_4$, $3\text{-}CH_3C_6H_4$, $4\text{-}CH_3C_6H_4$, $2\text{-}CH_3OC_6H_4$, $3,4\text{-}(CH_3)_2C_6H_3$, $4,5\text{-}(CH_3)_2C_6H_4$, $2\text{-}HOOCC_6H_4$, $1\text{-}C_{10}H_7$ and $2\text{-}C_{10}H_7$), with sodium borohydride in ethanol/benzene yielded the compounds RTeNa, which were not isolated but immediately reacted with β-chloropropionic acids[40] (see section VI-A2).

Ethyldiacetylenyl sodium telluride was obtained from the sodium acetylide and tellurium in liquid ammonia. It was immediately reacted with methyl iodide[26].

The organyl sodium tellurides **12** were presumably formed as intermediates in a reaction starting with β-chlorovinylaldehydes and sodium telluride in dimethylformamide (eqn. 16) and leading to tellurophene derivatives[17] (see section IX-B).

(16)

12

Phenyl and 4-methylphenyl bromomagnesium tellurides - conventionally prepared from aryl magnesium bromide and tellurium - were used to synthesize tellurium containing transition metal complexes[24] (see section VIII-D).

None of these organyl alkali metal tellurides, which are extremely oxygen and water sensitive, were isolated. They were used in-situ.

Siebert[56] in a review of the bonds formed between boron and sulfur, selenium or tellurium stated that boron-tellurium compounds containing an sp^2-hybridized boron atom are unknown. Complexes of the type $R_2Te{\cdot}BX_3$, in which the boron atom employs sp^3-type orbitals, have been described[2].

B. Organic Compounds of Tellurium Containing a Tellurium-Selenium Bond

Three new diorganyl selenide tellurides were prepared from aryl tellurium bromides and phenyl bromomagnesium selenide in tetrahydrofuran[37] (eqn. 17).

$$(17) \qquad C_6H_5\text{-Se-MgBr} + 4\text{-}RC_6H_4TeBr \xrightarrow[0°]{THF} 4\text{-}RC_6H_4\text{-Te-Se-}C_6H_5$$

R = H, 63% yield, mp. 47-8°; R = CH_3, 42% yield, oil;

R = CH_3O, 87% yield, bp. 155-8°/0.01 torr

These compounds were purified by chromatography on silicagel. When diphenyl selenide telluride was treated with 2 moles of bromine at 0^o in carbon tetrachloride, phenyl tellurium tribromide precipitated. Phenyl selenium bromide was the selenium containing product.

Bis(pentafluoroethyl) selenide telluride was obtained from $(C_2F_5Te)_2Hg$ and C_2F_5SeCl at room temperature. After two weeks' storage at -18° it had decomposed slightly to $(C_2F_5)_2Te_2$ and $(C_2F_5)_2Se_2$[30].

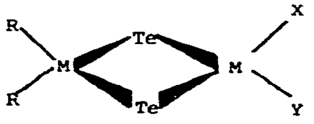
C. Organic Compounds of Tellurium Containing a Tellurium-Mercury Bond

As reported earlier[2], $(C_2F_5Te)_2Hg$ was obtained by shaking the ditelluride $(C_2F_5)_2Te_2$ with mercury and extracting the product with acetone. This reaction has been used to separate $(C_2F_5)_2Te$ from $(C_2F_5)_2Te_2$. The tellurium-mercury compound reacted with C_2F_5SeCl. A v.p.c. analysis of the liquid formed showed the presence of $C_2F_5SeTeC_2F_5$(60%), $(C_2F_5)_2Se$(34%) and $(C_2F_5)_2Te$(6%)[30].

D. Organic Compounds of Tellurium Containing a Tellurium-Transition Element Bond

To the already long list of transition element complexes containing covalently or coordinate-covalently bonded tellurium ligands[1,2], niobium derivatives were added. The new complexes of this element and of titanium, molybdenum, tungsten, platinum and mercury are summarized in Table 6. The mode of preparation of these complexes and their pertinent data are also listed. The Ti, Nb, Mo and W derivatives have an aryl telluro group, RTe-, covalently bonded to the metal atom.

The structure 13 has been suggested for the complexes $(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2\cdot L$ [L = Fe(CO)NO, $Co(CO)_2$] and for $(\pi\text{-}C_5H_5)_2Ti(TeC_6H_5)_2\cdot Fe(NO)_2$. These complexes are stable as solids under nitrogen, but decompose in solution and in air[57].



M = Ti, Nb

M' = Co, Fe

X, Y = CO, NO

13

The niobium complexes are diamagnetic. Several isomeric forms of these complexes are present in the solution as shown by nmr techniques[24].

The complexes $(\pi\text{-}C_5H_5)_2M(TeR)_2$ (M = W, Mo; R = C_6H_5, 4-$CH_3C_6H_4$) are quite stable in air. They decompose in methylene chloride solution within a day. The corresponding niobium complex (R = C_6H_5) is unstable in air and decomposes immediately when its benzene solution is brought in contact with air. Treatment of these complexes with concentrated hydrochloric acid or with methyl iodide in benzene cleaved the tellurium ligand forming $(\pi\text{-}C_5H_5)_2MCl_2$ and $(\pi\text{-}C_5H_5)_2MI_2$, respectively[24].

TABLE 6

ORGANIC COMPOUNDS OF TELLURIUM CONTAINING A TELLURIUM-TRANSITION ELEMENT BOND

Compound†	Reactants	Conditions	Yield %	m.p. °C	Ref.
$(C_6H_5Te)_2Ti(\pi\text{-cp})_2 \cdot Fe(NO)_2$	$(RTe)_2Ti(\pi\text{-cp})_2 + Hg[Fe(CO)_3NO]_2$	acetone, stir 2 hrs.	24	157*	57
$(C_6H_5Te)_2Nb(\pi\text{-cp})_2$	$RTeLi + (\pi\text{-cp})_2NbCl_2$	ether/benzene, 0°	80	137-42	24
$(C_6H_5Te)_2Nb(\pi\text{-cp})_2 \cdot Fe(CO)NO$	$(RTe)_2Nb(\pi\text{-cp})_2 + Hg[Fe(CO)_3NO]_2$	acetone, stir 1 hr.	80	171*	57
$(C_6H_5Te)_2Nb(\pi\text{-cp})_2 \cdot Co(CO)_2$	$(RTe)_2Nb(\pi\text{-cp})_2 + Hg[Co(CO)_4]$	acetone, 3 hrs, r.t.	90	157-60*	57
$(C_6H_5Te)_2Mo(\pi\text{-cp})_2$	$RTeMgBr + (\pi\text{-cp})_2MoCl_2$	THF, r.t.	75	198-9	24
$(4\text{-}CH_3C_6H_4Te)_2Mo(\pi\text{-cp})_2$	$RTeMgBr + (\pi\text{-cp})_2MoCl_2$	THF, r.t.	73	192-4	24
$(C_6H_5Te)_2W(\pi\text{-cp})_2$	$RTeMgBr + (\pi\text{-cp})_2WCl_2$	THF, r.t.	71	213	24
$(4\text{-}CH_3C_6H_4Te)_2W(\pi\text{-cp})_2$	$RTeMgBr + (\pi\text{-cp})_2WCl_2$	THF, r.t.	79	212-4	24
$(C_4H_9)_4N[(CH_3)_2Te \cdot PtX_3]^{\dagger\dagger}$	-	-	-	-	59
$[(C_4H_9)_4N]_2[(CH_3)_2Te \cdot (PtX_3)_2]^{**}$	$2[R_2Te \cdot PtX_3]^- + Pt_2X_6^{--}$	-	-	-	59
$[CH_2{=}CH\text{-}C{\equiv}C\text{-}TeCH_3] \cdot 2HgCl_2$	$RR'Te + HgCl_2$	diethyl ether	100	76	49
$[CH_2{=}CH\text{-}C{\equiv}C\text{-}TeCH_3] \cdot Hg(CH_3COO)_2$	$RR'Te + HgX_2$	CH_3COOH	-	52-4*	49

† π-cp = π-cyclopentadienyl (C_5H_5).

†† X = Cl, Br, I.

* The compound decomposed on melting.

** X = Cl, Br.

Cross and coworkers[58] detected with nmr techniques the exchange between free and coordinated $(C_2H_5)_2Te$-ligands in the complexes trans- $(C_2H_5)_2Te\ _2MX_2$ (M = Pd, Pt; X = halogen). The coalescence phenomena shown by these complexes could not unambiguously be distinguished from ligand exchange processes. The fluxional behavior of these molecules remains, therefore, uncertain.

The platinum complexes $[(C_4H_9)_4N]_n[(PtX_3)_n{\cdot}Te(CH_3)_2]$ (n = 1,2; X = halogen) were reported, but experimental details were not given. The spin-spin coupling constants $J_{^{195}Pt-\ ^{125}Te}$ were determined[59].

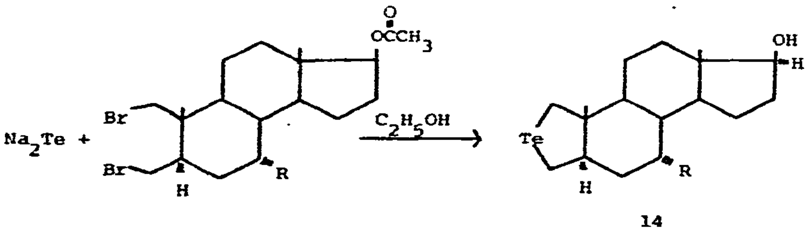
A mercury(II) acetate and chloride adduct of vinylacetylenyl methyl telluride was prepared by Radchenko[49] by mixing the components in the appropriate medium.

The metal complex formation constants for the ligand $(HOOCCH_2CH_2)_2Te$ with Mn^{+2}, Co^{+2}, Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, Pb^{+2} and Ag^{+} were determined. The complexes are rather weak. Species of the composition M(L), M(HL) and $M(H_2L)$ were detected. It is postulated that chelate formation occurred through the tellurium atom. Thermodynamic data for the silver complexes Ag(HL) and $Ag(H_2L)$ are reported[13].

IX. Heterocyclic Tellurium Compounds

A number of new heterocyclic, tellurium containing compounds were prepared. These include tetrahydrotellurophene derivatives, C-substituted tellurophenes, derivatives of benzotellurophene, 1-phospha-4-telluracyclohexanes, C-substituted 1-thia-4-telluracyclohexanes and telluracyclohexane derivatives.

(18)



14

2-Tellura-A-nor-5α-androstan-17β-ol

R = H, mp. 145-6°; R = CH_3, mp. 154-6°; 20% yield.

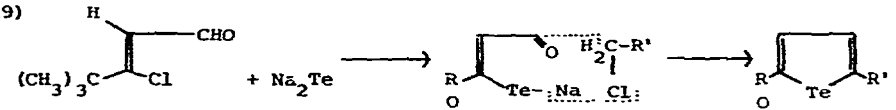
A. Tetrahydrotellurophene

The tetrahydrotellurophene derivatives 14 were synthesized[16] according to eqn. 18 (see previous page).

B. Tellurophene

Tellurophenes bearing substituents in the 2- and 5-positions were synthesized in 30% yield by adding a substituted chloroalkane to a solution of β-chlorovinylaldehydes and sodium telluride in dimethylformanide (eqn. 19)[17].

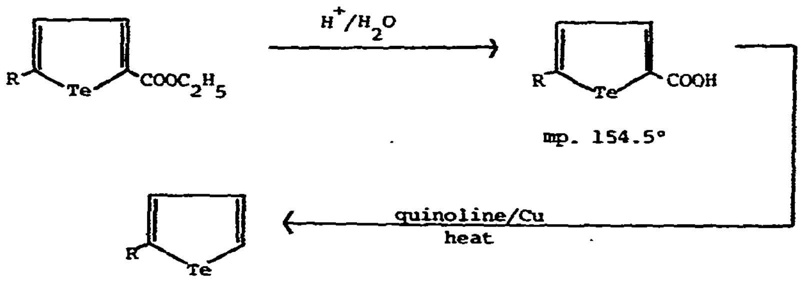
(19)



R', bp. °C/torr: $-CHO$, 153°/17 ; $-\overset{O}{C}CH_3$, 157°/15, mp. 57°; $-\overset{O}{C}-OC_2H_5$, 160°/16; $-NO_2$, 120°/0.9, mp. 30°

The oximes of the formyl and acetyl derivatives melted at 165.5° and 150.5°, respectively. Eqn. 20 describes the reactions carried out starting with the ethyl ester of 2-carboxy-5-*tert*-butyltellurophene[17].

(20)



90% yield, bp. 88°/16 torr   R = $(CH_3)_3C$

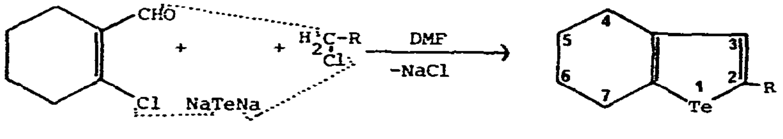
N,N-Dimethyl-2-tellurophenecarboxamide[60] was synthesized by heating 2-carboxytellurophene with $[(CH_3)_2N]_3PO$ at 180° for 3 hrs. The compound boiled at 114-6°/0.05 torr and melted at 70°.

Tellurophene formed a charge-transfer complex with tetracyanoethylene in methylene chloride[61].

C. 4,5,6,7-Tetrahydrobenzotellurophene

Three derivatives of 4,5,6,7-tetrahydrobenzotellurophene 15 with NO_2, $COOC_2H_5$ or $COCH_3$ as substituents in the 2-position were synthesized in 25% yield according to eqn. 21. The 2-acetyl derivative was converted to the oxime, which melted at 205.5°. Acid hydrolysis of the 2-carbethoxy compound yielded the free acid (mp. 199°), which lost carbon dioxide upon heating in quinoline in the presence of copper. 4,5,6,7-Tetrahydrobenzotellurophene boiled at 135°/17 torr[17].

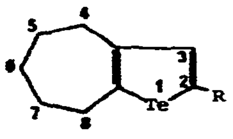
(21)



15

D. Cyclohept-1-eno[1,2-b]tellurophene

2-Carbethoxycyclohept-1-eno[1,2-b]tellurophene 16 was obtained in 25% yield according to eqn. 21 employing 2-chlorocyclohept-1-en-1-carbaldehyde and ethyl chloroacetate. The ester was hydrolyzed in acidic medium to the acid, which was decarboxylated in pyridine in the presence of copper[17].



16

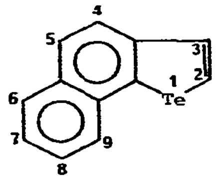
R = $COOC_2H_5$, bp. 154°/0.2 torr

R = COOH, mp. 194°

R = H, bp. 132.5°/15 torr

E. Naphtho[1,2-b]tellurophene

Dehydrogenation of 4,5-dihydronaphtho[1,2-b]tellurophene with dichlorodicyanobenzoquinone produced naphtho[1,2-b]tellurophene 17 (mp. 72.5°) in 90% yield.

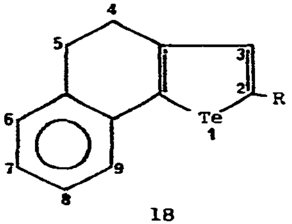


17

Compound 17 formed 1:1 adducts with picric acid and 2,4,7-trinitrofluorenone, which melted at 158° and 201° (dec), respectively[17].

F. 4,5-Dihydronaphtho[1,2-b]tellurophene

2-Carbethoxy-4,5-dihydronaphtho[1,2-b]tellurophene 18 was prepared in 25% yield from sodium telluride, ethyl chloroacetate and 1-chloro-3,4-dihydronaphthalene-2-carbaldehyde. The free acid was obtained by acid hydrolysis of the ester. Heating in pyridine in the presence of copper decarboxylated the acid[17].



18

R = $COOC_2H_5$, bp. 195°/0.3 torr

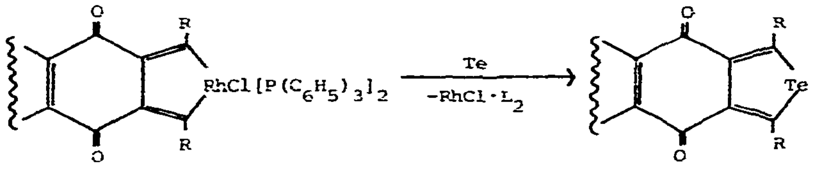
R = COOH, mp. 215°

R = H, bp. 167°/0.7 torr, mp. 45°

G. 1,4-Benzoquinono[c]tellurophene

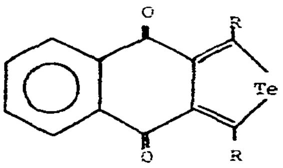
The rhodium heterocyclic compounds 19 (R = aryl) were refluxed in xylene under a nitrogen atmosphere with freshly precipitated, amorphous tellurium for 7-10 hrs. Tellurium replaced the $RHCl[P(C_6H_5)_3]_2$ group (eqn. 22). Aliphatic derivatives ($R = CH_3$) did not react under these conditions.

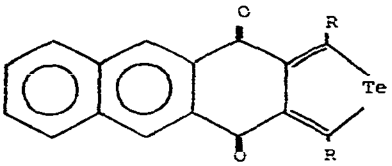
(22)



19

The following tellurium containing heterocyclic compounds were prepared in this manner[28,29]:





$R = C_6H_5$[28], 63% yield, mp. 215-6°

UV; 320.0 nm, log ε = 4.361

$R = 4\text{-}CH_3C_6H_4$[28], 20% yield, mp. 160-1°

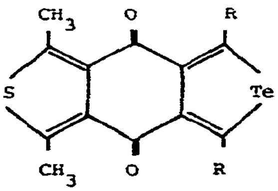
UV: 321.0 nm, log ε = 4.334

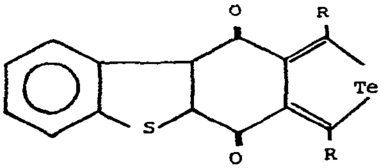
$R = C_6H_5$[28], 29% yield, mp. 290°

UV: 329.0 nm, log ε = 4.487
292.0 nm, log ε = 4.639

$R = 4\text{-}CH_3C_6H_4$[28], 10% yield, mp. 255°

UV: 333.0 nm, log ε = 4.475
291.0 nm, log ε = 4.649





$R = C_6H_5$[28], 33% yield, mp. 316°

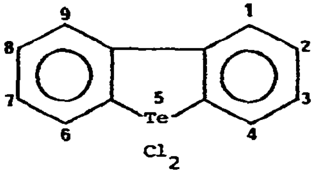
UV: 321.0 nm, log = 4.408

$R = C_6H_5$[28,29], 38% yield, mp. 248°

UV: 325.0 nm, log ε = 4.539

H. Dibenzotellurophene

McCullough[19] heated 2-biphenylyl tellurium trichloride at 210° (refluxing nitrobenzene) for 20 minutes. Crude dibenzotellurophene 5,5-dichloride 20 was isolated in quantitative yield. The purified product melted at 354° with decomposition. The dichloride was reduced with $K_2S_2O_5$ to dibenzotellurophene (mp. 94.5°). Chloroform solutions of dibenzotellurophene became turbid upon exposure to air. Addition of bromine and iodine to dibenzotellurophene in carbon tetrachloride caused the quantitative formation of the 5,5-dibromide (mp. 355°, dec) and the 5,5-diiodide (mp. 335°, dec), respectively. Grinding of the dichloride under 2-butanone with potassium iodide gave the diiodide in 83% yield.

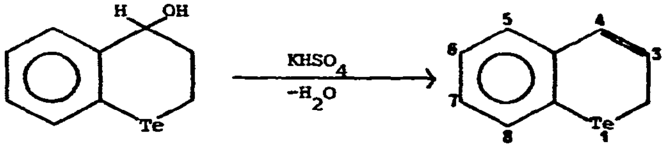


20

I. 1-Tellura-1,2-dihydronaphthalene

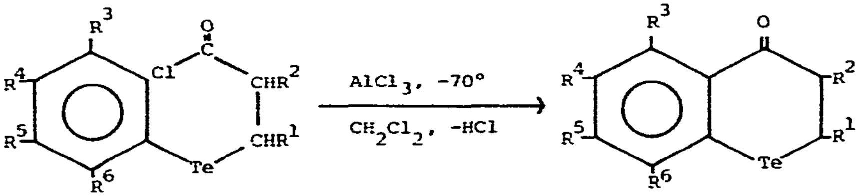
1-Tellura-1,2-dihydronaphthalene, boiling at 140°/0.8 torr was obtained in 85% yield upon distillation of 1-tellura-4-hydroxy-1,2,3,4-tetrahydronaphthalene[40] (eqn. 23).

(23)



J. Tellurochromanones and Tellurochromanols

When aryl 2-(chlorocarbonyl)ethyl tellurides 22, were treated with aluminum chloride in methylene chloride at -70° and the reaction mixtures carefully warmed to -5°, cyclization to tellurochromanones 21 occurred[40] (eqn. 24).



22 21

All R's = H except as stated otherwise.

R^n, n, yield %, mp. °C: -, -, 60%, 34° (bp. 150°/0.8 torr);

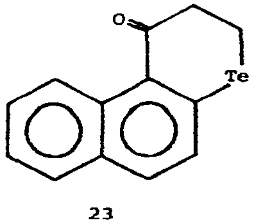
CH_3, 2, 60%, 24-5°; CH_3, 3, 55%, 62-3°

CH_3, 5, 45%, 48-50°; CH_3, 6, 45%, 48-9°;

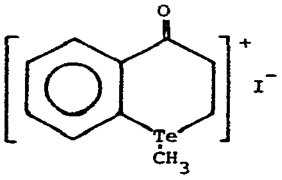
CH_3, 3, CH_3, 6, 13%, 41-2°;

CH_3, 4, CH_3, 5, 2%, 85-8°.

The naphtho[1,2-b]tellurochromanone 23 (mp. 104-6°) was similarly prepared in 66% yield from 2-naphthyl 2-(chlorocarbonyl)ethyl telluride. The aryl 2-(chlorocarbonyl)ethyl tellurides, $R-TeCH_2CH_2COCl$ (R = $2-CH_3OC_6H_4$, $4-CH_3C_6H_4$, 2,4-$(CH_3)_2C_6H_4$ and $1-C_{10}H_7$) could not be converted to tellurochromanones.



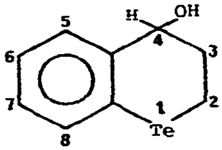
23



24

The tellurochromanone 21 (R^1-R^6 = H) formed a 2,4-dinitrophenylhydrazone (mp. 215°, dec.) and gave with methyl iodide the telluronium salt 24 (mp. 168°).

The tellurochromanones were reduced by sodium borohydride in ethanol to the tellurochromonols 25.



25

Position-Substituent, % yield, mp. °C:

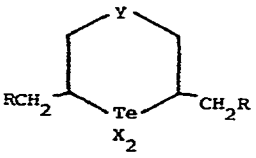
all H, 66%, 124°; 2-CH_3, 65%, 105-7°;
3-CH_3, 74%, 79-81°; 7-CH_3, 55%, 133-4°
8-CH_3, 63%, 86-7°

The tellurochromanol prepared from the chromanone 23 melted at 127-8° and was isolated in 60% yield.

Tellurochromanol distilled over $KHSO_4$ produced 1-tellura-1,2-dihydronaphthalene (section IX-I).

K. 1-Oxa-4-telluracyclohexane and 1-Aza-4-telluracyclohexane

A Russian patent[P-1] claims the preparation of the heterocyclic compounds 26 from tellurium tetrachloride or tellurium tetrabromide and diolefins in aqueous/ organic solutions.



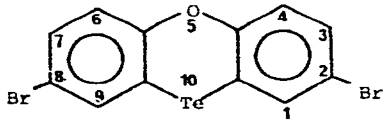
26

Y = O, NH, C_6H_5N
X = Cl, Br

L. Phenoxtellurine

Gioaba[62] reported that tellurium tetrachloride and bis(4-bromophenyl) ether did not condense to 2,8-dibromotellurophene 10,10-dichloride. This compound was successfully synthesized by bromination of phenoxtellurine 10,10-dihalides with elemental bromine in the presence of iodine or iron as catalyst. The highest yield (86%) of the 2,8-dibromophenoxtellurine 10,10-dibromide (mp. > 350°) was obtained by bromination of phenoxtellurine 10,10-diiodide.

2,8-Dibromophenoxtellurine 27 (mp. 93-4°), obtained in 96% yield by reduction of its 10,10-dibromide with aqueous $K_2S_2O_5$ solutions, was decomposed to bis(4-bromophenyl) ether by refluxing aqueous 30% potassium hydroxide.



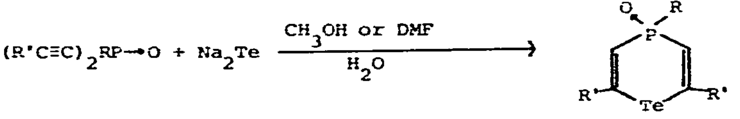
27

2-Bromophenoxtellurine 10,10-dibromide was formed as a by-product of the bromination reactions. Properties are not reported for this compound[62].

M. 1-Phospna-4-telluracyclohexane

Sodium telluride and organyldialkynylphosphine oxides combined in aqueous ethanol or dimethylformamide to give the heterocyclic compounds 28 (eqn. 25)[15].

(25)



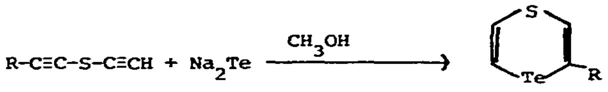
28

R, R', yield%, mp. °C: C_6H_5, H, 70%, 193-4°; $\underline{c}$-C_6H_{11}, H, 65%, 181-3°; C_6H_4, CH_3, 71%, 179-82°; $\underline{c}$-C_6H_{11}, CH_3, 58%, 172-3°; C_6H_5, $(CH_3)_3C$, 25%, 169-72°; $\underline{c}$-C_6H_{11}, $(CH_3)C$, 45%, > 200° (dec).

N. 1-Thia-4-tellurocyclohexane

When the dialkynyl sulfides, RC≡C-S-C≡CH, were treated with sodium telluride in methanol 1-thia-4-telluracyclohexane compounds 29 were obtained in good yields[14] (eqn. 26).

(26)



29

R, yield %, bp. °C/torr or mp. °C: CH_3, 55%, 41°/0.001;

C_2H_5, 54%, 49°/0.001;

$CH_2=C(CH_3)$, 56%, 55-8°/0.001;

$(CH_3)_3C$, 53%, 37°.

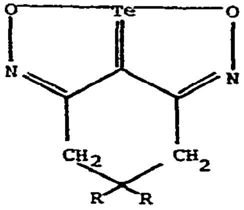
It was postulated that the nucleophile Te^{-2} attacked the -C≡CH group leading to RC≡C-S-CH=CH-Te⁻ followed by ring closure.

O. 2,5-Diaza-3,4-dioxa-3a-tellura-3,4-dihydropentalene

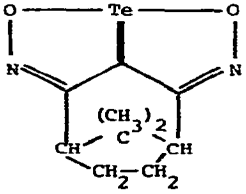
The diaza-dioxapentalenes shown below were synthesized from tellurous acid anhydride and the dioximes of 1,3-dioxo compounds (eqn. 27).

(27)

R = H; 25% yield, m. 200°
R = CH_3; 20% yield, m. 145°



R = H; 30% yield, m. 167°
R = CH_3; 30% yield, m. 167°



50% yield, m. 125°

X. Physicochemical Investigations of Organic Tellurium Compounds

Infrared, Raman, uv-visible, nmr, electron, Moessbauer and mass spectroscopy, structural analysis and dipole moment measurements were employed to characterize organic tellurium compounds.

A. Infrared and Raman Spectroscopy

Infrared data for a large number of tellurium-containing organic compounds were reported. Most of these data are presented without an attempt of assigning bands to certain vibrations. Many times only bands caused by characteristic groups such as multiple bonded carbon atoms or carbonyl groups are mentioned.

Only a few studies were devoted to a detailed analysis of the infrared spectra of organic tellurium compounds. Rodionov[63] interpreted the spectrum of diphenyl telluride on the basis of the experimental data and the results of the calculation of the wave numbers and modes of the in-plane vibrations.

Dance and McWhinnie[20] investigated the low frequency ir and Raman spectra of isotopically pure ^{126}Te- and ^{130}Te-$(C_6H_5)_2TeX_2$ (X = Cl, Br) and $(4\text{-}CH_3C_6H_4)_2TeBr_2$. Some bands in the spectra were shifted by 1 to 2 cm^{-1}, whereas others were completely unaffected by substitution of ^{126}Te with ^{130}Te. Bands at 270 and 245 cm^{-1} in the spectrum of $(C_6H_5)_2TeCl_2$ underwent shifts and are therefore ν(TeC). The ν(TeCl) modes at 286 and 245 cm^{-1} were also shifted.

The TeBr-modes did not show a shift. This observation was explained on the basis of the known Br-Te-Br angle of 178° and the large energy difference of 100 cm^{-1} between ν(TeBr) and ν(TeC). A frequency shift of ν_{sym} (TeBr) can occur only if ν(TeBr) is coupled with ν(TeC). Such coupling is weak at best under these conditions. The energies of ν(TeCl) and ν(TeC) are closer, leading to stronger coupling and a frequency shift on isotopic substitution.

In the compilation of infrared and Raman data the following abbreviations are used:

ir	infrared	n	neat
R	Raman	N	Nujol
l	liquid	soln	solution
s	solid	v	vapor

The frequency ranges used in the investigations or, if these ranges are not reported, the frequency spans tabulated or discussed in the papers are given.

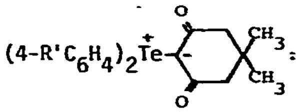
$TeCN^-$: ir[32] CH_3CN soln, $\nu(TeCN)$ 2081 cm^{-1};
$\nu(Te^{13}CN)$ 2035 cm^{-1};

CH_3-Te-CF_3: ir[43] v, 3660-725 cm^{-1}
CF_3-Te-CF_3: ir[18] v; 1178-740 cm^{-1}; ir[43] v, 2280-735 cm^{-1};
CH_3-Te-C_2F_5: ir[43] v, 2950-620 cm^{-1};
C_2F_5-Te-C_2F_5: ir[43] v, 1330-630 cm^{-1};
CH_3-Te-C≡CC≡CC_2H_5: ir[26], 2082 cm^{-1} (C≡CTe), 2200 cm^{-1} (C≡C);
CH_3-Te-C[OC(O)CH_3]=CH-CH=CH_2: ir[49]n, 1760 cm^{-1}(OC=O), 1562 cm^{-1} (C=CTe),
910,990, 1620 cm^{-1}(CH_2=CH);

The association of vinylacetylenyl methyl telluride with phenol, 4-chlorophenol and diphenylamine via hydrogen bonds was investigated by determining the ν(OH) shift[49].

C_6H_5-Te-$C_{10}H_{21}$: ir[25] n, 2960-690 cm^{-1};
C_6H_5-Te-$CH_2C(OH)(C_6H_5)_2$: ir[25] KI, 3500-590 cm^{-1};
C_6H_5-Te-$CH(CH_2C_6H_5)$-Te-C_6H_5: ir[25] n, 3060-690 cm^{-1};
C_6H_5-Te-CH_2-Te-C_6H_5: ir[25] n, 3050-690 cm^{-1};

$[(CH_3)_2Te\text{-}C{\equiv}CC{\equiv}CC_2H_5]^+I^-$: ir[26], 2110 cm^{-1} (C=C-Te);



: ir[53] n, R' = H: 1589, 1545 cm^{-1} ν(CO);
R' = CH_3: 1590, 1542 cm^{-1} ν(CO);
R' = CH_3O: 1589, 1545 cm^{-1} ν(CO);

$(\pi\text{-}C_5H_5)_2Ti(TeC_6H_5)_2\cdot Fe(NO)_2$: ir[57] KBr, 1675, 1708 cm^{-1} $\nu(NO)$;

$(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2\cdot Fe(NO)CO$: ir[57] KBr, 1623 cm^{-1} $\nu(NO)$, 1845 cm^{-1} $\nu(CO)$;

$(\pi\text{-}C_5H_5)_2Nb(TeC_6H_5)_2\cdot Co(CO)_2$: ir[57] KBr, 1859, 1911 cm^{-1} $\nu(CO)$;

$CH_2{=}CHC{\equiv}C\text{-}TeCH_3\cdot 2HgCl_2$: ir[49] KBr, 940, 980, 1625 cm^{-1} (C=C), 2150 cm^{-1} (C C);

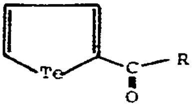
$CH_2{=}CHC{\equiv}C\text{-}TeCH_3\cdot Hg(CH_3COO)_2$: ir[49] KBr, 2150 cm^{-1} $\nu(C{\equiv}C)$, 1550 cm^{-1} ν(C C);

———— · ————

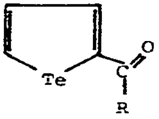
2-formyltellurophene: ir[64] C_2Cl_4 soln, 1691, 1666 cm^{-1} $\nu(CO)$,
1537, 1527, 1443, 1427 cm^{-1} $\nu(CO)$;

2-acetyltellurophene: ir[64] C_2Cl_4 soln, 1677, 1656.5 cm^{-1} $\nu(CO)$,
1531, 1521.5, 1428 cm^{-1} $\nu(C{=}C)$;

An analysis of the $\nu(CO)$ doublets[64] at various temperatures suggested that comparable amounts of the two conformers 30 and 31 of 2-formyl- or 2-acetyltellurophene are present in CS_2 solution. These results are in agreement with Lumbroso's conclusions derived from dipole moment measurements[65] but not with those of Caccamese[60] based on nmr results indicating the preponderance of conformer 30.

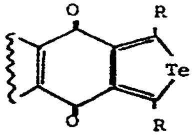


30



31

2-(N,N-dimethylaminocarbonyl)tellurophene: ir[60] CCl_4 soln, 1627 cm^{-1} $\nu(CO)$;



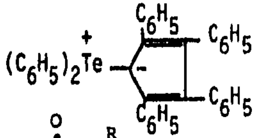
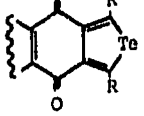
ir[28,29] KBr, 1650-1675 cm^{-1} $\nu(CO)$; for a list of compounds see section IX-G;

———— · ————

tellurochromanone: ir[40] CCl_4, 1679 cm^{-1} $\nu(CO)$;

———— · ————

TABLE 7. ULTRAVIOLET AND VISIBLE ABSORPTION SPECTRA OF ORGANIC TELLURIUM COMPOUNDS

Compound	λ_{max} X 10^9 m (log ε)†	Solvent	Ref.
$(CH_3)_2Te$	vacuum uv data	–	66
CH_3-Te-C_6H_5	330.5(2.865), 269.5(3.702), 254.7sh(3.505), 224.5(3.943)	cyclohexane	42
C_2H_5-Te-C_6H_5	329.6(2.834), 269.7(3.570), 2533sh(3.354), 227.0(4.107)	cyclohexane	42
C_3H_7-Te-C_6H_5	329.3(2.839), 271.1(3.581), 253.3sh(3.354), 225.1(4.097)	cyclohexane	42
i-C_3H_7-Te-C_6H_5	333.9(2.785), 270.8(3.400), 252.0sh(3.283), 227.7(4.204)	cyclohexane	42
C_4H_9-Te-C_6H_5	328.4(2.860), 270.0(3.584), 253.1sh(3.350), 224.1(4.093)	cyclohexane	42
$(C_6H_5)_3Te^+$ $CH_3C(NO)_2^-$	718.3(1.67), 448.5(-), 336.8(4.52) 662.1(1.67), 512.6(1.55), 333.1(4.35)	benzene CH_3OH	54 54
$(C_6H_5)_3Te^+$ $C_6H_5C(NO)_2^-$	717.8(1.74), 460.8sh(-), 346.0(4.39) 665.7(1.76), 521.9(1.56), 343.0(4.33)	benzene CH_3OH	54 54
tellurophene·$(CN)_2C{=}C(CN)_2$	530(-), 465(-)	CH_2Cl_2	61
	335(-)*, 286sh(-) 347(-) , 280sh(-)	CH_3OH benzene	55 55
	uv-visible data are listed in section IX-G	$CHCl_3$	28
tellurochromanone	375(3.816), 246(4.155), 238(3.949)	ethanol	40

†sh = shoulder *longest wavelength absorption

2,8-dibromophenoxtellurine: ir[62] KBr, 1385, 1463, 1585 cm^{-1} $\nu(C=C)$, 1238 cm^{-1} $\nu(COC)$, 835 cm^{-1} $\gamma 2H$;

2,8-dibromophenoxtellurine 10,10-dibromide: ir[62] KBr, 1380, 1455, 1580 cm^{-1} $\nu(C=C)$, 1225 cm^{-1} $\nu(COC)$, 810 cm^{-1} $\gamma 2H$.

B. Ultraviolet-Visible Spectroscopy

The ultraviolet-visible spectral data for organic tellurium compounds which have been reported during this survey period, are summarized in Table 7.

The vapor phase vacuum-ultraviolet spectral data for dimethyl telluride were used to compare its Rydberg term values with those of Xenon. Best agreement was found for the np series[66].

Alosi[61] measured the light absorption of the charge transfer complex formed between tellurophene and tetracyanothylene (Table 7). The formation constant was found to be 1.20 $dm^3 mol^{-1}$ in methylene chloride at 20°. The charge transfer band is a doublet. The ionization potentials of the tellurophone π_2 (8.32 eV) and π_3 (8.76 eV) orbitals were calculated from the charge transfer data. It has been suggested that inner orbitals of the donor in addition to the π_2 orbital are involved in the complex formation.

C. Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy was widely used to characterize organic tellurium compounds. The following nuclei were employed as probes: ^{1}H, ^{19}F, ^{125}Te and ^{195}Pt.

1. ^{1}H NMR Spectroscopy

The ^{1}H nmr data, which appeared in the literature during the survey period, are summarized in Table 8. Pertinent ^{1}H-^{1}H and ^{1}H-^{125}Te coupling constants are also listed.

(Continued on p. 466)

TABLE 8

^1H NMR SPECTRAL DATA FOR ORGANIC TELLURIUM COMPOUNDS

Compound	Solvent	Chemical Shift, ppm* TMS = 0 ppm	Coupling Constants Hz	Ref.
$C_6H_5TeCl \cdot [(CH_3)_2N]_2CS$	$CHCl_3$	CH_3 3.04 (s)	-	35
	CH_2Cl_2	CH_3 3.01 (s)	-	35
$C_6H_5TeBr \cdot [(CH_3)_2N]_2CS$	$CHCl_3$	CH_3 3.05 (s)	-	35
	CH_2Cl_2	CH_3 3.03 (s)	-	35
4-$CH_3C_6H_4TeCl_3$	DMSO-d_6	ortho H (to Te) 8.09 (d), meta H 7.18 (d)	$J_{\text{ortho-meta}}$ 8-9	38
4-$CH_3C_6H_4TeBr_3$	DMSO-d_6	8.23 7.15		38
4-$CH_3C_6H_4TeI_3$	DMSO-d_6	8.19 7.41		38
4-$CH_3OC_6H_4TeF_3$	DMSO-d_6	8.08 7.26		38
4-$CH_3OC_6H_4TeCl_3$	DMSO-d_6	8.35 7.16		38
4-$CH_3OC_6H_4TeBr_3$	DMSO-d_6	8.50 7.01		38
4-$CH_3OC_6H_4TeI_3$	DMSO-d_6	8.26 6.85		38
4-$C_2H_5OC_6H_4TeF_3$	DMSO-d_6	8.20 7.20		38
4-$C_2H_5OC_6H_4TeCl_3$	DMSO-d_6	8.32 7.13		38
4-$C_2H_5OC_6H_4TeBr_3$	DMSO-d_6	8.60 7.20		38
4-$C_2H_5OC_6H_4TeI_3$	DMSO-d_6	8.22 6.91		38

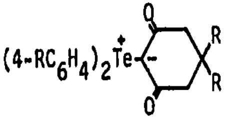
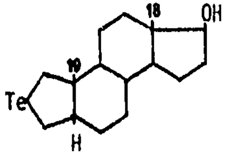
$(4-CH_3C_6H_4)_2Te_2$	DMSO-d_6	7.71	7.09		38
$(4-CH_3OC_6H_4)_2Te_2$	DMSO-d_6	7.86	6.99		38
$(4-C_2H_5OC_6H_4)_2Te_2$	DMSO-d_6	7.64	6.78		38
$CH_3-Te-CF_3$	C_6F_6	CH_3-2.57 (s)		$J_{^{1}H-^{125}Te}$ 22	43
$CH_3-Te-C_2F_5$	C_6F_6	CH_3-2.38 (s)			43
$CH_3-Te-C\equiv CC\equiv CC_2H_5$	-	CH_3Te 2.13 (s)		-	26
$CH_3-Te-C_6H_5$	CCl_4	CH_3 2.16 (s), 6.96-7.25 (3H,m), 7.43-7.75 (2H,m)		-	42
	CCl_4	CH_3 2.11 (s,d), 7.1 (3H,m), 7.5 (2H,m)		$J_{^{1}H-^{125}Te}$ 21.5	25
$CH_2D-Te-C_6H_5$	CH_2Cl_2	CH_2 2.10 (t)		J_{H-D} 1.6	25
$CH_3CH_2-Te-C_6H_5$	CCl_4	CH_3 1.63 (t), CH_2 2.82 (q), 6.98-7.30 (m) 7.53-7.83 (m)		J_{H-H} 7.5	42
$CH_3CH_2CH_2-Te-C_6H_5$	CCl_4	CH_3 0.98 (t), CH_2 1.75 (m), CH_2Te 2.90 (t) 7.02-7.30 (m), 7.57-7.80 (m)		$J_{CH_2CH_2}$ 7.5	42
$(CH_3)_2CH-Te-C_6H_5$	CCl_4	CH_3 1.58 (d), CH 3.52 (sept), 7.03-7.33 (m) 7.62-7.90 (m)		J_{CHCH_3} 7.0	42
$CH_2=CHCH_2-Te-C_6H_5$	CCl_4	CH_2Te 3.52 (d), $CH_2=CH$ 4.5-6.5 (m), $CH_2=$ 4.65 (d), 4.70 (d), CH 5.9 (t of d of d) 7.20 (3H,m), 7.65 (2H,m)		J_{TeCH_2CH} 8.0 $J_{CH_2=CH}$ 10, 16	25

TABLE 8 (continued)

Compound	Solvent	Chemical Shift, ppm* TMS = 0 ppm	Coupling Constants Hz	Ref.
$CH_3CH_2CH_2CH_2$-Te-C_6H_5	CCl_4	CH_3 0.88 (t), CH_2CH_2 1.08-2.05 (m), CH_2Te 2.88 (t), 7.00-7.28 (m), 7.53-7.80 (m)	$J_{TeCH_2CH_2}$ 7.0	42
	CCl_4	CH_2Te 2.86 (t)	-	25
$(CH_3)_3C$-Te-C_6H_5	CCl_4	CH_3 1.58 (s)	-	25
$C_6H_5CH(OH)CH_2$-Te-C_6H_5	CCl_4	CH_2 3.15 (d), CH 4.75 (t), 7.15 (8H,m) 7.60 (2H,m)	J_{CH_2CH} 6.5	25
$(C_6H_5)_2C(OH)CH_2$-Te-C_6H_5	CCl_4	HO 3.15 (s), CH_2 3.81 (s,d), 7.2 (13H,m) 7.65 (2H,m)	$J_{^1H-^{125}Te}$ 20	25
$C_{10}H_{21}$-Te-C_6H_5	CCl_4	CH_3 0.88 (t), $7CH_2$ 1.25, $TeCH_2CH_2$ 1.4-2.0 (m), $TeCH_2$ 2.83 (t), 7.1 (3H,m), 7.65 (2H,m)	$J_{TeCH_2CH_2}$ 7	25
$(4-CH_3C_6H_4)_2Te$	DMSO-d_6	ortho H 7.51 (d), meta H 7.03 (d)		38
$(4-CH_3OC_6H_4)_2Te$	DMSO-d_6	7.75 6.98	$J_{ortho-meta}$ 8-9	38
$(4-C_2H_5OC_6H_4)_2Te$	DMSO-d_6	7.73 6.98		38
$C_6H_5Te-CH_2-Te-C_6H_5$	CCl_4	CH_2 3.80 (s,d), 7.15 (6H,m), 7.65 (4H,m)	$J_{^1H-^{125}Te}$ 19	25
$C_6H_5Te-CH(CH_2C_6H_5)-TeC_6H_5$	CCl_4	CH_2 3.33 (d), CH 4.53 (t), 7.1 (11H,m), 7.7 (4H,m)	J_{CHCH_2} 7.5	25

$[(C_6H_5)_2C=CH]_2TeCl_2$	$CDCl_3$	CH 7.99 (s), 7.45 (10H,m), 7.36 (10H,m)	-	22
$4-CH_3C_6H_4(CH_3)TeI_2$	DMSO-*d*$_6$	ortho H 7.83 (d), meta H 6.67 (d)		38
$4-CH_3OC_6H_4(CH_3)TeI_2$	DMSO-*d*$_6$	8.00 7.08		38
$4-C_2H_5OC_6H_4(CH_3)TeI_2$	DMSO-*d*$_6$	7.92 7.01		38
$(4-CH_3C_6H_4)_2TeCl_2$	DMSO-*d*$_6$	7.83 7.32		38
$(4-CH_3C_6H_4)_2TeBr_2$	DMSO-*d*$_6$	7.88 7.29		38
$(4-CH_3C_6H_4)_2TeI_2$	DMSO-*d*$_6$	7.89 7.24		38
$(4-CH_3OC_6H_4)_2TeF_2$	DMSO-*d*$_6$	7.93 7.26		38
$(4-CH_3OC_6H_4)_2TeCl_2$	DMSO-*d*$_6$	7.98 7.12		38
	$CDCl_3$	CH_3 3.83 (s), 7.95 (2H,d), 6.98 (2H,d)	J_{H-H} 9	22
$(4-CH_3OC_6H_4)_2TeBr_2$	DMSO-*d*$_6$	ortho H 8.14 (d), meta H 7.24 (d)	$J_{ortho-meta}$ 8-9	38
$(4-CH_3OC_6H_4)_2TeI_2$	DMSO-*d*$_6$	8.87 7.07		38
$(4-C_2H_5OC_6H_4)_2TeF_2$	DMSO-*d*$_6$	7.92 7.23		38
$(4-C_2H_5OC_6H_4)_2TeCl_2$	DMSO-*d*$_6$	7.88 7.09		38
$(4-C_2H_5OC_6H_4)_2TeBr_2$	DMSO-*d*$_6$	8.10 7.21		38
$(4-C_2H_5OC_6H_4)_2TeI_2$	DMSO-*d*$_6$	8.05 7.16		38
$[4-CH_3C_6H_4(CH_3)_2Te]^+I^-$	DMSO-*d*$_6$	7.93 7.56		38
$[4-CH_3OC_6H_4(CH_3)_2Te]^+I^-$	DMSO-*d*$_6$	7.80 7.11		38
$[4-C_2H_5OC_6H_4(CH_3)_2Te]^+I^-$	DMSO-*d*$_6$	7.80 7.05		38
R = H	CH_2Cl_2	CH_3 1.05 (s), CH_2 2.25 (s), 7.25-7.28	-	53

TABLE 8 (continued)

Compound	Solvent	Chemical Shift, 0 ppm TMS = 0 ppm	Coupling Constants Hz	Ref.
		(10H,m)		
 R = CH_3	CCl_4	CH_3 1.02 (s), CH_2 2.12 (s), CH_3 (arom.) 2.30 (s)		53
		ortho H (Te) 7.09 (d), meta H (Te) 7.52 (d)	$J_{ortho-meta}$ 7.8	
R = CH_3O	CCl_4	CH_3 1.03 (s), CH_2 2.15 (s), CH_3O 3.75 (s)		53
		ortho H (Te) 7.55 (d), meta H (Te) 6.80 (d)	$J_{ortho-meta}$ 8.3	
$(\pi\text{-cp})_2Ti(TeC_6H_5)_2\cdot Fe(NO)_2^{**}$	$(CD_3)_2CO$	cp 5.17 (s), 5.29 (s), 5.32 (s); C_6H_5 7.16-7.40 (m)	-	57
$(\pi\text{-cp})_2Nb(TeC_6H_5)_2\cdot Fe(NO)_2^{**}$	$(CD_3)_2SO$	cp 4.69 (s), 4.75 (s), 4.93 (s), 5.10 (s) 5.17 (s), 5.36 (s), C_6H_5 7.26-7.50 (m)	-	57
$(\pi\text{-cp})_2Nb(TeC_6H_5)_2\cdot Co(CO)_2^{**}$	$(CD_3)_2SO$	cp 4.69 (s), 5.01 (s), 5.27 (s), C_6H_5 7.15-7.55 (m)	-	57
$(\pi\text{-cp})_2Mo(TeC_6H_5)_2$	$(CD_3)_2SO$	cp 5.28 (s), C_6H_5 6.85-7.50 (m)	-	24
$(\pi\text{-cp})_2MO(Te4\text{-}C_6H_4CH_3)_2$	$CDCl_3$	cp 5.32 (s), C_6H_4 6.99 (d), 7.69 (d)	-	24
$(\pi\text{-cp})_2W(TeC_6H_5)_2$	$CDCl_3$	cp 5.34 (s), C_6H_5 7.05-7.90 (m)	-	24
$(\pi\text{-cp})_2W(Te4\text{-}CH_3C_6H_4)_2$	$CDCl_3$	cp 5.31 (s), C_6H_4 6.98 (d), 7.69 (d)	-	24
	-	H (C_{18}) 0.78, H (C_{19}) 0.85	-	16

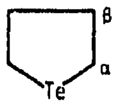
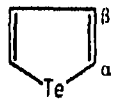
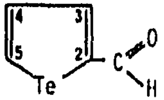
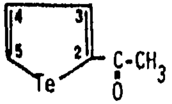
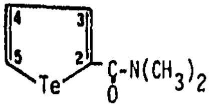
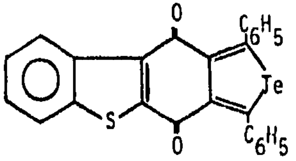
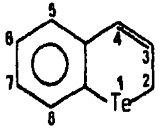
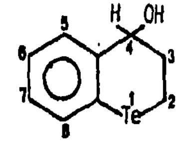
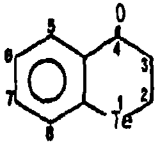
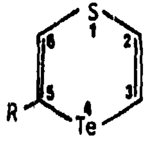
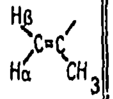
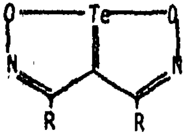
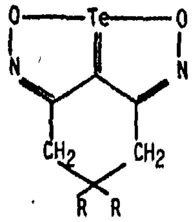
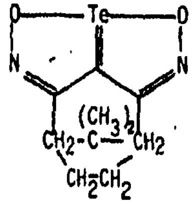
	CCl_4	α 3.10, β 2.03	-	67
	C_6D_6	α 2.91, β 1.69	-	67
	C_6F_6	α 3.18, β 2.10	-	67
	CCl_4	α 8.77, β 7.70	-	67
	C_6D_6	α 8.50, β 7.58	-	67
	C_6F_6	α 8.72, β 7.59	-	67
	$CDCl_3$	H 9.50, H3 8.50, H4 8.00, H5 9.43	$^3J_{34}4.02$, $^3J_{45}6.48$ $^4J_{35}1.28$, $^5J_{5\text{-}CHO}0.90$	60
	$CDCl_3$	CH_3 2.55, H3 7.17, H4 6.55, H5 7.60	$^3J_{34}4.15$, $^3J_{45}6.60$, $^4J_{35}1.21$	60
	$CDCl_3$	CH_3 3.15, H3 7.84, H4 7.84, H5 9.05	$^3J_{34}4.10$, $^3J_{45}6.69$ $^4J_{35}1.24$	60
	$CDCl_3$	arom. H 7.2-7.6 (m)	-	29
	$CDCl_3$	H2 3.26, H3 5.31, H4 6.10	$J_{23}5.9$, $J_{34}10.8$ $J_{24}1.5$, $J_{^1H\text{-}^{125}Te}32$	40

TABLE 8 (continued)

Compound		Solvent	Chemical Shift, ppm* TMS = 0 ppm	Coupling Constants Hz	Ref.
		DMSO-d_6	H3, OH 2.1 (m), H2 3.21 (m), H4 4.6 (m) arom. H 7(m)	-	40
		$CDCl_3$	H5, H8 8.1, H6, H7 7.4, CH_2 3.1	-	40
	R = CH_3	CCl_4	H2 7.41, H3 6.84, H6 6.19, CH_3 2.38	$J_{HC=C-CH_3}$1.5 $J_{HC=CH}$7.3	14
	R = CH_3CH_2	CCl_4	H2 7.38, H3 6.84, H6 6.36, CH_3 1.09 CH_2 2.58	$J_{HC=C-CH_2}$1.3 $J_{HC=CH}$7.2	14
	R = $(CH_3)_3C$	CCl_4	H2 7.45, H3 6.89, H6 6.36, CH_3 1.21	$J_{HC=CH}$7.0	14
	R = 	CCl_4	H2 7.48, H3 6.88, H6 6.66, CH_3 2.06, Hα 5.02, Hβ 5.18	$J_{HC=CH}$7.4	14
	R = H	$CDCl_3$	CH 10.37 (s)	-	62a
	R = CH_3	$CDCl_3$	CH_3 3.25 (s)	-	62a

	R = H	$CDCl_3$	CH_2-(C=N) 2.17-2.57 (m); CH_2 3.48-3.68 (m)	-	62a
	R = CH_3	$CDCl_3$	CH_3 1.18 (s); CH_2 3.41 (s)	-	62a
		$CDCl_3$	CH_3 0.57 (s), 1.36 (s), 1.78 (s); CH 3.82; CH_2 1.52-2.88 (m);	$J_{^1H-^{13}C}$ 6.5	62a

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[*] s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet

[**] cp = cyclopentadienyl; the various cp-singlet signals are caused by the presence of isomers.

The ^{1}H nmr spectra of some aryl tellurium derivatives, prepared from tellurium tetrachloride and methyl phenyl ether or ethyl phenyl ether, confirmed the known fact, that the tellurium atom in these compounds is bonded to the ring carbon atom in para-position to the alkoxy groups. The chemical shift difference between the ortho and meta hydrogen atoms (relative to the tellurium atom) in these compounds increases for a particular solvent in the sequence $R_2Te<R_2TeX_2<RTeX_3$ (R = 4-R'C_6H_4, R' = CH_3, CH_3O, C_2H_5O). For a particular compound in various solvents this difference increases in the order DMSO<CCl_4<C_6H_6[38].

Fringuelli[67] used the orientational influence between dipolar solutes and the aromatic solvents C_6D_6 and C_6F_6 as expressed by changes of the ^{1}H-chemical shifts of tellurophene and tetrahydrotellurophene, to confirm that the negative part of the dipole in these heterocycles is located on the tellurium atom.

Computer simulation of the lanthanide [Eu(fod)$_3$] induced shifts was applied to determine the relative concentrations of the conformers of 2-formyl- and 2-acetyltellurophene present in $CDCl_3$ solutions. It was concluded that 96% of the formyl derivative and 90% of the acetyl derivative were present as the conformer 30 (section X-A) with the carbonyl group close to the tellurium atom[60]. Different relative conformer concentrations were obtained from ir band analyses of ν(CO)[64] (section X-A). The torsional barrier about the C-N bond in 2-N,N-dimethylaminocarbonyltellurophene was determined by nmr measurements to be 13.7 - 13.8 kcal mol^{-1} in the temperature range -11°to + 13.8°[60].

2. ^{19}F NMR spectroscopy

The 19F chemical shifts of fluroalkyl tellurides and ditellurides are summarized in Table 9.

3. INDOR NMR spectroscopy (^{195}Pt-^{125}Te)

Values for the spin-spin coupling constants $^{1}J_{^{195}Pt-^{125}Te}$ in platinum-dimethyl telluride complexes were determined. The following values are reported (complex, $J_{^{195}Pt-^{125}Te}$,Hz): $M[(PtCl_3)_2L]$, -1553; $M[PtBr_3L]$, -1092; $M[PtI_3L]$, -400; $M_2[(PtCl_3)_2L]$, 5923; $M_2[(PtBr_3)_2L]$, 5088; $M=[(C_4H_9)_4N]^+$, $L = (CH_3)_2Te$.

D. Electron Spectroscopy

The compounds $(CH_3)_2Te$, $(SiH_3)_2Te$ and $(GeH_3)_2Te$ were studied by photoelectron spectroscopy to elucidate the role of d-orbital participation in bonding. It was concluded that the Si d-orbitals have only a minor influence on the chemical bond. The following vertical ionization potentials are reported: $(CH_3)_2Te$, 7.89 eV; $(SiH_3)_3Te$, 8.63 eV; $(GeH_3)_2Te$, 8.34 eV[68]. The multi-peak photoelectron spectrum of tellurophene in the C_{1s} region was interpreted as arising from shake up phenomena involving charge transfer from the heteroatom to the carbon atoms. The C_{1s} shake up eoergy is 4.1 eV. The spin-orbit splittings in the Te_{3d} and Te_{4d} regions are 10.5 eV and 1.4 eV, respectively[69].

E. ^{125}Te Moessbauer Spectroscopy

The ^{125}Te Moessbauer spectra, which are summarized in Table 10, were obtained at 4.2°K[70,71]. Enriched ^{125}Te (91.2%) was used to prepare the dimethyl tellurium compounds[71]. The large positive isomer shift values of the aryl tellurium derivatives are indicative of a high s-electron density at the tellurium nucleus[70]. The quadrupole splittings of the organic tellurium halides decrease in the order Cl<Br<I consistent with decreasing sterochemical activity of the non-bonding electrons and increasing symmetry with increasing size of the halide[70]. References to ^{125}Te Moessbauer work on inorganic tellurium compounds are given in Berry's paper[70]. Moessbauer data for inorganic tellurium compounds were also reported by Mahmud[73].

F. Mass Spectroscopy

Mass spectroscopy was used routinely for the characterization of organic

(Continued on p. 470)

TABLE 9

^{19}F NMR DATA FOR ORGANIC TELLURIUM COMPOUNDS

Compound	Solvent	Chemical Shift, ppm	Coupling Constants, Hz	Ref.
CH_3-Te-CF_3	C_6F_6	27.5(s)*	-	43
CF_3-Te-CF_3	-	-54(s)†	$J_{^{19}F-^{125}Te}$ 22	18
	C_6F_6	22.7(s)*	$J_{^{19}F-^{125}Te}$ 25	43
CH_3-Te-CF_2CF_3	C_6F_6	CF_3 85.0(t), CF_2 92.1(q)*	J_{F-F} 19	43
CF_3CF_2-Te-CF_2CF_3	C_6F_6	CF_3 84.6(s), CF_2 84.0(s)*	-	43
	-	CF_3 84.8, CF_2 84.1*	J_{F-F} 3.3	30
CF_3CF_2-Te-$CF_2CF_2CF_2CF_3$	-	$\underline{CF}_3CF_2Te$ 84.4, $CF_3\underline{CF}_2Te$ 84.7*	complex splitting	30
		$\underline{CF}_3(CF_2)_3$ 81.9(t,t), $CF_3CF_2(CF_2)_2$ 126.1(t,q)	$J_{CF_3CF_2}$ 2.6	
		$CF_3CF_2\underline{CF}_2CF_2$ 116.4 (broad),	$J_{CF_2CF_2}$ 12.0	
		$C_3F_7CF_2$ 79.2 (broad)		
$(CF_3)_2Te_2$	-	CF_3 -49.8(s)†	$J_{^{19}F-^{125}Te}$ 92.6	18
$(CF_3CF_2)_2Te_2$		CF_3 83.1(t), CF_2 86.5(q)*	J_{F-F} 3.3	30

*Chemical shift relative to CCl_3F. †Chemical shift relative to external TFA.

TABLE 10. ^{125}Te MOESSBAUER SPECTRAL DATA FOR ORGANIC TELLURIUM COMPOUNDS

Compound	Source	Chemical Isomer Shift, δ(I-Cu) mm s^{-1}	Quadrupole Splitting Δ, mm s^{-1}	Line Width 2Γ, mm s^{-1}	Ref.
C_6H_5TeI*	I-Cu	0.6	9.5	11.7	70
$C_6H_5TeI_3$	I-Cu	0.9	3.9	8.4	70
4-$CH_3OC_6H_4TeCl_3$	PbTe	0.9	9.2	7.4	70
4-$C_2H_5OC_6H_4TeCl_3$	PbTe	1.1	9.2	6.9	70
4-$C_2H_5OC_6H_4TeBr_3$	PbTe	1.0	8.0	6.9	70
4-$C_2H_5OC_6H_4TeI_3$	PbTe	1.0	5.2	7.1	70
(4-$CH_3C_6H_4)_2Te_2$	I-Cu	0.6	9.9	11.5	70
(4-$CH_3OC_6H_4)_2Te_2$	PbTe	0.3	10.3	6.5	70
(4-$C_6H_5OC_6H_4)_2Te_2$	PbTe	0.3	10.3	6.9	70
(4-$CH_3C_6H_4)_2Te$	I-Cu	0.7	10.1	10.9	70
(4-$CH_3OC_6H_4)_2Te$	PbTe	0.3	11.3	6.7	70
$(CH_3)_2TeCl_2$	SbCu	+0.272**	9.970	7.548	71
$(CH_3)_2TeBr_2$	SbCu	+0.241**	8.763	7.480	71
$(CH_3)_2TeI_2$	I-Cu	+0.55 ± 0.20	-	-	72
	SbCu	+0.248**	7.052	7.884	71
$(CH_3)_2TeI_4$	SbCu	+0.209**	7.078	6.966	71
$(C_6H_5)_2TeCl_2$	PbTe	0.5	9.2	6.6	70
$(C_6H_5)_2TeBr_2$	PbTe	0.5	8.1	7.4	70
$(C_6H_5)_2TeI_2$	I-Cu	0.7	5.9	6.3	70
(4-$CH_3C_6H_4)_2TeCl_2$	I-Cu	1.6	8.1	12.4	70
(4-$CH_3C_6H_4)_2TeI_2$	PbTe	0.6	6.3	6.5	70
(4-$C_2H_5OC_6H_4)_2TeCl_2$	PbTe	0.7	9.1	6.4	70

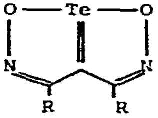
*The identity of this compound is uncertain. The melting point reported in ref. 70 does not agree with the one given in ref. 33.

** Shifts relative to Te matal.

tellurium compounds. Tellurium containing ions are easily identified through the characteristic pattern generated by the naturally occurring isotopes of tellurium. Such patterns for Te_n[76,79,80], Te_nSe_m[79,80], $TeCl_m$[76,81], Te_nBr_m[76,79] were published.

The mass spectral data reported for organic tellurium compounds during the survey period are summarized below. The spectra were obtained by electron impact at an energy of 70 eV unless otherwise stated. For singly charged ions the charge signs are omitted.

Only few detailed investigations of fragmentation pathways were carried out. Fragmentation schemes for diorganyl ditellurides[75a], methyl 2-carboxyphenyl telluride[75a], methyl 4-acetylphenyl telluride[75a], diphenyl tellurium dichloride[76], bis(4-methoxyphenyl) tellurium dichloride[76], diorganyl tellurium dicarboxylates[77] and the heterocyclic ring compounds[78] 32 (R = H, CH_3) are reported.



32

A detailed analysis of the mass spectra of the diorganyl tellurium dicarboxylat $R_2Te(O_2CR')_2$ (R = C_6H_5, 4-$CH_3C_6H_4$; R' = CH_3, C_6H_5), $C_6H_5(4\text{-}C_2H_5OC_6H_4)Te(O_2CCH_3)_2$ and trimethylene tellurium diacetate and dibenzoate[77] indicated that the ease of the cleavage of groups bonded to the tellurium atom decreases in the order acetate ∿ benzoate > $C_2H_5OC_6H_4$ ∿ $CH_3OC_6H_4$ > C_6H_5. The fragment ions $Ar_2Te(O_2CCH_3)$ lost ketene producing the ion Ar_2TeOH. There was no evidence that the entire acetate group was cleaved in a one step process. Fragments containing the benzoate group expelled carbon dioxide leaving the phenyl groups bonded to the tellurium atom.

$(CF_3)_2Te_2$[18]: base peak CF_3; relative abundances of ^{130}Te fragments: $C_2F_6Te_2$ (74%), CF_3Te_2 (66%), Te_2 (49%), CF_3Te (56%), CF_2Te (50%), CFTe (7%), FTe (16% Te (100%).

R_2Te_2 (R = C_6H_5, 4-$CH_3C_6H_4$), 1-$C_{10}H_7$, 2-$C_{10}H_7$)[75a]: R_2Te_2, R_2Te, RTe, R_2, R.

$(CH_3)_2Te$[74]: R_2Te (92%), RTeH (1.9%), RTe (100%), CH_2Te (19%), CHTe (23%), H_2Te (1%), HTe (20%), Te (44%), R_2Te^{++} (0.8%), RTe^{++} (0.2%), Te^{++} (1.2%); ratio of Te containing ions/CH only ions = 98.7/1.3.

CH_3-Te-CF_3[43]: CF_3-$TeCH_3$, CF_3Te, CH_3Te.

CF_3-Te-CF_3[18]: C_2F_6Te (90%), C_2F_5Te (20%), CF_3Te (100%), CF_2Te (60%), CFTe (11%), FTe (23%), Te (70%).

CF_3-Te-CF_3[43]: $(CF_3)_2{}^{130}Te$, CF_3Te.

CH_3-Te-C_2F_5[43]: $CH_3TeC_2F_5$, C_2F_5Te, CH_3Te.

$(C_2H_5)_2Te$ and $(\underline{i}\text{-}C_3H_7)_2Te$[75]: 30 eV, 12 eV spectra; $R_2Te^{\cdot+}$ fragments to $RTeH^{\cdot+}$ by olefin elimination; $RTe{=}CHR^+$ (R=H, CH_3) is not formed.

$(C_2F_5)_2Te$[43]: $(C_2F_5)_2Te$, C_2F_5Te.

(4-$CH_3C_6H_4)_2Te$[22]: R_2Te.

(2-$HO_2CC_6H_4)CH_3Te$[75a]: $R(CH_3)Te$, RTe, C_6H_4Te, C_6H_3COTe;

(4-$CH_3COC_6H_4)CH_3Te$[75a]: $R(CH_3)Te$, RTe, C_6H_3COTe, C_6H_4Te.

$[(C_6H_5)_2C{=}CH]_2TeCl_2$[22]: R_2TeCl, R_2Te

$(C_6H_5)_2TeCl_2$[76]: R_2TeCl, RTeCl, R_2Te, RTe, TeCl, Te, R_2, R, no R_2TeCl_2 ion.

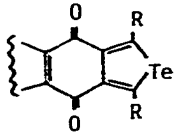
(4-$CH_3OC_6H_4)_2TeCl_2$[76]: R_2TeCl, RTeCl, R_2Te, RTe, TeCl, Te, C_6H_4OTe, C_5H_4Te, R_2, R, several other CH and CHO fragments; no R_2TeCl_2-ion.

(4-$CH_3OC_6H_4)_2TeCl_2$[22]: R_2TeCl, R_2Te;

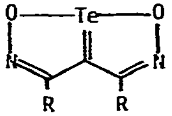
(4-$RC_6H_4)_2Te(O_2CR')_2$ (R = H, R' = CH_3, C_6H_5; R = CH_3O, R' = CH_3)[77]: no molecular ions; R_2TeX, $RTeX_2$, R_2Te, RTeX, RTe, TeX_2, TeX, R_2TeOH, RTeOH (X = acetate, benzoate).

$Te(O_2CR')_2$(R' = CH_3, C_6H_5)[77]: no molecular ion; R_2TeX, R_2Te, CH_2Te, Te, R_2TeOH (for R' = CH_3); R_2TeR' (R' = C_6H_5), C_6H_5Te (for R' = C_6H_5).

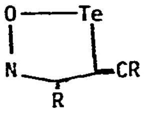
2-Tellura-A-nor-5α-androstan-17β-ol[16]: molecular ion (see section IX-A for structure



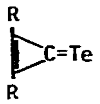
: (see section IX-G for complete formulas)[28,29]: molecular ions.



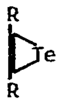
: (relative abundances of ^{130}Te fragments; R = H, CH$_3$; fragment formula, relative abundance R=H, relative abundance R=CH$_3$ given)[78]: molecular ion (95%, 100%);



(13%, 8%);

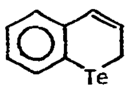


(100%, 97%);

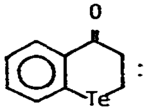


(26%, 13%);

RC≡CC≡Te (37%, 6%);

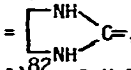
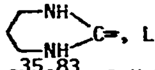


: (relative abundances of ^{130}Te fragments)[40]: molecular ion (25.9%), base peak at m/e 115; m/e 116 (92.4%).

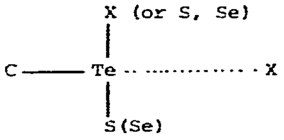


: (relative abundances of ^{135}Te fragments)[40]: molecular ion (74.4%), m/e 234 (100%), C$_6$H$_4$Te (62.8%).

G. X-Ray Structure Analyses

Space groups and unit cell dimensions were reported for the following compounds (L = , L' = , L" = [(CH$_3$)$_2$N]$_2$C=): 2-H(O)CC$_6$H$_4$TeX (X = Cl, Br, I)[82], C$_6$H$_5$TeCl·LS[35,83], C$_6$H$_5$TeCl·(LS)$_2$[35], C$_6$H$_5$TeCl·LSe[34], C$_6$H$_5$TeCl·L'S[35], C$_6$H$_5$TeCl·L"S[35], C$_6$H$_5$TeCl·L"Se[34], C$_6$H$_5$TeBr·LS[35,84], C$_6$H$_5$TeBr·LSe[34,83], C$_6$H$_5$TeBr·L'S[35], C$_6$H$_5$TeBr·L'Se[34], C$_6$H$_5$TeBr·L"S[35], C$_6$H$_5$TeBr·L"Se[34], C$_6$H$_5$TeI·LS[36], C$_6$H$_5$TeI·LSe[36], C$_6$H$_5$TeSCN·LS[35], [(CH$_3$)$_4$N]$^+$ [C$_6$H$_5$Te(YCN)$_2$]$^-$ (Y = S, Se)[85], dibenzotellurophene[19,86] and dibenzotellurophene 5,5-diiodide[19].

Singel crystal X-ray structural analyses of the compounds C$_6$H$_5$TeX·LS (X = Cl[83], Br[84], I[36]), C$_6$H$_5$TeX·LSe (X = Br[83], I[36]) and of [(CH$_3$)$_4$N]$^+$ [C$_6$H$_5$Te(YCN)$_2$]$^-$ (Y = S, Se)[85] produced the following bond lengths: Te-C, 2.100-2.124Å; Te-Cl, 2.848Å, Te-Br, 2.835-3.054Å; Te-I, 3.003-3.095Å, Te-S, 2.521-2.702Å; Te-Se, 2.616-2.823Å. The coordination of the tellurium atom in these compounds depicted in structure 33 can be described as approximately square planar with an almost linear arrangement of the X-Te-S(Se) group. The Te-C bond almost bisects the X-Te-S(Se) angle. The fourth position can be vacant as is the case in $C_6H_5Te(YCN)$ (Y = S, Se)[85], one crystalline form of $C_6H_5TeBr{\cdot}LS$ (space group C2/c)[84] and $C_6H_5TeI{\cdot}LS(Se)$[36] or is occupied by a halogen atom from another molecule.



33

The Te....X bond lengths[83] for X = Cl and Br are 3.740Å and 3.849Å, approximately 1Å longer than the corresponding Te-X bonds.

McCullough[86] found the dibenzotellurophene molecule to be slightly folded with dihedral angles of 1.4° and 0.6° between the five-membered and six-membered rings. The Te-C bond distances are 2.084 and 2.089Å and the C-Te-C bond angle is 81.7°.

H. Dipole Moment Measurements

The electric dipole moments of the diaryl ditellurides, $(RC_6H_4)_2Te_2$ (R = H, 4-F, 4-Br, 4-CH_3, 3-F) were measured in benzene solutions[87] at 25° and 45°. The following values were obtained (R, μ^{25}, μ^{45}): H, 1.26, 2.82; 4-Br, 0.89, 0.88; 4F, 1.05, 0.36; 4-CH_3, 2.16, 2.17; 3-F, 1.86, 0.66. These data indicate that the ditellurides with R = 4-Br and 4-CH_3 exhibit free rotation about the Te-Te bond at both temperatures. The other three compounds seem to have a more rigid conformation at 25° characterized by dihedral angles between the C-Te-Te planes of 89.7° (R = H), 47.7° (R = 4-F), and 89.7° (R = 3-F). No good explanation is available for the high dipole moment of diphenyl ditelluride at 45°.

Kataeva[88] determined experimentally and calculated with quantum mechanical methods the dipole moments of the tellurides 4-RC_6H_5-Te-C≡C-C_6H_5. The results indicated that all bonds in this molecule have multiple bond character and that the tellurium atom acted as π-electron donor to the carbon π-system.

Fringuelli[67] established by nmr methods (section X-C1) that the tellurium atom is the negative end of the dipole in tetrahydrotellurophene and tellurophene.

XI. Analytical Techniques

A gelatin reference material containing 25 trace elements among them tellurium in the μg/g range was developed[89].

The book "Analytical Chemistry of Selenium and Tellurium" by Nazarenko and Ermakov[11] has a small section devoted to the determination of selenium or tellurium in organic compounds and biological materials.

XII. Biology of Organic Tellurium Compounds

2-Tellura-A-nor-5α-androstan-17β-ol was tested for its androgenic activity[16].

Tellurium was found to be ineffective as a protective agent toward methyl mercury poisoning in the Japanese quail[90].

An attempt to synthesize ^{123m}Te-telluromethionine by growing baker's yeast in the presence of H_2TeO_3 was unsuccessful[91]. The telluromethionine was intended to be used as an agent for the diagnostic visualization of the pancreas by scintigraphy.

The reactions which occur in living organisms and lead to the formation of a carbon-tellurium bond were reviewed by Imura[10].

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