TELLURIUM
LITERATURE SURVEY COVERING THE YEAR 1976 *

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* Tellurium, Literature Survey covering the year 1975 see J. Organometal. Chem., 130 (1977) 411-479.

I. Introduction

This annual survey of the organic chemistry of tellurium covers the literature abstracted in Chemical Abstract Volume 84, No. 10 through Volume 86, No. 9. 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 papers are generally not cited; instead the reader is referred to previous surveys[1,2,3] which will provide access to the pertinent 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.

Ylides of Group V and VI Elements (D. Lloyd, 1975)[4]: A review of Se and Te ylides and a comparison of them with ylides of group V and other group VI elements.

Organic Derivatives of thio- (seleno-, telluro-)phosphoric acid (D. E. Ailman and R. J. Magee, 1976)[5]: A compilation of S-, Se-, and Te-phosphoric acids with synthetic information and physical data; three tellurophosphoric acids are listed on p. 801.

Tellurophene: A New Interesting Heteroaromatic Ring (G. Marino, 1975)[6]: A review of tellurophene research carried out at the Institute of Organic Chemistry at the University of Perugia; physical, spectroscopic and chemical properties of tellurophene are summarized and critically compared with those of furan, thiophene and selenophene.

Compounds with five-membered rings having one heteroatom from Group VI; Sulfur and Its Analogs (R. Livingstone, 1973)[7]: Review of synthetic information and physical data on group VI heterocycles including tellurophenes, hydrotellurophenes, benzotellurophenes and dibenzotellurophenes.

Recent Aspects of the Chemistry of Benzo[b]selenophene and Benzo[b]tellurophene (M. Renson, 1975)[8]: A review of the methods of preparation of these heterocycles and their electrophilic substitution and metalation reactions.

Stereochemistry of Tellurium (E. A. Meyers et al., 1975)[9]: The stereochemistry of inorganic and organic tellurium compounds is discussed in light of recent results of X-ray diffraction studies; VSEPR and three-center bonding theory is used in the interpretation of the structures.

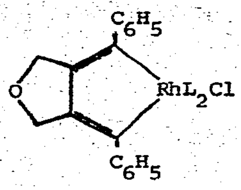
X-Ray Diffraction of Oxygen, Selenium and Tellurium Compounds (M. B. Hursthouse, 1975)[10]: A review of the molecular structures of inorganic and organic compounds published during the period 1973-1974.

Determination of Selenium and Tellurium in Organic Compounds and Organic Materials (M. R. Masson, 1976)[11]: A review of the various techniques (wet digestion, combustion, bomb fusion) for the decomposition of organic materials containing Se or Te and the various types of reactions which have been used to determine these elements after mineralization; instrumental methods are not discussed.

III. Methods for the Introduction of Tellurium into Organic Molecules

During the time covered by this survey tellurium, hydrogen telluride, sodium telluride and tellurium tetrachloride were employed as reagents to introduce tellurium into organic molecules. Most of these reactions are extensions or modification of previously reported preparative methods.

Tellurium powder heated at 450° in a sealed tube with 1,2-diiodotetrafluorobenzene yielded octafluorodibenzotellurophene[12]. Tellurium[13] refluxed in toluene with compound **1** produced the tellurophene derivative **2**.



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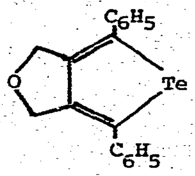

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Sodium telluride and phenylbutadiene in absolute methanol combined to form 2-phenyltellurophene[14]. Butadiene[15] and CH_3OD gave tellurophene-d_4. Hydrogen telluride[16] and $[(CH_3)_nH_{3-n}GeN]_2C$ yielded $[(CH_3)_nH_{3-n}Ge]_2Te$. The corresponding silicon compound did not react. Berry, Smith and Jones[17] reinvestigated the reaction between tellurium tetrachloride and acetic anhydride[1]. Gioaba[18,19] condensed 4-fluoro-, 4-chloro-, 4-bromo- and 4-iodo-diphenyl ethers with tellurium tetrachloride. The bromo- and iodo compounds did not produce the expected phenoxtellurines. Tellurium tetrachloride and 2-lithioheptafluorobiphenyl yielded bis(2-heptafluorobiphenylyl) telluride[12].

The reactions of organic tellurium compounds which were used to produce new organic tellurium derivatives are summarized in Fig. 1. All of these reactions are discussed in the sections devoted to the pertinent tellurium compounds. Reactions of heterocyclic tellurium compounds are not included in the figure.

IV. Tellurocyanates

Tetraethylammonium tellurocyanate, a very hygroscopic solid, which melts at 158-160° and blackens in air, was prepared from tellurium and tetraethylammonium cyanide in acetonitrile[20]. The electrochemical oxidation of the tellurocyanate ion in acetonitrile produced tellurocyanogen, $(TeCN)_2$, via the $(TeCN)_3^-$ ion as the intermediate. Tellurocyanogen decomposed to tellurium and cyanogen, $(CN)_2$, and formed upon electrochemical reduction tellurocyanate and cyanogen[20]. The instability of tellurocyanogen will make it difficult to use this compound as a reagent to introduce the TeCN-group into organic molecules.

V. Compounds Containing a Single Carbon-Tellurium Bond

During the survey period organyl tellurium halides and pseudohalides, RTeX, organyl tellurium trihalides, $RTeX_3$, organyltetrahalotellurates, $[RTeX_4]^-$, and diorganyl ditellurides received attention. No new results were reported for tellurols, RTeH, organyldihalotellurium compounds, $[RTeX_2]^+$ or $[RTeX_2]^-$, organyl tellurium pentahalides or tellurinic acids.

Tellurium derivatives, in which the second tellurium valence is satisfied by group I to V element atoms, sulfur or selenium are discussed in section VIII.

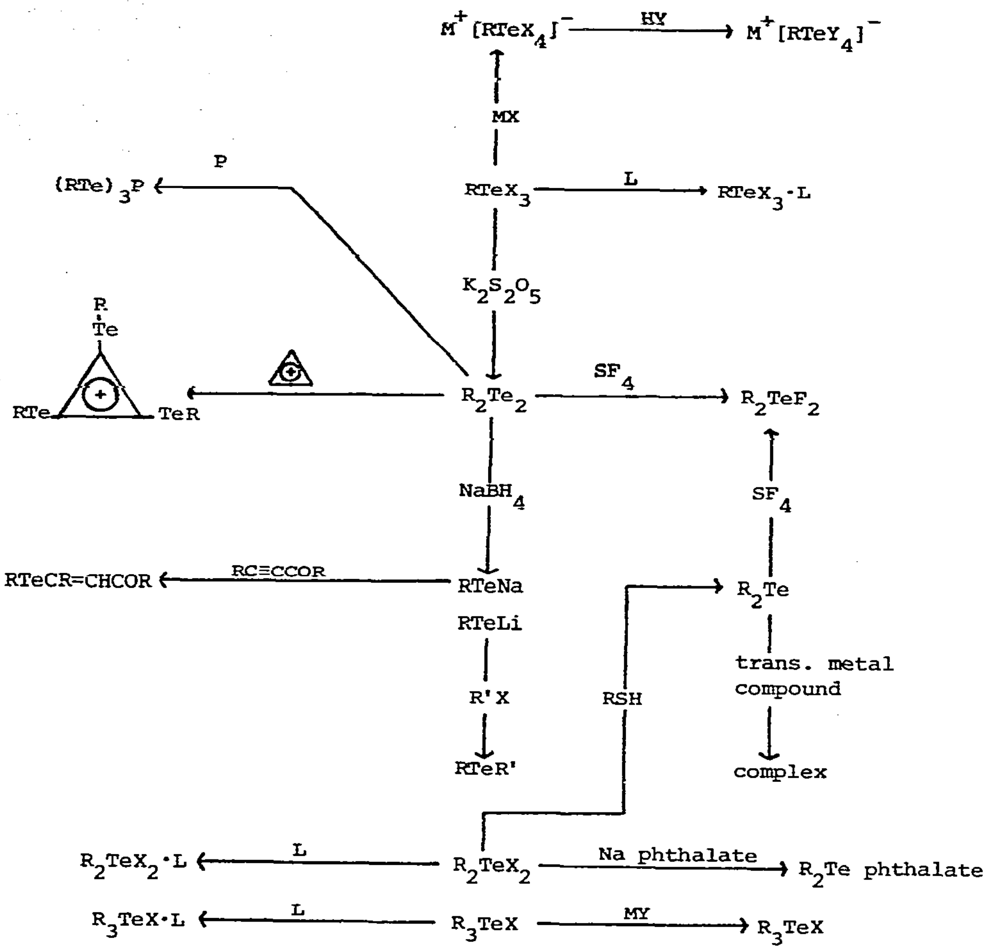
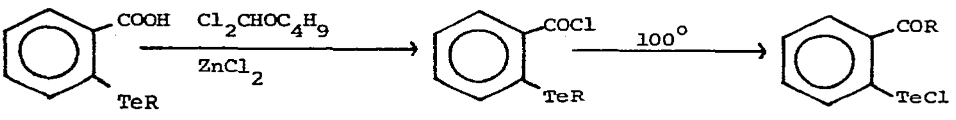


Fig. 1: Transformation of Organic Tellurium Compounds

A. Tellurenyl Compounds

When 2-carboxyphenyl aryl tellurides were treated with dichloromethyl butyl ether at 100° in the presence of zinc chloride 2-benzoylphenyl tellurium chlorides were isolated[21] (eqn. 1). The 2-chloroformylphenyl aryl telluride, expected in this reaction, was obtained only when the temperature was kept

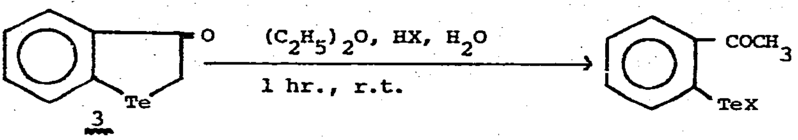
(1)



R = C_6H_5, 2,4,6-$(CH_3)_3C_6H_2$

at 50-60°. At 100° the chloride ion migrated to the tellurium atom with a concomitant shift of the aryl group R to the carbonyl carbon atom[21].

2-Acetylphenyl tellurium halides were isolated in 50% yield after an ether solution of 3-oxo-2,3-dihydrobenzotellurophene 3 had been treated with aqueous hydrohalic acids at room temperature for one hour[22] (eqn. 2).

(2) 

X, mp. °C: Cl, 120°; Br, 115° (ref. 2); I, 85°; CN 117°

The 2-acetylphenyl tellurium bromide reverted back to the heterocycle 3 upon treatment with ethanolic potassium hydroxide[22].

B. Organyl Tellurium Trihalides, $RTeX_3$

New organyl tellurium trihalides were not synthesized during the survey period.

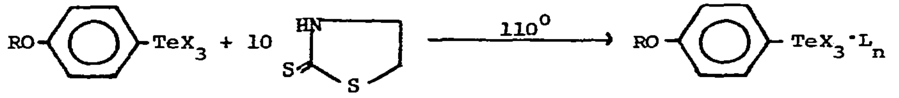
A reinvestigation of the reaction of tellurium tetrachloride with acetic anhydride in chloroform solution proved that the products, which precipitated during the reaction, are carboxymethyl tellurium trichloride and bis(trichlorotelluro)acetic anhydride. Methylene bis(tellurium trichloride) was obtained upon evaporation of the filtrate[17].

Conductance studies with 4-ethoxyphenyl tellurium trichloride in acetonitrile and cryoscopic molecular mass determinations in benzene suggested that the compound is present in solution mainly in molecular form. The conductivity increased with dilution. A molar conductance of 120-160 ohm^{-1} cm^{-2} mol^{-1} was found[23].

The complexes formed by phenyl tellurium halides, $(C_6H_5)_nTeX_{4-n}$ (X = Cl, Br, n = 1-3[24], n = 0-2[25]) with $AlBr_3$[24,25], $GaCl_3$[25], dialkyl sulfoxides[24,25] and diorganyl sulfides[25] were investigated by dipole moment, electric conductance, ^{35}Cl-nqr[25] and calorimetric methods[24,25]. The tellurium compounds formed 1:1 adducts with the compounds tested. The electron donating properties of the tellurium compounds increased, and the electron accepting properties decreased with an increasing number of phenyl groups bonded to the tellurium atom.

The aryl tellurium trihalides 4 produced yellow-orange complexes upon heating with thiazolidine-2-thione at 110° (eqn. 3). It was suggested on the basis of ir-spectral results that the nitrogen atom of the ligand serves as the electron-donor atom[26].

(3)



R, n, mp. °C (dec): CH_3, Br, 4, 128-32°; C_2H_5, Cl, 1, 114-6°;
C_6H_5, Cl, 2, 196-201°

The formation of aryltetrahalotellurates from organyl tellurium trihalides[27] is discussed in the next section.

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

Ammonium, arsonium, solfonium, selenonium and iodonium aryltetrahalotellurates(IV) were prepared[27] employing improved versions of earlier reported methods[2]. The addition of an equivalent amount of the onium halide dissolved in dry methanol or ethanol to the stirred solution of the aryl tellurium trihalide in the same solvent at room temperature precipitated the aryltetrahalotellurates (eqn. 4).

(4) $$RTeX_3 + [R'_nY]^+X^- \xrightarrow{ROH} [R'_nY]^+[RTeX_4]^-$$

Alternately, the aryl tellurium trihalides, $RTeX_3$, were dissolved in aqueous hydrochloric or hydrobromic acid and the onium halides added to this solution (eqn. 5).

(5) $$RTeX_3 + [R'_nY]^+X^- \xrightarrow{H_2O/HX} [R'_nY]^+[RTeX_4]^-$$

Halogen exchange reactions were carried out as described in eqn. 6.

(6) $$\begin{array}{lll} & \xrightarrow[10\%\ HBr/H_2O]{X\,=\,Cl} [R'_nY]^+[RTeBr_4]^- & (6a) \\ [R'_nY]^+[RTeX_4]^- & \xrightarrow[HCl\ conc.]{X\,=\,Br} [R'_nY]^+[RTeCl_4]^- & (6b) \\ & \xrightarrow[THF/10\%\ HI/H_2O]{X\,=\,Cl\ or\ Br} [R'_nY]^+[RTeI_4]^- & (6c) \end{array}$$

The compounds prepared according to these methods are summarized in Table 1.

The aryltetrachlorotellurates are colorless, and the bromo derivatives yellow. The phenyltetraiodotellurates are green, and the 4-ethoxyphenyltetraiodo compounds purple. All compounds behave as 1:1 electrolytes in nitromethane[27].

D. Diorganyl Ditellurides

New diorganyl ditellurides were not synthesized during the survey period.

The reduction of a mixture of $HOOCCH_2TeCl_3$ and $(Cl_3TeCH_2CO)_2O$ with aqueous $K_2S_2O_5$ produced bis(carboxymethyl) ditelluride[17] as reported earlier[1]. The reduction product of methylene bis(tellurium trichloride) formulated earlier as ditelluromethane[1] is according to mass spectral, nmr and Moessbauer spectral evidence 1,2,4,5-tetratelluracyclohexane[17].

A patent was issued for the preparation of bis(trifluoromethyl) ditelluride[3] from tellurium tetrahalides and CF_3-radicals in a low energy plasma[P-1].

The previously reported bis(2-acetylphenyl) ditelluride[2] has now been prepared by treatment of 3-oxo-2,3-dihydrobenzotellurophene with hypophosphorous acid[28] or with sodium hydrogen sulfite in refluxing ethanol[22]. The ditelluride (mp. 185°) was obtained in 80% yield[22].

The failure to isolate unsymmetric diorganyl ditellurides[2], R-TeTe-R', led to the investigation of the properties of mixtures of symmetric ditellurides, R_2Te_2. Mass spectral and nmr data gave evidence of redistribution of the R groups. Radical intermediates were not detected in these reactions[29].

Diaryl ditellurides reacted with sulfur tetrafluoride to produce diaryl tellurium difluorides[30]. Bis(4-methoxyphenyl) ditelluride and white phosphorus yielded tris(aryltelluro)phosphine[31].

Dimethyl ditelluride, but not diaryl ditellurides, reacted with trichloropropenium salts to give tris(methyltelluro)propenium compounds[32].

VI. Compounds Containing a Carbon-Tellurium-Carbon Moiety

Diorganyl tellurides, diorganyl tellurium dihalides and diorganyl tellurium dicarboxylates are discussed in this section. No reports about diorganyl tellurium dihalides of the type R_2TeXY, tetrahalides of the formula R_2TeX_4 or $R_2TeX_2Y_2$, compounds of the type $[R_2TeX]^+$ and $[R_2TeX_3]^-$, diorganyl telluroxides, R_2TeO, or diorganyl tellurones, R_2TeO_2, appeared during the survey period.

A. Diorganyl Tellurides

Several new diorganyl ditellurides were prepared. 4-Methoxyphenyl sodium telluride reacted with acetylenic oxo compounds in absolute ethanol. The nucleophilic addition of the RTe-anion across the triple bond produced aryl 1-phenyl-3-oxo-1-alkenes[33] (eqn. 7).

(7)

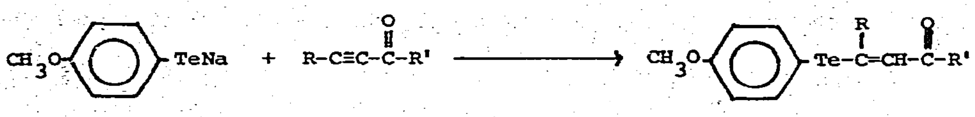


TABLE 1

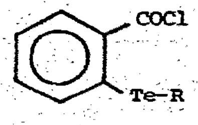
ORGANYTETRAHALOTELLURATES(IV)[27], $M^+[4\text{-}RC_6H_4TeX_4]^-$

R	X	M^+	Mode of Preparation eqn.	mp. °C
H	Cl	$(CH_3)_4N$	4	312°(dec)
		$(C_2H_5)_4N$	6b	176-8°
		$(C_6H_5)_4As$	4	217-9°
		$(C_6H_5)_3S$	5	165-6°
		$(C_6H_5)_3Se$	4	134-5°
		$(C_6H_5)_2I$	4	205°
	Br	$(CH_3)_4N$	6a	320°(dec)
		$(C_2H_5)_4N$	4	175-6°
		$(CH_3)_3C_6H_5N$	4	220-1°(dec)
		$(C_6H_5)_3S$	4	170-2°
		$(C_6H_5)_3Se$	6a	175°
		$(C_6H_5)_2I$	4	217-9°
	I	$(C_3H_7)_4N$	4	144-6°
		$(CH_3)_3S$	4	193-6°(dec)
C_2H_5O	Cl	$(CH_3)_4N$	4	224-7°
		$(C_2H_5)_4N$	6b	168-9°
		$(C_6H_5)_4As$	4	193-6°
		$(C_6H_5)_3S$	5	139-42°
		$(C_6H_5)_3Se$	4	158-9°
		$(C_6H_5)_2I$	4	157-8°
C_2H_5O	Br	$(CH_3)_4N$	6a	238-41°
		$(C_2H_5)_4N$	4	141°
		$(CH_3)_3C_6H_5N$	4	202-5°(dec)
		$(C_6H_5)_3S$	4	189-92°
		$(C_6H_5)_3Se$	6a	178-80°
		$(C_6H_5)_2I$	4	160-3°
	I	$(C_3H_7)_4N$	4	98-9°
		$(CH_3)_3S$	4	162-4°(dec)
		$(C_6H_5)_3Se$	6c	170-2°

R,R', mp. or bp. °C, yield %: C_6H_5, H, 83-4°, 71%; C_6H_5, C_4H_9, 79-80°, 68%; C_6H_5, C_6H_5, 151°, 74%; C_4H_9, CH_3, b_1 195-200°, 71%.

Tellurium tetrachloride mixed with 2-lithio-octafluorobiphenyl in diethyl ether at -78° produced a 32% yield of bis(2-octafluorobiphenylyl) telluride, which melted at 111-3° after purification by vacuum sublimation.[12]

The unsymmetric diorganyl tellurides 5 [R = C_6H_5, 2,4,6-$(CH_3)_3C_6H_2$] were obtained from the carboxy derivatives upon treatment with dichloromethyl butyl ether in the presence of zinc chloride at 50-60°. A chlorine-R group exchange occurred when the reactions were carried out at 100° forming 2-acylphenyl tellurium halides 6, which were converted to the aryl methyl tellurides 7 in reactions with dimethyl cadmium[21]. Data for these compounds were not reported.



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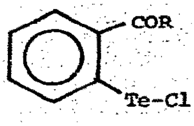

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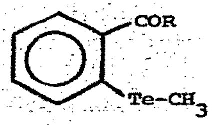

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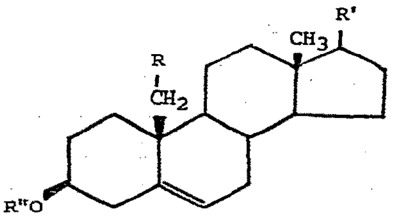
The telluride 8 (R = CH_3Te) was synthesized from the compound 8 (R = Br, 4-$CH_3C_6H_4SO_3$) and methyl lithium telluride in tetrahydrofuran medium[P-2]. These tellurides are claimed to be useful as X-ray contrast media.



R = Br, 4-$CH_3C_6H_4SO_3$

R' = C_8H_{17}, $C_{10}H_{21}$

R" = H, linoleoyl

8

A patent[P-1] was issued for the preparation of bis(trifluoromethyl) telluride from tellurium tetrahalides and CF_3-radicals. Details for this synthesis were published[3] previously.

Diaryl tellurides were obtained by reduction of diaryl tellurium dihalides with various dithiols, which were oxidized to disulfides[34] during the reaction.

The pyrolysis of dimethyl telluride at 350° under static conditions produced methane, carbon and tellurium via intramolecular disproportion of the methyl group with $(CH_2Te)_n$ as intermediates and via a radical decomposition mechanism which is more important at higher temperatures[35]. Results of vapor pressure measurements on dimethyl telluride by a static method with a membrane null-manometer indicated that $(CH_3)_2Te$ is the only species present in the gas phase. The following thermodynamic quantities for the evaporation process were found[36]: $\Delta H = 32.84 \pm 1.7$ kcal mol^{-1}; $\Delta S = 89.1 \pm 5.4$ cal mol^{-1} deg^{-1}. Quite different values were reported earlier[3].

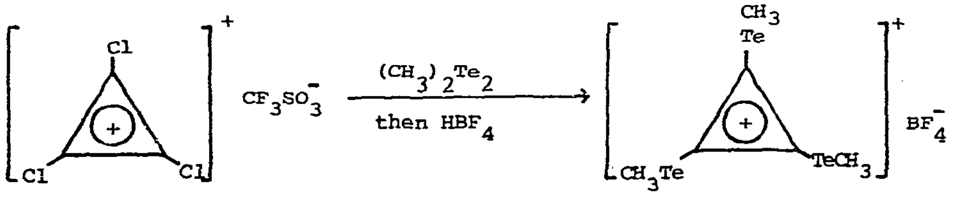
A nmr and CNDO study of the proton- and electron-donor capability in a hydrogen-bond shared with O, S, Se or Te compounds was carried out[37]. Details are not available. For earlier work on Te-hydrogen bonding consult pertinent sections in ref. 2 and 3.

Diaryl tellurides reacted with sulfur tetrafluoride[38] and $C_6T_5^+$ (from the β-decay of T in C_6T_6)[39] to form diaryl tellurium difluorides and $[(C_6H_5)_2C_6T_5Te]^+$, respectively.

The ligand exchange reactions of $(CH_3)_2Te\cdot TaX_5$ are discussed in section VIII.

The reaction of excess dimethyl ditelluride with trichlorocyclopropenium trifluoromethanesulfonate 9 in diethyl ether yielded the tris(methyltelluro)-cyclopropenium cation which was isolated in 40% yield as the tetrafluoroborate (eqn. 8). The colorless compound decomposed at 100° and developed an obnoxious odor when exposed to air[32]. The isolation of the compound $[(CH_3S)_3]^+SbCl_6^-$ from the mother liquor of the reaction of 9 with dimethyl disulfide suggests the following mechanism (eqn. 9).

(8)



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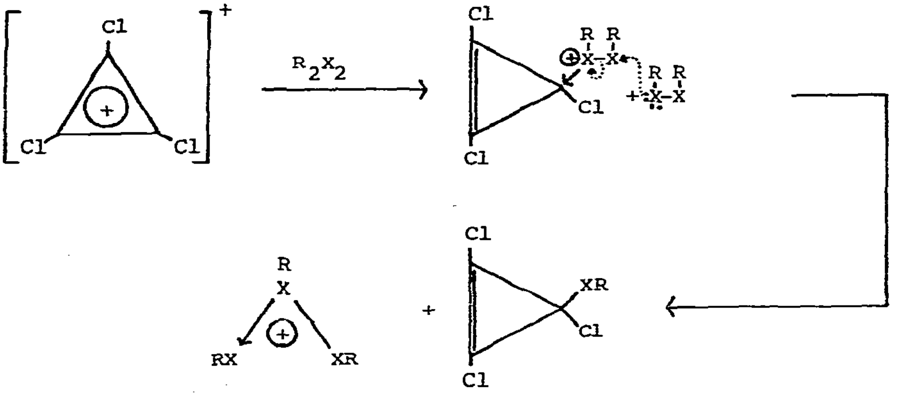

B. Diorganyl Tellurium Compounds, R_2TeX_2

Sadekov[38] prepared diphenyl tellurium difluoride (mp. 152°) and bis(4-methoxyphenyl) tellurium difluoride (mp. 131°) in yields ranging from 77-92% by passing sulfur tetrafluoride through refluxing benzene solutions of the diaryl tellurides or the diaryl ditellurides. These difluorides had been previously synthesized by a halogen exchange reaction employing silver fluoride[1,3].

Diaryl tellurium dicarboxylates 10 were formed in 50-85% yield when diaryl tellurium dichlorides in chloroform solution were shaken for 48 hours at room temperature with the freshly prepared sodium carboxylates[40] (eqn. 10). The reactions of the sodium carboxylates with diaryl tellurium dibromides proceeded only very slowly giving low yields. Pure products were not obtained from the reactions of the sodium salts of maleic, fumaric, formic, or iso- or terephthalic acid with diaryl tellurium dichlorides. Sodium sebacate gave a glassy material whose molecular mass suggested the compound to be a trimer in contrast to results of earlier experiments which had produced polymers (ref. 3, chapter XIII).

The products obtained in these reactions with the sodium salts of carboxylic acids seem to differ from those formed when the silver salts were employed[34].

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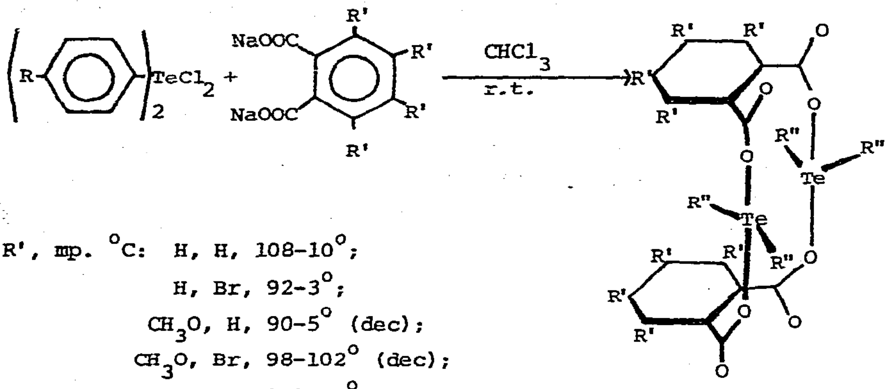


R,R', mp. °C: H, H, 108-10°;
H, Br, 92-3°;
CH_3O, H, 90-5° (dec);
CH_3O, Br, 98-102° (dec);
C_2H_5O, H, 129-31°.

R" = 4-$C_2H_5OC_6H_4$

10

The ^{1}H-nmr spectrum of the bis(4-ethoxyphenyl) tellurium phthalate contained two triplets of equal intensity for the methyl resonances. Only one methylene quartet was observed. It was suggested[40] that "the steric cone swept out by the large CH_3CH_2O-group brings the CH_3 protons sufficiently close to the aromatic ring of the phthalate for the chemical shift to be marginally affected." The observation of two methyl resonances is consistent with structure 10. Infrared data indicate that all four carboxylate groups are in similar environments within the dimeric molecule[40] and thus support structure 10.

Cryoscopic molecular mass determinations in benzene and conductivity measurements in acetonitrile showed that bis(4-methoxyphenyl) tellurium dichloride is not appreciably dissociated in solution. A conductance of 120-160 ohm^{-1} cm^{-2} mol^{-1} was found for 0.001M solutions. The conductivity increased with dilution[23].

Diphenyl tellurium dihalides, $(C_6H_5)_2TeX_2$ (X = Cl, Br) formed 1:1 complexes with $AlBr_3$[24,25], $GaCl_3$[25], dialkyl sulfoxides[24,25] and dialkyl sulfides[25]. The enthalpy of formation of $(C_6H_5)_2TeCl\cdot(C_6H_{13})_2SO$ in benzene solution[24] was found to be -1.0 kcal mol^{-1}.

Bis(benzoylmethyl) tellurium dichloride is claimed to be a thermal development type photographic material which releases tellurium on heating after exposure to light to form a black image[P-3], and has been shown to be an efficient photoinitiator for free radical polymerization of methyl methacrylate under conditions which rigorously exclude ionic processes[42]. Mechanistic schemes were developed for the thermolysis and photolysis of bis(benzoylmethyl) tellurium dichloride. Radical scission to $RTeCl_2\cdot$ appears to be an essential step in the extrusion sequence[41]. The photochemical reaction (at 313 nm) is initiated by formation of the ${}^3\pi, \pi^*$ state. Tellurium, chloroacetophenone and acetophenone are formed in concerted steps. Phenacyl radicals, which are produced by tellurium-carbon bond cleavage, abstract hydrogen from good hydrogen-donor solvents to give acetophenone. In inert solvents the radicals abstract hydrogen and chlorine from bis(benzoylmethyl) tellurium dichloride and combine to form 1,2-dibenzoylethane. Tellurium may be produced by disproportionation of $TeCl_2$ or directly in concerted photochemical steps.[43]

Diaryl tellurium dihalides reacted with dithiols to produce diaryl tellurides and disulfides and not $R_2Te{<}^{S}_{S}]$compounds[34].

The reaction of diaryl tellurium dibromides with 1,1-dimethyl-3,5-cyclohexanedione to yield ylides[44] is discussed in section VII.

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

Anion exchange reactions using triphenyl telluronium chloride as starting material produced several new triphenyl telluronium pseudohalides[45] (eqn. 11).

$$[(C_6H_5)_3Te]^+Cl^- \xrightarrow[-MCl]{+MY} [(C_6H_5)_3Te]^+Y^- \tag{11}$$

MY, yield %, mp. °C: NaN_3, 75-85%, 156°; CN-resin, 85% 183-4° (dec); AgOCN, 90%; 151-2°; NaCNS, 90%, 165-6°; KCNSe, 90-95%, 165°.

The telluronium cyanide was obtained by loading the telluronium chloride on a Baker CGA-541 resin in the cyanide form and eluting with ethanol. The other reactions were carried out in aqueous medium or in the case of the azide in a water/$CHCl_3$ system. Upon recrystallization of the cyanate from chloroform the compound $[(C_6H_5)_3Te]CNO\cdot0.5CHCl_3$ was obtained, which melted at 140° with decomposition.

Infrared data indicate that triphenyl telluronium bromide was formed when the azide or cyanate was mixed with potassium bromide and pressed into a pellet.

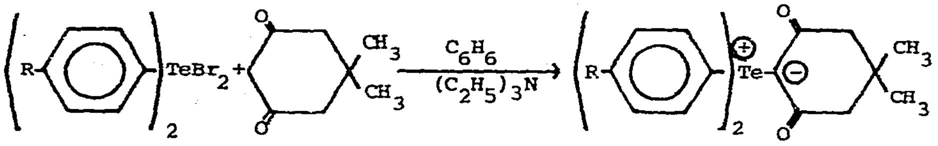
The azide did not detonate when heated or exposed to mechanical shock or light. Results of differential thermal and thermogravimetric analyses suggest that these telluronium salts decompose to diphenyl telluride and phenyl pseudohalides. Tellurium was not formed in these decomposition reactions[45].

The diphenyl pentatritiophenyl telluronium cation was produced from diphenyl telluride and $C_6T_5^+$ ions formed by β-decay of T in C_6T_6[39].

Gol'dshtein and coworkers[24] claimed to have prepared 1:1 adducts between triphenyl telluronium chloride and bromide and $AlBr_3$ or dihexyl sulfoxide.

Refluxing diaryl tellurium dibromides and 1,1-dimethyl-3,5-dioxocyclohexane in benzene in the presence of triethylamine yielded the ylides 11 (eqn. 12) as colorless needles[44].

(12)



11

R, mp. °C, yield %: H, 156-7°, 100%; CH_3, 136-7°, 75%; CH_3O, 143-4°, 88%.

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

During the period covered by this survey new organic tellurium compounds containing a tellurium-lithium, -sodium, -aluminum, -gallium, or -germanium bond have been synthesized.

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

Methyl lithium telluride, whose preparation was not reported in the abstract[P-2], was reacted with the organyl bromide or 4-methylbenzenesulfonate 8 (section VI-A) to yield the methyl organyl telluride 8 (R = CH_3Te). 4-Methoxyphenyl sodium telluride, synthesized by reduction of the diaryl ditelluride with sodium borohydride in absolute ethanol (for an earlier preparation see ref. 2), added across the triple bond in acylacetylenes to produce aryl acylalkenyl tellurides (see section VI-A).

Aluminum tribromide and gallium trichloride (in benzene solution) formed

1:1 adducts with phenyl tellurium halides, $(C_6H_5)_nTeX_{4-n}$ (X = Cl, Br; n = 1, 2, 3). The tellurium atom serves in these complexes as electron pair donor[24,25]. The enthalpies of formation of the aluminum bromide adducts were -41.0 kcal mol^{-1} $[C_6H_5TeCl_3]$, -43.8 kcal mol^{-1} $[(C_6H_5)_2TeCl_2]$ and -25.3 kcal mol^{-1} $[(C_6H_5)_2TeBr_2]$[24].

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

New germyl tellurides were obtained from digermylcarbodiimides and hydrogen telluride (eqn. 13). The reagents were mixed at -196°.

$$(CH_3)_nH_{3-n}Ge\text{-}N{=}C{=}N\text{-}GeH_{3-n}(CH_3)_n \xrightarrow{H_2Te} [(CH_3)_nH_{3-n}Ge]_2Te + H_2NCN \qquad (13)$$

n, yield %: 1, 62%; 2, 79%; 3, 89%.

The mixture was then allowed to warm to room temperature. After one hour the liquid germyl tellurides were isolated by vacuum fractionation. When the germyl tellurides were treated at room temperature with excess hydrogen telluride the tellurols, $(CH_3)_nH_{3-n}Ge\text{-}TeH$, were formed. Gaseous hydrogen iodide cleaved the Ge-Te bond producing germyl iodides and hydrogen telluride[16].

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

White phosphorus reacted with bis(4-methoxyphenyl) ditelluride in acetone solution in the presence of potassium hydroxide[31]. The new compound, tris(4-methylphenyltelluro)phosphite, was obtained (36% yield) as shiny, rusty-brown crystals, which decomposed rapidly at room temperature. The compound was stable for several months in acetone solution at -20°.

Tellurium and tris(tert-butyl)phosphine produced the phosphine telluride $(tert\text{-}C_4H_9)_3P{=}Te$. In mixtures made from $(tert\text{-}C_4H_9)_3P{=}Te$ and $[(CH_3)_2N]_3P$ tellurium was transferred from the trialkyl- to the aminophosphine. When phosphine telluride was treated with an equimolar amount of the phosphine, the compound $(R_3P)_2Te$ [R = $tert\text{-}C_4H_9$, $(CH_3)_2N$] was present in solution according to ^{31}P-nmr data[46].

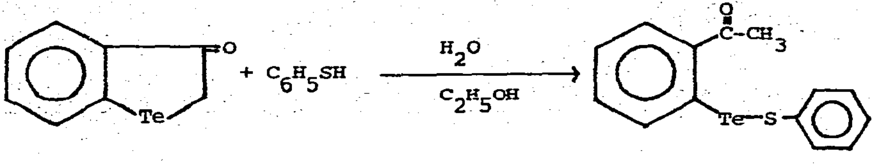
D. Organic Compounds of Tellurium with a Tellurium-Sulfur Bond

The sulfide telluride **12** melting at 105° was obtained by stirring benzenethiol and 3-oxo-1,2-dihydrobenzotellurophene in aqueous ethanol at room temperature for one hour[22] (eqn. 14).

E. Organic Tellurium Compounds as Ligands in Transition Metal Complexes

The hitherto unreported complexes $[(C_2H_5)_2Te]_2MX_2$ (M = Pd, Pt; X = Br, I)[48] were prepared according to literature procedures[1]. The complexes had the following melting points (M, X, color, mp. °C): Pt, Cl, brown-yellow, 126-9°; Pt, Br, brown-yellow, 127-8°; Pt, I, maroon, 87-9°; Pd, Cl, maroon, 97-9°; Pd, Br, maroon, 110-2°; Pd, I, black, 87-9°. The complexes $PdCl_2 \cdot L_2$, $PtCl_2 \cdot L_2$ and $PtBr_2L_2$ [L = $(C_2H_5)_2Te$] were isolated as the cis-isomers. However, all six complexes were present in the trans-configuration in benzene solution according to dipole moment, ^1H-nmr, Raman and ir data. The report by Jensen [Z. Anorg. Allg. Chem. 231, 365 (1937)] that the complex $\{PtCl_2 \cdot [(C_2H_5)_2Te]_2\}$ has cis-geometry is probably incorrect.

(14)



12

Variable temperature nmr spectra showed that ligand exchange in the systems $(C_2H_5)_2Te/PtI_2 \cdot [(C_2H_5)_2Te]_2$ or $PdBr_2 \cdot [(C_2H_5)_2Te]_2$ is fast[49].

The ligand exchange reactions in methylene chloride containing dimethyl telluride and the complex $TaX_5 \cdot Te(CH_3)_2$ (X = Cl, Br) is second order and proceeds via an associative mechanism[47]. Thermodynamic quantities for these reactions were determined.

IX. Heterocyclic Tellurium Compounds

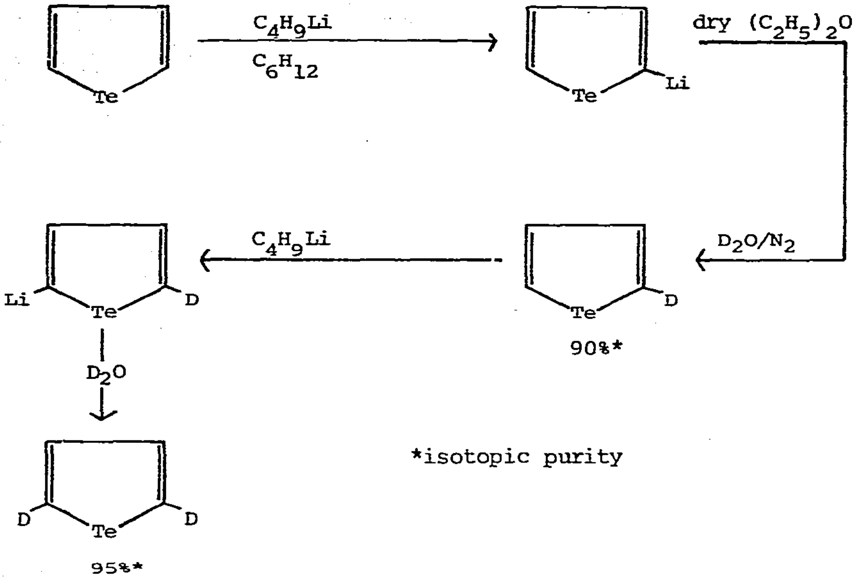
A number of new heterocyclic tellurium compounds were prepared. These include deuterated tellurophenes, 3,4-substituted 2,5-diphenyltellurophenes, 2,3-dihydrobenzotellurophenes, telluroindigo, benzotellurophenes, octafluorodibenzotellurophene, 1-telluracyclohexa-3,5-dienes and phenoxtellurines.

A. Tellurophene

Deuterated tellurophenes[15] were prepared by H-D or D-H exchange via lithiotellurophenes as outlined by eqn. 15 and 16. All the tellurophenes boiled between 90° and 92° at 100 torr. They were purified by treatment with bromine in chloroform followed by reduction of the tellurophene dibromides with zinc powder in glacial acetic acid.

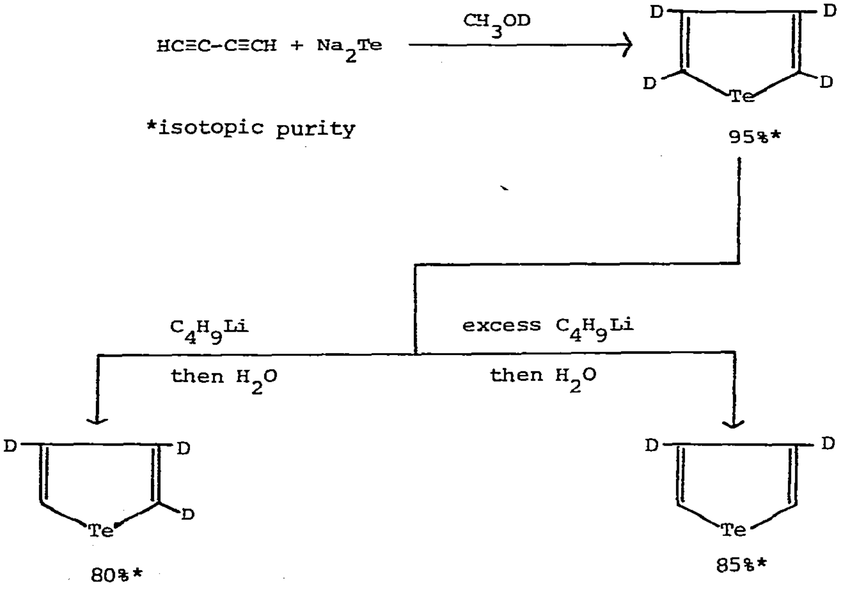
2- Phenyltellurophene, its 5-deuterio and trideuterio derivatives were prepared according to eqn. 17.

(15)



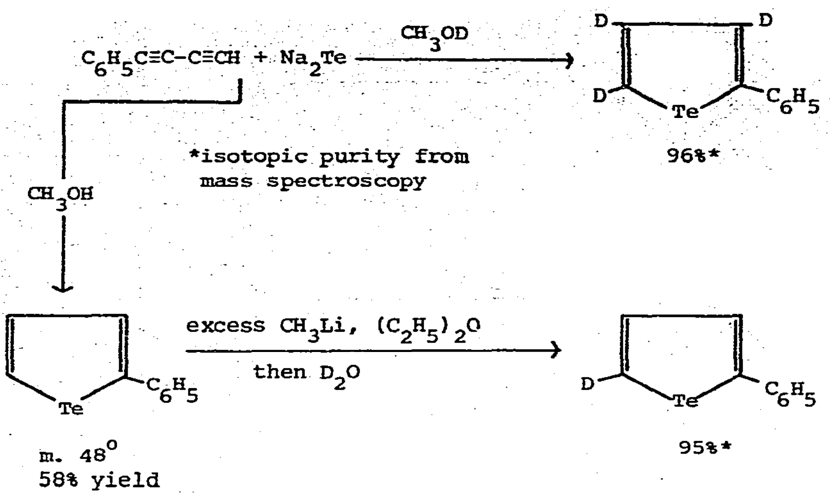
*isotopic purity

(16)



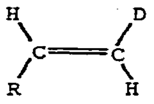
*isotopic purity

(17)



During the chromatographic purification of the trideuteriotellurophene on activated alumina some H-D exchange occurred at the 5-position. The H-hydrogen was supplied by moisture on the alumina[14]. The eluted tellurophene was treated with methyl lithium and then with D_2O. The final product had an isotope purity of 96%.

Irradiation of diethyl ether solutions of these 2-phenyltellurophenes with a 300 nm lamp through Pyrex for at least ten hours produced tellurium and phenyl(vinyl)acetylenes (equal amounts of 13 and 14 from 2-phenyl-5-deuteriotellurophene, and 15 and 16 from 2-phenyl-trideuteriotellurophene).



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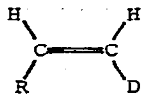
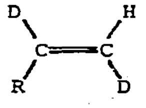


14



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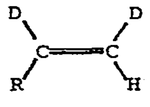


16

Experiments with the deuterium-labeled tellurophenes revealed that the phenyl(vinyl)acetylenes did not form via a unimolecular reaction but involved hydrogen abstraction from the solvent[14]. The results were interpreted within an extension of van Tamelen's general mechanism for the photochemistry of aromatic heterocyclopentadienes.

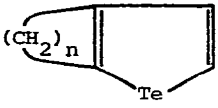
The reactions of 2,5-diphenyltellurophene[50] leading to new 3,4-disubstituted derivatives are summarized in eqn. 18. The 3,4-bis(chloromethyl)-2,5-diphenyltellurophene 17 was obtained when hydrogen chloride was passed through a solution of formaldehyde and diphenyltellurophene in glacial acetic acid for

15 hours. When hydrogen bromide was used, the tellurophene decomposed. The reactive chloromethyl groups allowed the preparation of other 3,4-disubstituted tellurophene derivatives. The pyridinium salt 18 and 4-nitrosodimethylaniline gave an impure product which could not be hydrolyzed to the dialdehyde. The dialdehyde 19 was, however, obtained through oxidation of the hydroxymethyl derivative 20 with selenium dioxide at 200° under a nitrogen atmosphere. Activated manganese dioxide gave only a 1% yield. Silver carbonate, lead tetraacetate or chromium trioxide did not produce the dialdehyde.

Most of these compounds were purified by chromatography on Silica Gel with benzene or benzene/acetone[50].

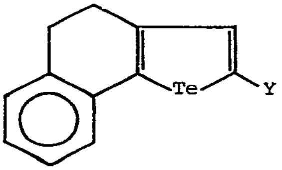
B. Cyclo(polymethylene)tellurophenes

An extension of the previously reported[3] base-catalyzed condensation of aldehydes of the type RCCl=CR'CHO with sodium telluride in dimethylformamide and compounds XCHR"R"' (X = Cl, Br, R" = H, CH_3, R"' = $COOC_2H_5$) produced the derivatives 21 and 22[51].



n = 4,5

21



Y = $COOC_2H_5$, COOH, H

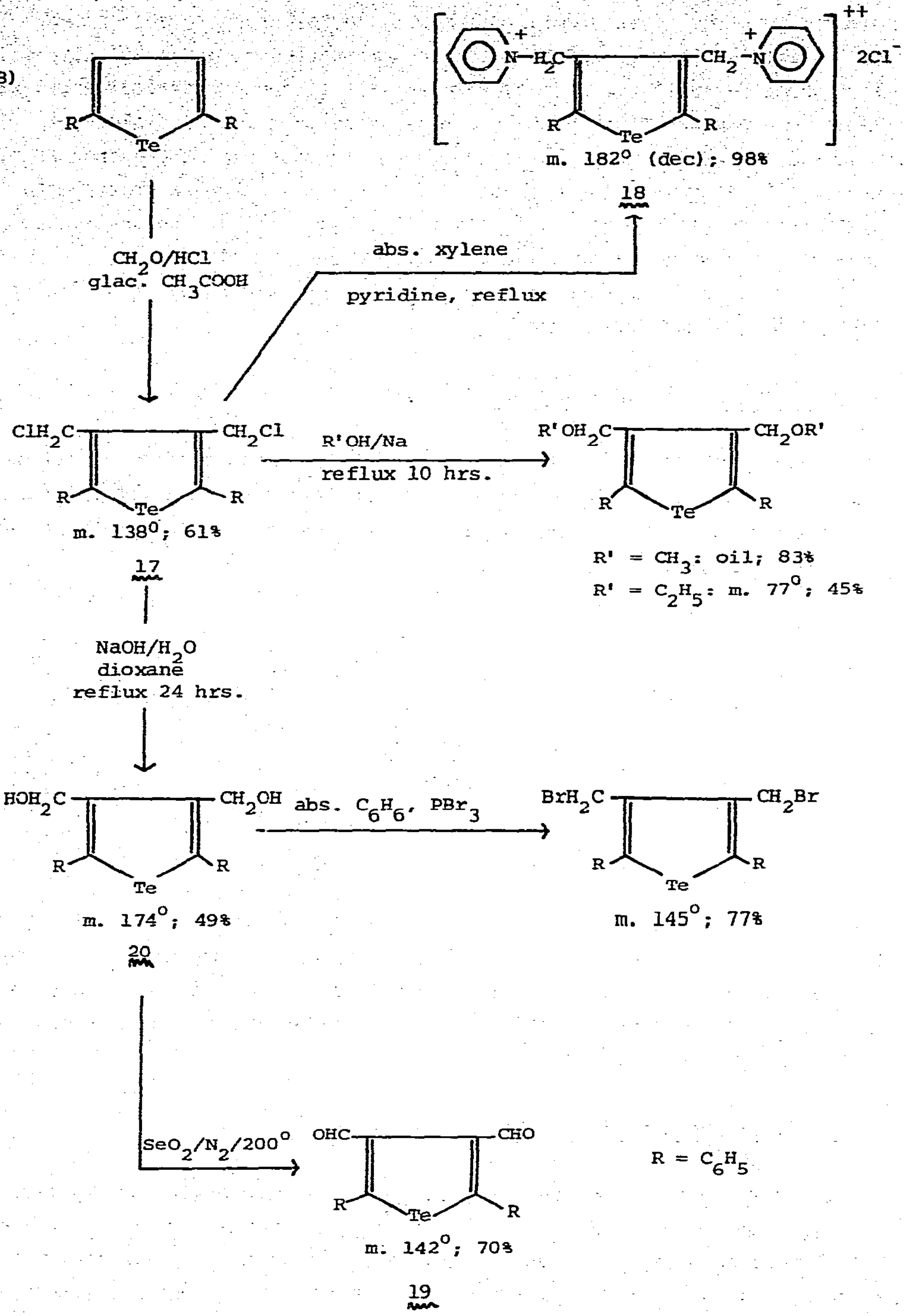
22

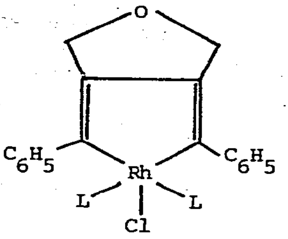
Refluxing the rhodium-heterocyclic compounds 23 in toluene with tellurium under nitrogen for forty hours produced the tellurophene derivative 24 (m. 145-6°) in 14% yield based on the bis(3-phenyl-2-propinyl) ether, from which the rhodium compound 23 had been prepared[13]. For other tellurophene compounds obtained by this method see ref. 3.

C. 2,3-Dihydrobenzotellurophene

3-Oxo-2,3-dihydrobenzotellurophene 25 (telluroindoxyl) was prepared by treating an ethanolic solution of 2-acetylphenyl tellurium bromide with a stoichiometric amount of ethanolic potassium hydroxide[22]. This new compound was converted to the 2-acetylphenyl tellurium halides by aqueous solutions of HX (X = Cl, Br, I, CN, C_6H_5S). The 2-hydroxybenzotellurophene does not seem to be present in basic solutions of the oxo-compound. Methylating agents [CH_3I, $(CH_3)_2SO_4$] did not yield 3-methoxybenzotellurophene in a basic reaction medium. With methyl iodide in chloroform the telluronium salt 26 was formed.

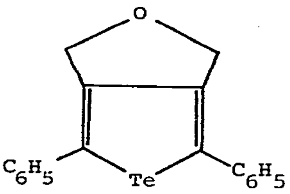
(18)


R
Te
R
CH2O/HCl
glac. CH3COOH
abs. xylene
pyridine, reflux
N
H2C
CH2
N
R
Te
R
2Cl⁻
++
m. 182° (dec); 98%
18
ClH2C
CH2Cl
R
Te
R
m. 138°; 61%
17
R'OH/Na
reflux 10 hrs.
R'OH2C
CH2OR'
R
Te
R
R' = CH3: oil; 83%
R' = C2H5: m. 77°; 45%
NaOH/H2O
dioxane
reflux 24 hrs.
HOH2C
CH2OH
R
Te
R
m. 174°; 49%
20
abs. C6H6, PBr3
BrH2C
CH2Br
R
Te
R
m. 145°; 77%
SeO2/N2/200°
OHC
CHO
R
Te
R
m. 142°; 70%
19
R = C6H5



L = $(C_6H_5)_3P$

23



24

The 3-oxo-2,3-dihydrobenzotellurophene was converted to the tellurium dihalides. It formed hydrazones and an oxime. Phenylhydrazine in acetic acid, however, produced the benzotellurophene derivative 27.

The methylene group condensed with aldehydes, acetals and 4-nitrosodimethylaniline. Treatment of telluroindoxyl with sodium hydrogen sulfite[22] or hypophosphorous acid[28] yielded bis(2-acetylphenyl) ditelluride. Reduction with sodium borohydride in ethanol gave benzotellurophene.

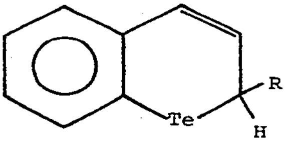
Telluroindigo 28, which is violet in solution, is obtained by refluxing the telluroindoxyl for 48 hours in dimethylformamide.

These reactions are summarized in eqn. 19.

D. Benzotellurophene

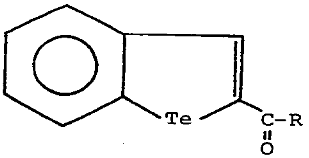
Benzotellurophene was obtained in 20% yield boiling at 115° (0.6 torr) by reducing 3-oxo-2,3-dihydrobenzotellurophene with sodium borohydride in ethanol[22]. Treatment of the dihydrobenzotellurophene with phenylhydrazine in glacial acetic acid produced[22] the benzotellurophene derivative 27 melting at 170° (section IX-C, eqn. 19).

Oxidation of compounds 29 with selenium dioxide or chromium trioxide gave 2-acylbenzotellurophenes 30.



R = H, CH_3

29

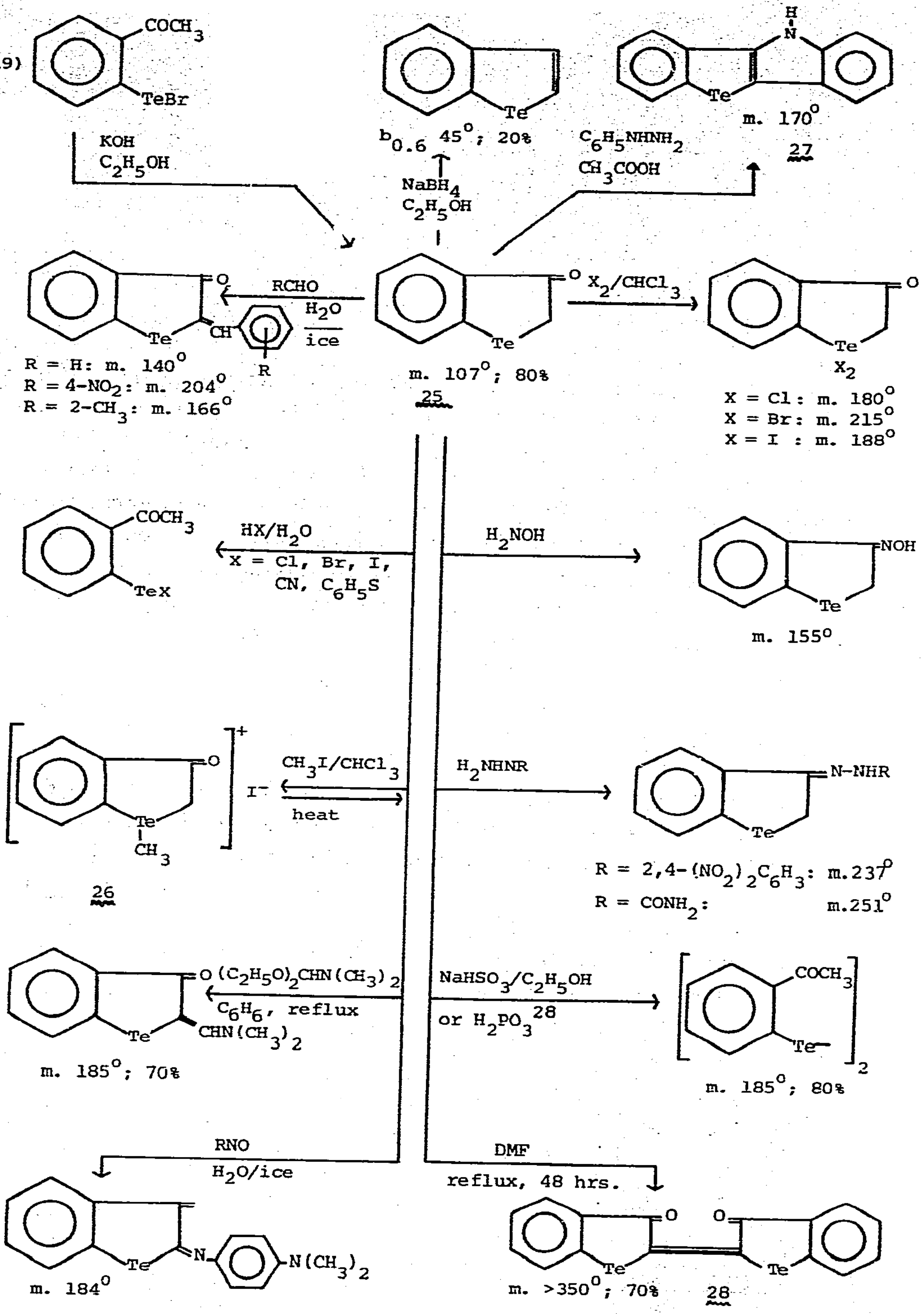


30

E. Dibenzotellurophene

Octafluorodibenzotellurophene melting at 115-6° was obtained in 17% yield when tellurium powder was heated with 1,2-diiodotetrafluorobenzene in

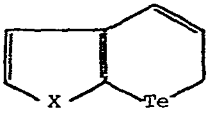
(19)


COCH3
TeBr
KOH
C2H5OH
Te
b0.6 45°; 20%
NaBH4
C2H5OH
H
N
Te
m. 170°
27
C6H5NHNH2
CH3COOH
O
Te
CH
R
R = H: m. 140°
R = 4-NO2: m. 204°
R = 2-CH3: m. 166°
RCHO
H2O
ice
O
Te
m. 107°; 80%
25
X2/CHCl3
O
Te
X2
X = Cl: m. 180°
X = Br: m. 215°
X = I : m. 188°
COCH3
TeX
HX/H2O
X = Cl, Br, I, CN, C6H5S
H2NOH
NOH
Te
m. 155°
O
Te
CH3
+
I⁻
26
CH3I/CHCl3
heat
H2NHNR
N-NHR
Te
R = 2,4-(NO2)2C6H3: m.237°
R = CONH2: m.251°
O
Te
CHN(CH3)2
m. 185°; 70%
(C2H5O)2CHN(CH3)2
C6H6, reflux
NaHSO3/C2H5OH
or H2PO3 28
COCH3
Te
2
m. 185°; 80%
RNO
H2O/ice
Te
N
N(CH3)2
m. 184°
DMF
reflux, 48 hrs.
O
O
Te
Te
m. >350°; 70%
28

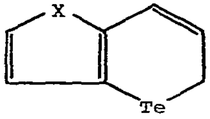
a sealed tube at 450° for three days[12].

F. 1-Telluracyclohexa-3,5-diene

The oxidation of compounds 29 (section IX-D) with selenium dioxide or chromium trioxide yielded 2-acylbenzotellurophenes[52]. Compound 31 and 32 are reported to produce upon treatment with SeO_2 or CrO_3 a variety of products[52].



31



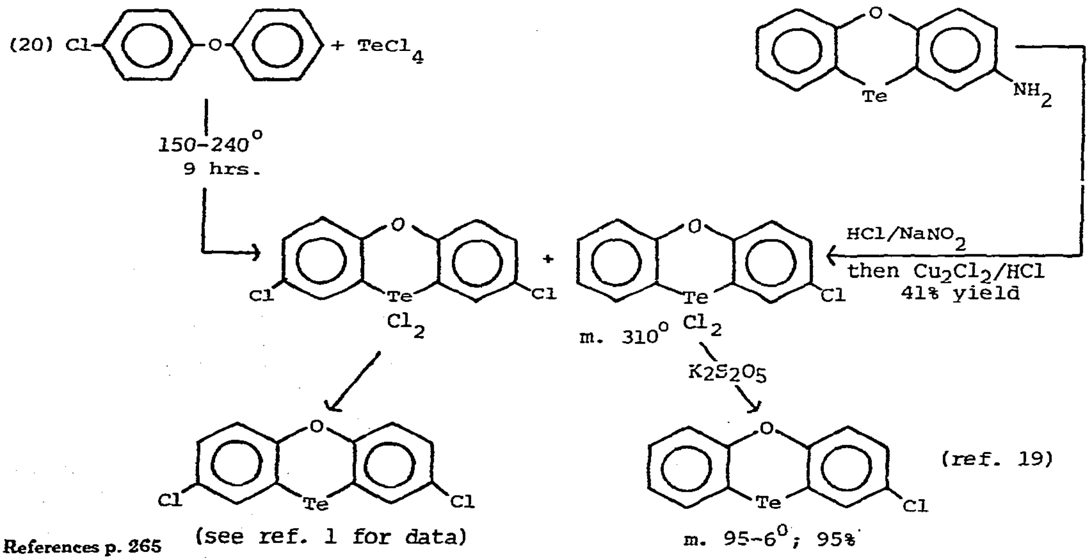
32

G. 1,2,4,5-Tetratelluracyclohexane

The reduction of methylene bis(tellurium trichloride) by cold aqueous potassium disulfite yielded a compound melting over the range 54-102°. Mass spectral, nmr and Moessbauer spectral data indicate that this compound is 1,2,4,5-tetratelluracyclohexane[17].

H. Phenoxtellurine

Gioaba and co-workers[18,19] prepared several new phenoxtellurine derivatives by heating tellurium tetrachloride with *para*-substituted diphenyl ethers. The successful reactions are summarized in eqn. 20-22.



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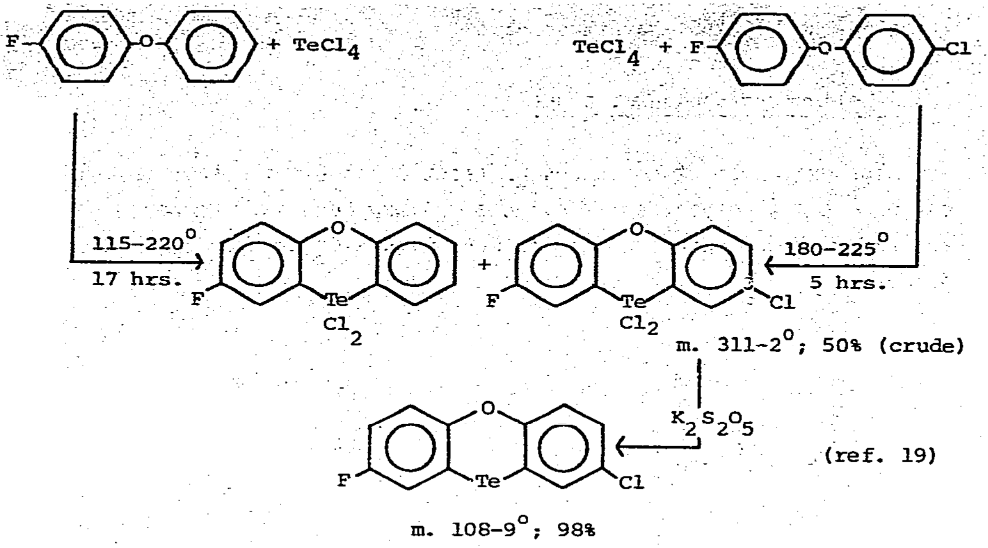

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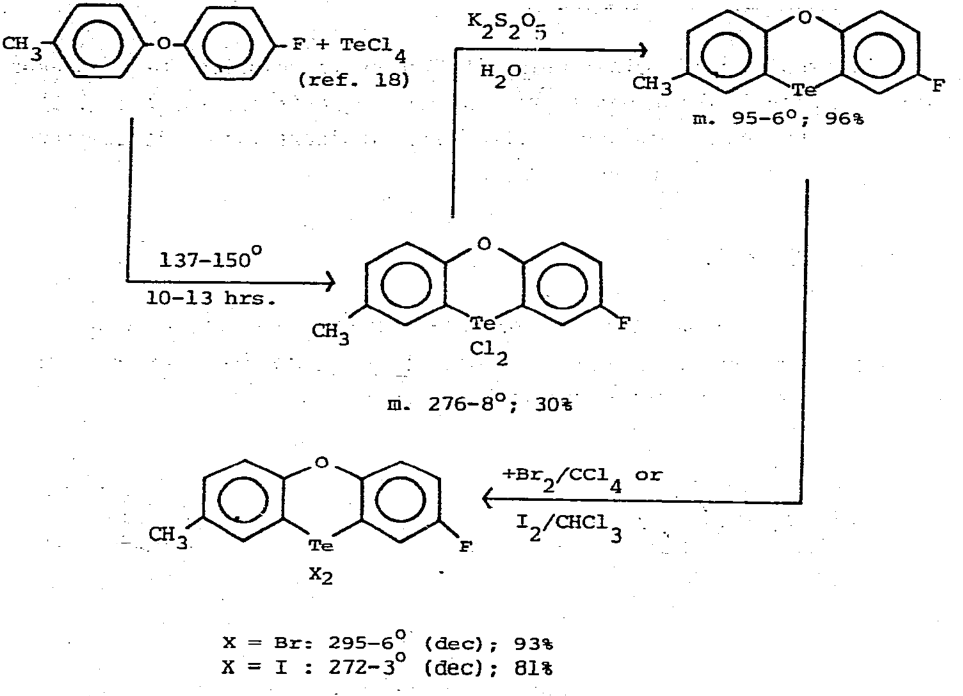


2-Chlorophenoxtellurine 10,10-dichloride was also obtained when the 2-aminophenoxtellurine was diazotized and the diazonium salt reacted with copper(I) chloride/hydrochloric acid[19].

Tellurium tetrachloride and 4-bromo-[19], 4-iodo-[19], 4-chloro-4'-bromo-[18], and 4-chloro-4'-nitrodiphenyl[18] ethers produced either mixtures of phenoxtellurine derivatives, which could not be satisfactorily separated, or no definite compounds at all.

The tellurium atom was replaced by a sulfur atom when the phenoxtellurines[18,19] were heated with molten sulfur. Phenoxtellurine dichlorides heated with degassed Raney Nickel in the presence of copper produced dibenzofurans[53]. 2-Fluoro-8-methylphenoxtellurine produced a purple color in concentrated sulfuric acid[18].

X. Physicochemical Investigations of Organic Tellurium Compounds

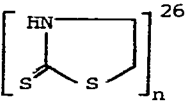
Infrared, Raman, ultraviolet-visible, ^{1}H-, ^{13}C-, ^{31}P-, ^{125}Te-nuclear magnetic resonance, ^{35}Cl-, ^{79}Br-, ^{127}I-nuclear quadruple resonance, electron, ^{125}Te-Moessbauer spectroscopy, mass spectrometry, X-ray structure analysis and dipole moment measurements were used to characterize organic tellurium compounds.

A. Infrared and Raman Spectroscopy

The infrared (ir) and Raman (R) spectral data for organic tellurium compounds reported during the survey period are summarized below. Frequencies are listed only for modes involving the tellurium atom. Other band assignments are indicated.

$4\text{-}C_2H_5OC_6H_4TeCl_3$[23]: ir, ν(COC), ν(TeC) 480 cm^{-1}; ν(TeCl) 320 cm^{-1}.

$4\text{-}ROC_6H_4TeX_3\cdot$



(R, X, n: CH_3, Br, 4; C_2H_5, Cl, 1; C_6H_5, Cl, 2)

ir, R; ν(TeN) 310-327 cm^{-1}; ν(TeS) 201-235 cm^{-1}; ν(TeCl) 255-286 cm^{-1}; ν(TeBr) 149-165 cm^{-1}; δ(TeS or TeX) 120-142 cm^{-1}.

$M^{+}[4\text{-}RC_6H_4TeCl_4]^{-}$ (see section V-C for individual compounds)[27]: ir, R; $ν_s$(TeCl) 285 cm^{-1}; $ν_{as}$ (TeCl) 265 cm^{-1}; ν(TeC), δ(TeC) incorporated into phenyl modes.

$(C_2F_5)_2Te_2$[54]: ir, R; ν(TeTe) 190 cm^{-1}.

$(C_2F_5)_2Te$[54]: ir, R; ν(TeC) ~300 cm^{-1}.

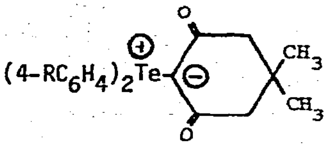
$4\text{-}CH_3OC_6H_4TeCR{=}CHC(O)R'$[33]: ir, ν(CO), ν(C=C).

55

$4\text{-}XC_6H_4Te\text{-}C{\equiv}CC_6H_5$: ν(TeC) 450-575 cm^{-1}.
tris(methyltelluro)cyclopropenium tetrafluoroborate[32]: ir.

$(4\text{-}CH_3OC_6H_4)_2TeCl_2$[23]: ir, ν(TeC) 480 cm^{-1}, ν(TeCl) 290 cm^{-1}.
$(C_6H_5COCH_2)_2TeCl_2$[43]: ir, ν(CO).
$(4\text{-}RC_6H_4)_2$Te-phthalates[40]: ir, ν(CO).

$[(C_6H_5)_3Te]^+$ pseudohalide$^-$: ir, R[45], ν(pseudohalide).



: ir[44], ν(CO).

$[(CH_3)_nH_{3-n}Ge]_2Te$[16]: R, ν(GeTe) 228 cm^{-1}, δ(GeTeGe) 63 cm^{-1}.
trans-$[MX_2(Te(C_2H_5)_2)_2]$[48]: ir, R, ν(MX) (M = Pt, Pd).

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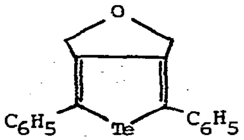
tellurophene[56]: ir; analysis of the CH stretching region in gas, liquid, solution phase and crystal spectra.
tellurophene and deuterated tellurophenes[15]: ir, R; vibrational assignment of fundamental frequencies on the basis of ir vapor band contours and depolarization states of Raman lines.



: ir,[13], ν(C-O).

2,5-diphenyl-3,4-R_2-tellurophene[50] (for individual compounds see section I

3-oxo-2,3-dihydrobenzotellurophene[22]: ir, ν(CO).
4,4-dimethyl-1-tellurocyclohexane-3,5-dione[57]: ir.

2-X-8-Y-phenoxtellurine[18]: ir, ν(COC), $\nu(CH_3)$, γ2H (X, Y: CH_3, CH_3; CH_3, F, F).

B. Ultraviolet-Visible Spectroscopy

Ultraviolet-visible spectral data were reported for $(TeCN)_3^-$ [20], thiazolidine-2-thione complexes of aryl tellurium trihalides[26], phenyl phenylacetylenyl tellurides[55], tris(methyltelluro)cyclopropenium tetrafluoroborate[32], bis(benzoylmethyl) tellurium dichloride[43] (uv; phosphorescence emission spectrum at 77° K, assignment of bands), and 2-phenyltellurophene[14].

C. Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy employing the nuclei ^1H, ^{13}C, ^{31}P, and ^{125}Te were used to characterize organic tellurium compounds. H-H, C-H and Te-H coupling constants, and ^{13}C-spin-lattice relaxation times for telluracyclohexane were reported.

1. ^1H-NMR Spectroscopy

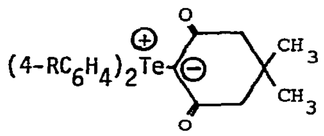
^1H-nmr data were reported for the following organic tellurium compounds:

CH_3TeH[58]: comparison with O, S, Se-derivatives.

$CH_2(TeCl_3)_2$[17]; $4\text{-}C_2H_5OC_6H_4TeCl_3$ (J_{H-H})[23]; $M^+[4\text{-}RC_6H_4TeX_4]^-$ (for individual compounds see section V-C)[27].

tris(methyltelluro)cyclopropenium tetrafluoroborate[32].

$(4\text{-}CH_3OC_6H_4)_2TeCl_2$ (J_{H-H})[23]; $(C_6H_5COCH_2)_2TeCl_2$[43]; $(4\text{-}RC_6H_4)_2Te$-phthalate[40].



(R = H, CH_3, CH_3O)[44].

$[(CH_3)_nH_{3-n}Ge]_2Te$ (J_{H-H}, $J_{^{13}C-H}$, $J_{H-^{125}Te}$)[16]; $(4\text{-}CH_3OC_6H_4Te)_3P$ (J_{H-H})[31]; $PtI_2[Te(C_2H_5)_2]_2/(C_2H_5)_2Te$ and $PdBr_2[Te(C_2H_5)_2]_2/(C_2H_5)_2Te$ (temperature dependence of ^1H-nmr signals)[49].

4,4-dimethyl-1-telluracyclohexane-3,5-dione ($^2J_{^{125}TeH}$)[57]; 1,2,4,5-tetratelluracyclohexane[17] tellurophene-2-*d*[15]; tellurophene-2,5-$\underline{d}_2$[15]; tellurophene-3,4-$\underline{d}_2$[15]; tellurophene-2,3,4-$\underline{d}_3$[15]; 2-phenyltellurophene[14]; 2-phenyltellurophene-5-*d*[14]; 2,5-diphenyltellurophene[50]; 2,5-diphenyl-3,4-R_2-tellurophene[50] (for individual compounds see section IX-A); 2,5-diphenyl-3,4-CH_2OCH_2-tellurophene[13]; 3-oxo-2,3-dihydrobenzotellurophene[22].

2. ^{13}C-NMR Spectroscopy

The ^{13}C-chemical shifts for telluracyclohexane and the telluronium salts obtained by protonating or methylating the tellurium atom in telluracyclohexane were measured and compared to the pentamethylene heterocycles of groups IV, V and other group VI elements. The effects of substituents on the tellurium atom on the ^{13}C-chemical shifts were elucidated[59]. The spin-lattice relaxation times were determined by the inversion-recovery method for the ring carbon atoms of telluracyclohexane[60]. ^{13}C-Chemical shifts and $^{1}J_{^{125}Te-^{13}C}$ for 4,4-dimethyl-1-telluracyclohexane-3,5-dione were measured[57].

3. ^{31}P-NMR Spectroscopy

^{31}P-NMR spectroscopy was used to study the tellurium atom transfer in the systems (*tert*-$C_4H_9)_3PTe/R_3P$ and $[(CH_3)_2N]_3PTe/R_3P$ [R = *tert*-C_4H_9, $(CH_3)_2N$]. ^{31}P-Chemical shifts and $^{31}J_{H-^{31}P}$ were measured[46].

4. ^{125}Te-NMR Spectroscopy

^{1}H-^{125}Te Heteronuclear magnetic double resonance experiments were carried with the following organic tellurium compounds containing ^{125}Te in natural abundance[61]: $CH_2(TeCl_3)_2$, $(Cl_3TeCH_2CO)_2O$, $(HOOCCH_2)_2Te_2$, $(C_6H_5)_2Te$, $(4\text{-}CH_3C_6H_4)_2Te$, $(C_6H_5)_2TeCl_2$, 4-R-$C_6H_4(CH_3)TeI_2$ (R = H, CH_3, CH_3O, C_2H_5O), (4-R-$C_6H_4)(CH_3)_2TeI$ (R = H, CH_3O, C_2H_5O), (R-$C_6H_4)_2CH_3TeI$ (R = H, 2-CH_3). ^{125}Te- and ^{1}H-chemical shifts and $^{2}J_{^{125}Te-H}$ are reported. The Te-H coupling constants have values between 24 and 36 Hz.

D. Nuclear Quadrupole Spectroscopy

The nuclear quadrupole spectra of ^{35}Cl, ^{79}Br and ^{127}I for the compounds $(C_6H_5)_2TeX_2$ (X = Cl, Br, I) were obtained. Each of the spectra consisted of a single line indicating the chemical and crystallographic equivalence of the halogen atoms in the molecules. The results agree with a trigonal bipyramidal structure with the halogen atoms occupying the axial positions[62].

The structures of the 1:1 adducts formed between $(C_6H_5)_nTeCl_{4-n}$ (n = 0, 1, 2) and $AlBr_3$, $GaCl_3$, R_2SO or R_2S were investigated by ^{35}Cl nqr techniques[25]

E. Electron Spectroscopy

The photoelectron spectra of 2-substituted tellurophenes were investigated and the vertical ionization energies of the two highest molecular orbitals and of orbitals mainly localized on the substituent of 2-R-tellurophenes [R = Cl, Br, I, CO_2H, CO_2CH_3, $CON(CH_3)_2$] assigned. The substituent effects confirmed the earlier suggested[2] reversal of the sequence of the two highest molecular orbitals in tellurophene ($\pi_3 > \pi_2$) in comparison with the other group VI derivatives ($\pi_2 > \pi_3$)[63].

The He(I) and He(II) photoelectron spectra of benzotellurophene were recorded and compared with those of similar heterocycles. The first four bands were correlated with π-molecular orbitals[64].

F. ^{125}Te-Moessbauer Spectroscopy

The ^{125}Te-Moessbauer spectrum of crystalline 1,2,4,5-tetratelluracyclohexane [$\delta(^{125}Sb/Cu)$ 0.27, 0.06; Δ9.33, 0.11, 2Γ 6.33 (mms^{-1})] confirmed the equivalence of the tellurium atoms and showed, that the sample did not contain elemental tellurium[17]. The ^{125}Te-Moessbauer spectra of inorganic tellurium(IV) oxides, oxyfluorides and fluorides were reported[65].

G. Mass Spectrometry

Mass spectral data were reported for alkyl phenyl tellurides[66], bis(nonafluoro-2-biphenylyl) telluride (only M^+)[12], tris(methyltelluro)cyclopropenium tetrafluoroborate (no M^+)[32], 2-phenyltellurophene[14], 2-phenyltellurophene-2-*d* (16 eV)[14], 2-phenyltellurophene-3,4,5-d_3 (16 eV)[14], 2,5-diphenyl-3,4-R_2-tellurophenes (only M^+; for individual compounds see section IX-A)[50]; 2,5-diphenyl-3,4-CH_2OCH_2-tellurophene (only M^+)[13]; 3-oxo-2,3-dihydrobenzotellurophene (only M^+)[22]; telluroindigo (only M^+)[22] and 1,2,4,5-tetratelluracyclohexane (no M^+)[17].

The mass spectra of the alkyl phenyl tellurides, C_6H_5-Te-R (R = CH_3, CD_3, C_2H_5, C_3H_7, *i*-C_3H_7, C_4H_9) exhibited intense parent ions. The fragmentation of the molecular ions produced C_6H_5Te, RTe, Te and the rearrangement ions C_6H_6Te, HTe, C_7H_7 and C_6H_6. Examination of the spectrum of the CD_3-derivative demonstrated that the HTe-ion derived its hydrogen from the phenyl group. The series of low intensity peaks caused by ions TeCpHq (p = 1-4, q = 1, 2), which was present in all the spectra, arises probably through fragmentation of the C_6H_5Te group[66].

H. X-Ray Structure Analyses

2-Biphenylyl tellurium triodide crystallizes in the monoclinic space group $P2_1/n$ with four molecules per unit cell. The tellurium atom is in a trigonal-bipyramidal environment with two iodine atoms occupying the axial positions (Te-$I_{ax.}$ 2.833, 3.099 Å; Te-$I_{eq.}$ 2.769 Å; Te-C 2.15 Å). Intermolecular I····I bonds link the molecules into chains[67].

Indexed powder patterns and unit cell dimensions were reported for the triphenyl telluronium pseudohalides, $(C_6H_5)_3TeX$ (X = N_3, CNO, CNS, CNSe)[68].

Preliminary X-ray results[57] for 4,4-dimethyl-1-telluracyclohexane-3,5-dione gave a Te-C bond length of 2.170 Å and a CTeC angle of 86.3°.

I. Dipole Moment Measurements

The dipole moments of bis(4-dimethylaminophenyl) telluride (3.72 D) and $4\text{-}RC_6H_5\text{-}TeC{\equiv}C\text{-}C_6H_5$ (R, μ: H, 1.20 D; CH_3, 1.60 D; F, 1.16 D; Cl, 1.47 D; Br, 1.36 D) were determined in benzene solution at 25°. The dipole moments of the sp^nC-Te bonds were determined by a vector scheme with consideration of weak dipoles. The moments for sp^3 (0.77 D) and sp^2 bonds (0.34 D) are directed from the carbon to the tellurium atom, whereas the sp-moment (0.76 D) points from the tellurium to the carbon atom[55].

Dipole moment measurements were employed to investigate the compounds $(C_6H_5)_nTeX_{4-n}\cdot L$ (X = Cl, Br; n = 0, 1, 2; L = $AlBr_3$, $GaCl_3$, R_2SO, R_2S)[25].

The dielectric constant-refractive index method was used to determine the dipole moments of the complexes trans-$[MX_2\cdot L_2]$ [L = $(C_2H_5)_2Te$] in benzene solution at room temperature[48] (M, X, μD): Pt, Cl, 2.3; Pt, Br, 1.9; Pt, I, 1.8; Pd, Cl, 1.8; Pd, Br, 1.8; Pd, I, 1.9). The dipole moment of 6D reported by Jensen [Z. Anorg. Chem., 231 (1937) 365] for the platinum chloride complex is probably incorrect.

XI. Analytical Techniques

Tellurium was determined in organic substances by decomposition with a mixture of concentrated sulfuric and nitric acids and potentiometric titration of the borate-buffered solution at pH 8.0-8.5 with silver nitrate. The results were within ±0.3% of the calculated values. The oxygen-flask combustion method did not give satisfactory results[69].

However, decomposition of organic tellurium compounds using the conventional oxygen flask method followed by treatment with aqueous hydrogen peroxide/hydrochloric acid solution and tellurium determination by atomic absorption spectrophotometry was recommended as a rapid micro-analytical procedure for tellurium. A standard deviation of 0.23 was calculated from the results obtained with 41 organic tellurium compounds. Only diaryl ditellurides were not completely oxidized by this method[70].

The methods available for the determination of tellurium in organic compounds were reviewed[11].

XII. Biology of Organic Tellurium Compounds

The ecological aspects of tellurium in human and animal health[71], the toxicity and metabolism of tellurium compounds[72], the toxicology of tellurium and its compounds[73], and the interaction of Na_2TeO_4 with mercury, cadmium, selenium, beryllium and arsenic[74] were reviewed.

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