

TELLURIUM

LITERATURE SURVEY COVERING THE YEAR 1977

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I. Introduction

This annual survey of the organic chemistry of tellurium covers the literature abstracted in Chemical Abstracts Volume 86, No. 10 through Volume 88, No. 13. The general symbol "R", for which the term "organyl" has been adopted, is used for alkyl as well as aryl groups. When reference is made to earlier work, the original papers are generally not cited; instead the reader is referred to the previous surveys 1-4, which will provide access to the pertinent literature.

The partial financial support of 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.

Tellurane, tetrahydrotelluropyran derivatives and related compounds (R. Livingstone, 1977)²: A very brief review of telluracyclohexane and its derivatives.

Aliphatic organo-sulfur compounds; compounds with exocyclic sulfur functional groups, and their selenium and tellurium analogs (G.C. Barret, 1977)³: This review is mainly devoted to organic sulfur compounds. Selenium and tellurium compounds are included, but pertinent data are dispersed throughout the text and are difficult to find.

Ylides of sulfur, selenium and tellurium, and related structures (E. Block and M. Haake, 1977)⁷: Three pages of this review deal with selenium and tellurium ylides.

Thiophenes and their selenium and tellurium analogs (S. Gronowitz, 1977)⁸: This review covers the period from April 1974 to March 1976. Tellurophenes are discussed on pages 298 and 299.

Tellurophenes and related compounds (F. Fringuelli et al., 1977)⁹: A very thorough and complete review of the synthesis and properties of tellurophene, tetrahydrotellurophene, benzotellurophene and dibenzotellurophene and their derivatives including uv, ir, Raman, microwave, nmr and photoelectron spectral characteristics, discussion of reactivity studies and tables of compounds.

Pharmacology and toxicology of heavy metals: tellurium (L.M. Klevay, 1976)¹⁰: This review discusses the absorption, distribution, excretion, metabolism, physiological effects and medical uses of inorganic tellurium compounds and dimethyl telluride and the treatment of tellurium poisoning.

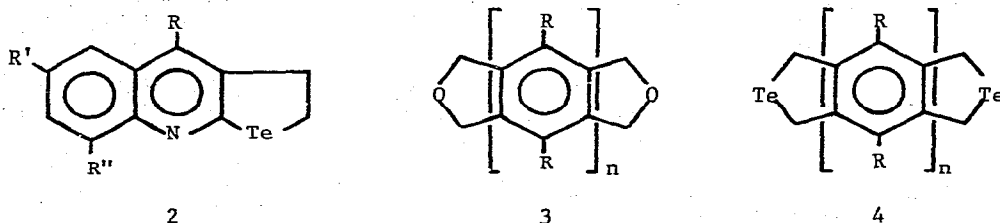
Tellur (Gmelin-Handbuch der Anorganischen Chemie, 1976)¹¹: This review is not devoted to organic tellurium compounds, but surveys the work on hydrogen telluride, alkali tellurides, tellurium oxides, tellurium(IV) acids, tellurium(VI) acids, alkali tellurites, alkali tellurates, tellurium-nitrogen compounds and tellurium nitrates reported in the literature up to the end of 1973.

III. Methods for the Introduction of Tellurium into Organic Molecules

During the period covered by this review tellurium, alkali metal tellurides and tellurium tetrahalides were used to introduce the tellurium atom into organic molecules. Most of these reactions, which are summarized in Fig. 1, are extension of previously reported preparative methods.

Of potential interest is the formation of divinyl telluride from acetylene and tellurium in a basic aqueous medium for the synthesis of unsaturated tellurides. The reaction conditions, reminiscent of those used for the preparation of tellurophene from tellurium and butadiyne¹, are not fully disclosed in the brief note reporting the synthesis of divinyl telluride.¹³ The reaction of tellurium with dimethyl tin dihydride¹² produced the 1,2,4-tristanna-3,5-ditelluracyclopentane 1 (Fig. 1).

A U.S.S.R. patent^{P-1} claims the preparation of alkyl derivatives of tellurium by reacting alkyl halides and tellurium in aqueous alkaline medium containing $\text{Na}_2\text{S}_2\text{O}_4$ or thiourea dioxide as a reducing agent. The condensation of sodium hydrogen telluride, obtained from tellurium and sodium borohydride in ethanol, with 2-chloro-4-(2-chloroethyl)quinolines²² yielded the dihydrotellurophene derivatives 2. Potassium telluride is claimed^{P-2}



to have converted the aromatic carboxylic anhydride 3 to the tellurium heterocycle 4. Chloromethyl(dimethyl)-3-chloropropylsilanes and potassium telluride yielded 1-sila-3-telluracyclohexanes²³ (eqn. 1).

Potassium tellurocyanate and benzyl chloride in dimethyl sulfoxide yielded benzyl tellurocyanate²¹.

The tellurium tetrahalides reacted with tetraphenyl tin in a refluxing mixture of toluene/diethyl ether to give diphenyl tellurium dihalides.

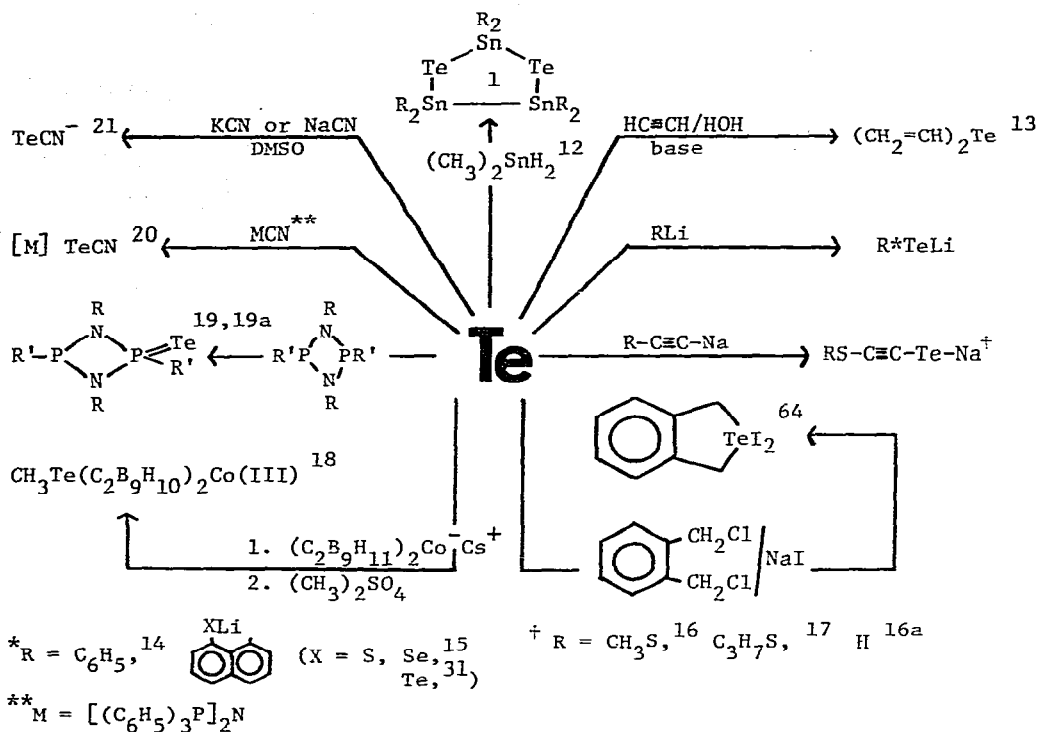
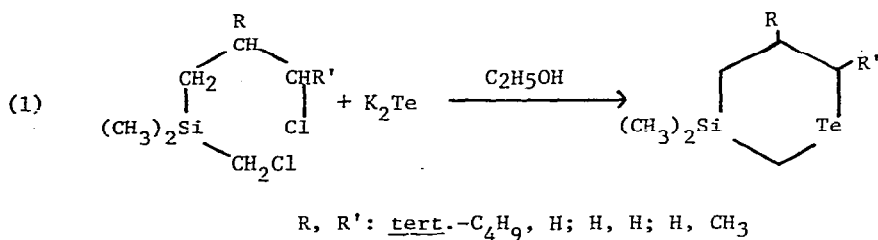


Fig. 1: Reactions Employing Elemental Tellurium as the Reagent for the Introduction of Tellurium into Organic Molecules

Triphenyl tin halides produced phenyl tellurium trihalides. The corresponding ethyl tin derivatives reacted similarly.²⁴ Tellurium tetrachloride was



arylated by aryltrimethylsilane in refluxing toluene to aryl tellurium trihalides.²⁵ Aryl mercuric chlorides and tellurium tetrachloride refluxed in dioxane produced diaryl tellurium dichlorides.^{26, 26a} Heating the complexes C₆H₅N(CH₃)₂·TeX₄ (X = Cl, Br) or the ammonium salts [(CH₃)₂NHC₆H₅]₂⁺TeX₆⁻ (X = Cl, Br, I) in dry methanol yielded 4-dimethylaminophenyl tellurium

trihalides²⁷. Condensation of tellurium tetrachloride with triphenylamine at room temperature in benzene in the presence of triethylamine gave bis(4-diphenylaminophenyl) tellurium dichloride.²⁸ Dimethylformamidyl tellurium trichloride, $(\text{CH}_3)_2\text{NC}(\text{O})\text{TeCl}_3 \cdot \text{DMF}$, was prepared from tellurium tetrachloride and dimethylformamidyl sodium.²⁹ A U.S. patent^{P-3} claims the tellurium tetrabromide and CF_3 radicals obtained from C_2F_6 in a corona or glow discharge plasma^{P-3} reacted to form $[(\text{CF}_3)_2\text{Te}]_n$ ($n = 1, m$) and $(\text{CF}_3)_2\text{Te}_2$.

The reactions of organic tellurium compounds which were used to produce new organic tellurium derivatives are summarized in Fig. 2. All of these reactions are discussed in the sections devoted to the pertinent tellurium compounds. The reactions of heterocyclic tellurium compounds are not included in Fig. 2.

IV. Tellurocyanates

The tellurocyanate, $[(\text{C}_6\text{H}_5)_3\text{P}=\text{N}=\text{P}(\text{C}_6\text{H}_5)_3]^+ \text{TeCN}^-$ was prepared by addition of black tellurium powder to a solution of the corresponding ammonium cyanide in acetone. The mixture was heated at 50° for 30 min. The tellurocyanate precipitated on addition of diethyl ether. The tellurocyanate (65% yield) melted after recrystallization from acetone at $190-3^\circ$ with decomposition. The Te^{13}CN -tellurocyanate, was similarly prepared from the ^{13}C -cyanide.

Potassium tellurocyanate obtained from tellurium and KCN in dimethyl sulfoxide reacted with benzyl chloride to yield benzyl tellurocyanate, the first alkyl tellurocyanate ever isolated.

V. Compounds Containing a Single Carbon-Tellurium Bond

Tellurools, benzyl tellurocyanate, organyl tellurium trihalides and diorganyl ditellurides were investigated during the survey period. Tellurium derivatives, in which the second tellurium valence is satisfied by group I to V element atoms, sulfur or selenium are discussed in section X

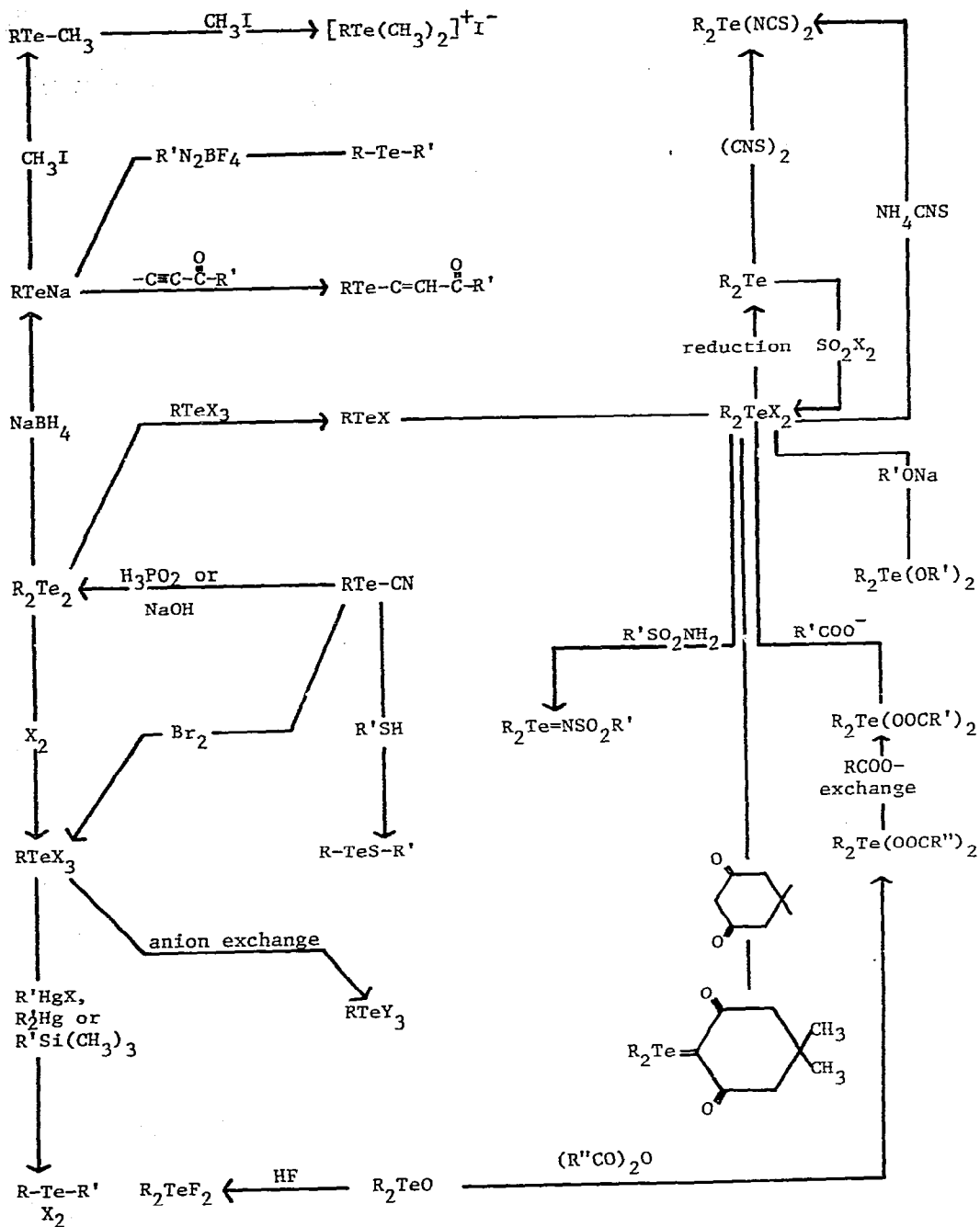


Fig. 2: Transformations of Organic Tellurium Compounds

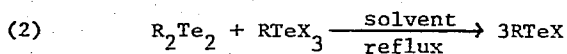
A. Tellurois

Methanetellurois, prepared from dimethyl ditelluride and sodium in liquid ammonia followed by addition of 2N sulfuric acid to the reaction mixture under an oxygen-free atmosphere, was found to be spontaneously flammable in air and to explode on contact with pure oxygen at room temperature. The tellurois was stable at liquid nitrogen temperatures, but decomposed to tellurium at room temperature.³⁰

The 8-hydrothio-¹⁵, 8-hydro-seleno-¹⁵ and 8-hydro-telluro-1-hydro-telluro-naphthalenes³¹ were obtained by protonation of the corresponding dilithium salts in tetrahydrofuran at -25°. The tellurois were not isolated but oxidized by air to heterocyclic compounds.¹⁵

B. Tellurenyl Compounds, RTeX

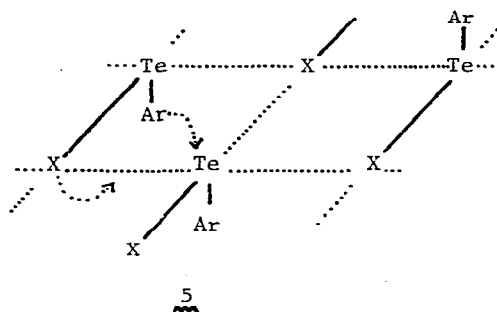
The preparation of aryl tellurium halides, RTeX, from equimolar amounts of diaryl ditellurides and aryl tellurium trihalides³² in refluxing organic solvents was attempted according to eqn. 2. These reactions led to the



R,X, % yield: 2-C₆H₅C₆H₄, Br, 73%; C₆H₅, I, 38%

desired products only with the 2-biphenyl (X = Br, in petroleum ether), and phenyl (X = I, in ClCH₂CH₂Cl) derivatives. All other compounds investigated [R,X: C₆H₅, Cl; C₆H₅, Br; 4-CH₃OC₆H₄, Cl and I; 3,4-(CH₃O)₂C₆H₃, Cl] produced only diaryl tellurium dihalides and tellurium. Phenyl tellurium iodide and 4-methoxyphenyl tellurium iodide subjected to the conditions employed for the reactions between R₂Te₂ and RTeX₃ generated the same products which were obtained from the ditellurides and aryl tellurium trihalides. These observations and results of experiments with ^{123m}Te-labeled starting materials suggest strongly, that aryl tellurium halides, RTeX, are intermediates in all these reactions. Petraghani and de Moura Campos³³ had earlier mentioned RTeX compounds among others as possible intermediates in reactions between ditellurides and aryl tellurium trihalides. Whether or not the aryl tellurium halide can be isolated, depends on the thermal

stability of the compound. Based on reaction times and yields the thermal stability of $R\text{TeX}$ compounds decreases in the sequence $3,4-(\text{CH}_3\text{O})_2\text{C}_6\text{H}_4$, $4-\text{CH}_3\text{OC}_6\text{H}_4 < \text{C}_6\text{H}_5$ and $\text{Cl} < \text{Br} < \text{I}$. It was postulated,³² that instability is caused by the facile migration of aryl groups in the associated aryl tellurium halides (structure 5). Such a migration should be facilitated



by small halogen atoms, which allow the tellurium atoms to be close to each other and by substituents in the benzene ring such as CH_3O . The observed stability order of $R\text{TeX}$ compounds and the fact, that the 4-methoxyphenyl group migrates preferentially before the phenyl group, are in agreement with the postulated mechanism. 2-Biphenyl tellurium bromide is monomeric in solution,³⁴ is not capable of an aryl group migration and is not converted to diaryl tellurium dibromide and tellurium.³²

Benzyl tellurocyanate, the first reported example of an alkyl tellurocyanate, was obtained in 61% yield from benzyl chloride and potassium tellurocyanate in dimethyl sulfoxide.²¹ The white needles melted at $126-7^\circ$. Benzyl tellurocyanate is light-sensitive, darkens in the presence of air, and is especially unstable in solution. It can be chromatographed and recrystallized under red light. The reactions²¹ of benzyl tellurocyanate are summarized in Fig. 3.

C. Organyldihalotellurium Compounds, $[R\text{TeX}_2]$

The compound $\text{C}_6\text{H}_4\text{CH}_2\text{TeCN} \cdot (\text{C}_6\text{H}_5)_4\text{AsBr}$, obtained previously from benzyl bromide and tetraphenylarsonium tellurocyanate,³⁵ was now prepared

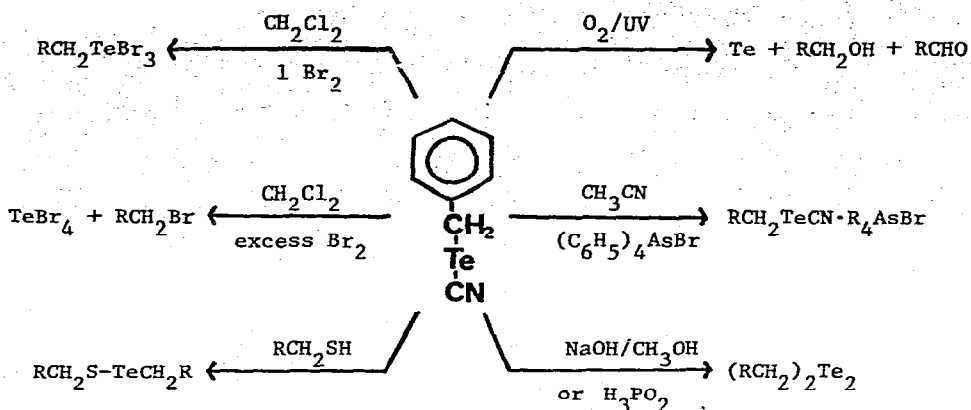


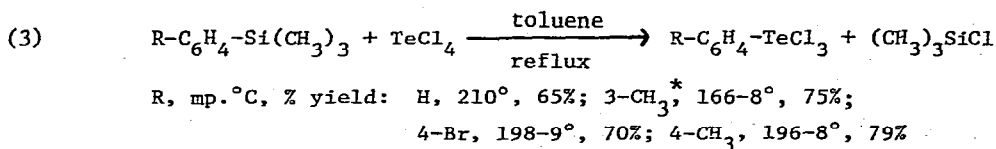
Fig. 3 : The Reactions of Benzyl Tellurocyanate

from benzyl tellurocyanate and tetraphenylarsonium bromide.²¹ The ir spectrum of the complex in KBr is virtually identical with a composite spectrum of the components. The low melting point of 118°, the ir and nmr data suggest the complex to be a loose association²¹ and not an ionic compound $[\text{C}_6\text{H}_5\text{CH}_2\text{Te}(\text{CN})\text{Br}]^-[(\text{C}_6\text{H}_5)_4\text{Br}]^+$ as suggested previously.³⁵ Chromatography of the complex on silica gel with chloroform or methanol as eluent regenerated benzyl tellurocyanate.²¹

D. Organyl Tellurium Compounds, RTeX_3

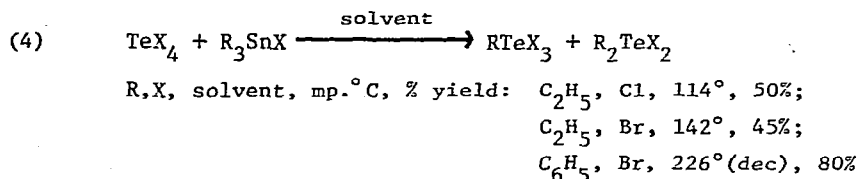
Several hitherto unreported organyl tellurium trihalides (marked by an asterisk) were prepared employing both previously developed and new preparative methods. Some known compounds were also synthesized by the new methods.

Tellurium tetrachloride and aryltrimethylsilanes gave aryl tellurium trichlorides²⁵ (eqn. 3). This reaction is a convenient one-step synthesis



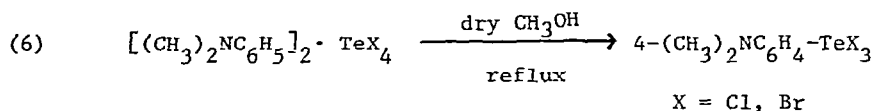
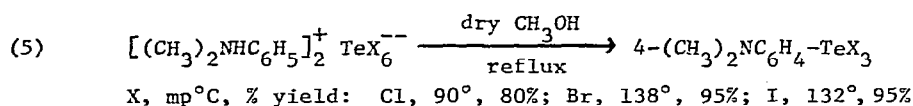
of aryl tellurium trichlorides using the easily accessible aryltrimethylsilanes.

Triorganylhalostannanes reacted similarly with tellurium tetrahalides²⁴
(eqn. 4).



Tellurium tetraiodide in non-polar solvents did not react with triorganylhalostannanes, probably because of poor solubility. In polar solvents such as methanol products were obtained which could not be characterized.²⁴

A.K. Gupta et al.²⁷ claimed the synthesis of 4-dimethylaminophenyl tellurium trihalides in almost quantitative yield by heating the dimethylphenylammonium hexahalotellurates(IV) (eqn. 5) or the adducts [(CH₃)₂NC₆H₅]₂ · TeX₄ (eqn. 6) in dry methanol. Treatment of 4-dimethylaminophenyl tellurium trichloride with potassium halides, KX (X = Br, I)



produced the aryl tellurium tribromide and triiodide in 95% yields²⁷ as precipitates upon addition of benzene to the reaction mixtures.

Treatment of bis(2-biphenyl) ditelluride with bromine in carbon tetrachloride gave 2-biphenyl tellurium tribromide*, in 72% yield. The compound melted at 183-4° with decomposition.^{32,40}

Benzyl tellurium tribromide*, which turned gray at 135-8° and melted at 150°, was the product of the reaction between equimolar quantities of bromine and benzyl tellurocyanate in methylene chloride.²¹

The compound (CH₃)NC(O)TeCl₃·DMF, a mustard-colored powder, which behaved in nitrobenzene as a 1:1 electrolyte, was obtained from (CH₃)₂NC(O)Na and tellurium tetrachloride in carbon tetrachloride after treatment of the precipitated brown solid with dimethylformamide.²⁹ Refluxing the CCl₄ suspension of the DMF-adduct with quinoline gave the white quinoline

adduct. The adducts decompose to tellurium dioxide on heating.²⁹

4-Methoxyphenyl tellurium trichloride labeled with the radioactive ^{123m}Te -isotope was prepared from $^{123m}\text{TeCl}_4$ and methoxybenzene.³²

The following reactions of organyl tellurium trihalides are discussed in the indicated sections: reactions with diaryl ditellurides³² to form aryl tellurium halides (section V-B) or diaryl tellurium dihalides (section VI-B1), the reduction to ditellurides with $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ^{25,32} or hydrazine hydrate³⁶ (section V-E), the reaction with diaryl mercury compounds and aryl mercuric chlorides^{26a,36,37,55} to give $\text{RR}'\text{TeCl}_2$, the reactions with aryltrimethylsilanes²⁵ yielding $\text{RR}'\text{TeCl}_2$ ($\text{R} = \text{R}'$, $\text{R} \neq \text{R}'$), the addition to cyclohexene²⁷ (section VI-B1) and the cyclization of 2-biphenyl tellurium tribromide to dibenzotellurophene dibromide⁴⁰ (section XI-D)

EHM and CNDO/2 calculations showed that those conformations of RTeX_3 with the greatest numbers of gauche interactions are the most stable.³⁸

E. Diorganyl Ditellurides

The following new diaryl ditellurides, $(\text{RC}_6\text{H}_4)_2\text{Te}_2$, were prepared (R , method of preparation): 4- NO_2 (no data reported);³⁶
 $\text{RC}_6\text{H}_4\text{TeCl}_3 + \text{N}_2\text{H}_4\cdot\text{H}_2\text{O}/\text{abs. C}_2\text{H}_5\text{OH}$ ³⁶; 3-Cl, $\text{RC}_6\text{H}_4\text{TeCl}_3 + \text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ³⁹;
 3-Br, $\text{RC}_6\text{H}_4\text{TeCl}_3 + \text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ ³⁹. The bis(3-halophenyl) ditellurides are oils, which could not be distilled.

The previously reported¹, exceedingly photosensitive dibenzyl ditelluride (mp. $80-1^\circ$) was obtained in 91% yield by treating powdered benzyl tellurocyanate with hypophosphorous acid (50%), or in 29% yield by stirring the tellurocyanate with methanolic sodium hydroxide solutions. Mechanisms for these reactions were proposed.²¹ A patent^{P-3} was issued for the preparation of bis(trifluoromethyl) ditelluride (bp. -53°) in 33% yield from tellurium tetrabromide and C_2F_6 in an electric discharge. Bis(4-methoxyphenyl) ditelluride labeled with the ^{123m}Te -isotope was synthesized by reduction of the 4-methoxyphenyl ^{123m}Te -tellurium trichloride with sodium sulfide.³²

Ultraviolet irradiation of solutions of diethyl ditelluride and

cut d-orbitals) for the cis- and trans- barriers, respectively. The conformation is mainly determined by the interaction of the electron pairs on tellurium.³⁹ The conformations of diaryl ditellurides as deduced from dipole moment studies were compared with the conformation of diaryl disulfides and diselenides⁴³ (for details see section XII-G).

VI. Compounds Containing a Carbon-Tellurium-Carbon Moiety

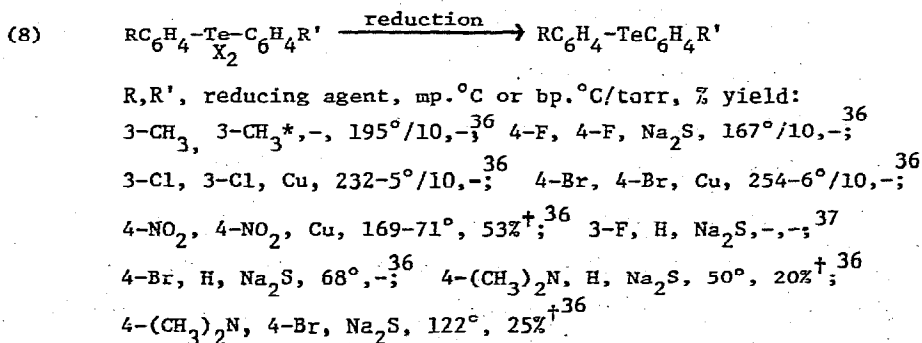
Symmetric and unsymmetric diorganyl tellurides, R_2Te , telluroamino acids, tellurides with two tellurium atoms in the molecule, symmetric and unsymmetric diorganyl tellurium dihalides, diaryl tellurium di(isothiocyanates), diorganyl dialkoxides, diaryl tellurium dicarboxylates and some reactions of diaryl telluroxides were investigated.

A. Diorganyl Tellurides

A number of new, diorganyl tellurides, which are with a few exceptions of the unsymmetric type, $R-Te-R'$, were prepared employing previously reported methods. Tellurides with two tellurium atoms in the molecule were also synthesized.

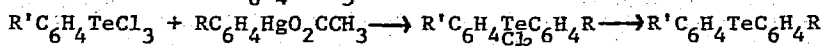
1. Symmetric and unsymmetric diorganyl tellurides

The reduction of diaryl tellurium dihalides with sodium sulfide monohydrate or with copper powder in dioxane yielded diaryl tellurides (eqn. 8).



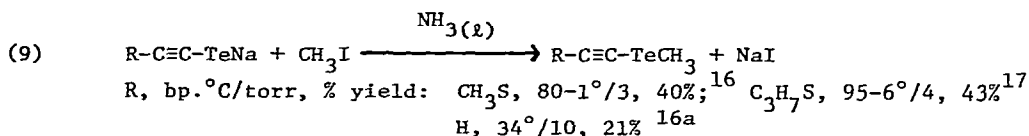
* Previously prepared from TeBr₂ and 3-methylphenylmagnesium bromide.¹

† Yield based on R'C₆H₄TeCl₃ employed in reaction sequence



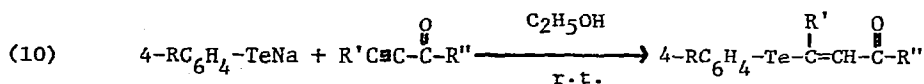
Sadekov and co-workers^{41a} prepared diaryl tellurides, R-Te-R' (R, R': C₆H₅, C₆H₅; C₆H₅, 4-CH₃C₆H₄; C₆H₅, 4-ClC₆H₄; 4-CH₃OC₆H₄, 4-CH₃C₆H₄) by reacting RTeNa, obtained from the ditelluride and sodium borohydride in ethanol/benzene, with the diazonium tetrafluoroborates, R'⁺N₂BF₄⁻. Only the 4-methoxyphenyl 4-methylphenyl telluride (m. 64°, 36% yield) was isolated and purified without being converted to the diaryl tellurium dichloride. The other compounds were treated with chlorine to give the diaryl tellurium dichlorides. The compound 2-methylphenyl 2,4,5-trimethylphenyl telluride was mentioned by Sadekov³⁶ but its preparation and physical characteristics were not given.

Alkylthioethynyl methyl tellurides^{10,17} and ethynyl methyl telluride^{16a} were isolated when methyl iodide was added to the ethynyl sodium telluride in liquid ammonia (eqn. 9). Hydrogen chloride did not add to the triple



bond in propylthioethynyl methyl telluride; instead, it caused tellurium-carbon-bond cleavage.¹⁷

The nucleophilic addition of arenetelluroolate ions to α-acetylenic oxo compounds in ethanolic medium at room temperature places the aryltelluro group on the β-carbon atom relative to the carbonyl group in accordance with the electron-density distribution in the carbonylethynyl compound⁴¹ (eqn. 10).



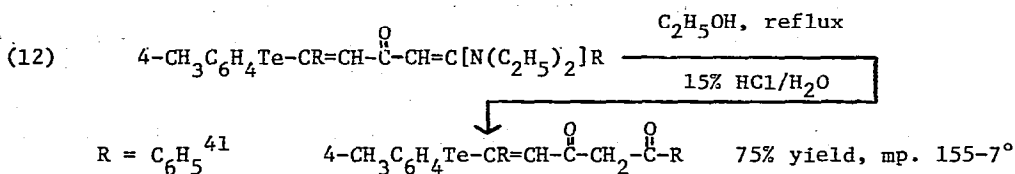
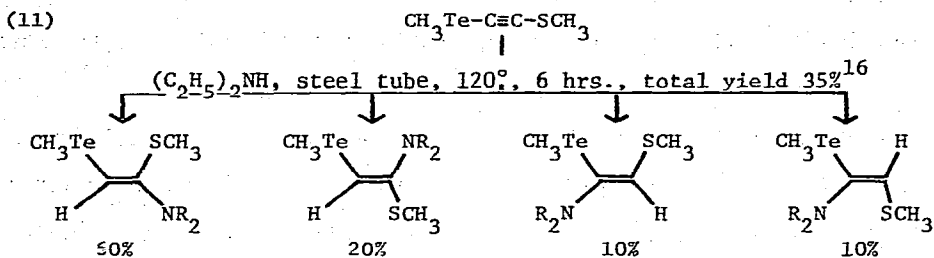
R = H; R', R'', mp.°C, % yield: C₆H₅, H, 94-95°, 88%; C₆H₅, OH, 132-3°, 14%;
 C₆H₅, C₂H₅O, 92-3°, 81%;
 C₆H₅, C₆H₅, 118-9°, 86%
 1-hydroxy-1-cyclohexyl, 112, 84%

R = CH₃; R', R'', mp.°C, % yield: H, C₂H₅O, 53-4°, 70%; C₆H₅, H, 93-4°, 76%;
 C₆H₅, CH=C(C₆H₅)OC₆H₅, 138-9°, 70%; C₆H₅, CH=C(C₆H₅)N(C₂H₅)₂, 143-4°, 68%;

R = CH₃O; R', R'', mp.°C, % yield: C₄H₉, C₆H₅, 80°, 68%; C₆H₅, H, 86-7°, 67%

The unsaturated tellurides $2,4-(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3\text{-Te-CR}'=\text{CHC}(\text{O})\text{R}''$ (R' , R'' , mp. °C, % yield: COOH , C_6H_5 , 215-8°, 21%; C_6H_5 , $\text{C}_2\text{H}_5\text{O}$, 73-4°, 70%) were obtained similarly.⁴¹

Modifications of the organic moieties in unsaturated diorganyl tellurides produced the new diorganyl tellurides in reactions described in eqns. 11 and 12. Attempts to replace the aryltelluro group in the compounds $\text{R}'\text{C}_6\text{H}_4\text{TeCR}=\text{CHCOR}''$ by a dialkylamino group were not successful.⁴¹



The telluroamino acids, $\text{RTe-CH}_2\text{CH}_2\text{CH}(\text{NH}_2)\text{COOH}$ ($\text{R} = \text{CH}_3$, telluromethionine; $\text{R} = \text{C}_6\text{H}_5$), the first examples of this class of tellurium compounds, were obtained by the hydantoin route employing methanetelluro or benzene-telluro.⁴⁴

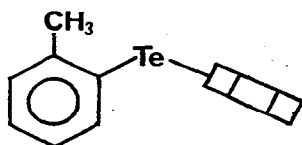
Divinyl telluride, $(\text{CH}_2=\text{CH})_2\text{Te}$, boiling at 131-2°/720 torr, was formed when the telluride ion, Te^{--} , generated from tellurium in basic aqueous medium, was reacted with acetylene. It was assumed that the tellurium disproportionated according to $4\text{Te} \rightarrow 3\text{Te}^{--} + \text{Te}^{+6}$. The yield of divinyl telluride based on the telluride ion was 55 percent.¹³

Diethyl telluride and dibenzyl telluride, which had previously been synthesized,¹ were produced when solutions of the appropriate ditellurides were exposed to uv-radiation. The dibenzyl telluride could not be isolated in pure form, because it decomposed under the reaction conditions to

dibenzyl and tellurium. Even diethyl telluride was cleaved to ethylene upon prolonged uv-irradiation.⁴²

Several patents claim the synthesis of diorganyl tellurides: diorganyl tellurides from Te/aqueous alkaline medium/ $\text{Na}_2\text{S}_2\text{O}_4$ or thiourea dioxide/RX;^{P-1} $(\text{CF}_3)_2\text{Te}$ and $[(\text{CF}_3)_2\text{Te}]_n$ from $\text{TeBr}_4/\text{C}_2\text{F}_6$ /electric discharge;^{P-3} $\text{C}_6\text{H}_5\text{C}\equiv\text{CTeR}$ from $\text{C}_6\text{H}_5\text{C}\equiv\text{CBr} + \text{RTeNa}/\text{NH}_3(\ell)$.^{P-4}

On the basis of the ^1H -nmr chemical shifts of the methyl groups the conformation 6 was suggested for 2-methylphenyl 2,4,6-trimethylphenyl telluride.³⁶ The conformations of other diaryl tellurides and the electronic



6

interactions between the tellurium atom and the aromatic rings as deduced from dipole moment measurements³⁶ are discussed in section XII-G.

A gas chromatographic separation of diethyl telluride from diethyl selenide with silicon rubber SKTFB-803 as the stationary liquid phase was developed.⁴⁵ Dipropyl telluride was found to be the best corrosion inhibitor for 99.99 percent iron in 3M perchloric acid among several propyl halides and dipropyl dichalcogenides tested. The efficiency of these inhibitors increased in the order $\text{RCl} < \text{RBr} < \text{RI}$, $\text{R}_2\text{O} < \text{R}_2\text{S} < \text{R}_2\text{Se} < \text{R}_2\text{Te}$ ($\text{R} = \text{C}_3\text{H}_7$).⁴⁶

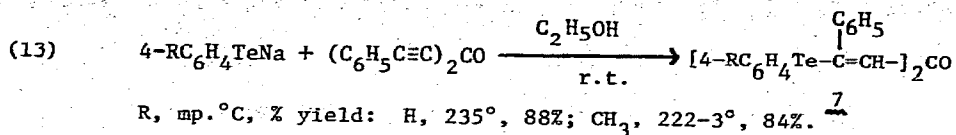
Diphenyl telluride was found to transfer both phenyl groups to ethyl acrylate molecules in acetonitrile solution in the presence of palladium diacetate. It was suggested that the phenyl group is first transferred to the palladium atom, followed by a shift to the olefin with formation of trans- ethyl phenylacrylate.⁴⁷ Diaryl tellurides do not exchange aryl groups⁴⁹ when heated at 140° .

The reactions of diorganyl tellurides with sulfuryl halides³⁷ and with thiocyanogen⁴⁸ are presented in section VI-B. The formation of telluronium salts from dialkyl tellurides is discussed in section VII. The results of the aryl group exchange upon heating a mixture of diphenyl telluride and

tetrakis(4-methylphenyl) tellurium⁴⁹ are summarized in section VIII.

2. Tellurides with two tellurium atoms in the molecule

The nucleophilic addition of arenetelluroate ions to bis(phenylethynyl) ketone⁴¹ yielded the tellurides 7 (eqn. 13). It was not possible to stop



the reaction after one telluroate ion had added to a triple bond.

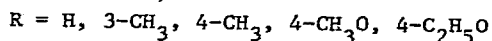
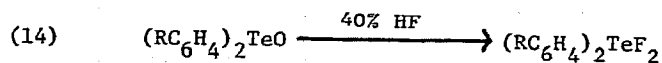
B. Diorganyl Tellurium Compounds, R₂TeX₂

New, symmetric and unsymmetric diaryl tellurium dihalides were prepared by novel as well as already known methods. A number of diaryl tellurium dithiocyanates, dicarboxylates, di(organyloxides), R₂Te(OR)₂, and compounds obtained from diorganyl tellurium dialkoxides and diols were synthesized.

1. Symmetric and unsymmetric diorganyl tellurium dihalides and diisothiocyanates

Treatment of dimethyl tellurium diiodide dissolved in chloroform with chlorine yielded dimethyl tellurium dichloride.⁵⁵

Sadekov³⁷ reported that aqueous solutions of diaryl telluroxides precipitated diaryl tellurium difluorides when treated with 40 percent aqueous hydrofluoric acid (eqn. 14). Symmetric and unsymmetric diaryl



tellurides were converted to the corresponding diaryl tellurium dihalides through reactions with sulfuryl dichloride, dibromide or diiodide in benzene or carbon tetrachloride solutions.³⁷ The tellurium dihalides were isolated in quantitative yields.

The reactions between diaryl ditellurides and aryl tellurium trihalides which produced diaryl tellurium dihalides³² via aryl tellurium halides as intermediates were discussed in section V-B. The compounds prepared

by this method are listed in Table 1.

Petragnani and co-workers⁵¹ refluxed dioxane solutions of tellurium tetrachloride and aryl mercuric chlorides (1:2 molar ratio).⁵¹ The diaryl tellurium dichlorides, $(4\text{-RC}_6\text{H}_4)_2\text{TeCl}_2$ ($R = \text{H}, \text{CH}_3$), were isolated in yields higher than 90 percent. Sadekov *et al.* prepared unsymmetric diaryl tellurium dichlorides by boiling equimolar mixtures of aryl tellurium trichlorides and aryl mercuric chlorides,^{37,55} aryl tellurium trichlorides and aryl mercuric acetates³⁶ or aryl tellurium trichlorides and diaryl mercury compounds (2:1 molar ratio)^{26a} in dioxane for several hours. Aryl-trimethylsilanes transferred in refluxing dioxane the aryl groups to aryl tellurium trichlorides²⁵ forming diaryl tellurium dichlorides in rather low yields. Tellurium tetrabromide and tetraphenyl tin produced after twelve hours in refluxing toluene/diethyl ether (5:1 v/v) diphenyl tellurium dibromide. A similar reaction with tellurium tetraiodide gave diphenyl tellurium diiodide in only 20 percent yield.²⁴ Tetraethyl tin reacted with tellurium tetrachloride and tetrabromide. The oily products, R_2TeX_2 and R_2SnX_2 , could not be separated.²⁴ All these arylation reactions are summarized in eqn. 15. Pertinent data for the compounds prepared in this manner are given in Tables 1 and 2 for symmetric and unsymmetric diaryl tellurium dihalides, respectively.

(15)

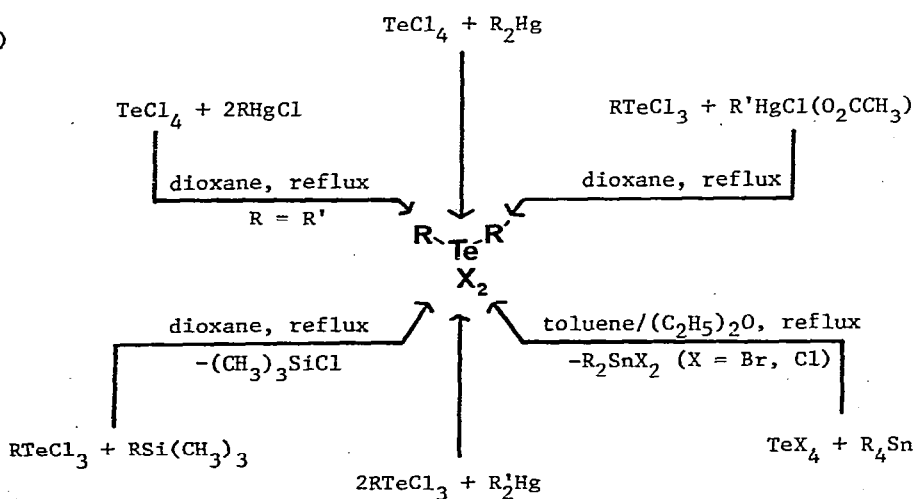


TABLE 1

SYMMETRIC DIARYL TELLURIUM DIHALIDES AND DITHIOCYANATES, R_2TeX_2

$(R'R''C_6H_3)_2TeX_2$		Method of Preparation	$(R'R''C_6H_3)_2TeX_2$		Ref.	
R'	X		mp., °C	% yield		
H	F*	$R_2TeO + HF$	153°	60	37	
	Cl*	$R_2Te + Cl_2$	160°	45**	41a	
	Cl*	$R_2Te_2 + RTeCl_3$	---	100	32	
	Cl*	$TeCl_4 + 2 RHgCl$	160-2°	>90	26	
	Cl*	$TeCl_4 + R_2Hg$	162-3°	98	26a	
	Br*	$R_2Te_2 + RTeBr_3$	---	96	32	
	Br*	$TeBr_4 + R_4Sn$	198-99°	92	24	
	I*	$R_2Te_2 + RTeI_3$	---	29	32	
	I*	$TeI_4 + R_4Sn$	236°	20	24	
	NCS	$R_2Te + (SCN)_2$	129-32° ^{††}	73	48,51	
	NCS	$R_2TeCl_2 + NH_4CNS$	140°	---	51	
	3-CH ₃	F	$R_2TeO + HF$	118°	---	37
		Cl*	$RTeCl_3 + RSi(CH_3)_3$	126-8°	32	25
4-CH ₃	F	$R_2TeO + HF$	163°	---	37	
	Cl*	$TeCl_4 + 2RHgCl$	166°	>90	26	
	Cl*	$TeCl_4 + R_2Hg$	162-3°	95	26a	
	Cl*	$RTeCl_3 + RSi(CH_3)_3$	163°	37	25	
	NCS	$R_2Te + (SCN)_2$	137° ^{††}	70	48	
4-(C ₆ H ₅) ₂ N	Cl	$TeCl_4 + 2(C_6H_5)_3N$	271-3°	---	28	
4-CH ₃ O	F*	$R_2TeO + HF$	131°	---	37	
	Cl*	$R_2Te_2 + RTeCl_3$	---	84	32	
	Cl*	$TeCl_4 + R_2Hg$	181-2°	86	26a	
	Cl*	$RTeCl_3 + RSi(CH_3)_3$	165°	58	25	
	I*	$R_2Te_2 + RTeI_3$	---	61	32	
4-CH ₃ O	NCS	$R_2Te + (SCN)_2$	106-8° ^{††}	72	48,51	
4-CH ₃ O	NCS	$R_2TeCl_2 + NH_4CNS$	110°	---	51	
R'' = ³ CH ₃ O	Cl*	$R_2Te_2 + RTeCl_3$	---	82	32	

$(R'R''C_6H_3)_2TeX_2$		TABLE 1 (CONT'D.)	$(R'R''C_6H_3)_2TeX_2$		Ref.
R'	X	Method of Preparation	mp., °C	% yield	
4-C ₂ H ₅ O	F	R ₂ TeO + HF	170°	---	37
	NCS	R ₂ Te + (SCN) ₂	100°	---	51
	NCS	R ₂ TeCl ₂ + NH ₄ CNS	100°	---	51
4-F	Cl	R ₂ Te + SO ₂ Cl ₂	128°	100	37
	Br	R ₂ Te + SO ₂ Br ₂	171°	100	37
3-Cl	Br	R ₂ Te ₂ + SO ₂ Br ₂	178°	100	37
4-Cl	I	R ₂ Te SO ₂ I ₂	220°	100	37
3-Br	Br	R ₂ Te + SO ₂ Br ₂	200°	100	37
4-Br	Cl*	TeCl ₄ + R ₂ Hg	189°	90	26a
	NCS	R ₂ Te + (SCN) ₂	158-60° ^{††}	75	48

† R'' = H unless otherwise stated †† with decomposition

* Compounds marked by an asterisk were prepared previously by a different method

** Yield based on C₆H₅TeNa for the reaction RTNa + RN₂BF₄ → R₂Te + R₂TeCl₂

Berry and co-workers²⁸ reported that tellurium tetrachloride and triphenylamine kept in benzene solutions in the presence of triethylamine at room temperature for 24 hours yielded bis(4-diphenylaminophenyl) tellurium dichloride, a yellow crystalline material. Tellurium was precipitated when tellurium tetrachloride reacted with (C₆H₅)M (M = P, As, Sb) forming (C₆H₅)₃MCl₂.

4-Dimethylaminophenyl tellurium trichloride and cyclohexene combined to give 4-dimethylaminophenyl 2-chlorocyclohexyl tellurium dichloride, which melted at 78°, in 80 percent yield. The use of bis(4-methoxyphenyl) tellurium dichloride^{P-5} and dibromide^{P-7} and bis(benzoylmethyl) tellurium dichloride^{P-6} as photosensitive imaging agents was claimed by several patents. Diaryl tellurium diisothiocyanates were prepared in yields between 70 and 75 percent from diaryl tellurides and thiocyanogen in diethyl

TABLE 2

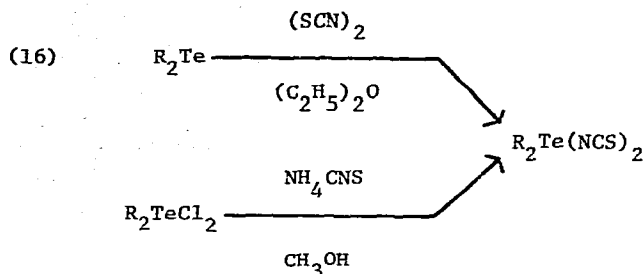
UNSYMMETRIC DIARYL TELLURIUM DIHALIDES[†], R-Te-R'
X₂

R''C ₆ H ₄ -Te-C ₆ H ₄ R''' X ₂				R''C ₆ H ₄ -Te-C ₆ H ₄ R''' X ₂				
R''	R'''	X	Method of Preparation	mp., °C	% yield	Ref.		
H	4-(CH ₃) ₂ N	Cl	RR'Te + SO ₂ Cl ₂	151°	100	37		
		Cl	C ₆ H ₅ TeCl ₃ + RHgOOCCH ₃	---	11**	35		
		Br	RR'Te + SO ₂ Br ₂	140°	100	37		
		I	RR'Te + SO ₂ I ₂	146°	100	37		
	4-CH ₃ O	Cl*	4-CH ₃ OC ₆ H ₄ TeCl ₃ + R ₂ Hg	112-3°	97	26a		
		3-F	Cl	C ₆ H ₅ TeCl ₃ + RHgCl	150°	---	37	
		4-F	Br	RR'Te + SO ₂ Br ₂	184°	---	37	
			Cl	C ₆ H ₅ TeCl ₃ + RHgCl	132°	---	37	
		4-Cl	Br	RR'Te + SO ₂ Br ₂	177-9°	---	37	
			Cl	RR'Te + Cl ₂	125°	39**	41a	
		4-Br	Cl	C ₆ H ₅ TeCl ₃ + RHgCl	144°	---	37	
		4-CH ₃	4-CH ₃ O	Cl	4-CH ₃ OC ₆ H ₄ TeCl ₃ + R ₂ Hg	163-4°	93	26a
		4-(CH ₃) ₂ CH	4-CH ₃ O	Cl	4-CH ₃ OC ₆ H ₄ TeCl ₃ + RHgCl	113-5°	72	55
4-(CH ₃) ₂ N	4-Br	Cl	C ₆ H ₅ TeCl ₃ + RHgOOCCH ₃	--- ^{††}	---	36		
		Cl	RR'Te + SO ₂ Cl ₂	152°	100	37		
		Br	RR'Te + SO ₂ Br ₂	169°	100	37		
		I	RR'Te + SO ₂ I ₂	145°	100	37		

† The reduction of these diaryl tellurium dichlorides by Na₂S·9H₂O is discussed in section VI-A1. †† Not purified

* Compounds marked by an asterisk were prepared previously by a different method. ** Crude product

ether solution^{48,51} or from diaryl tellurium dichlorides and ammonium thiocyanate in methanol⁵¹ (eqn. 16). The diisothiocyanates are white⁴⁸ or pale yellow⁵¹ solids, which according to infrared data contain nitrogen-tellurium bonds.^{48,51} The compounds are sparingly soluble in ethanol, diethyl ether and carbon tetrachloride and insoluble in petroleum ether.⁴⁸

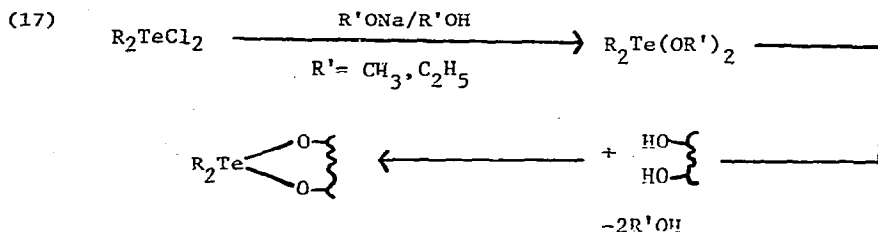


The colorless nitromethane solutions of diaryl tellurium diisothiocyanates conduct electricity suggesting a dissociation⁵¹ to $[\text{R}_2\text{Te(NCS)}]^{+}$, $[\text{R}_2\text{Te}]^{++}$ and $[\text{NCS}]^{-}$. Pertinent data for the diisothiocyanates are collected in Table 1.

The reactions of diorganyl tellurium dihalides with 1,1-dimethyl-3,5-cyclohexanedione to yield tellurium ylides⁵⁵ are discussed in section IX.

2. Diorganyl dialkoxides and dicarboxylates

Diorganyl tellurium dihalides and sodium alkoxides form diorganyl tellurium dialkoxides (eqn. 16), which are rather stable toward air and moisture.⁵² Phenols and diols react with these alkoxides according to eqn. 17. The data for these compounds are listed in Table 3. Dithiols

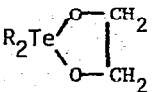
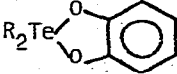
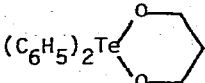
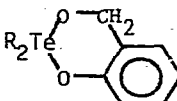
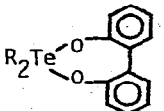
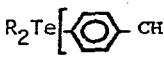
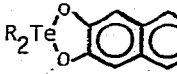


do not produce the expected heterocyclic compounds; instead they are oxidized to disulfides with a concomitant reduction of the diorganyl tellurium dialkoxide to the telluride.⁵²

A number of new and already known diaryl tellurium dicarboxylates, $\text{R}_2\text{Te(OOCR}^\prime\text{)}_2$ (Table 4), were prepared by improved methods. When a solution of the diaryl tellurium dichlorides (0.001 mol) dissolved in

TABLE 3

DIORGANYL TELLURIUM DIALKOXIDES

Compound	mp., °C	bp., °C/torr	% yield
$R_2Te(OCH_3)_2$: R = CH ₃ [*]	---	60°/1	89
R = C ₆ H ₅ ^{**}	53°	---	83
$R_2Te(OC_2H_5)_2$: R = CH ₃ [*]	---	52°/1	61
R = C ₆ H ₅ ^{**}	52°	---	75
 R = CH ₃ [†]	142°	---	69
R = C ₆ H ₅ [†]	impure oil, which crystallized at -18°		
 R = CH ₃ [†]	149°	---	83
R = C ₆ H ₅ [†]	101°	---	85
 (C ₆ H ₅) ₂ Te	115°	---	43
 R = CH ₃ [†]	178°	---	57
R = C ₆ H ₅ [†]	180°	---	69
 R = CH ₃ [†]	213°	---	41
R = C ₆ H ₅ [†]	212°	---	78
 R = CH ₃ [†]	20°	---	59
R = C ₆ H ₅ [†]	148°	---	61
 R = CH ₃	166°	---	63
R = C ₆ H ₅	131°	---	41

* Prepared from (CH₃)₂TeI₂ + R'ONa/R'OH

** Prepared from (C₆H₅)₂TeCl₂ + R'ONa/R'OH

† Prepared from R₂Te(OC₂H₅)₂ + diol or alcohol

C₂H₅OH/THF (1:1 v/v, 20 ml) was passed over an Amberlite IR45 resin in the carboxylate form (5g), the resin then rinsed with the solvent mixture (50 ml) and the solvent removed from the eluate, the diaryl tellurium carboxylates were obtained in yields as high as 99 percent.²⁶

Several diaryl tellurium dicarboxylates were prepared earlier from

TABLE 4

DIORGANYL TELLURIUM DICARBOXYLATES

(4-RC ₆ H ₄) ₂ Te(OOCR') ₂		Method of Preparation	(4-RC ₆ H ₄) ₂ Te(OOCR') ₂		Ref.
R	R'		mp., °C	% yield	
H	H	Ar ₂ Te(O ₂ CCH ₃) ₂ + HCO ₂ H/CHCl ₃	122-4°	97	53
		Ar ₂ TeO + HCO ₂ H/CHCl ₃	122-4°	95	53
	CH ₃ [†]	Ar ₂ TeCl ₂ + AERIC*	138°	70	26
		Ar ₂ TeO + (R'CO) ₂ O	143-5°	89	53
		Ar ₂ TeO + R'COOH	143-5°	97	53
	C ₂ H ₅	Ar ₂ TeCl ₂ + AERIC*	100-3°	73	26
	(CH ₃) ₂ CH	Ar ₂ TeCl ₂ + AERIC*	109°	70	26
		Ar ₂ TeO + (R'CO) ₂ O	108-9°	93	53
		Ar ₂ TeO + R'COOH	108-9°	91	53
		Ar ₂ Te(O ₂ CCH ₃) ₂ + R'COOH	108-9°	68	53
	(CH ₃) ₃ C	Ar ₂ TeCl ₂ + AERIC*	141°	70	26
		Ar ₂ TeO + R'COOH	137-40°	87	53
		Ar ₂ Te(O ₂ CCH ₃) ₂ + R'COOH	137-40°	56	53
	C ₆ H ₅ [†]	Ar ₂ TeCl ₂ + AERIC*	165°	94	26
		Ar ₂ TeO + (R'CO) ₂ O	161-3°	88	53
		Ar ₂ TeO + R'COOH	161-3°	77	53
		Ar ₂ Te(O ₂ CCH ₃) ₂ + R'COOH	161-3°	77	53
	C ₆ H ₅ CH ₂	Ar ₂ TeCl ₂ + AERIC*	86-8°	70	26
		Ar ₂ TeO + R'COOH	99-100°	92	53
	(C ₆ H ₅) ₂ CH	Ar ₂ TeCl ₂ + AERIC*	167-8°	78	26
	C ₆ H ₅ CH=CH	Ar ₂ TeCl ₂ + AERIC*	175°	82	26
CH ₃	CH ₃ [†]	Ar ₂ TeCl ₂ + AERIC*	177°	70	26
	C ₂ H ₅	Ar ₂ TeCl ₂ + AERIC*	185-7°	97	26
	C ₃ H ₇ [†]	Ar ₂ TeCl ₂ + R'COOH + Ag ₂ O	125-7	>90	26
	(CH ₃) ₂ CH	Ar ₂ TeCl ₂ + AERIC*	140-2°	83	26
	(CH ₃) ₃ C	Ar ₂ TeCl ₂ + AERIC*	140-3°	90	26

TABLE 4 (CONT'D.)

$(4-RC_6H_4)_2Te(OOCR')_2$		Method of Preparation	$(4-RC_6H_4)_2Te(OOCR')_2$		Ref
R	R'		mp., °C	% yield	
CH ₃	C ₇ H ₁₅ [†]	Ar ₂ TeCl ₂ + R'COOH + Ag ₂ O	84-6°	>90	26
	C ₁₁ H ₂₃ [†]	Ar ₂ TeCl ₂ + R'COOH + Ag ₂ O	67-8°	>90	26
	C ₆ H ₅ [†]	Ar ₂ TeCl ₂ + AERIC*	230-4°	>90	26
		Ar ₂ TeCl ₂ + R'COOH + Ag ₂ O	230-4°	>90	26
	C ₆ H ₅ CH ₂	Ar ₂ TeCl ₂ + AERIC*	95°	80	26
	(C ₆ H ₅) ₂ CH	Ar ₂ TeCl ₂ + AERIC*	147-9°	90	26
	C ₆ H ₅ CH=CH	Ar ₂ TeCl ₂ + AERIC*	207-9°	86	26
CH ₃ O	CH ₃ [†]	Ar ₂ TeCl ₂ + AERIC*	135°	98	26
	C ₂ H ₅	Ar ₂ TeCl ₂ + AERIC*	168-70°	96	26
	(CH ₃) ₂ CH	Ar ₂ TeCl ₂ + AERIC*	176-8°	99	26
	(CH ₃) ₃ C	Ar ₂ TeCl ₂ + AERIC*	176-8°	85	26
	C ₆ H ₅ [†]	Ar ₂ TeCl ₂ + AERIC*	210°	86	26
	C ₆ H ₅ CH ₂	Ar ₂ TeCl ₂ + AERIC*	90-1°	81	26
	(C ₆ H ₅) ₂ CH	Ar ₂ TeCl ₂ + AERIC*	141°	68	26
	C ₆ H ₅ CH=CH	Ar ₂ TeCl ₂ + AERIC*	162-5°	80	26

* Amberlite IR 45 Ion Exchange Resin in the Carboxylate Form

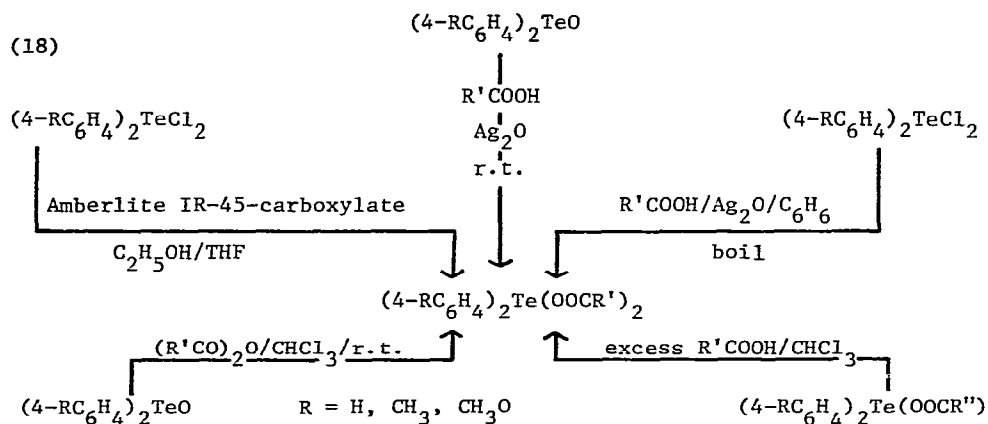
† Previously Reported^{1,2,3,4}

the diaryl tellurium dichlorides and silver salts of carboxylic acids. In the improved version of this method the cumbersome synthesis of the silver carboxylates is avoided by simply mixing the tellurium dichloride, the carboxylic acid and the silver oxide in a 1:2:1 molar ratio in benzene and refluxing the mixture for several hours. The diaryl tellurium dicarboxylates were obtained in yields higher than 90 percent. It was observed that carboxylic acids react under these conditions much faster with silver oxide than do the diaryl tellurium dichlorides. It is, therefore, likely that the dicarboxylates are formed from the silver carboxylates and the

diaryl tellurium dichlorides, rather than from the carboxylic acid and the diaryl telluroxide²⁶.

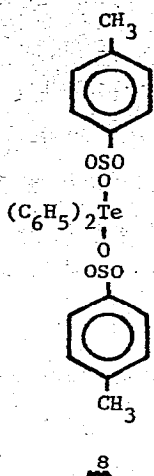
Tamagaki *et al.*⁵³ synthesized diphenyl tellurium dicarboxylates in high yields employing diphenyl telluroxide and carboxylic acid anhydrides, a method used previously by Sadekov and co-workers³, or diphenyl telluroxide and carboxylic acids. The easily accessible diphenyl tellurium diacetate was reacted with an excess of the carboxylic acids, R'COOH (R' = H, *i*-C₃H₇, tertiary-C₄H₉, C₆H₅), to produce diphenyl tellurium dicarboxylates *via* carboxylate exchange. All these reactions were carried out at room temperature with chloroform as the solvent. It is noteworthy, that the reaction between diphenyl tellurium dichloride and sodium formate did not produce diphenyl tellurium diformate.⁵⁰

Pertinent data for the diaryl tellurium dicarboxylates prepared by these methods (eqn. 18) are summarized in Table 4.

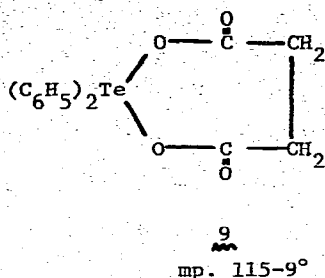


In addition to the diphenyl tellurium dicarboxylates listed in Table 4, Tamagaki *et al.*⁵³ synthesized diphenyl tellurium bis(4-methylphenylsulfonate) 8 and the carboxylates 9 and 10 derived from dicarboxylic acids. Propiolactones gave oligomeric compounds with a molecular mass larger than 1000.

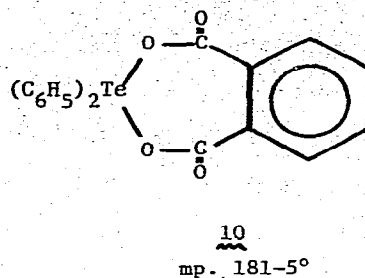
The diphenyl tellurium *ortho*-phthalate 10 obtained by Tamagaki⁵³ (mp. 181-5°) is different from the product (mp. 108-10°) of the reaction between diphenyl tellurium dichloride and disodium phthalate^{4,50} for



mp. 282-5°; $R_2TeO + (R'SO_2)_2O$: 79% yield; $R_2TeO + R'SO_3H$: 71%
 $R_2Te(OOCH_3)_2 + R'SO_3H$: 74% yield



mp. 115-9°



mp. 181-5°

$R_2TeO + (R'CO)_2O$: 93% yield $R_2TeO + (R'CO)_2O$: 99% yield

which a dimeric structure was suggested.⁵⁰

C. Diorganyl Telluroxides

The reactions of diaryl telluroxides with hydrofluoric acid to give diaryl tellurium difluorides³⁷ are discussed in section VI-B1. The preparation of diphenyl tellurium dicarboxylates from diphenyl telluroxide and carboxylic acids or carboxylic acid anhydrides⁵³ is described in section VI-B2. Diphenyl telluroxide and 4-methylbenzenesulfonic acid yielded diphenyl tellurium bis(4-methylbenzenesulfonate).⁵³ The synthesis of bis(4-methoxyphenyl) tellurium benzenesulfonimides from the diaryl telluroxide and arylsulfonamides⁵⁴ is treated in section IX.

A pKa value of 14.9 was reported for bis(4-methoxyphenyl) telluroxide in acetonitrile.⁵⁴

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

The reaction of $C_3H_7S-C\equiv C-TeCH_3$ with methyl iodide at 35° and then at room temperature for two days produced the telluronium iodide $[C_3H_7S-C\equiv C-Te(CH_3)_2]^+I^-$ in 76 percent yield. The compound melted at 196-8° with decomposition.¹⁷

VIII. Tetraorganyl Tellurium Compounds, R_4Te

The mechanism of the thermal decomposition of tetraaryl tellurium compounds was investigated. Tetraphenyl tellurium decomposed at 140° in vacuo in a sealed tube to diphenyl telluride (92%), biphenyl (89%) and benzene (10%). Similar decomposition experiments under a nitrogen atmosphere but at 80° in the presence of toluene, triethylsilane, furan or styrene gave similar results indicating that there is little radical trapping. Only traces of polymer were formed during the decomposition of tetraphenyl tellurium in styrene, whereas decomposition of dibenzyl peroxide under similar conditions produced polystyrene in 77 percent yield.⁴⁹

Tetrakis(4-methylphenyl) tellurium likewise decomposed on melting at 124-7° to the diaryl telluride, 4,4'-dimethylbiphenyl and a small amount of toluene. The decomposition in the presence of a 2:1 mixture of benzene/1,4-dihydroxybenzene, a powerful hydrogen atom transfer reagent, yielded less toluene than the decomposition of the neat tetrakis(4-methylphenyl) tellurium.⁴⁹

These results indicate that radicals, which can be trapped, are not formed during the decomposition reactions. However, the decomposition of the mixtures $(C_6H_5)_4Te / ((4-CH_3C_6H_4)_4Te$ and $(C_6H_5)_4Te / (C_6D_5)_4Te$ yielded large quantities of mixed biaryls and unsymmetric diaryl tellurides. The experimental molar ratios of the products agree reasonably with those calculated assuming random exchange of aryl groups among the tetraaryl tellurium compounds before decomposition and equal likelihood for the decomposition of the various tetraaryl tellurium compounds. Aryl groups exchange was observed in mixtures of tetrakis(4-methylphenyl) tellurium and diphenyl telluride but not between diaryl tellurides.⁴⁹

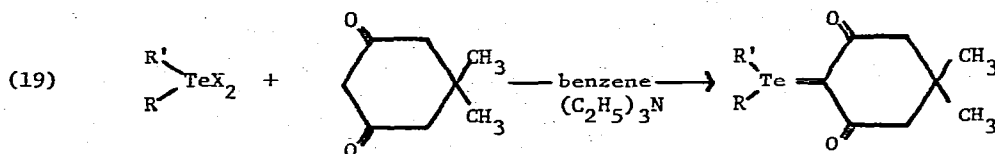
Barton, Glover and Ley⁴⁹ concluded "that tetraaryl tellurium compounds exchange ligands by a fast non-radical process prior to decomposition to diaryl tellurides and biaryls. The decomposition process itself is concerted, does not involve radicals, and represents an interesting procedure for the formation of carbon-carbon bonds."⁴⁹

tert-Butanethiol and tetraphenyl tellurium reacted exothermically at

room temperature. Benzene, diphenyl telluride and di(*tert*-butyl) disulfide were the only products. The reaction is considered to be heterolytic.⁴⁹

IX. Tellurium Ylides

Sadekov and co-workers⁵⁵ prepared fourteen ylides from diorganyl tellurium dihalides and 1,1-dimethyl-3,5-cyclohexanedione employing a technique reported previously^{3,4} (eqn. 19). Ylides were not formed when diorganyl



R, R', X, mp. °C, % yield: CH₃, CH₃, Cl, 98°, 80%; CH₃, C₆H₅, Br, 148°, 89%; CH₃, 4-CH₃C₆H₄, Br, 113-5°, 93%; CH₃, 4-CH₃OC₆H₄, Br, 156°, 100%; CH₃, 4-C₂H₅OC₆H₄, Br, 97°, 92%; C₆H₅, C₆H₅*, Br, 159°, 100%; 4-CH₃C₆H₄, 4-CH₃C₆H₄*, Br, 137°, 75%; 4-(CH₃)₂NC₆H₄, 4-(CH₃)₂NC₆H₄, Cl, 150°, 91%; 4-CH₃OC₆H₄, 4-CH₃OC₆H₄*, Br, 144°, 89%; 4-C₂H₅OC₆H₄, 4-C₂H₅OC₆H₄, Cl, 143°, 97%; 4-FC₆H₄, 4-FC₆H₄, Cl, 128°, 83%; 4-BrC₆H₄, 4-BrC₆H₄, Br, 157°, 95%; 4-CH₃OC₆H₄, C₆H₅CH₂, Cl, 141-3°, 97%; 4-CH₃OC₆H₄, 4-(CH₃)₂CHC₆H₄, Cl, 104°, 91%.

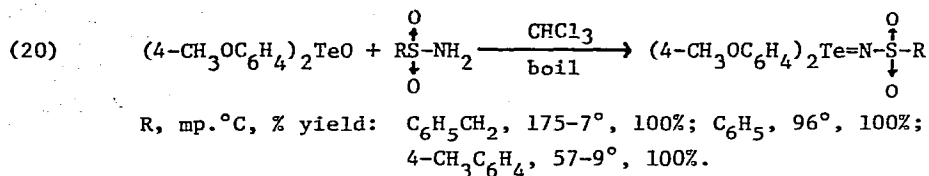
* Reported previously

tellurium dihalides were reacted with acetylacetone, dibenzolymethane, ethyl acetylacetate, malonic ester or malonitrile. With dimethyl tellurium diiodide a mixture of unidentified compounds was obtained.⁵⁵

The tellurium ylides are colorless, crystalline substances, readily soluble in benzene, carbon tetrachloride and methylene chloride but insoluble in petroleum ether. The thermodynamic basicity constants, pK_a, of these ylides in acetonitrile at 25° lie in the range 10.07 to 12.07, indicating that they are fairly strong bases comparable to aromatic amines. The ylides possess trigonal-pyramidal structure. The tellurium pyramid is configurationally stable at room temperature according to nmr data.⁵⁵

The tellurium ylides, R₂Te=NSO₂R (diaryl tellursulfonimides), were

prepared from diaryl telluroxides and the sulfonamides⁵⁴ (eqn. 20).



X. Organic Tellurium Compounds Containing a Tellurium-Metal, a Tellurium-Metalloid or a Tellurium-Nitrogen Bond

During the period covered by this survey organic tellurium compounds containing a Te-Li, Te-Na, Te-B, Te-Si, Te-Sn, Te-P, Te-N, Te-S, Te-Se, Te-Mo, Te-Re, Te-Mn, or Te-Pt were investigated.

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

Phenyl lithium telluride, C₆H₅TeLi, was used to prepare molybdenum complexes containing the phenyltelluro group¹⁴. For details on the complex see section X-E.

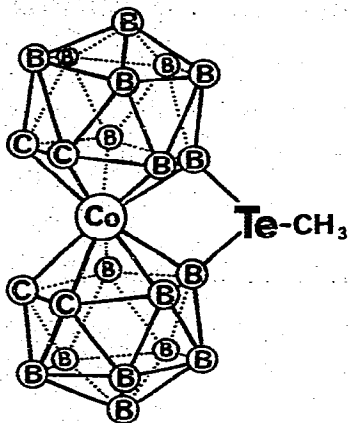
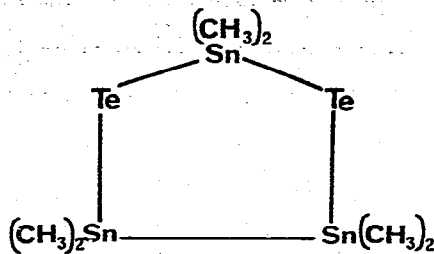
Methyl sodium telluride, CH₃TeNa, was obtained by reacting dimethyl ditelluride with sodium in liquid ammonia at -78° under a nitrogen atmosphere. The compound was not purified. Evaporation of the ammonia followed by treatment of the residue with 2N sulfuric acid produced methanetelluro³⁰.

The aryl sodium tellurides, 4-RC₆H₄TeNa (R = H, CH₃, CH₃O) and 2,4-(CH₃O)₂C₆H₃TeNa, were obtained by treating the solutions of diaryl ditellurides in absolute methanol with sodium borohydride.⁴¹ These tellurides were not isolated.

They were used as sources of telluroate ions for the addition to acetylene derivatives⁴¹ (section VI-A1), reaction with phenylethynyl bromide^{P-4} or reaction with aryldiazonium tetrafluoroborates.⁴¹

Several new ethynyl sodium tellurides, RC≡C-TeNa (R = H,^{16a} CH₃S¹⁶, C₃H₇S¹⁷) were synthesized by reacting tellurium with sodium acetylides in liquid ammonia. Addition of methyl iodide to the reaction mixtures containing the ethynyl sodium tellurides yielded ethynyl methyl tellurides (section VI-A1).

The first compound with a tellurium-boron bond, $\text{CH}_3\text{Te}(\text{C}_2\text{B}_9\text{H}_{10})\text{Cs}$ 11, aside from the adducts $\text{R}_2\text{Te}\cdot\text{BX}_3$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) and $(\text{R}_2\text{TeBr}_2)_2\cdot\text{BBr}_3$, was prepared from tellurium and the carborane derivative $[(\text{C}_2\text{B}_9\text{H}_{10})_2\text{Co}]^-\text{Cs}^+$ in an acetic anhydride/sulfuric acid medium followed by addition of dimethyl sulfate.¹⁸ The red compound 11 was isolated in 3.1 percent yield. It decomposed above 300° .

11

28.5% yield
mp. 55°

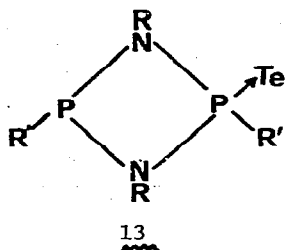
12

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

Bis(triorganylsilyl) tellurides, $(\text{R}_3\text{Si})_2\text{Te}$, were employed to produce SiTe -films by thermal decomposition at 450° on a glass-ceramic substrate.^{P-8} Bis(trimethylstannyl) telluride reacted with $(\text{CO})_5\text{MBr}$ ($\text{M} = \text{Mn}, \text{Re}$) to give $[(\text{CO})_4\text{M}-\text{Te}-\text{Sn}(\text{CH}_3)_3]_2$.⁵⁶ The reaction of tellurium with dimethylstannane, $(\text{CH}_3)_2\text{SnH}_2$, in diethyl ether/dimethylformamide at room temperature produced the thermally labile and air-sensitive heterocyclic compound 12.¹²

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

The phosphine telluride 13a was isolated in quantitative yield as pale yellow crystals from a reaction mixture containing the parent phosphine and tellurium in benzene at room temperature.¹⁹ Compound 13a is stable in benzene solution for several weeks in daylight in contrast to other phos-



13a R, R': CH₃, (CH₃)₃C¹⁹

13b R, R': (CH₃)₃C, (CH₃)₂N^{19a}

phine tellurides.¹ The crystalline solid softens between 77° to 83° and melts in the range 83° to 90°. The phosphine telluride 13b was prepared similarly.^{19a} It decomposed at 120°. According to nmr data the tellurium atom migrates in both of these compounds between phosphorus atoms inter- and intramolecularly.^{19,19a}

The formation of (C₆H₅)₂CH₃P=Te was observed during the photolytic decomposition of dibenzyl or diethyl ditelluride in C₆D₆ solutions. An equilibrium between R₃P and R₃P=Te exists in these solutions with rapid exchange (on the nmr time scale) of the tellurium atom.⁴²

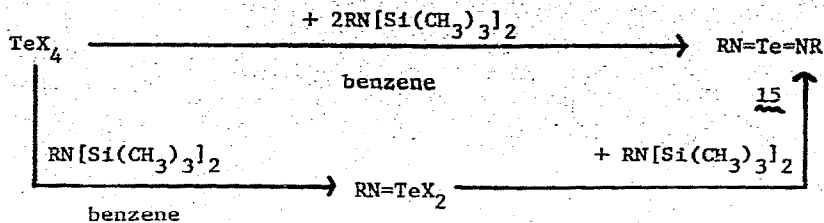
Organic tellurium compounds containing a tellurium-nitrogen bond have hardly been investigated at all. Until recently, the only known example was the adduct¹ (CH₃)₂TeI₂·nNH₃. The first representatives of compounds with tellurium-nitrogen bonds have now been reported. The reactions between bis(4-methoxyphenyl) telluroxide and arene- or phenylmethanesulfonamides yielded diaryl tellurimides, R'₂Te=NSO₂R. Pertinent data for these derivatives are given in section IX.

Examples of another class of tellurium-nitrogen compounds were prepared from tellurium tetrafluoride or tetrachloride and bis(trimethylsilyl)-carboxylic acid amides or sulfonamides (eqn. 21).⁵⁷

The compounds, 4-RC₆H₄SO₂N=TeF₂ (R = H, CH₃) reacted with N-trimethylsilylmorpholine in benzene solution to produce the tellurium derivatives 16.⁵⁷

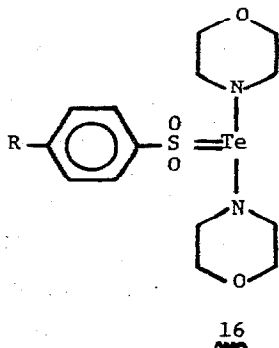
The tellurium-nitrogen bonds in the compounds 14, 15 and 16 are hydrolyzed upon boiling with water producing tellurium dioxide and the amide. Bubbling hydrogen chloride through diethyl ether solutions of these compounds gave tellurium tetrachloride and the amides. With elemental chlorine

(21)



14 (R, X, mp. °C, % yield): CH₃CO, F, 111-3°, 96%; CH₃CO, Cl, 121-3°, 55%;
 C₆H₅SO₂, F, 238-40°, 91%; C₆H₅SO₂, Cl, 250°(dec), 72%;
 4-CH₃C₆H₄SO₂, F, 246°(dec), 96%; 4-CH₃C₆H₄SO₂, 237°(dec), 64%

15 (R, mp. °C, % yield): CH₃CO, 150-2°, 77%; C₆H₅SO₂, 257°, 90%;
 4-CH₃C₆H₄SO₂, 258°, 96%.



R = H: m. 109-12°(dec), 74% yield

R = CH₃: m. 110-1°(dec), 77% yield

RSO₂NCl₂ and tellurium tetrachloride were formed.⁵⁷

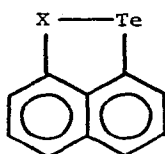
D. Organic Compounds of Tellurium with a Tellurium-Sulfur or Tellurium-Selenium Bond

Dibenzyl sulfide telluride was obtained as a yellow crystalline product melting at 68-9° from benzyl tellurocyanate and phenylmethanethiol in carbon tetrachloride solution.²¹

The heterocyclic compounds 17 containing a tellurium-sulfur or -selenium bond are discussed in section XI-E.

E. Organic Tellurium Compounds as Ligands in Transition Metal Complexes

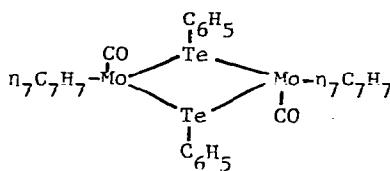
The phenyltelluro-bridged dinuclear molybdenum complex 18 was prepared.



X = S, Se

17

in 54% yield from phenyl lithium telluride and $(C_7H_7)Mo(CO)_2Br$ in methylene chloride.⁴¹ The compound melted with decomposition at 118° .



18

Bis(trimethylsilyl) telluride heated with $(CO)_5MnBr$ in benzene or with $(CO)_5ReCl$ in 1,2-dimethoxyethane gave $[(CH_3)_3Sn-Te-Re(CO)_4]_2$, a red-golden solid, in 11 percent yield and $[(CH_3)_3Sn-Te-Re(CO)_4]_2$ as orange crystals in very low yield.⁵⁶ The manganese complex decomposed at 150° , but was stable in air at room temperature. Treatment of the manganese complex in diethyl ether solution with hydrogen chloride produced the air sensitive compound $[(CO)_4Mn-TeH]_2$ in 57% yield.

XI. Heterocyclic Tellurium Compounds

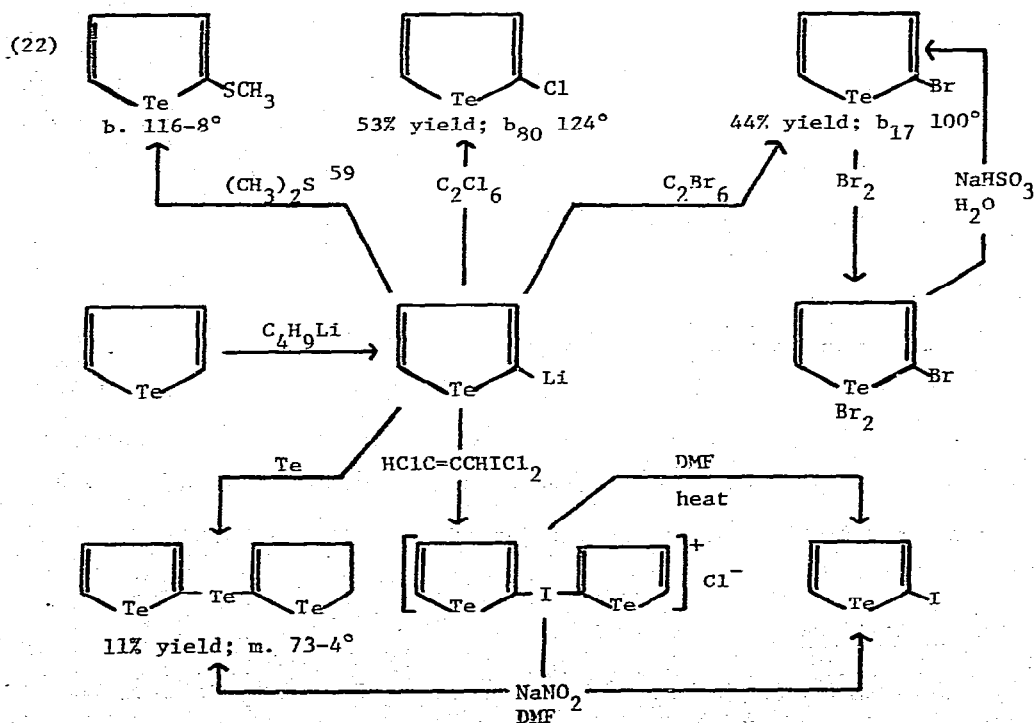
Tellurophene derivatives, polycyclic fused tellurophenes, benzotellurophene, 1-chalcogena-2-telluraacenaphthenes, 1-tellura-2,5-cyclohexanedione-containing merocyanine dyes, 1-sila-3-telluracyclohexane derivatives and the anion radicals of nitrophenoxtellurines were investigated.

A. Tellurophene

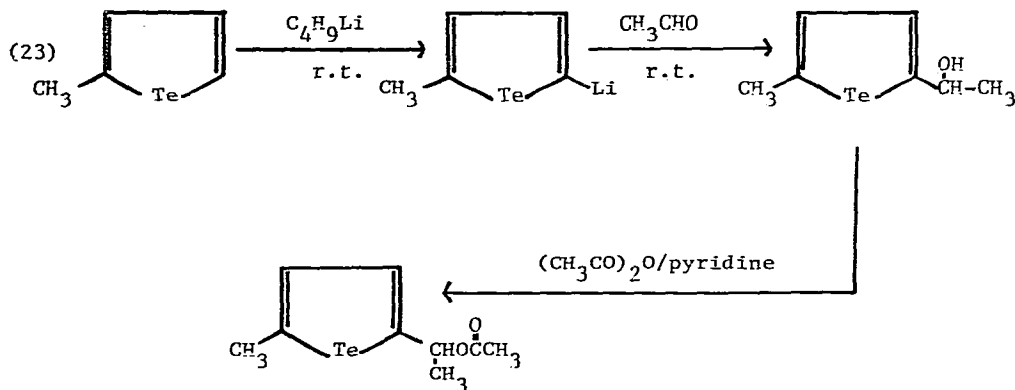
A convenient method for the preparation of 2-halotellurophenes was

discovered in the reaction of 2-lithiotellurophene with hexachloro- or hexabromoethane. 2-Fluorotellurophene could not be obtained from 2-lithio-tellurophene and perchloryl fluoride, FClO_3 . Bis(2-tellurophene-yl) iodonium chloride was isolated as the product of the reaction between 2-lithiotellurophene and perchloryl fluoride, FClO_3 . Bis(2-tellurophene-yl) iodonium chloride was isolated as the product of the reaction between 2-lithiotellurophene and trans- $\text{ClCH}=\text{CHICl}_2$. When the iodonium chloride was heated in dimethylformamide, 2-iodophenyltellurophene was formed. Attempts to prepare 2-nitrotellurophene from 2-lithiotellurophene and ethyl nitrate or bis(tellurophene-yl) iodonium chloride and sodium nitrate were unsuccessful; bis(tellurophene-yl) telluride was isolated from both reaction mixtures. This telluride was also formed when 2-lithiotellurophene was reacted with tellurium.⁵⁸ These reactions are summarized in eqn. 21.

Lumbroso et al.⁵⁹ prepared 2-methylthiotellurophene from 2-lithiotellurophene and dimethyl sulfide (eqn. 22) and 2-hydroxymethyltellurophene ($b_{0.05}$ 88-9°) by reduction of 2-carboxytellurophene with lithium aluminum hydride in diethyl ether.

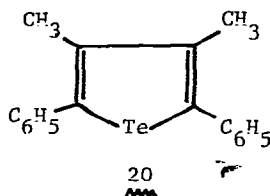
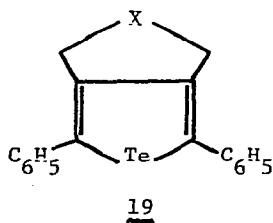


The preparation of 2-methyl-5-(1'-hydroxyethyl)tellurophene and its acetyl derivative⁶⁰ is outlined in eqn. 23.



The rate of formylation and trifluoroacetylation of 2-methyltellurophene and the rate of solvolysis of 2-methyl-5-(1'-hydroxyethyl)tellurophene in 30 percent ethanol was studied and compared to the rates of these reactions observed for the corresponding oxygen, sulfur and selenium heterocycles.⁶⁰

The reaction of 2,5-diphenyl-3,4-bis(chloromethyl)tellurophene with sodium chalcogenides, Na_2X , yielded the heterocyclic compounds 19. Whereas



the sulfur and selenium derivatives 19 ($\text{X} = \text{S}, \text{Se}$) could be isolated (see section XI-B); the tellurium compound 19 ($\text{X} = \text{Te}$) decomposed to 2,5-diphenyl-3,4-dimethyltellurophene 20 upon concentrating its benzene/methanol solution. This tetra-substituted tellurophene derivative was isolated in 30 percent yield.⁶¹ It melted at 96° .

The reactions of 2,5-diphenyl-3,4-diformyltellurophene⁶² with hydrazine,

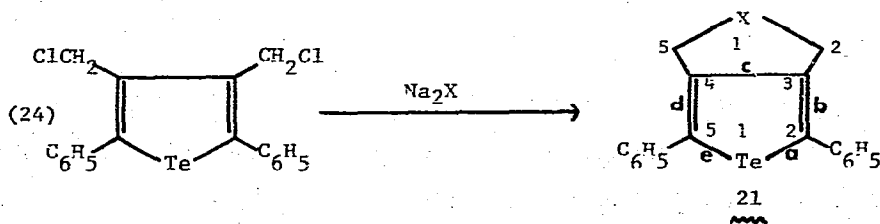
diaminobenzene, carbonyl compounds and carboxylic acid esters are discussed in section XI-B.

2,5-Diphenyltellurophene reacted with butyl lithium in diethyl ether in the presence of N,N,N',N'-tetramethylethylenediamine at room temperature to give 1,4-dilithio-1,4-diphenylbutadiene, which was used to prepare a variety of 1,4-disubstituted butadienes.⁶³

2-Methylthiophene and 2-iodothiophene were reported to react with tetramethylsilane in acetone-d₆.⁵⁸

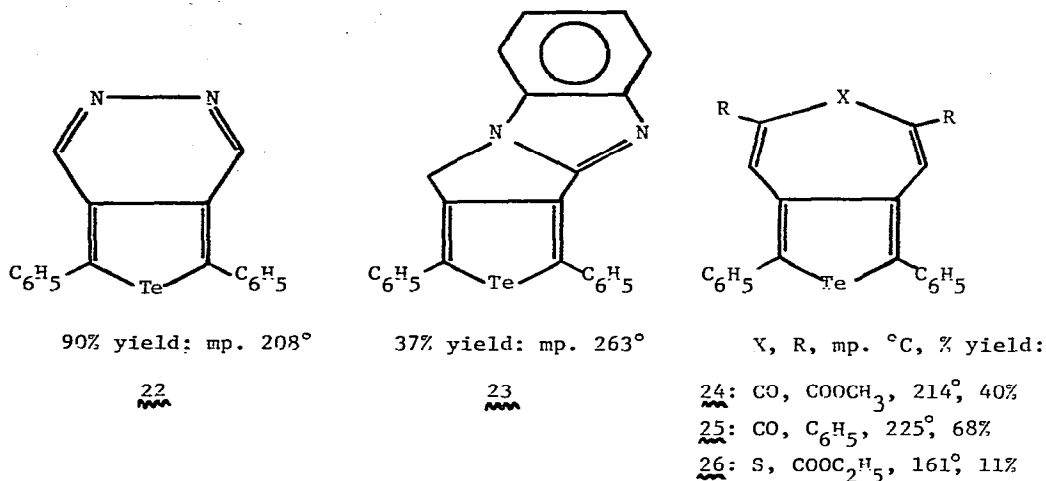
B. Polycyclic [3,4-c]-Fused Tellurophenes and Dihydrotellurophenes

Benzo[3,4-c]-2,5-dihydrotellurophene 1,1-diiodide was prepared in 83 percent yield by boiling a solution of bis(1,2-chloromethyl)benzene and sodium iodide with tellurium powder (< 100 μm) in 2-methoxyethanol.⁶⁴ The diiodide was obtained in two crystalline forms. The α-form precipitated upon recrystallization from dimethylformamide as yellow to orange holohedral monoclinic needles, which melted at 225° (dec). The β-form was obtained upon recrystallization from ethyl acetate as orange-red monoclinic crystals resembling octahedra, which melted at 222° (dec).⁶⁴ The reaction of 2,5-diphenyl-3,4-bis(chloromethyl)tellurophene with sodium chalcogenides, Na₂X, in refluxing absolute methanol (X = Se, Te) or ethanol (X = S) yielded the 2,5-diphenyl-2',5'-dihydrochalcopheno[3,4-c]tellurophenes 21 (eqn. 24).⁶¹ The compound 21 with X=Te decomposed to 2,5-diphenyl-3,4-dimethyltellurophene when its solution in benzene/methanol was concentrated.⁶¹

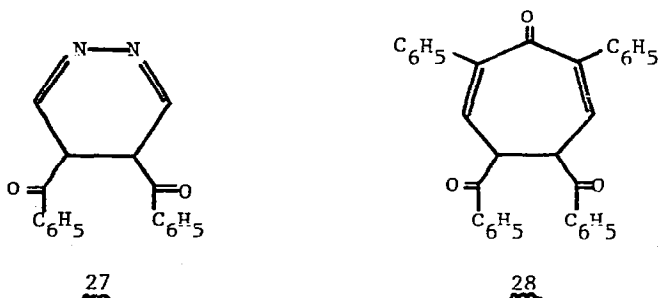


X = S: 82% yield; mp. 167°
X = Se: 60% yield; mp. 220°

The condensation of hydrazine, 1,2-diaminobenzene, $(\text{CH}_3\text{OOCCH}_2)_2\text{CO}$, dibenzyl ketone or $(\text{C}_2\text{H}_5\text{OOCCH}_2)_2\text{S}$ with 2,5-diphenyl-3,4-diformyltellurophene yielded the polycyclic tellurophene derivatives 22-26.⁶²



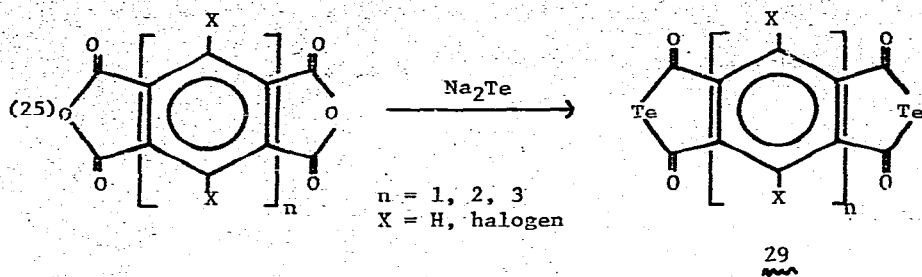
Compounds 22 and 25 eliminated the tellurium atoms upon exposure of their chloroform solutions to air and daylight forming the tellurium-free compounds 27 and 28 respectively.⁶²



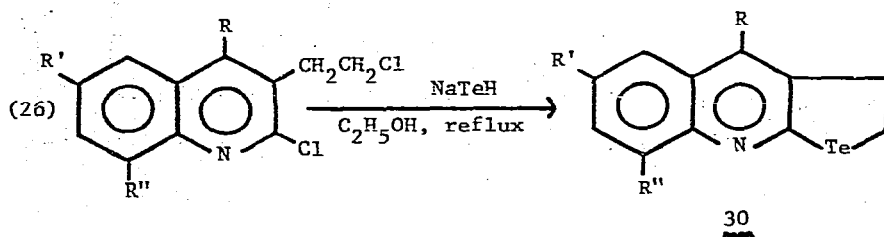
A Russian patent^{P-2} claims photosensitizing properties for the 2,5-dioxo-2,5-dihydrotellurophene derivatives 29, which were prepared according to eqn. 25.

C. Polycyclic [4.5-d]-Fused Tellurophenes and Dihydrotellurophenes

The condensation of sodium hydrogen telluride, obtained from tellurium



and sodium borohydride in ethanol, with 2-chloro-3-(chloroethyl)pyridines produced [4,5-d]-fused 2,3-dihydrotellurophenes 30 (eqn. 26).²²



$R=R'=R''=\text{H}$: 30% yield, mp. 122-4°

$R'=R''=\text{H}$, $R=\text{C}_6\text{H}_5$: 44% yield, mp. 143°

$R=R''=\text{H}$, $R'=\text{CH}_3$: 49% yield, mp. 143-5°

$R=R'=\text{H}$, $R''=\text{CH}_3$: 38% yield, mp. 98.5°

2-Acetyl-benzo[4,5-d]tellurophene was reduced to the corresponding hydroxy derivative with sodium borohydride in diethyl ether, which was then acetylated with acetic anhydride/pyridine to 2-[acetoxy(methyl)methyl]-benzo[4,5-d]tellurophene. The acetylated compound melted at approximately 30°. It was obtained in 70 percent yield. The rate of solvolysis in 30 percent ethanol at 60° was determined and compared to the rates observed for the corresponding furan, thiophene and selenophene derivatives.⁶⁰

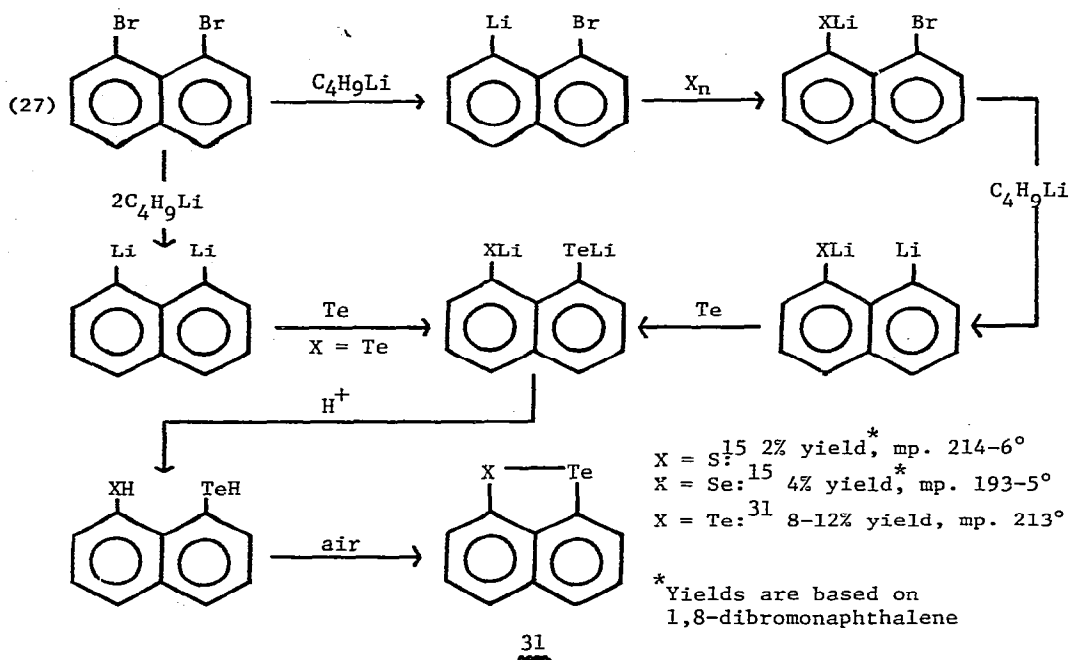
D. Benzotellurophene

Benzotellurophene 1,1-dibromide⁴⁰ was formed when 2-biphenyl tellurium

tetrabromide was heated at 180°.

E. 1-Chalcogena-2-telluraacenaphthenes

The 1-chalcogena-2-telluraacenaphthenes were prepared according to eqn. 27.



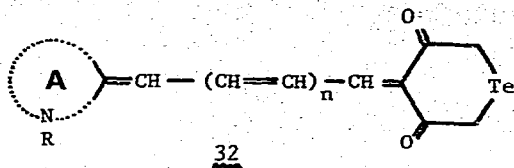
The compounds 31 form 1:1 adducts with 7,7,8,8-tetracyanoquinodimethane.^{15,31}

The adduct with compound 31 (X = Te) is deeply colored and appears to be metallic at room temperature according to its resistivity.³¹ The selenium derivative of 31 (X = Se) is reported to complex with iodine.¹⁵

When compound 31 (X = Te) was reacted with methyl lithium in tetrahydrofuran 2,8-dimethylnaphthalene and traces of perylene were produced.³¹

F. 1-Tellura-3,5-cyclohexanedione Derivatives

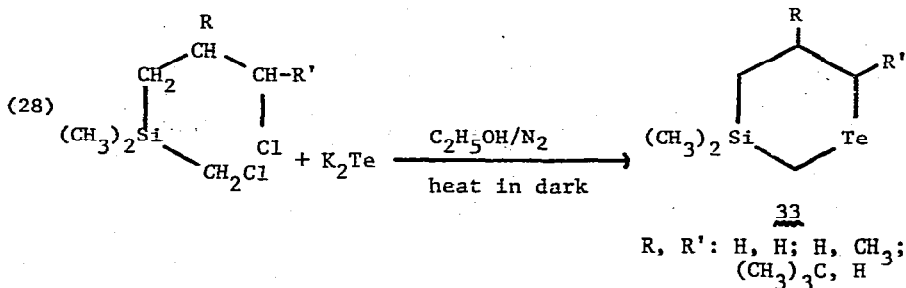
Tellurium containing merocyanine dyes 32, useful as photosensitizers, were prepared from 1-tellura-3,5-cyclohexanedione.^{P-9, P-10} The quinoline derivative 32 (R = C₂H₅, n = 0) melted at 220-30°.^{P-9}



A: quinoline, iodoline, benzoselenazole, benzoxazole,
 benzothiazole, naphthothiazole; R = CH₃, C₂H₅;
 n = 0, 1, 2.

G. 1-Sila-3-telluracyclohexane

The reaction of potassium telluride with dimethyl(chloromethyl)-4-chloro propylsilane²³ (eqn. 28) produced the unstable 1-sila-3-telluracyclohexanes



33 in yields higher than 50 percent. The silatelluracyclohexanes adopt the chair conformation according to nmr data with ring torsion angles in the aliphatic region somewhat more puckered than in cyclohexane.⁶⁵

H. Phenoxtellurine

The electrolytic reduction of 2,8-dinitro- and 2-nitrophenoxtellurine in dimethyl sulfoxide/tetrabutylammonium perchlorate generated anion radicals. The electron spin resonance spectrum of the 2,8-dinitrophenoxtellurine anion radical is consistent with the presence of two asymmetric conformers undergoing exchange.⁶⁶ MO calculations were performed for the anion radicals.

XII. Physicochemical Investigations of Organic Tellurium Compounds

Infrared, Raman, ultraviolet-visible, ^1H -, ^{11}B -, ^{13}C -, ^{19}F -, and ^{31}P -nuclear magnetic resonance, electron and mass spectroscopy, 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 (cm^{-1}) are listed only for modes involving the tellurium atom. Other band assignments are indicated. If ir spectra of a series of similar compounds are reported, only the general formula for these compounds is given, with the reference to the section where the individual compounds can be found.

$\text{CH}_3\text{TeH}^{30}$: ir (gas), Raman (solid, -196°), assignment of frequencies; comparison with CH_3X (X = Br, OH, SH, SeH); $\nu_s(\text{TeH})$ 1984 vs(R), 1995 vs(ir); $\nu_s(\text{CTe})$ 521 m(R), 515 m(ir); $\rho_r(\text{TeH})$ 857 m(R), 860s(ir).

$\text{C}_6\text{H}_5\text{CH}_2\text{TeCN}^{21}$: ir (KBR) $\nu(\text{TeCN})$ 2180.

$\{[(\text{C}_6\text{H}_5)_3\text{P}]_2\text{N}\}\text{TeCN}^{20}$: ir (CH_3CN soln.) $\nu(\text{TeC}^{12}\text{N})$ 2081; $\nu(\text{TeC}^{13}\text{N})$ 2034.

$(\text{CH}_3)_2\text{NC(O)TeCl}_3 \cdot \text{L}$ (L = quinoline, dimethylformamide) 29 : $\nu(\text{TeCl})$ 370; $\nu(\text{CO})$.

$(\text{CF}_3)_2\text{Te}_2^{\text{P-3}}$: ir bands listed

$(\text{CH}_3)_2\text{Te}^{67}$: ir; on the basis of analysis of the ir spectrum D_{3d} symmetry with a linear C-Te-C group was suggested for $(\text{CH}_3)_2\text{Te}$.

$(\text{CF}_3)_2\text{Te}^{\text{P-3}}$: ir bands listed.

$(\text{CH}_2=\text{CH})_2\text{Te}^{13}$: ir $\nu(\text{CTe})$ 515, 550; (C=C, $\text{CH}_2=$, HC=).

$\text{HC}\equiv\text{C}-\text{Te}-\text{CH}_3^{16a}$: ir $\nu(\text{C}\equiv\text{C}, \text{HC}\equiv)$. $\text{CH}_3\text{SC}\equiv\text{C}-\text{Te}-\text{CH}_3^{16}$: ir $\nu(\text{C}\equiv\text{C})$.

$\text{C}_3\text{H}_7\text{SC}\equiv\text{C}-\text{Te}-\text{CH}_3^{17}$: ir (neat), bands listed.

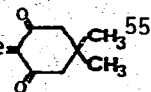
$\text{RC}_6\text{H}_4\text{TeC(R)=CHC(O)R}'^{41}$: ir (CCl_4) $\nu(\text{CO})$.

$(\text{RC}_6\text{H}_4)_2\text{Te}(\text{OOCR}')_2^{26,53}$: ir (KBr) $\nu(\text{CO})$; (section VI-B2).

$(\text{C}_6\text{H}_5)_2\text{Te}(\text{O}_3\text{SC}_6\text{H}_4\text{CH}_3)_2^{53}$: ir (KBr), bands listed.

$(\text{RC}_6\text{H}_4)_2\text{Te}(\text{NCS})_2^{48,51}$: ir (mineral oil) $\nu(\text{NCS})$; (section VI-B1).

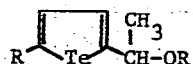
$[\text{C}_3\text{H}_7\text{SC=C-Te}(\text{CH}_3)_2]^+\text{I}^-^{17}$: ir(KBr), bands listed.


$(\text{RC}_6\text{H}_4)_2\text{Te}$  55 : ir (mineral oil) $\nu(\text{CO})$ (section IX).

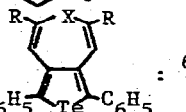
$(4\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{Te=NSO}_2\text{R}^{54}$: ir (vaseline oil), bands listed (section IX).

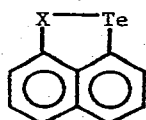
$[(\text{C}_7\text{H}_7)(\text{CO})\text{Mo}(\text{TeC}_6\text{H}_5)]_2^{14}$: ir (CH_2Cl_2 or KBr) $\nu(\text{CO})$.

$[\text{HTe-Mn}(\text{CO})_4]_2(\text{M=Mn, Re})^{56}$: ir (cyclohexane) $\nu(\text{CO})$.

R  CH_3 $\text{CH-OR}'$ (R, R': H, CH_3CO ; CH_3 , H; CH_3 , CH_3CO):⁶⁰ ir (film) $\nu(\text{CO})$, $\nu(\text{OH})$.

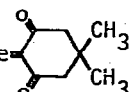
 TeI_2 :⁶⁴ ir (Nujol), bands listed.

 Te C_6H_5 C_6H_5 :⁶² ir (KBr), $\nu(\text{CO})$ (section XI-C).

 (X = S, Se¹⁵, Te³¹): ir (KBr), bands listed.

B. Ultraviolet-Visible Spectroscopy

Ultraviolet-visible spectral data were reported for diethyl ditelluride,

dibenzyl ditelluride,⁴² $\text{C}_6\text{H}_5(\text{R})\text{Te}$  (R = CH_3 , C_6H_5),⁵⁵

$\text{CH}_3\text{Te}(\text{C}_2\text{B}_9\text{H}_{10})\text{Co}^{18}$ (section XI-A, compound 11), [3,4-c]benzo-2,5-dihydro-tellurophene 1,1-diiodide⁶⁴, the polycyclic [3,4-c]-fused tellurophenes⁶² (section XI-B, compounds 22-26), 1,2-ditelluraacenaphthenes³¹, and the

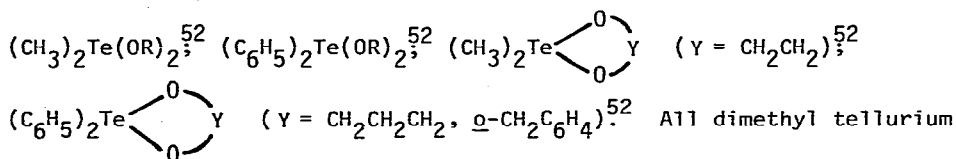
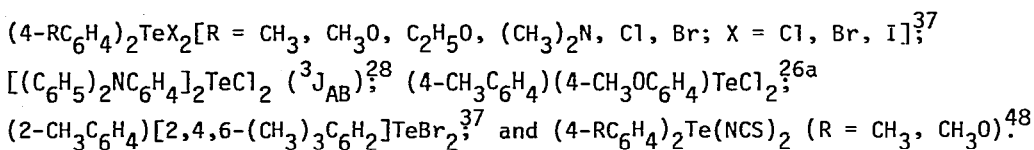
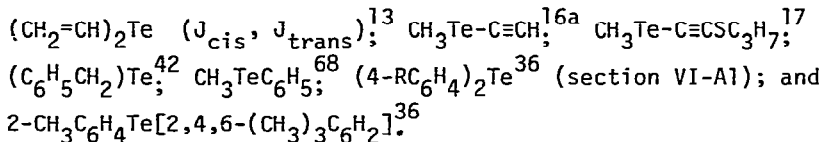
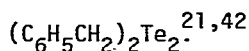
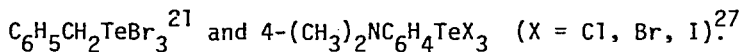
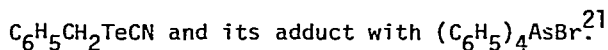
tellurium containing merocyanine dye 32 (section XI-F) (A = quinoline, R = C₂H₅, n = 0)^{P-9, P-10}.


C. Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy employing the nuclei ¹H, ¹¹B, ¹³C, ¹⁹F and ³¹P were used to characterize organic compounds.

1. ¹H-NMR Spectroscopy

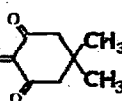
¹H-nmr data were reported for the following compounds:



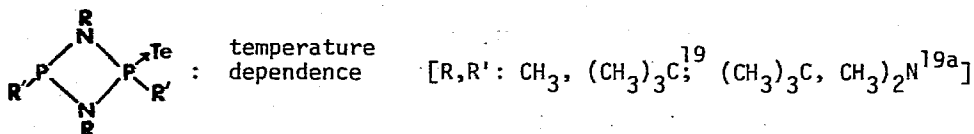
dialkoxides give only one methyl signal although two signals would be expected for (CH₃)₂Te  on the assumption of a trigonal bipyramidal structure. A fast ligand exchange in the trigonal bipyramidal molecule or a rigid tetragonal pyramidal structure could account for the single methyl

resonance.⁵²

$(4\text{-RC}_6\text{H}_4)_2\text{Te}(\text{OOCR}')_2$ ($J_{\text{H-H}}$) (section VI-B2);^{26,53} $(\text{C}_6\text{H}_5)_2\text{Te}(\text{O}_3\text{SC}_6\text{H}_4\text{CH}_3)_2$;⁵³
 diphenyl tellurium ortho-phthalate and malonate.⁵³

$(4\text{-RC}_6\text{H}_4)_2\text{Te}$

 (section IX);⁵⁵ and $(4\text{-CH}_3\text{OC}_6\text{H}_4)_2\text{Te}=\text{NSO}_2\text{R}$
 $(\text{R} = \text{C}_6\text{H}_5\text{CH}_2, \text{C}_6\text{H}_5, 4\text{-CH}_3\text{C}_6\text{H}_4)$.⁵⁴

$\text{CH}_3\text{Te}(\text{C}_2\text{B}_9\text{H}_{10})\text{Co}$ ¹⁸ (section X-A compound 11); $[(\text{CH}_3)_3\text{Sn}]_2\text{Te}$;⁵⁶



1,2,4-hexamethyl-1,2,4-tristanna-3,5-ditelluracyclopentane (J_{SnCH});^{12,69}
 (J_{SnSnCH}) ;⁶⁹ and $\text{C}_6\text{H}_5\text{CH}_2\text{-S-Te-CH}_2\text{C}_6\text{H}_5$.²¹

$[(\text{C}_7\text{H}_7)(\text{CO})\text{Mo}(\text{TeC}_6\text{H}_5)]_2$;¹⁴ $[(\text{CO})_4\text{Mn-TeH}]_2$;⁵⁶ and $[(\text{CH}_3)_3\text{SnTeM}(\text{CO})_4]_2$ ($\text{M} = \text{Mn}, \text{Re}$).⁵⁶

2-R-tellurophene [$\text{R} = \text{CH}_3, \text{CH}_3\text{CH}(\text{OOCCH}_3)\text{-}, (\text{CH}_3)_2\text{NC}(\text{O}), \text{Cl}, \text{Br}, \text{I}$] (J_{HH});⁵⁸
 bis(2-tellurophene-yl) telluride (J_{HH});⁵⁸ 2-R-5- CH_3 -tellurophene [$\text{R} = \text{CHO},$
 $\text{CH}_3\text{CH}(\text{OH}), \text{CH}_3\text{CH}(\text{OOCCH}_3)$];⁶⁰ 2,5-diphenyl-3,4-dimethyltellurophene;⁶¹
 benzo[3,4-c]-2,5-dihydrotellurophene 1,1-diodide⁶⁴; polycyclic [3,4-c]-
 fused tellurophenes (section XI-B, compounds 21,⁶¹ 22-26;⁶²); polycyclic
 (4,5-d)-fused 2,3-dihydrotellurophenes (section XI-C, compounds 30);²² and
 2-[acetoxymethyl)methyl]benzo[4,5-d]tellurophene.⁶⁰

1-chalcogena-2-telluraacenaphthene (section XI-E, compounds 31).^{15,31}

1-sila-3-telluracyclohexanes (section XI-G, compounds 33) (J_{HH}).^{23,65}

2. ^{11}B -NMR Spectroscopy

The structure of the compound $\text{CH}_3\text{Te}(\text{C}_2\text{B}_9\text{H}_{10})\text{Co}$ (section X-A, compound 11) was ascertained by ^{11}B -nmr spectroscopy.¹⁸

3. ^{13}C -NMR Spectroscopy

The ^{13}C spin-lattice relaxation times were measured^{70,71} for diphenyl dichalcogenides, $(\text{C}_6\text{H}_5)_2\text{X}_2$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$) and analyzed to obtain information on the relative order of the magnitude of internal motion rates.⁷⁰ The analyses provided evidence that the internal motion for the diselenide and ditelluride is much faster than that for the disulfide, in which conformational motions about the $\text{C}_6\text{H}_5\text{-S}$ bond occur at a rate comparable to that of overall molecular reorientation.⁷⁰

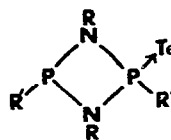
^{13}C -nmr data were also reported for 2-R-tellurophenes [$\text{R} = \text{CH}_3$, $\text{CH}_3\text{CH}(\text{OOCCH}_3)\text{-}$, Cl , Br , I]⁵⁸ and 1,2-ditelluraacenaphthene.³¹

4. ^{19}F -NMR Spectroscopy

According to ^{19}F -nmr spectra of the bis(3-fluorophenyl) and bis(4-fluorophenyl) tellurium dichlorides and dibromides^{36,37} the resonance component of the σ -constant arising from the RTeX_2 group is less than 10 percent.³⁷ ^{19}F -nmr data and $J_{125\text{Te-F}}$ values were reported for $(\text{CF}_3)_2\text{Te}_n$ ($n = 1, 2$).^{P-3}

5. ^{31}P -NMR Spectroscopy

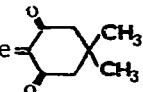
^{31}P -nmr data were reported for the compounds [$\text{R}, \text{R}' = \text{CH}_3, (\text{CH}_3)_3\text{C}; (\text{CH}_3)_3\text{C}, (\text{CH}_3)_2\text{N}^{19a}$]. They indicate that exchange of tellurium atoms occurs between the phosphorus atoms^{19,19a} and that the rotation about the exocyclic P-N bond [$\text{R}' = (\text{CH}_3)_2\text{N}$]^{19a} is restricted.

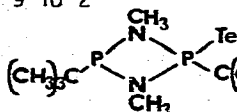


D. Electron Spectroscopy

The He(I) photoelectron spectrum of phenyl methyl telluride was investigated including EHMO calculations. The low energy region of the spectrum displays overlapping bands of gas-phase conformers. The π -conjugation between the phenyl ring and a tellurium lone electron pair is small in contrast to the considerable better conjugation in the analogous oxygen, sulfur and selenium derivatives. Comparisons between phenyl methyl chalcogenides and dimethyl chalcogenides are also presented.⁶⁸ Reference was made⁶⁸ to the photoelectron spectrum of tellurium dicyanide described in the dissertation by H. Stafast, Universität Frankfurt, 1974.

E. Mass Spectrometry

Mass spectral data were reported for benzyl tellurocyanate²¹, $C_6H_5CH_2TeCN \cdot (C_6H_5)_4AsBr$,²¹ $(CF_3)_2Te_2$,^{P-3} $(C_6H_5CH_2)_2Te_2$,²¹ $[(CF_3)_2Te]_n$ ($n = 1, m$),^{P-3} diphenyl tellurium dialkoxides and dimethyl tellurium dialkoxides⁵² (section VI-B2), $(4-RC_6H_4)_2Te$  (R = H, CH₃O),⁵⁵ $CH_3Te(C_2B_9H_{10})_2Co$ (section X-A, compound 11),¹⁸



$(CH_3)_3C-P-N(CH_3)-P(CH_3)_3-Te-C(CH_3)_3$ (ref. 19), 1,2,4-hexamethyl-1,2,4-tristanna-3,5-telluracyclopentane,¹² $C_6H_5CH_2-S-Te-CH_2C_6H_5$,²¹ $[(C_7H_7)(CO)Mo(TeC_6H_5)]_2$,¹⁴ 2,5-diphenyl-3,4-dimethyltellurophene,⁶¹ polycyclic [3,4-c]-fused 2,5-diphenyltellurophenes [section XI-B, compounds 21] (X = S, Se)⁶¹ and 22-26⁶², benzo[3,4-c]-2,5-dihydrotellurophene 1,1-diiodide,⁶⁴ 2',3'-quinolino[4,5-d]-2,3-dihydrotellurophene,²² and 1-chalcogena-2-telluraacenaphthenes (X = S, Se,¹⁵ Te³¹).

F. X-Ray Structure Analyses

Crystals of $(CH_3COCH_2COCH_2)_2TeCl_2$ suitable for X-ray analysis could not be grown.⁷²

The orange crystals of 2-biphenyl tellurium tribromide are triclinic,

space group $P\bar{1}$ with two molecules per unit cell. The molecule is trigonal bipyramidal with two bromine atoms in the axial positions (Te-Br distances 2.647 and 2.675 Å, Br-Te-Br angle 178.46°). The third bromine atom, a carbon atom and a lone electron pair occupy the equatorial positions with Te-Br and Te-C distances of 2.49 Å and 2.136 Å, respectively. The Br-Te-C angle is 97.1°. A very short intramolecular Te····C separation of 2.945 Å is probably related to the ease with which the tribromide is converted to dibenzotellurophene dibromide.⁴⁰

The structure of the β -form of 2-biphenyl tellurium triiodide is very similar to that of the tribromide described above. The red crystals are monoclinic with the space group $P2_1/c$. The pertinent distances in the molecule are: Te-I_{axial} 2.828 Å and 3.028 Å, angle I-Te-I 176.02°; Te-I_{eq.} 2.748 Å, Te-C_{eq.} 2.15 Å and angle I-Te-C 98.1°. The principal differences between the crystal structures of the α - and the β -form are in the intermolecular bonding arrangements of the heavy atoms.⁷³

Triphenyl telluronium thiocyanate forms triclinic crystals of space group $P\bar{1}$. The structure consists of triphenyl telluronium cations and thiocyanate anions with six molecules per unit cell associated into one dimer and one tetramer. The thiocyanate anions serve as bridging groups between the tellurium atoms using the nitrogen and sulfur atoms for coordination. The Te-N and Te-S distances range from 2.963 Å to 3.182 Å and 3.526 Å to 3.616 Å, respectively. The triphenyl telluronium cations have a trigonal-pyramidal shape but possess no symmetry. The mean Te-C distance is 2.13 Å and the mean C-Te-C angle^{74,75} is 97.3°.

Crystals of the compound $[(C_6H_5)_2Te(NCS)]_2O$ belong to the space group $C2/c$ and have four molecules per unit cell. The Te-O-Te angle is 121.7° with a Te-O distance of 1.985 Å. An intermolecular Te-S contact completes a square pyramidal geometry around the tellurium atom.⁷⁷ The Te-N distance is 2.40 Å.

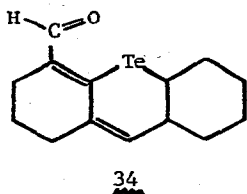
The compound $(C_6H_5)_3Te(NCO) \cdot 0.5CHCl_3$ exists as tetramer in the solid state with cyanate groups serving as bridges between the tellurium atoms. The Te-N and Te-O distances are 2.02 Å and 1.98 Å, respectively. The chloro-

form molecules are possibly hydrogen-bonded to the tetramer.⁷⁶

The compound $[(C_6H_5)_4P]^+[Hg(TeC_6H_5)_3]^-$ crystallizes in the space group $P2_1/c$ and has an ionic structure with isolated cations and anions. The anion has a trigonal-planar shape with a mean Hg-Te distance⁷⁸ of 2.697Å.

Crystals of 1-tellura-3,5-cyclohexanedione are orthorhombic. The heterocyclic ring with Te-C distances^{72,79} of 21.6Å and a C-Te-C angle of 90° is present in the chair conformation. 1-tellura-3,5-cyclohexanedione 1,1-dichloride adopts also the chair conformation with a Te-Cl distance of 2.49Å, a Cl-Te-Cl angle of 171.8° and a C-Te-C angle⁷² of 95.5°.

The telluraanthracene derivative 34 crystallizes in the space group $Pca2_1$ with eight molecules per unit cell.⁸⁰ The molecules are almost planar.



The Te-C distances are in the range 2.05Å to 2.08Å with a C-Te-C angle of 94°.

G. Dipole Moment Measurements

Dipole moments were measured for the diaryl ditellurides, $(RC_6H_4)_2Te_2$ ($R = H, 4-CH_3, 4-CH_3O, 4-C_2H_5O, 4-Cl, 3-Cl, 4-Br, 3-Br$) in benzene at 25°. In most cases the dipole moments calculated assuming a dihedral angle of 75° agreed with the experimental values. The dipole moment of diphenyl ditelluride (1.40 D) differs little from that of dimethyl ditelluride. This was taken as an indication that there is no appreciable mesomeric interaction of the ring π -system with unshared electrons of the tellurium atom.³⁹ An analysis of the dipole moments obtained at 25° and 45° for the diaryl dichalcogenides, $(RC_6H_4)_2X_2$ ($R = H, 3-F, 4-Br, 4-CH_3; X = S, Se, Te$) showed that the conformational properties of these compounds are explicable in terms of a decreasing repulsion between the lone electron pairs of the chalcogen atoms on going from the disulfides to the ditellurides and a

concomitant reduction of the barrier to rotations about the X-X bonds⁴³

On the basis of dipole moments for the diaryl tellurides, $(RC_6H_4)_2Te$ ($R = H, 3-CH_3, 4-CH_3, 4-CH_3O, 4-C_2H_5O, 4-F, 3-Cl, 4-Cl, 3-Br, 4-Br, 4-NO_2, 2-C_{10}H_7$), $4-RC_6H_4-Te-C_6H_5$ [$R = (CH_3)_2N, CH_3O, Br$] and $4-(CH_3)_2NC_6H_4-Te-(4-RC_6H_4)$ ($R = CH_3O, Br$), a butterfly conformation was assigned to all these compounds.³⁶ The $C_{aryl}-Te$ bond moment (0.90 D) and the C-Te-C angle (103°) were deduced from the dipole moment values of the diaryl tellurides. The dipole moment data are consistent with practically no $p_{Te} \rightarrow \pi$ bonding unless a strong electron acceptor substituent such as a nitro group is present in the ring. The tellurium atom acts as a π -acceptor presumable using its vacant 5d orbitals when a powerful π -donor group, e.g., the $(CH_3)_2N$ group, is in the para-position.³⁶

A similar investigation of a large number of symmetric and unsymmetric diaryl tellurium dihalides, $(RC_6H_4)_2TeX_2$ [$R, X: H, F, Cl, Br, I$;^{37,38} 2- CH_3, Cl ; 3- CH_3, F, Cl, Br ; 4- CH_3, F, Cl, Br, I ; 4- $(CH_3)_2N, Cl, Br, I$; 4- CH_3O, F, Cl, Br, I ; 4- C_2H_5O, F, Cl, Br, I ; 4- F, Cl, Br ; 3- Cl, Cl, Br ; 4- Cl, F, Cl, Br, I ; 3- Br, Cl, Br ; 4- Br, Cl, Br, I ; 2- $C_{10}H_7, Cl$], $RC_6H_4(C_6H_5)TeX_2$ [$R, X: 4(CH_3)_2N, Cl, Br, I$; 4- CH_3O, Cl ; 4- F, Cl ; 4- Br, Cl], $4-(CH_3)_2NC_6H_4(4-RC_6H_4)TeX_2$ [$R, X: 4-CH_3O, Cl, Br, I$; 4- Br, Cl, Br, I]³⁷ $C_6H_5(CH_3)TeX_2$ ($X = Cl, Br, I$)³⁸ and $(CH_3)_2TeX_2$ ($X = Cl, Br, I$)^{37,38} produced the same results with regard to $p_{Te} \rightarrow \pi_{ring}$ and $\pi_{ring} \rightarrow 5d_{Te}$ interactions³⁷ as obtained for the diaryl tellurides (see above). The aryl groups are very likely in a butterfly configuration.³⁷ The increase in the dipole moments of diaryl tellurium dihalides in the series $Cl < Br < I$ is caused-- according to CNDO/2 calculations--by an increase in the point component of the total dipole moment and a decrease in the pd hybridization component.³⁸

The dipole moments of the tellurium ylides obtained from diaryl tellurium dihalides and 1,1-dimethyl-3,5-cyclohexanedione (for individual compounds see section IX) are in the range 1.74 D to 5.49D (benzene solutions, 30°) depending on the nature of the substituents in the aryl group. These values are much lower than those for sulfur ylides (7-8 D), because the Te-C group moment opposes the cyclohexanedione group moment.⁵⁵

The dipole moments of tetrahydrotellurophene, tellurophene, 2-R-tellurophenes [R = CH₃, CH₂OH, CHO, CH₃CO, CH₃OOC, (CH₃)₂NCO, CH₃S, Cl, Br] and 2-methoxycarbonyl-5-R-tellurophenes (R = CH₃OOC, CH₃CO) were determined in benzene solutions at 25°. The mesomeric moments of the 2-halotellurophenes and the methyl conjugation moment in 2-methyltellurophene are directed from the substituents toward the ring. The conformational properties of 2-methylthiotellurophene and the 2-RCO-tellurophenes are discussed.⁵⁹

XIII. Analytical Techniques

Tellurium was determined in biological materials by radiochemical neutron activation analysis using the 25 min. ¹³¹I_gTe isotope. After activation the tellurium was separated by reduction to the element with sulfur dioxide in 3M HCl. The sensitivity of this method was estimated to be approximately 10 ng.⁸¹

Tellurium was determined in ilmenite and titanium dioxide pigments by generating hydrogen telluride which was then passed into an atomic absorption spectrometer.⁸²

XIV. Biology of Organic Tellurium Compounds

The safe use of selenium and tellurium in industry and agriculture was discussed by Frost.⁸³ The complex cis-dichlorobis(dimethyl telluride)-platinum(II) did not have antileukemic activity in mice.⁸⁴ Tellurium as TeCl₄ fed to ducklings at 500 ppm caused pathological alterations and clinical signs of selenium-vitamin E deficiencies. A supplement of selenium and/or vitamin E partially protected against the tellurium effects.⁸⁵ Tellurite produced no increase in glutathione peroxidase activity in mouse neuroblastoma cells, but did inhibit induction when present with selenite.⁸⁶

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