TELLURIUM
LITERATURE SURVEY COVERING THE YEAR 1978 *

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* Tellurium; Literature Survey covering the year 1977
see J. Organometal. Chem., Vol. 158(1978)267-323.

I. Introduction

This annual survey of the organic chemistry of tellurium covers the literature abstracted in Chemical Abstracts Volume 88, No. 14 through Volume 90, No. 10, papers which had appeared earlier but had not been included in previous surveys, and publications abstracted in Chemical Abstracts Volume 90, No. 11 through No. 26, provided copies of the original articles were available. The 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 previous surveys [1-5] which will provide access to the pertinent literature.

The assistance of the investigators, who provided reprints and preprints of their papers, and the partial financial support of this endeavor by the Robert A. Welch Foundation of Houston, Texas is gratefully acknowledged.

II. Reviews

The following reviews, which were published during the survey period, and a few reviews, which had appeared earlier but had not been included in previous surveys, are of interest to organic tellurium chemists.

Stereochemistry of Tellurium(II) Complexes and Related Compounds (O. Foss, 1970) [6]: The stereochemistry of tellurium complexes of the type L_2TeX_2, L_4TeX_2 and $C_6H_5Te(L_n)X$ (n = 1,2) and the transition states in nucleophilic substitutions at divalent sulfur, selenium and tellurium are discussed.

Conformational Analysis of Pentamethylene Heterocycles (J.B. Lambert and S.I. Featherman, 1975) [7]: The conformational properties of pentamethylene heterocycles containing group III, IV, V, VI, VII and metallic heteroatoms, the conformational preferences of substituents on the heteroatom and the barriers to ring reversal as deduced mainly from nmr studies are reviewed.

Selenocyanates and Related Compounds (E. Bulka, 1977) [8]: Selenocyanic acid, its esters, selenenyl selenocyanates, sulfenyl selenocyanates and isoselenocyanates and tellurocyanates are reviewed.(147 references).

Moessbauer Isomer Shifts for the 5s-5p Elements Beyond Tin: Antimony, Tellurium, Iodine and Xenon (S.L. Ruby and G.K. Shenoy, 1978) [9]: Moessbauer data for inorganic tellurium compounds are included in this review.

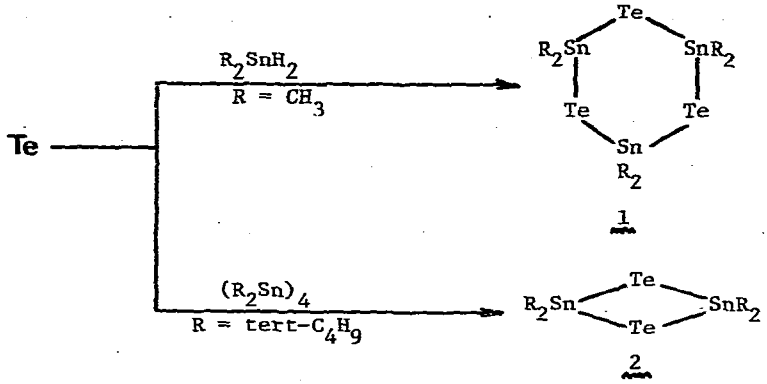
Industrial Exposure to Tellurium: Atmospheric Studies and Clinical Evaluation (H.H. Steinberg et al., 1942) [10]: The effects of exposure of workers to tellurium fumes are reported.

III. Methods for the Introduction of Tellurium into Organic Molecules

Tellurium, disodium telluride, disodium ditelluride and tellurium tetrahalides were employed to prepare organic tellurium compounds.

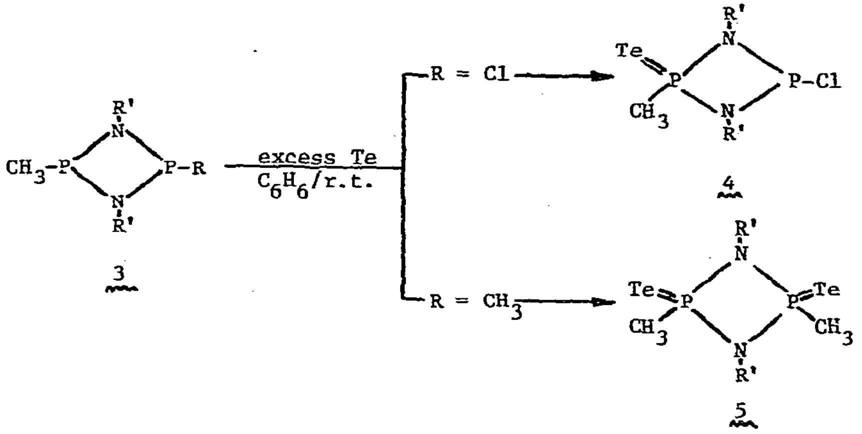
The previously reported reaction of tellurium with aryl magnesium bromide [11] was used to synthesize bis(4-pentylphenyl) ditelluride [12]. Tellurium combined with $(CH_3)_2SnH_2$ and $[(\underline{tert}\text{-}C_4H_9)_2Sn]_4$ to produce the heterocycles 1 [13] and 2 [14], respectively (eqn. 1).

(1)



The phosphorus-nitrogen heterocycles 3 and tellurium suspended in benzene gave at room temperature the phosphine tellurides 4 and 5 (eqn. 2) [15].

(2)



Tellurium and diethyl sodium phosphite in absolute ethanol yielded $(C_2H_5O)_2P(O)TeNa$ [16].

Tellurium was converted to sodium telluride [17,18,19,20] by sodium formaldehyde sulfoxylate dissolved in aqueous sodium hydroxide [17,18,19] or by sodium borohydride in aqueous medium [18,20]. Sodium telluride was also obtained from tellurium and sodium (1 : 2 molar ratio) in liquid ammonia [21]. When tellurium was reacted with sodium borohydride in ethanol, sodium hydrogen telluride, NaHTe, was claimed to be the product [22,23]. A chronoamperometric method was employed to study the reduction of polycrystalline and monocrystalline tellurium to hydrogen telluride and ditelluride [24].

The reactions of sodium tellurides leading to organic tellurium compounds are summarized in Fig. 1.

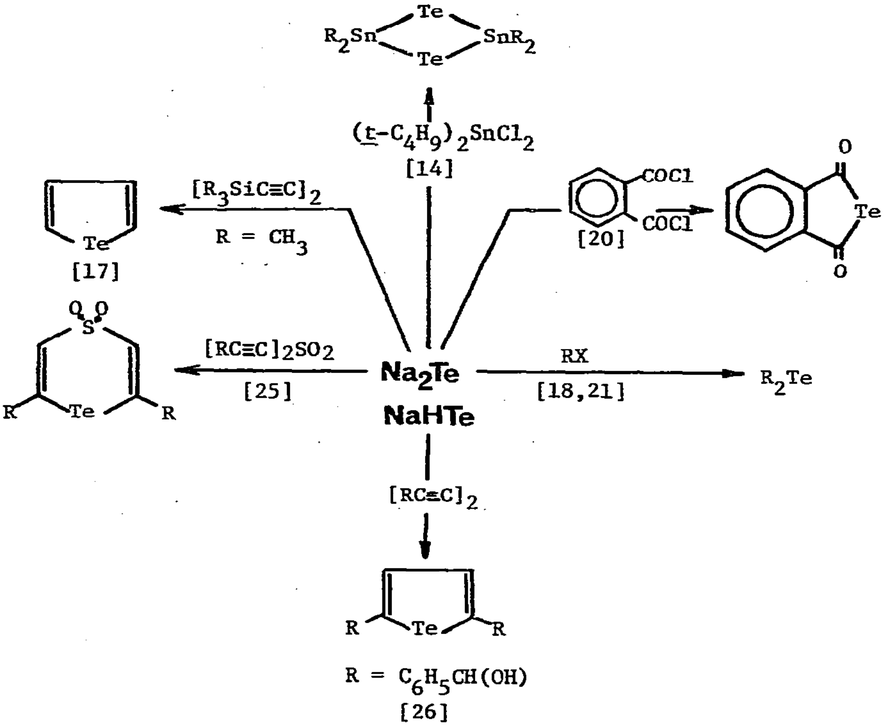


Fig. 1: Reactions Employing Sodium Telluride as the Reagent for the Introduction of Tellurium into Organic Molecules

Sodium ditelluride was reacted with alkyl halides to yield dialkyl ditellurides [19,21]. Most of these reactions are extensions of previously developed methods.

Sodium hydrogen telluride, prepared from tellurium and sodium borohydride in ethanol, has been found to be a convenient reagent for the debromination of vic-dibromides to olefins [23], for the reduction of olefins to saturated hydrocarbons [27] and the conversion of $C_6H_5C[=N(CH_3)_2]OR$ (R = cholesteryl) to $C_6H_5CH_2OR$ [22]. Sodium hydrogen telluride produced the olefins in the debromination reactions in good yields. The olefins did not polymerize. Tellurium can be recovered and reused [23].

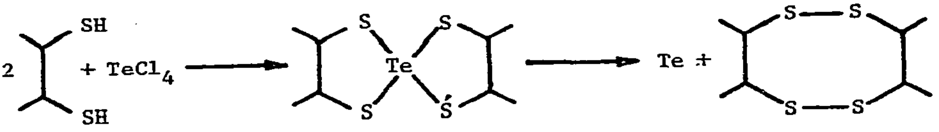
Tellurium dioxide and $NaB_{11}H_{14}$ reacted in water/heptane to yield $B_{11}H_{11}Te$ [28]. Telluric acid and sucrose formed complexes [29].

Acetic acid in the presence of tellurium dioxide combined with aromatic compounds to produce acetoxymethyl derivatives [30]. Tellurium dioxide served as a catalyst in the conversion of ethylene to ethylene glycol [31]. Organic tellurium compounds have been suggested as intermediates.

The reactions of tellurium tetrahalides, which were carried out during the survey period, are summarized in Fig. 2.

Tellurium tetrahalides formed complexes with $(HOCH_2CH_2)_2NCSS^-$ [40], tetramethylmalonamide [41], tetramethylurea [41], dithiooxamides [42] and $RC(S)NHC_6H_5$ (R = morpholino) [43]. Tellurium tetrachloride reacted with monothiols. The products, $Te(SR)_4$, were isolated at low temperature. They thermally decomposed to tellurium and the disulfides. A similar reaction sequence employing 1,2-dithiols yielded the compound **6** (eqn.3)[44].

(3)



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The reactions of organic tellurium compounds which were used to produce other organic tellurium derivatives are summarized in Fig. 3. All of these reactions are discussed in the sections devoted to the particular tellurium compounds. The reactions of heterocyclic tellurium compounds are not included in Fig. 3.

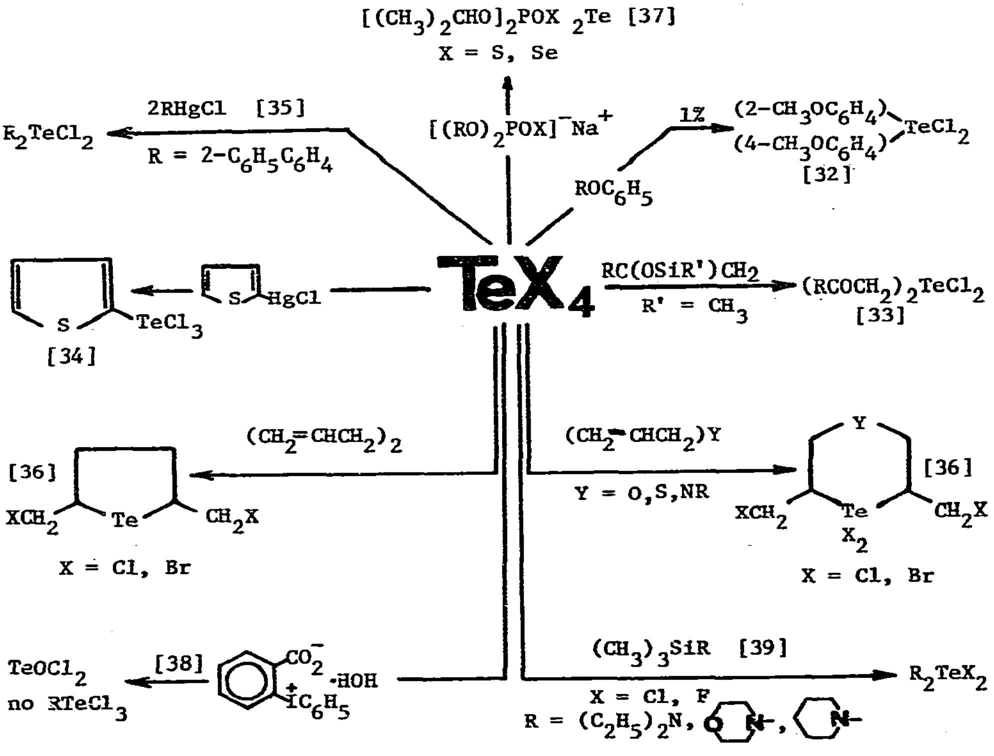


Fig. 2: Reactions Employing Tellurium Tetrahalides as the Reagents for the Introduction of Tellurium into Organic Molecules

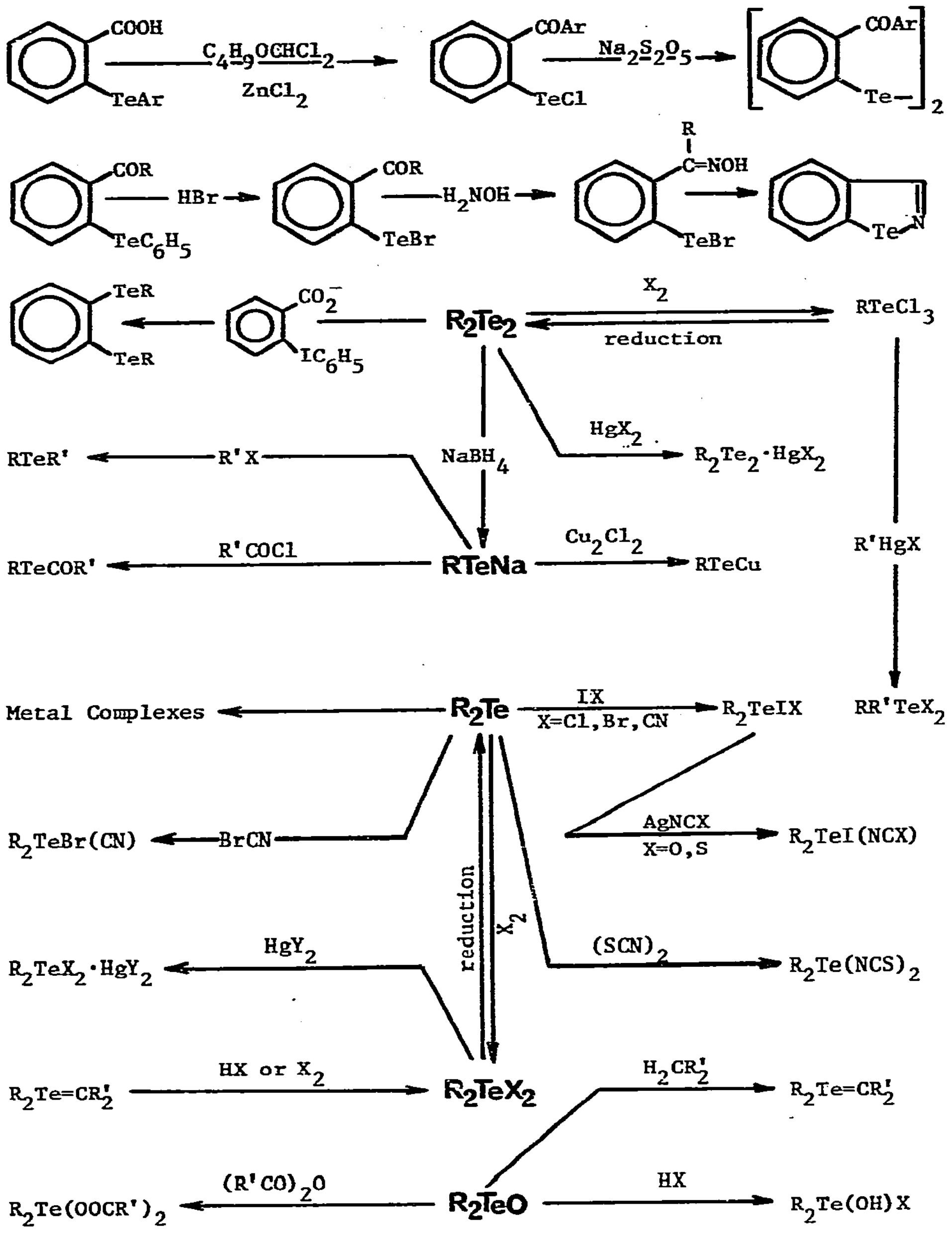


Fig. 3: Transformations of Organic Tellurium Compounds

IV. Tellurocyanates

No papers on ionic tellurocyanate compounds appeared during the survey period. Aryl tellurocyanates are discussed in section V-B, devoted to Tellurenyl Compounds.

V. Compounds Containing a Single Carbon-Tellurium Bond

Aryl tellurium halides, 2-benzoylphenyl tellurocyanate, organyl tellurium trihalides and diorganyl ditellurides were investigated during the survey period. Tellurium derivatives, in which the second tellurium valence is satisfied by a group I to V element atom, sulfur or selenium are discussed in section X.

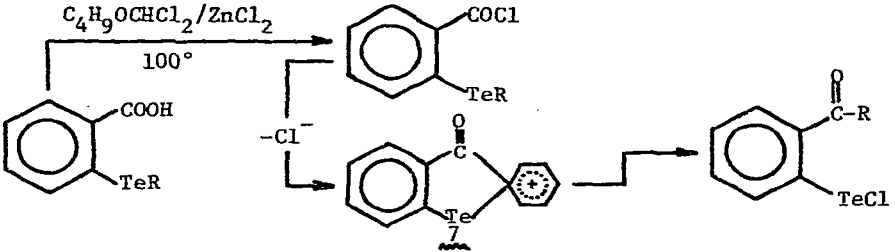
A. Tellurols

No papers on tellurols, RTeH, appeared during the survey period. The alkali metal salts of tellurols, RTeM, are discussed in section X-A.

B. Tellurenyl Compounds, RTeX

Several new ortho-substituted aryl tellurenyl halides were prepared from aryl 2-carboxyphenyl tellurides upon treatment with butyl dichloromethyl ether/$ZnCl_2$ [45] (eqn. 4).

(4)



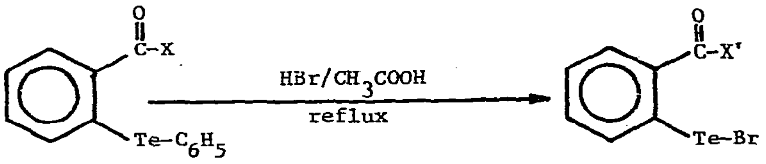
not isolated

R, % yield, mp. °C: C_6H_5, 80%, 114°; 4-$CH_3C_6H_4$, 80%, 116; 3-thienyl, 53%, 165°.

The reaction has been postulated to proceed via the carbonium ion 7 [45].

When 2-alkoxycarbonylphenyl phenyl tellurides were refluxed for 24 hours in a mixture of hydrobromic and acetic acid, the tellurium-C(phenyl) bonds were cleaved and 2-alkoxyphenyl tellurium bromides formed [45] (eqn. 5).

(5)



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X,X', % yield, mp. °C: Cl, HO, 64%, 184°; CH_3O, CH_3O, 87%, 128°; C_2H_5O, C_2H_5O, –, 112°.

The chlorocarbonyl group in compound 8 was hydrolyzed to the acid during the reaction.

The 2-benzoylphenyl tellurium chloride was fused with silver cyanide to produce 2-benzoylphenyl tellurocyanate in 80% yield. The orange crystals melted at 135° [45].

Heating 2-formylphenyl tellurium bromide with hydroxylamine hydrochloride, potassium acetate and absolute ethanol yielded the oxime [46], which was not purified but converted to 2-azabenzotellurophene (section XI-F).

The conversions of aryl tellurium halides to diaryl tellurides (section V-D), to aryl tellurium trihalides (section V-C), to aryl methyl tellurides (section VI-2) and heterocyclic tellurium compounds (sections XI-C, F) are discussed in the indicated sections.

C. Organyl Tellurium Trihalides

Four new aryl tellurium trihalides were prepared. 4-Fluorophenyl tellurium trichloride (mp. 241-2°, dec.) and 3-fluorophenyl tellurium tribromide (mp. 220-2°, dec.) were obtained in 100% yield from the ditellurides and SO_2Cl_2 and bromine in benzene, respectively [47]. 2-Thienyl tellurium trichloride was isolated from a reaction mixture containing tellurium tetrachloride and 2-thienyl mercury chloride in dioxane. The compound was not purified [34]. 2-Benzoylphenyl tellurium chloride and chlorine in an organic solvent yielded 2-benzoylphenyl tellurium trichloride (mp. 212°) [45].

Sadekov [47] reported the synthesis of 4-fluorophenyl tellurium tribromide (mp. 265-7°, 100% yield) from the ditelluride and bromine in benzene solution. The same compound prepared from the ditelluride but with carbon tetrachloride as the medium, melted at 291° (dec.) [11].

3-Fluorophenyl tellurium trichloride (mp. 203-6°) obtained quantitatively from the ditelluride and SO_2Cl_2 in benzene [47] had been synthesized previously from tellurium tetrachloride and the aryl mercury chloride [48] with a melting point of 195°.

A number of patents claim the use of organyl tellurium trihalides as components of heat developable photographic materials [P-2, P-8, P-11, P-13].

The reduction of 2-thienyl tellurium trichloride to the ditelluride [34] (section V-D), the reactions of aryl tellurium trichlorides with aryl mercury acetates [49,50] to produce unsymmetric diaryl tellurium dichlorides and with $C_6H_5C[OSi(CH_3)_3]{=}CH_2$ to yield aryl benzoylmethyl tellurium dichlorides [33] (section VI-B2) are discussed in the indicated sections.

The aryl tellurium trichlorides, $4\text{-}RC_6H_4TeCl_3$ (R=H, CH_3O, C_2H_5O) were converted to the known $4\text{-}RC_6H_4Te(O)Cl$ [1] upon heating with 2-(phenyliodonio)benzoate monohydrate. No reaction occurred with the anhydrous iodonium salt [38].

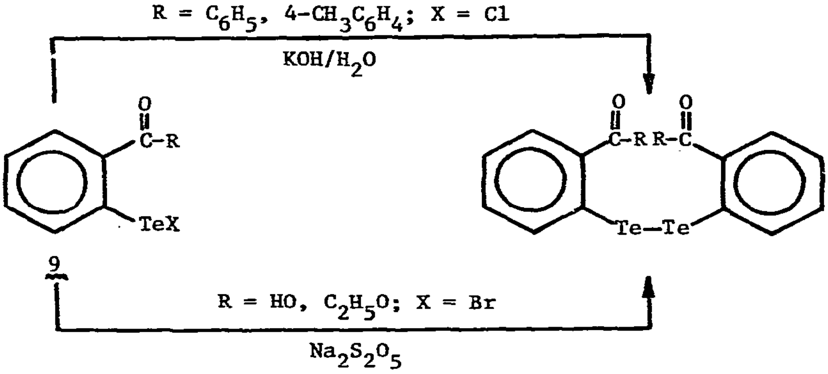
D. Diorganyl Ditellurides

Seven new diorganyl ditellurides were prepared during the survey period. Dipentyl ditelluride and the already known diethyl and dibutyl ditelluride [1] were prepared from alkyl bromides and aqueous solutions of sodium ditelluride obtained from tellurium and Rongalite [19]. Bogolyubov [21] prepared dimethyl ditelluride (48% yield, bp. 97°/9 torr), diethyl ditelluride (71% yield, bp. 92°/10 torr) and dibenzyl ditelluride (82% yield, mp. 79°) employing sodium ditelluride (obtained from sodium and tellurium in liquid ammonia) and the appropriate alkyl halide. These ditellurides had been synthesized earlier [1] in comparable yields from the same starting materials used by Bogolyubov. Orange bis(2-thienyl) ditelluride(mp. 88°) was the product of the reduction of 2-thienyl tellurium trichloride with hydrazine hydrate in hot ethanol [34].

Tellurium and 4-pentylphenyl magnesium bromide in tetrahydrofuran under an oxygen atmosphere produced bis(4-pentylphenyl) ditelluride (mp. 29°) in 92% yield. This ditelluride is sensitive to heat, air, moisture and light [12].

The ortho-substituted phenyl tellurium halides 9 were converted to ditellurides upon treatment with sodium disulfite or potassium hydroxide in water [45] (eqn. 5a).

(5a)

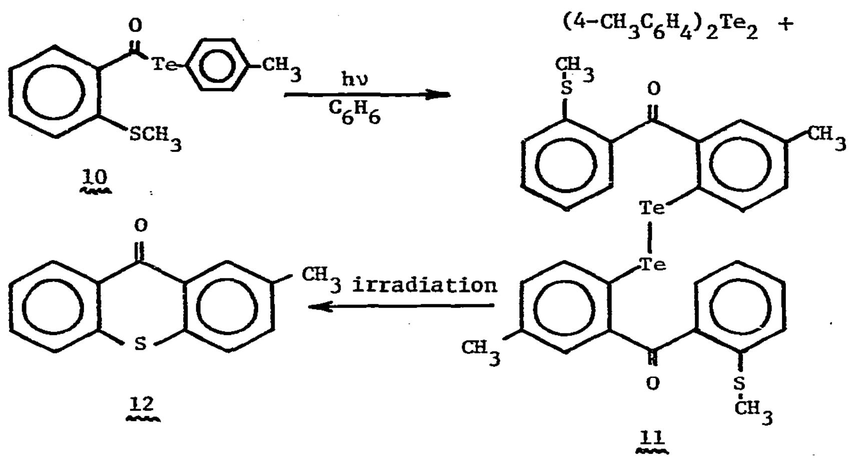


R, % yield, mp. °C: HO*, 52%, 216°(dec); C_2H_5O, 80%, 116°; C_6H_5, 83%, 139°; 4-$CH_3C_6H_4$, -, 178°.

* Previously prepared from other starting materials [1,3].

Irradiation of the Te-4-methylphenyl 2-methylthiotellurobenzoate 10 in dry benzene with a mercury lamp produced, among other compounds, bis(4-methylphenyl) ditelluride and the ditelluride 11 via a radical mechanism [51,52] (eqn. 6).

(6)



11% yield; m. 172-3°

Irradiation of the solid ditelluride 11 with the light from a mercury lamp [51] or exposure of a chloroform solution of the ditelluride to daylight produced thioxanthone 12 [51,52] (eqn. 6).

The photochemically very labile dibenzyl ditelluride [5] precipitated tellurium when its solutions were exposed to daylight at room temperature. The ditelluride could be crystallized and chromatographed only under red photographic safety lights. At 120° under nitrogen even red light caused decomposition to tellurium and dibenzyl telluride. Irradiation of the ditelluride dissolved in $CDCl_3$ with a mercury lamp under oxygen yielded benzaldehyde, toluene, benzyl alcohol and 1,2-diphenylethane. Excess bromine added to a carbon tetrachloride solution of dibenzyl ditelluride cleaved the carbon-tellurium bonds to form tellurium tetrabromide and benzyl bromide. With an equimolar amount of bromine dibenzyl tellurium dibromide and tellurium were obtained. [18].

Pulse radiolysis of an acidic or neutral methanolic solution of bis(4-methoxyphenyl) ditelluride yielded the radical $4\text{-}CH_3OC_6H_4Te\cdot$ [53]. A number of diaryl ditellurides were proposed as components of heat developable photographic emulsions [P-14].

The diorganyl ditellurides were subjected to the following reactions which are discussed in the indicated sections: the reaction with sodium borohydride in ethanol to yield RTeNa [12,19,45,47,52,54,55], the conversion to RTeM (M = Na, K) by the alkali metals in liquid ammonia [56] (section X-A); the reactions with SO_2Cl_2 or bromine to give $RTeX_3$ [47] (section V-C); the reactions of $(4\text{-}RC_6H_4)_2Te_2$ with 2-(phenyliodonio)benzoate to produce $1,2\text{-}(RC_6H_4Te)_2C_6H_4$ [R = CH_3, CH_3O, C_2H_5O; diphenyl ditelluride and bis(2-naphthyl) ditelluride did not react] [38] (section VI-A4); and the reactions with copper(I) halides [19,57], $[(C_6H_5CN)_2PdCl_2]$ [34], $[(C_6H_5)_3P]_4Pd$ [34], mercury(II) halides and elemental mercury [58] to form complexes (section X-E, F).

VI. Compounds Containing A Carbon-Tellurium-Carbon Moiety

Symmetric and unsymmetric diorganyl tellurides, aryl organyl tellurides, tellurides with two tellurium atoms in the molecule, symmetric and unsymmetric diorganyl tellurium dihalides, diorganyl tellurium dipseudohalides, diorganyl tellurium compounds of the type R_2TeXX', diorganyl tellurium dicarboxylates and some reactions of diaryl telluroxides were investigated.

A. Diorganyl Tellurides

Several new diorganyl tellurides, which are with a few exceptions of the unsymmetric type R-Te-R', were prepared generally employing previously reported methods. Acyl organyl tellurides, and tellurides with two tellurium atoms or one selenium and one tellurium atom in the molecule were also synthesized.

1. Symmetric diorganyl tellurides

Bogolyubov [21] prepared diethyl telluride boiling at 78°/123 torr in 38% yield from sodium telluride (obtained from sodium and tellurium in a 2:1 molar ratio in liquid ammonia) and ethyl bromide. This method had been used previously [1] to synthesize diethyl telluride.

Dibenzyl telluride, which has been known since 1914 [1,2], has now been obtained [18] from benzyl chloride and an alkali metal telluride and by decomposition of dibenzyl ditelluride. When the telluride had been prepared from tellurium and tetramethylammonium borohydride in water, the yield of dibenzyl telluride was 82%. With sodium telluride synthesized according to the Rongalite method [1] the yield dropped to 70%. When dibenzyl ditelluride was irradiated in $CDCl_3$ solution with the light from a mercury lamp, dibenzyl telluride was formed as the only product. Heating the ditelluride at 120° without solvent for ten minutes under nitrogen and under red lights also gave the telluride [18]. Dibenzyl telluride is an almost colorless, crystalline material melting at 49-57°. Irradiations of $CDCl_3$ solutions of dibenzyl telluride under nitrogen with the light of a mercury lamp proved that decomposition is very slow. Decomposition products could not be detected by nmr methods after irradiation for four hours. Although dibenzyl telluride solutions were found to be stable under an oxygen atmosphere in the absence of light, irradiation of such solutions caused complete decomposition of the telluride in five hours. Benzaldehyde, benzyl alcohol, toluene, 1,2-diphenylethane and benzyl chloride were identified as the major products. Excess bromine added to a CCl_4 solution of dibenzyl telluride yielded tellurium tetrabromide and benzyl bromide, whereas an equimolar amount of bromine in a reaction carried out in the dark produced dibenzyl tellurium dibromide [18].

Bis(2-biphenylyl) telluride was the product of the reduction of bis(2-biphenylyl) tellurium dichloride with hydrazine in ethanol. To convert the ditelluride present as an impurity in the product of the reduction to the telluride the solution of the mixture in dioxane was treated with copper. The overall yield of the telluride based on the starting materials tellurium tetrachloride and 2-biphenylyl mercury chloride was 19 percent [35].

Diphenyl telluride was hydrogenated to benzene on the surface of Raney-Nickel. The tellurium remained on the surface of the Raney-Nickel and was liberated as hydrogen telluride upon treatment with mineral acids [59].

Pulse radiolysis of bis(4-methoxyphenyl) telluride in acidic or neutral solutions of methanol generated the radical ArTe•, which was detected by means of its absorption at 508 nm. Hydrogen radicals formed by radiolysis of methanol (eqn. 7) attacked methanol (eqn. 8) and the diaryl telluride (eqn. 9) in competitive reactions. The rate constant k = 1.5×10^{10} $\mathrm{mol^{-1}\ sec^{-1}}$ was found for reaction (9) [53].

$$(7) \quad CH_3OH \xrightarrow{h\nu} CH_3O\cdot + H\cdot$$

$$(8) \quad H\cdot + CH_3OH \longrightarrow H_2 + \cdot CH_2OH$$

$$(9) \quad H\cdot + Ar_2Te \longrightarrow ArTe\cdot + ArH$$

The second-order rate constants for the transfer of chlorine from a diaryl tellurium dichloride to bis(4-methoxyphenyl) telluride (eqn. 10) were determined from the intensities of the methoxy-nmr signals. The rates are very sensitive to catalytic impurities and the method used for the purification of the solvents. The exchange rates decreased for the reaction with $(4\text{-}CH_3C_6H_4)_2TeCl_2$ along the solvent series $C_6H_5CN > C_6H_5NO_2 >$ $1,2\text{-}Cl_2C_6H_4 > CH_3C_6H_5$ and increased with the substituent R in $(4\text{-}RC_6H_4)_2TeCl_2$ in the sequence $Br < Cl < CH_3$. The nature of the halogen atoms bonded to the tellurium atom substantially influenced the rate of the exchange reactions. The rates decreased in the order Br>>Cl>F [60].

$$(10) \quad (4\text{-}CH_3OC_6H_4)_2Te + (4\text{-}RC_6H_4)_2TeCl_2 \xrightarrow[40^\circ]{C_6H_5NO_2} (4\text{-}CH_3OC_6H_4)_2TeCl_2 + (4\text{-}RC_6H_4)_2Te$$

R, rate constant, % $(4\text{-}RC_6H_4)_2Te$ at equilibrium: Br, 0.00091, 93%;
Cl, 0.0014, 85%;
CH_3, 0.0045, 60%.

Diaryl tellurides are claimed to be components of heat developable photographic materials [P-14]. Bis(4-ethoxyphenyl) telluride increased the sensitivity of photographic silver halide emulsions [P-10].

Dimethyl telluride is generally considered to possess C_{2v} symmetry and a bent C-Te-C skeleton. However, Hamada and Morishita [64] argue for a linear C-Te-C arrangement with D_{3d} symmetry for dimethyl telluride on the basis of Raman and infrared spectral data.

The reactions of diaryl tellurides with halogens [35] (section VI-B1), with ICl, IBr, ICN or BrCN [62] (section VI-B4), $(SCN)_2$ [61,62] (section VI-B3) and with silver halides [P-12], K_2PtCl_4/LiI [63] or $(C_6H_5CN)_2PdCl_2$ to form complexes with diorganyl tellurides as ligands (section X-E), are described in the indicated sections.

2. Unsymmetric diorganyl tellurides

Several new alkyl aryl tellurides, unsymmetric dialkyl tellurides and diaryl tellurides were prepared. These new compounds are marked with an asterisk in Table 1, which also contains already known compounds synthesized by new methods or variants of previously developed procedures.

Because diaryl ditellurides are rather easily accessible and convertible to aryl sodium tellurides through reduction with sodium borohydride [3,4,5], these tellurides are convenient starting materials for the preparation of unsymmetric tellurides employing dimethyl sulfate or alkyl bromides as the source of alkyl groups (eqn. 11).

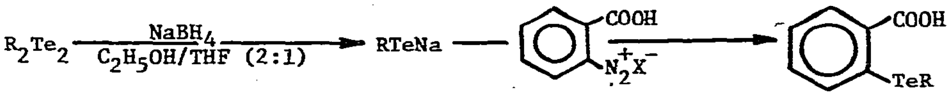
$$(11)\quad (YC_6H_4)_2Te_2 \xrightarrow{NaBH_4} YC_6H_4TeNa \xrightarrow{RX} YC_6H_4\text{-}Te\text{-}R$$

Vinylacetylenyl alkyl tellurides were obtained from the vinylacetylenyl sodium telluride and an alkyl halide (eqn. 12) [67] according to a procedure developed earlier [1,5].

$$(12)\quad CH_2{=}CH\text{-}C{\equiv}CH \xrightarrow[NH_3(\ell)]{Na} CH_2{=}CH\text{-}C{\equiv}CNa \xrightarrow{Te} CH_2{=}CH\text{-}C{\equiv}C\text{-}TeNa$$

A rare example of the successful use of diazonium salts for the synthesis of organic tellurium compounds was reported by Piette and coworkers [45]. The aryl sodium telluride, generated by reduction of the appropriate diaryl ditelluride with sodium borohydride in ethanol/tetrahydrofuran (1:2 v/v), was rapidly combined with the neutral diazonium salt solution (eqn. 13). The unsymmetric diaryl tellurides were obtained in fair yields (Table 1). In order to obtain reproducible yields tetrahydrofuran must be used as one of the solvents.

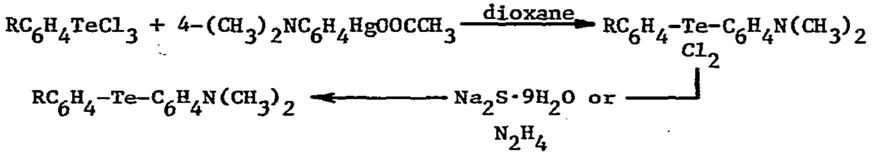
(13)



R = C_6H_5, 4-$CH_3C_6H_4$, 3-thienyl

The 2-carboxyphenyl phenyl telluride thus prepared was treated with diazomethane to give the methyl ester and with butyl dichloromethyl ether/$ZnCl_2$ at room temperature to produce the acid chloride. Diethyl cadmium was employed to convert the acid chloride to 2-ethoxycarbonylphenyl phenyl telluride [45].

Either hydrazine or sodium sulfide nonahydrate was used to reduce several 4-dimethylaminophenyl aryl tellurium dichlorides (obtained as shown in eqn. 14) to the corresponding tellurides [49]. The pK_a values

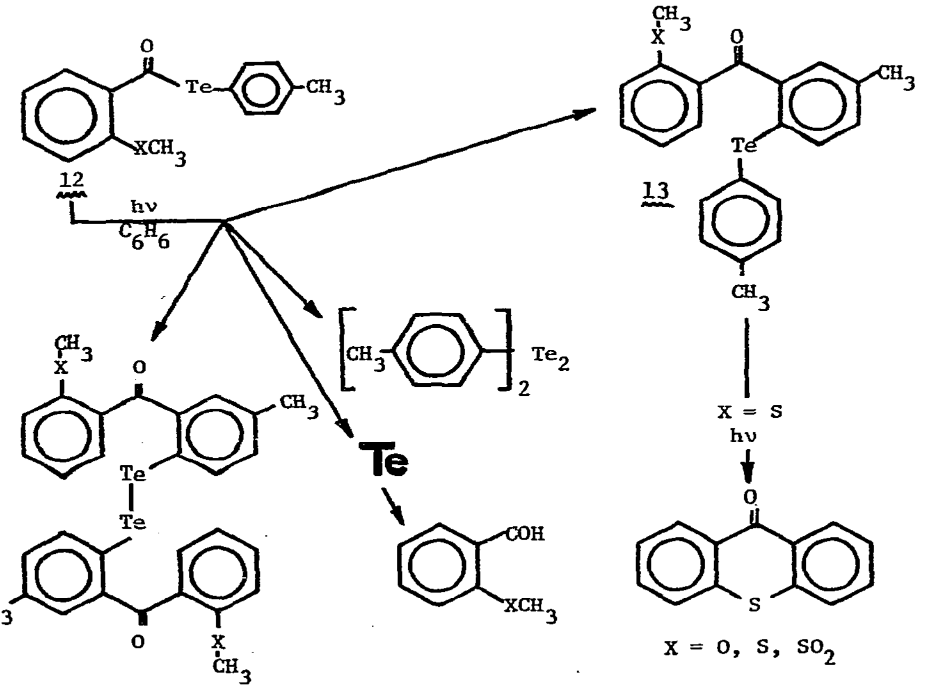
(14) 

$$RC_6H_4TeCl_3 + 4\text{-}(CH_3)_2NC_6H_4HgOOCCH_3 \xrightarrow{\text{dioxane}} RC_6H_4\text{-}\underset{Cl_2}{Te}\text{-}C_6H_4N(CH_3)_2$$

$$RC_6H_4\text{-}Te\text{-}C_6H_4N(CH_3)_2 \xleftarrow{\quad} \underset{N_2H_4}{Na_2S\cdot 9H_2O \text{ or }}$$

of these tellurides in acetonitrile at 25° are in the range 9.5 to 10.3. According to results of dipole moment measurements the tellurium atoms in 4-dimethylaminophenyl aryl tellurides participate in the transmission of electronic effects through the conjugation of vacant d_{xz} and d_{yz} orbitals with the π-orbitals of the $C_6H_4N(CH_3)_2$ group. This π-acceptor function of the aryltelluro group is observable only in the presence of powerful π-donor groups such as $(CH_3)_2N$.

Irradiation of the benzoyl aryl tellurides **12** under a nitrogen atmosphere at 20° for up to 40 hours with the light from a mercury lamp yielded among other products aryl benzoylphenyl tellurides **13** (eqn. 15). These reactions probably proceed via tellurium-centered radicals [52].

(15) 

(Continued on p. 82)

TABLE 1

UNSYMMETRIC DIORGANYL TELLURIDES, R-Te-R'

R	R'	Method	mp. °C bp. °C/torr	Yield %	Ref.
CH_3	C_6H_5	$R'TeNa + R_2SO_4$	94°/11	62	54
	$2\text{-}HOOCC_6H_4$	$R'TeNa + R_2SO_4$	195°	--	66
	$3\text{-}FC_6H_4{*}$	$R'TeNa + R_2SO_4$	113°/6	--	47
	$4\text{-}FC_6H_4{*}$	$R'TeNa + R_2SO_4$	111°/6	--	47
	$2\text{-}C_6H_5COC_6H_4{*}$	$R'TeCl + R_2Cd$	75°	50	45
		$2\text{-}ClCOC_6H_4TeCH_3 + (C_6H_5)_2Cd$	75°	52	45
C_2H_5	C_6H_5	$R'TeNa + RBr$	96°/8	65	54
C_3H_7	$CH_2{=}CH\text{-}C{\equiv}C{*}$	$R'TeNa + RBr$	66°/3	35	67
$\underline{i}\text{-}C_3H_7$	C_6H_5	$R'TeNa + RBr$	98°/4	71	54
C_4H_9	$CH_2{=}CH\text{-}C{\equiv}C{*}$	$R'TeNa + RBr$	78°/3	37	67
C_6H_5	$2\text{-}HOOCC_6H_4{*}$	$RTeNa + R'N_2^+X^-$	185°	43	45
	$2\text{-}ClCOC_6H_4{*}$	$2\text{-}HOOCC_6H_4TeR + C_4H_9OCHCl_2$, r.t.	89-91°	64	45
	$2\text{-}CH_3OOCC_6H_4{*}$	$2\text{-}HOOCC_6H_4TeR + CH_2N_2$	96°	72	45
	$2\text{-}C_2H_5OOCC_6H_4{*}$	$2\text{-}ClCOC_6H_4TeR + (C_2H_5)_2Cd$	118°	--	45

TABLE 1 (CONT'D)

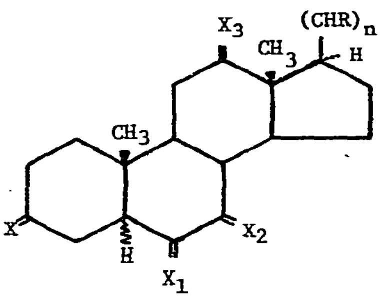
UNSYMMETRIC DIORGANYL TELLURIDES, R-Te-R'

R	R'	Method	mp. °C bp. °C/torr	Yield %	Ref.
4-$CH_3C_6H_4$	2-$HOOCC_6H_4$*	RTeNa + $R'N_2^+X^-$	212°	30	45
	2-(2'-$CH_3OC_6H_4CO$)-4-$CH_3C_6H_3$*	see eqn. (15)	108°	6	52
	2-(2'-$CH_3SC_6H_4CO$)-4-$CH_3C_6H_3$*	see eqn. (15)	110°	2	51,52
	2-(2'-$CH_3SO_2C_6H_4CO$)-4-$CH_3C_6H_3$*	see eqn. (15)	212°	10	52
4-$(CH_3)_2NC_6H_4$	4-$CH_3C_6H_4$*	$RR'TeCl_2$ + Na_2S	70°	40**	49
	4-$CH_3OC_6H_4$	$RR'TeCl_2$ + Na_2S	97°	57**	49
	4-$C_2H_5OC_6H_4$	$RR'TeCl_2$ + Na_2S	127°	44**	49
	4-$C_6H_5OC_6H_4$	$RR'TeCl_2$ + Na_2S	75°	25**	49
	3-ClC_6H_4*	$RR'TeCl_2$ + Na_2S	61°	17**	49
	4-ClC_6H_4*	$RR'TeCl_2$ + Na_2S	111°	40**	49
	3-BrC_6H_4*	$RR'TeCl_2$ + Na_2S	72°	18**	49
	4-BrC_6H_4	$RR'TeCl_2$ + Na_2S	122°	25**	49
	3-$O_2NC_6H_4$*	$RR'TeCl_2$ + N_2H_4	86°	41**	49
3-thienyl	2-$HOOCC_6H_4$*	RTeNa + $R'N_2^+X^-$	205°	15	45

* New Compounds.

** Yields are based on $R'TeCl_3$ for the reaction given in eqn. (14).

The tellurium derivatives of steroids 14 [P-4] and bile acids 15 [P-5a] were prepared from RTeLi or RTeH and an appropriate halogen derivative of the steroids or bile acids.



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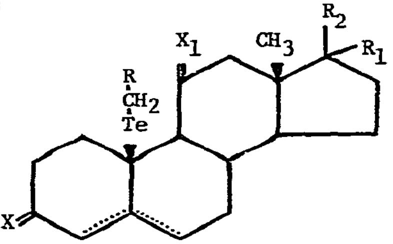


14

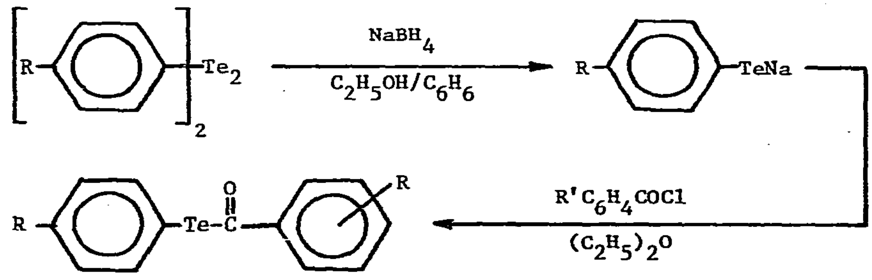
The resonance constants for the phenyl alkyl tellurides C_6H_5Te-R (R = CH_3, C_2H_5, i-C_3H_7, tert-C_4H_9), decrease with increasing chain length of the alkyl group. The electron donating properties of the CH_3E group (E = O, S, Se, Te) decrease steadily in the series O S Se Te because of the increasing energy difference between the π-ring orbitals and the unfilled orbitals of the chalcogen atom E [68].

The reactions of the unsymmetric diorganyl tellurides with chlorine, sulfuryl chloride, bromine or iodine are presented in section VI-B2. The preparation of $RR'Te(NCS)_2$ from tellurides is discussed in section VI-B3. The conversion of 2-RC_6H_4Te-R' to tellurenyl compounds is dealt with in section V-B. Silver halide complexes of phenyl alkyl telluride are listed in section X-E.

3. Acyl organyl tellurides

The method orginally developed by Piette and Renson [1] for the synthesis of aryl acyl tellurides was used to prepare several new compounds of this type (eqn. 16). A similar reaction with terephthaloyl dichloride

(16)



R, R' mp. °C, % yield: CH_3, H, 65°, 85% [52]; CH_3, 4-C_5H_{11}, 38°, 10% [70];
C_5H_{11}, 4-$C_8H_{17}O$, 41°, 62% [12];
CH_3, 4-CH_3O, 75°, 68% [52,70];
CH_3, 2-CH_3O, 72°, 64% [52]; CH_3, 2-Cl, 97°, 75% [52];
CH_3, 2-CH_3SO_2, 91°, 75% [52]; CH_3, 2-CH_3S, 50°, 83% [52].

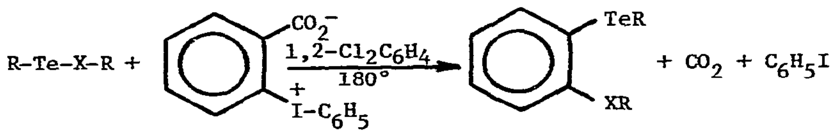
gave compound **16** (R' = $OCTeC_6H_4CH_3$) (mp. 167°) in 10% yield [70].

Irradiation of the yellow aryl acyl tellurides with the light of a mercury lamp produced diaryl ditellurides, benzaldehydes, unsymmetric diaryl tellurides and tellurium [52]. An example of such a reaction is given in eqn. 15 (section VI-A2). Two of the aryl tellurides **16** (R = CH_3; R' = 4-CH_3O or 4-C_5H_{11}) were investigated as to their ability to form liquid crystals [70].

4. Tellurides with two tellurium atoms in the molecule

The reaction of diaryl ditellurides (or of diaryl selenide tellurides) **17** with 2-(phenyliodonio)benzoate first reported in 1970 [1] and at that time found to be not entirely reproducible was made more reliable by using iodonium salts recrystallized from water in the presence of EDTA. The compounds **18** containing two tellurium atoms or one selenium and one tellurium atom in the molecule were thus obtained (eqn. 17) [38]. A similar reaction between bis(4-methoxyphenyl) ditelluride and 5-methyl-2-(phenyliodonio)benzoate in triglyme at 220° gave 1,2-bis(4-methoxyphenyltelluro)-5-methylbenzene melting at 74° in 32% yield [38].

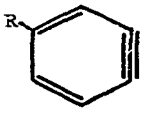
(17)



R, X, mp. °C, % yield: 4-$CH_3C_6H_4$, Te, 83°, 50%;
4-$CH_3OC_6H_4$, Te, 80°, 53%;
4-$C_2H_5OC_6H_4$, Te, 115°, 64%;
4-$CH_3OC_6H_4$, Se, 95°, 26%.

To obtain some information, whether singlet benzyne **19**, triplet benzyne **20**, or the carbonium ion **21** is the intermediate attacking the dichalcogenide group, bis(4-methoxyphenyl) selenide telluride was reacted with 5-methyl-2-(phenyliodonio)benzoate. The reaction produced an inseparable 1:1 mixture of the selenide tellurides **22** and **23** melting at 98° in 31 percent yield. No evidence for the presence of 1,2-bis(aryltelluro)-

benzene or 1,2-bis(arylseleno)benzene could be obtained. These results strongly favor the concerted insertion of singlet benzyne into the selenium-tellurium bond [38].



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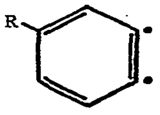

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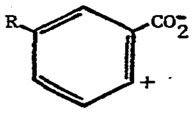

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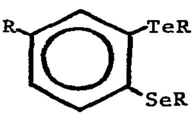

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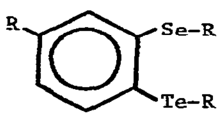


23

The telluride 1,4-$[4'-CH_3C_6H_4TeC(O)]_2C_6H_4$ obtained from terephthaloyl dichloride and 4-methylphenyl sodium telluride in 10 percent yield melted at 167° [70].

B. Diorganyl Tellurium Compounds, R_2TeX_2

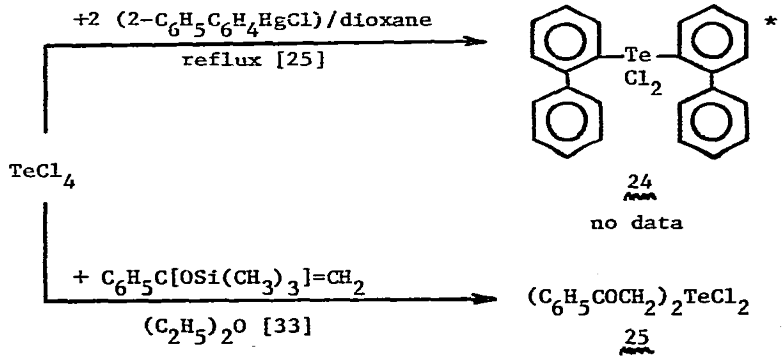
New, symmetric and unsymmetric diorganyl tellurium dihalides were prepared by novel as well as already known methods. Several diaryl tellurium di(pseudohalides), diaryl tellurium compounds of the type R_2TeXX' and diaryl tellurium dicarboxylates were also synthesized. The compounds $[R_4N]_2^+[R'_2TeX_4]^{--}$ (R'_2 = pentamethylene) are discussed in section XI-A.

1. Symmetric diorganyl tellurium dihalides, R_2TeX_2 (X = F, Cl, Br, I)

The five new diorganyl tellurium dihalides prepared during the survey period are marked by asterisks in the equations given below.

Tellurium tetrachloride reacted with 2-biphenylyl mercury chloride or 1-phenyl-1-trimethylsiloxyethylene to yield the diorganyl tellurium dichlorides 24 and 25, respectively (eqn. 18).

(18)



24

no data

25

63% yield; mp. 176-8°

Diorganyl tellurides and elemental halogens dissolved in carbon tetrachloride produced diorganyl tellurium dihalides (eqn. 19).

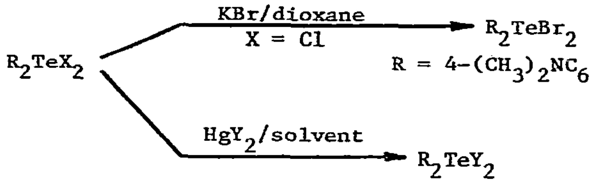
(19) $$R_2Te + X_2 \xrightarrow{CCl_4} R_2TeX_2$$

R, X, % yield, mp.°C: $C_6H_5CH_2$, Br, 63%, 136–7° [18];
$2\text{-}C_6H_5C_6H_4$, Cl*, 100%, not reported [35];
$2\text{-}C_6H_5C_6H_4$, Br*, 100%, not reported [35];
$2\text{-}C_6H_5C_6H_4$, I*, 100%, not reported [35].

Dibenzyl telluride and bromine, both in carbon tetrachloride solution, must be mixed in the dark and very carefully to avoid a local excess of bromine, which would decompose the tellurium compounds to benzyl bromide and tellurium tetrachloride. Dibenzyl tellurium dibromide was also obtained from equimolar amounts of dibenzyl ditelluride and bromine dissolved in carbon tetrachloride. The yield from this reaction was 72 percent [18]. Dibenzyl tellurium dibromide was first synthesized by McWhinnie [71].

Halogen exchange reactions were carried out between diorganyl tellurium dihalides and mercury(II) halides or potassium bromide (eqn. 20).

(20)



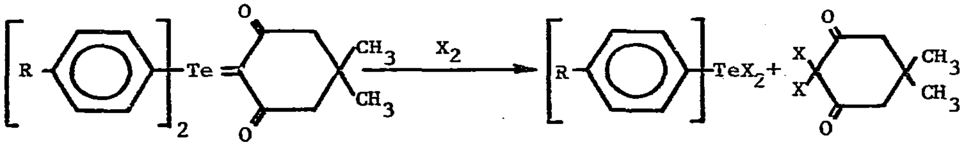
R = $4\text{-}(CH_3)_2NC_6H_4$,* 91% yield, mp. 150° [50]

R, X, Y, solvent, % yield, mp.°C:
CH_3, I, Cl, boiling $CHCl_3$, 95%, 89° [35];
CH_3, I, Br, boiling $CHCl_3$, 95%, 90–92° [35];
C_6H_5, Br, Cl, ethanol, high yield, 160° [35].

The halogen exchange reactions employing mercury(II) halides, claimed to be superior to older methods [35], can be performed by boiling solutions of the complexes $R_2TeX_2 \cdot HgY_2$ or mixing solutions of the reactants.

Treatment of the tellurium ylides **26** with elemental halogens or concentrated hydrohalic acids produced diaryl tellurium dihalides in 100 percent yield (eqn. 21) [72]. This reaction is not of importance for the preparation of diaryl tellurium dihalides, because the dihalides are

(21)



R, X, mp.°C: CH_3O, Cl, 183°; CH_3O, Br, 199°; CH_3O, I, 182°; $(CH_3)_2N$,* Br, not reported [72].

starting materials for the synthesis of the ylides [4,5].

Sadekov and coworkers [73] observed, that diaryl telluroxides, $(4\text{-}RC_6H_4)_2TeO$ (R = CH_3, CH_3O) reacted with acyl chlorides R'COCl [R' = CH_3, C_6H_5, $(CH_3)_2N$] to give in almost quantitative yields either diaryl tellurium dichlorides ($R_2TeO/R'COCl \leq 0.5$) or an equimolar mixture of R_2TeCl_2 and $R_2Te(OOCR')_2$ ($R_2TeO/R'COCl = 1$). Diaryl tellurium dicarboxylates refluxed with acyl chlorides (1:2 molar ratio) in toluene produced diaryl tellurium dichlorides [73].

Moessbauer data for bis(2-biphenylyl) tellurium dihalides indicate [35] that the structure of these compounds might differ from the trigonal bipyramidal arrangement found in diaryl tellurium dihalides with less bulky groups.

The following thermodynamic basicity constants, pK_a, for bis(4-dimethylaminophenyl) tellurium dihalides, $[4\text{-}(CH_3)_2NC_6H_4]_2TeX_2$ were determined in acetonitrile at 25° (X, pK_a^1, pK_a^2): Cl, 8.39, 6.79; Br, 8.12, 6.54; I, 7.67, 6.32 [50].

Pyrolysis of bis(4-methoxyphenyl) tellurium dichloride at 250° generated tellurium and 4-methoxychlorobenzene as the main product. Refluxing in bis(methoxyethyl) ether in the presence of specially prepared Raney-Nickel produced a 90 percent yield of 4,4'-dimethyoxybiphenyl. Commercial Raney-Nickel gave a lower yield of the diaryl compound and caused the formation of some diaryl telluride [32].

The reaction of diphenyl tellurium dibromide with diphenyl mercury led to the formation of triphenyl telluronium bromide but not tetraphenyl tellurium [35].

Diaryl tellurium dihalides, R_2TeX_2 (R, X: $C_6H_5CH_2$, Br [P-14]; $C_6H_5CH_2$, I [P-13]; $C_6H_5COCH_2$, Cl [P-2,P-6,P-7,P-9,P-14]; $4\text{-}CH_3OC_6H_4$, Cl [P-14]; other organic tellurium compounds [74,75,76,P-1], tellurium di(methyl xanthate) [P-5] and bis(thiourea)tellurium dichloride [76,P-3] are claimed as components of heat-developable photographic materials.

The reduction of diaryl tellurium dichlorides with hydrazine [34,35] and the halogen exchange reactions between R_2TeX_2 and R'_2Te [60] have been described in section VI-A1. The conversion of diaryl tellurium dihalides to $R_2Te(NCS)_2$ [61] and the formation of mercury(II) halide adducts of dimethyl tellurium dihalides [35] are discussed in sections VI-B3 and X-E, respectively.

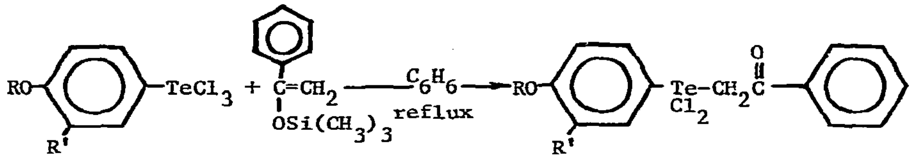
2. Unsymmetric diorganyl tellurium dihalides, $RR'TeX_2$ (X = F, Cl, Br, I)

A number of new unsymmetric diorganyl tellurium dihalides were prepared employing with few exceptions well-established methods. The new compounds marked by an asterisk are listed in Table 2.

Several diorganyl tellurium difluorides, $RR'TeF_2$, were obtained by treating the diiodides with silver oxide followed by addition of hydrofluoric acid [69] or by reacting diorganyl telluroxides with hydrofluoric acid [69].

Most of the diorganyl tellurium dichlorides, dibromides and diiodes were obtained from the tellurides and chlorine, sulfuryl dichloride, bromine or iodine. Aryl tellurium trichlorides reacted with 1-phenyl-1-trimethylsiloxyethylene to produce aryl benzoylmethyl tellurium dichlorides [33] in yields as high as 90 percent (eqn. 22).

(22)



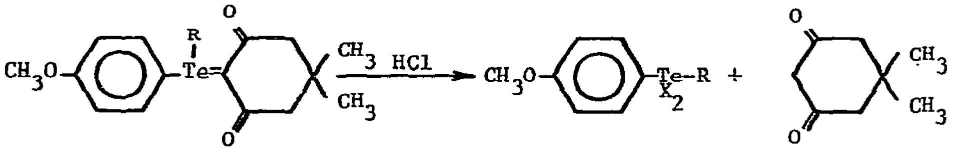
R, R': CH_3, H; C_2H_5, H; CH_3, CH_3O

The reaction between 4-dimethylaminophenyl mercury acetate and aryl tellurium trichlorides was used to synthesize 4-dimethylaminophenyl aryl tellurium dichlorides [49].

The product of the reaction between tellurium tetrachloride and methoxybenzene at 160° contained in addition to bis(4-methoxyphenyl) tellurium dichloride approximately one percent 4-methoxyphenyl 2-methoxyphenyl tellurium dichloride [32].

Boiling the tellurium ylides 27 in ethanol with concentrated hydrochloric acid or treating them with bromine in $CHCl_3$/hexane yielded diorganyl tellurium dihalides [72] (eqn. 23).

(23)



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The tellurium atoms in 4-dimethylaminophenyl aryl tellurium dihalides use their d-orbitals to accept electrons from the amino group. This conclusion is based on dipole moment measurements (section XII-H) and the observation that $\mu_{calcd.} < \mu_{exp.}$ [50]. The values for the thermodynamic basicity constants pK_a (Table 2) indicate that the TeX_2 groups do not transmit electronic effects as well as the tellurium atoms in diorganyl

(Continued on p. 91)

TABLE 2

UNSYMMETRIC DIORGANYL TELLURIUM DIHALIDES, RR'TeX$_2$ (X = F, Cl, Br, I)

R	R'	X	Method	mp.°C	Yield %	$pK_a^{25°}$ (CH$_3$CN)	Ref.**
CH$_3$	4-CH$_3$C$_6$H$_4$	Br	**27** + conc. HCl/C$_2$H$_5$OH (eqn. 23)	-	-	-	72 [5]
CH$_3$	3-FC$_6$H$_4$	F*	RR'TeI$_2$ + Ag$_2$O, then HF	118-9°	-	-	69
		Cl*	RR'Te + SO$_2$Cl$_2$/benzene	94°	100	-	47
		Br*	RR'Te + Br$_2$/benzene	137°	100	-	47
		I*	RR'Te + I$_2$/benzene	126°(dec)	100	-	47
	4-FC$_6$H$_4$	F*	RR'TeI$_2$ + Ag$_2$O, then HF	78-9°	-	-	69
		Cl*	RR'Te + SO$_2$Cl$_2$/benzene	111°	100	-	47
		Br*	RR'Te + Br$_2$/benzene	133-4°	100	-	47
		I*	RR'Te + I$_2$/benzene	128°(dec)	100	-	47
C$_6$H$_5$CH$_2$	4-CH$_3$OC$_6$H$_4$	Cl	**27** + conc. HCl/C$_2$H$_5$OH (eqn. 23)	-	-	-	72 [1]
C$_6$H$_5$COCH$_2$	4-CH$_3$OC$_6$H$_4$	Cl	R'TeCl$_3$ + C$_6$H$_5$C(OSiMe$_3$)=CH$_2$	133-5°	87	-	33
	4-C$_2$H$_5$OC$_6$H$_4$	Cl	R'TeCl$_3$ + C$_6$H$_5$C(OSiMe$_3$)=CH$_2$	136-7°	88	-	33
	3,4-(CH$_3$O)$_2$C$_6$H$_3$	Cl*	R'TeCl$_3$ + C$_6$H$_5$C(OSiMe$_3$)=CH$_2$	189°	91	-	33
C$_6$H$_5$	3-FC$_6$H$_4$	F*	RR'TeO + HF	118-9°	-	-	69
	4-FC$_6$H$_4$	F*	RR'TeO + HF	78-9°	-	-	69
	2-CH$_3$OOCC$_6$H$_3$	Cl*	RR'Te + Cl$_2$	141°	100	-	45
4-(CH$_3$)$_2$CHC$_6$H$_4$	4-CH$_3$OC$_6$H$_4$	Cl	**27** + Br$_2$/CHCl$_3$, hexane (eqn. 23)	-	-	-	72 [5]
2-CH$_3$OC$_6$H$_4$	4-CH$_3$OC$_6$H$_4$	Cl*	TeCl$_4$ + CH$_3$OC$_6$H$_5$/160°	not pure	1	-	32

TABLE 2 (CONT'D)

UNSYMMETRIC DIORGANYL TELLURIUM DIHALIDES, RR'TeX_2 (X = F, Cl, Br, I)

R	R'	X	Method	mp. °C	Yield%	$pK_a^{25°}$ (CH_3CN)	Ref.**
4-$(CH_3)_2NC_6H_4$	C_6H_5	Cl†	RR'Te + SO_2Cl_2/CCl_4	150-1°	89	7.83	50
		Cl†	R'$TeCl_3$ + $RHgOOCCH_3$/dioxane	-	-	-	49
		Br	RR'Te + Br_2/CCl_4	140°	84	7.56	50 [5]
		I	RR'Te + $I_2/CHCl_3$	145-6°	86	7.12	50 [5]
	4-$CH_3C_6H_4$	Cl*	RR'Te + SO_2Cl_2/CCl_4	165-6°	88	7.87	50
		Cl*	R'$TeCl_3$ + $RHgOOCCH_3$/dioxane	-	-	-	49
		I*	RR'Te + $I_2/CHCl_3$	134°	97	7.19	50
	4-$CH_3OC_6H_4$	Cl	RR'Te + SO_2Cl_2/CCl_4	170-1°	-	7.91	50 [1]
		Cl	R'$TeCl_3$ + $RHgOOCCH_3$/dioxane	-	-	-	49 [1]
		Br	RR'Te + Br_2/CCl_4	183-4°	78	7.61	50 [1]
		I†	RR'Te + $I_2/CHCl_3$	130°	85	7.32	50 [1]
	4-$C_2H_5OC_6H_4$	Cl	RR'Te + SO_2Cl_2/CCl_4	153-4°	86	7.95	50 [1]
		Cl	R'$TeCl_3$ + $RHgOOCCH_3$/dioxane	-	-	-	49 [1]
		Br	RR'Te + Br_2/CCl_4	121-3°	91	7.61	50 [1]
		I†	RR'Te + $I_2/CHCl_3$	96-7°	94	7.37	50 [1]
	4-$C_6H_5OC_6H_4$	Cl	RR'Te + SO_2Cl_2/CCl_4	194-5°	50	-	50 [1]
		Cl	R'$TeCl_3$ + $RHgOOCCH_3$/dioxane	-	-	-	49 [1]
		Br	RR'Te + Br_2/CCl_4	188-9°	89	-	50 [1]
		I†	RR'Te + $I_2/CHCl_3$	135-6°	91	-	50 [1]

TABLE 2 (CONT'D)

UNSYMMETRIC DIORGANYL TELLURIUM DIHALIDES, $RR'TeX_2$ (X = F, Cl, Br, I)

R	R'	X	Method	mp. °C	Yield %	$pK_a^{25°}$ (CH_3CN)	Ref.**
4-$(CH_3)_2NC_6H_4$	3-BrC_6H_4	Cl*	$RR'Te + SO_2Cl_2/CCl_4$	149°	87	7.73	50
		Cl*	$R'TeCl_3 + RHgOOCCH_3$/dioxane	-	-	-	49
		Br*	$RR'Te + Br_2/CCl_4$	133°	84	7.44	50
		I*	$RR'Te + I_2/CHCl_3$	116-8°	85	6.95	50
	4-Br-C_6H_4	Cl†	$RR'Te + SO_2Cl_2/CCl_4$	151-2°	94	7.76	50 [5]
		Cl†	$R'TeCl_2 + RHgOOCCH_3$/dioxane	-	-	-	49 [5]
		Br	$RR'Te + Br_2/CCl_4$	168-9°	85	7.49	50 [5]
		I	$RR'Te + I_2/CHCl_3$	144-5°	87	-	50 [5]
	3-ClC_6H_4	Cl*	$R'TeCl_3 + RHgOOCCH_3$/dioxane	-	-	-	49
	4-ClC_6H_4	Cl*	$RR'Te + SO_2Cl_2/CCl_4$	151-2°	86	7.76	50
		Cl*	$R'TeCl_3 + RHgOOCCH_3$/dioxane	-	-	-	49
		Br*	$RR'Te + Br_2/CCl_4$	146°	75	7.51	50
		I*	$RR'Te + I_2/CHCl_3$	124°	82	-	50
	3-$O_2NC_6H_4$	Cl*	$R'TeCl_3 + RHgOOCCH_3$/dioxane	138°	50	7.56	50
		Cl*	$R'TeCl_3 + RHgOOCCH_3$/dioxane	-	-	-	49

* New Compounds.

† These compounds were prepared previously using exactly the same reactions as described in the column labeled "Method". Compounds which are not marked by an asterisk or a dagger were synthesized previously by reactions different from those listed in this table.

** References in brackets refer to the review articles, in which the compounds in question were described for the first time.

tellurides [50]. Fluorine nmr chemical shifts obtained from the compounds m-(or p-)$FC_6H_4Te(R)X_2$ (R = CH_3, C_6H_5) were used to determine the induction and resonance constants employing the Taft equation. The results suggested that the $RTeX_2$ groups interact with the π-systems of the phenyl rings mainly through the inductive effect [47,69].

The reduction of diorganyl tellurium dihalides by sodium sulfide is discussed in section VI-A2. The cyclization of the oxime of 2-formylphenyl butyl telluride at 100° in the presence of polyphosphoric acid to give 2-azabenzotellurophene [46] is described in section X-C.

3. Diorganyl tellurium compounds, R_2TeX_2 (X = CN, NCO, NCS, NCSe)

Diorganyl tellurium di(pseudohalides) were prepared from diorganyl tellurides and thiocyanogen, $(SCN)_2$, [62,69] a reaction reported previously [5], from diorganyl tellurium dichlorides and ammonium thiocyanate [61] and from R_2TeClI and silver pseudohalides, AgX (X = CN, OCN, SCN, SeCN) [62]. The yields and the melting points of the products of these reactions are listed in Table 3. Dibutyltin diisothiocyanate did not react with diaryl tellurium dichlorides [61].

The ν(C-X) infrared modes of the pseudohalide groups in the diorganyl tellurium di(pseudohalides) suggest the presence of Te-N bonds in these molecules [62]. The ν(CN) vibrations in the spectra of diphenyl and bis(4-methoxyphenyl) tellurium diisothiocyanate are split implying either a non-linear N-Te-N arrangement or molecular association via weakly bridging SCN groups.

The ν(CN) region in the spectrum of bis(4-ethoxyphenyl) tellurium isothiocyanate is characterized by a broad band which indicates much stronger covalent interaction for one SCN group than for the other. The telluronium structure $[R_2TeNCS]^+SCN^-$ has been suggested for this compound. These differences among the assumed structures were attributed to the influence of the para-substituents on the relative lattice energies of the two structures [61]. The molar conductances of diorganyl tellurium di(pseudohalides) (10^{-3}M solutions) in acetonitrile or methanol indicate that these compounds are non-electrolytes [62]. However, according to values of the molar conductances measured in 10^{-3}M solutions of $(4\text{-}ROC_6H_4)_2Te(NCS)_2$ (R = CH_3, C_2H_5) in nitromethane and extrapolated to infinite dilution, complete dissociation to $(ROC_6H_4)_2Te^{++}$ and NCS^- has taken place [61].

The diaryl tellurium di(pseudohalides) are yellow, crystalline substances, generally soluble in common organic solvents, and monomeric in benzene solution. They can be stored unchanged for several weeks. Among the compounds investigated only the diphenyl tellurium di(pseudohalides) decomposed slowly even at low temperatures [62].

TABLE 3

DIORGANYL TELLURIUM DI(PSEUDOHALIDES), $RR'TeX_2$, (X = CN, OCN, SCN, SeCN)

R	R'	X	Method	mp. °C	Yield %
C_6H_5	C_6H_5	-NC	$R_2TeICN + AgCN/CHCl_3$	70°	100
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	-NC	$R_2TeICN + AgCN/CHCl_3$	75°	100
C_6H_5	C_6H_5	-NCO	$R_2TeClI + AgOCN$	85-90°(dec)	100
C_6H_5	C_6H_5	-NCS	$R_2Te + (SCN)_2/CCl_4$	128°	90
		-NCS	$R_2TeClI + AgSCN/CHCl_3$	128°	100
		-NCS	$R_2TeCl_2 + NH_4SCN/CH_3OH$	-	-
	$3\text{-}FC_6H_4$	-NCS	$RR'Te + (SCN)_2/(C_2H_5)_2O$	115-8°	-
	$4\text{-}FC_6H_4$	-NCS	$RR'Te + (SCN)_2/(C_2H_5)_2O$	123-5°(dec)	-
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	-NCS	$R_2Te + (SCN)_2/CCl_4$	138-40°**	90
		-NCS	$R_2TeClI + AgSCN/CHCl_3$	138-40°	100
		-NCS	$R_2TeCl_2 + NH_4SCN/CH_3OH$	-	-
C_6H_5	C_6H_5	-NCSe	$R_2TeClI + AgSeCN/CHCl_3$	110-2°	100
$4\text{-}CH_3OC_6H_4$	$4\text{-}CH_3OC_6H_4$	-NCSe	$R_2TeClI + AgSeCN/CHCl_3$	220°	-

*Previously reported mp. 140° [5].

**Previously reported mp. 106-108°(dec) and 110° [5].

Based on fluorine nmr shifts obtained from the compounds m-(or p-)$FC_6H_4Te(C_6H_5)(NCS)_2$ Sadekov and coworkers [69] concluded that the $C_6H_5Te(NCS)_2$ groups interact with the π-system of the phenyl rings mainly through the inductive effect.

4. Diorganyl tellurium compounds, R_2TeXX'

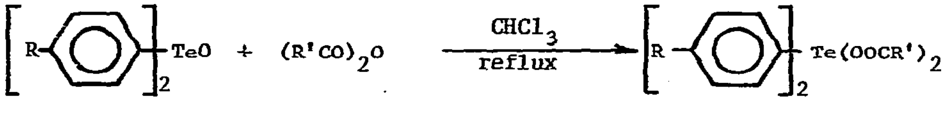
The diorganyl tellurium compounds of the general formula R_2TeXX' were prepared from diorganyl tellurides and ICl, IBr, ICN or BrCN, from diorganyl tellurium chloride iodides and AgCN, AgNCO or AgNCS, or from diorganyl telluroxides and perchloric acid or trichloroacetic acid. Details for these reactions and data for the products are listed in Table 4.

Infrared data indicate [62], that the CN, OCN and SCN groups are bonded to the tellurium atom via the nitrogen atom. The diorganyl tellurium halide pseudohalides, R_2TeXX' (X = Cl, Br; X' = CN, OCN, SCN) are non-electrolytes in acetonitrile and methanol. They are monomeric in benzene [62]. The good solubility of $(4\text{-}CH_3OC_6H_4)_2Te(OH)(CCl_3COO)$ in carbon tetrachloride and in benzene suggests that the compound is not a telluronium salt $[R_2Te(OH)]^+CCl_3COO^-$ [73].

5. Diorganyl tellurium dicarboxylates

The reaction of diorganyl telluroxides with carboxylic acid anhydrides in 1:1 molar ratio produced diorganyl tellurium dicarboxylates in high purity and quantitative yields [73] (eqn. 24). This method had been used previously [3,5]. The new compounds are marked in eqn. (24) by an asterisk. Diphenyl tellurium diacetate was previously reported to melt at 138° [2,5] and at 145° [5], whereas now a melting point of 164° was determined [73].

(24)



R, R', mp.°C: H, CH_3, 164°; H, CH_2Cl*, 107-9°; CH_3, CH_3, 182°; CH_3, CH_2Cl*, 163°; CH_3, C_3H_7, 142°; CH_3, C_6H_5, 231°; CH_3O, CH_3, 136°; CH_3O, CH_2Cl*, 160°; CH_3O, CCl_3*, 122-5°; CH_3O, CF_3, 152°; CH_3O, C_3H_7, 128°; CH_3O, C_6H_5, 210°; $(CH_3)_2N$, CH_3*, 184°; $(CH_3)_2N$, CH_2Cl*, 167°; $(CH_3)_2N$, C_3H_7*, 133°; $(CH_3)_2N$, C_6H_5*, 189°.

Boiling a suspension of bis(4-methoxyphenyl) telluroxide in carbon

TABLE 4

DIORGANYL TELLURIUM COMPOUNDS, R_2TeXX'

R	X	X'	Method	mp. °C	Yield %
C_6H_5	I	Cl	$R_2Te + ICl/(C_2H_5)_2O$	205°	90
		Br	$R_2Te + IBr/(C_2H_5)_2O$	213°	90
		-NC	$R_2Te + ICN/(C_2H_5)_2O$	142°	90
		-NC	$R_2TeClI + AgCN/CHCl_3$	142°	100
		-NCO	$R_2TeClI + AgNCO/CHCl_3$	78-80°	100
		-NCS	$R_2TeClI + AgNCS/CHCl_3$	170°	100
	OH	ClO_4	$R_2TeO + HClO_4$	251-3°	64
	-NC	Br	$R_2Te + BrCN/(C_2H_5)_2O$	225°	90
		-NCO	$R_2TeI(CN) + AgNCO/CHCl_3$	175°(dec)	100
		-NCS	$R_2TeI(CN) + AgNCS/CHCl_3$	142°(dec)	100
$4\text{-}CH_3OC_6H_4$	I	Cl	$R_2Te + ICl/CHCl_3$	145°	90
		Br	$R_2Te + IBr/CHCl_3$	160°	90
		-NC	$R_2Te + ICN/CHCl_3$	176°	90
		-NC	$R_2TeClI + AgCN/CHCl_3$	176°	100
		-NCO	$R_2TeClI + AgNCO/CHCl_3$	138-40°	100
		-NCS	$R_2TeClI + AgNCS/CHCl_3$	110°	100
	OH	ClO_4	$R_2TeO + HClO_4$	220°	74
		CCl_3COO^-	$R_2TeO + CCl_3COOH/C_6H_6$	116-9°	95
	-NC	Br	$R_2Te + BrCN/CHCl_3$	230°	90

tetrachloride with acetic acid or trichloroacetic acid and filtering the mixture through anhydrous calcium chloride gave the expected bis(4-methoxyphenyl) tellurium dicarboxylates in quantitative yields [73].

Diaryl tellurium dicarboxylates refluxed in toluene with acyl chlorides (1:2 molar ratio) produced diorganyl tellurium dichlorides in quantitative yields [73].

C. Diorganyl Telluroxides, R_2TeO

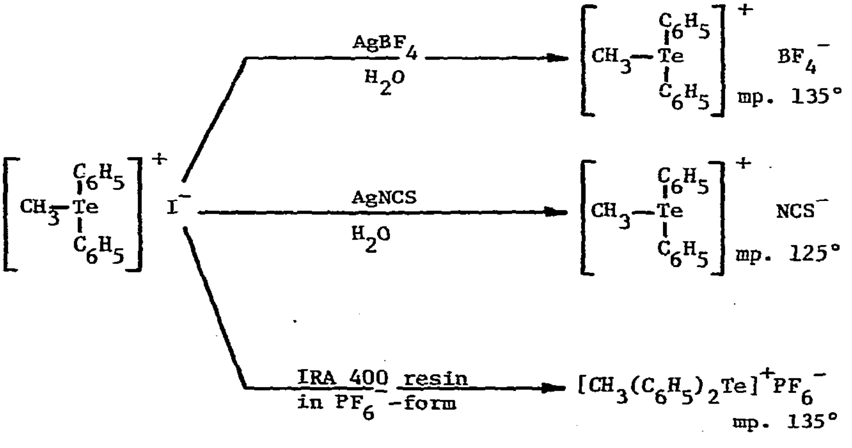
SCF-Mo Methods in the CNDO/2 approximation and the Extended Hückel Method were employed to calculate the barriers to pyramidal inversion and internal rotation for the molecules $R_2M{=}X$ ($M = S, Se, Te$; $X = O, NH, PH, CH_2$). The tellurium compounds had the highest inversion barrier and the lowest barriers to rotation relative to the M=X bond [77].

The reactions of diaryl telluroxides with hydrofluoric acid [69] (section VI-B2), and with carboxylic acids and anhydrides [73] (section VI-B5) and those leading to tellurium ylides [78] (section VIII) are discussed in the indicated sections.

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

Anion exchange reactions employing diphenyl methyl telluronium iodide as starting material yielded the telluronium tetrafluoroborate, hexafluorophosphate and thiocyanate [61] (eqn. 25).

(25)



The telluronium thiocyanate behaves as 1:1 eletroclyte in DMSO and DMF. In $CDCl_3$ solution it exists in a covalent form from which reductive elimination of methyl thiocyanate occurs. The rate of this decomposition was studied [61].

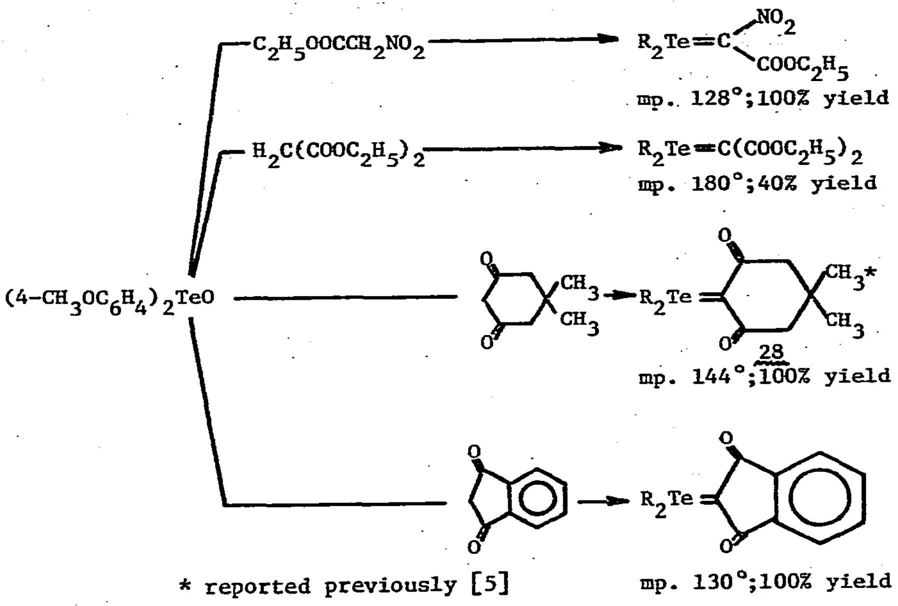
Tris(4-methoxyphenyl) telluronium chloride was claimed to be a component of heat-developable photographic materials [P-14].

VIII. Tellurium Ylides

A new method for the synthesis of tellurium ylides was developed. Diaryl telluroxide and a compound with an active methylene group were refluxed in benzene (eqn. 26). The water formed in the reactions was removed by azeotropic distillation [78].

The reactions of the tellurium ylides 28 (eqn. 26) with elemental halogens to form diorganyl tellurium dihalides and 1,1-dihalo-2,6-dioxo-4,4-dimethylcyclohexane or with concentrated hydrochloric acid to give diorganyl tellurium dichlorides and 2,6-dioxo-4,4-dimethylcyclohexane are discussed in sections VI-B1 and VI-B2 [72].

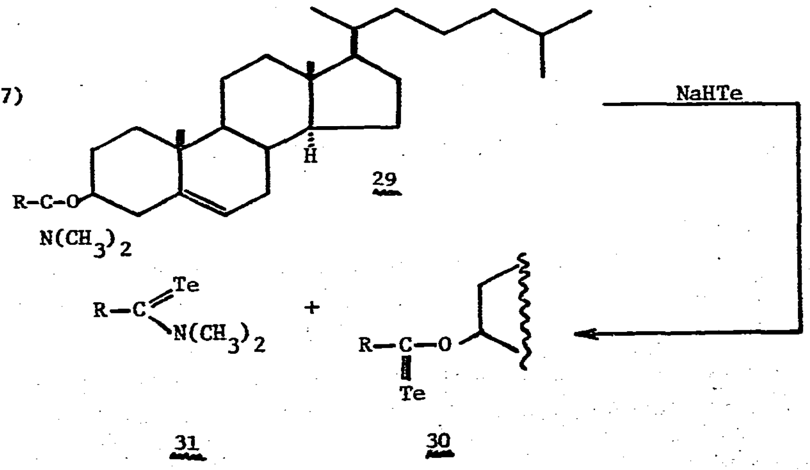
(26)



IX. Tellurocarboxylic Acids, RC(=Te)X

The tellurocarboxylic acid derivatives 30 and 31 (R=H) were obtained

(27)



when the cholesteryl ester 29 was treated with sodium hydrogen telluride in ethanol at -20° [22] (eqn. 27). Both of these yellow to orange tellurocarboxylic acid derivatives were highly unstable and were not completely characterized. When reaction (27) was carried out with the benzoyl ester 29 (R = C_6H_5) only tellurium and the benzyl cholesteryl ether were obtained [22].

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

During the period covered by this survey, organic tellurium compounds containing a Te-Li, Te-Na, Te-K, Te-B, Te-Ge, Te-Sn, Te-N, Te-P, Te-S, Te-Se, Te-Cu, Te-Pd, Te-Pt, Te-Ag and Te-Hg bond were investigated.

A. Organic Compounds of Tellurium with Elements of Group I or III

Alkyl lithium tellurides, RTeLi, were reacted with 19-bromoprogesterone to produce 19-alkyltelluroprogesterones [P-4].

The following organyl sodium tellurides, RTeNa, were generated (but not isolated) by reduction of diorganyl ditellurides with sodium borohydride in ethanol/1M aqueous NaOH [19], ethanol/benzene/aqueous NaOH [12,47,52,55] or ethanol/benzene/1M aqueous NaOH [45] as the reaction medium (R given): $C_2H_5^*$, $C_4H_9^*$, $C_5H_{11}^*$ [19]; C_6H_5 [19,45,54,55]; 4-$CH_3C_6H_4$ [45,52,55]; 4-$C_5H_{11}C_6H_4^*$ [12]; 4-$CH_3OC_6H_4$ [55]; 4-$C_2H_5OC_6H_4^*$ [19]; 3-$FC_6H_4^*$, 4-$FC_6H_4^*$ [47]; 4-BrC_6H_4 [55]; 3-thienyl* [45]. New compounds are marked by an asterisk.

Liesk, Schulz and Klar [56] reacted diphenyl ditelluride with sodium as well as with potassium in liquid ammonia. Upon evaporation the phenyl alkali metal tellurides were obtained in 95 percent yields as grey powders, which were moisture and air sensitive but stable for months under a nitrogen atmosphere. The compounds are soluble in acetone and tetrahydrofuran. Phenyl potassium telluride and tetraphenyl phosphonium chloride suspended in liquid ammonia produced orange-red tetraphenyl phosphonium benzenetellurolate $[(C_6H_5)_4P]^+[C_6H_5Te]^-$, a compound, which is soluble in ethanol and chloroform, but insoluble in petroleum ether, benzene, diethyl ether and tetrahydrofuran.

The reaction of organyl sodium tellurides with dimethyl sulfate [47,54] or alkyl halides [54], diazonium salts [45] (section VI-A2), carboxylic acid chlorides [12,52] (section VI-A3), compounds of the type $(C_6H_5)_3MTeR$ (M = Ge, Sn, Pb) [55] (section X-B), and copper(I) chloride [19] (section X-F) are discussed in the indicated sections.

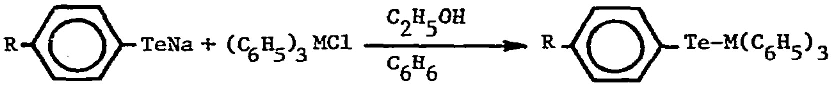
Sodium polytelluride, prepared from sodium and tellurium in liquid ammonia, reacted with $B_{10}H_{14}$ in deoxygenated water to give the anion

$B_{10}H_{11}Te^-$. Upon acidification $B_{10}H_{12}Te$, which melted at 244-6° with decomposition, was obtained in 79 percent yield. The following compounds were prepared from $B_{10}H_{12}Te$ (% yield and mp. given): $[(CH_3)_4N]^+[B_{10}H_{11}Te]^-$, 97%, -; $[(CH_3)_4N]^+[(B_{10}H_{10}Te)_2Co]^-$, 10%, -; $C_5H_5Co(B_{10}H_{10}Te)$, 56%, 290-2°; $[(CH_3)_4N]^+[(B_{10}H_{10}Te)_2Fe]^-$, 30%, - [79]; $B_{11}H_{11}Te$, 25%, ~480°(dec) [28]. The compound $B_{11}H_{11}Te$, which probably has a closo, nearly icosahedral cage structure, was also prepared from tellurium dioxide and $NaB_{11}H_{14}$ [28].

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

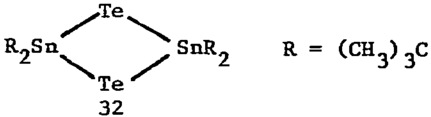
A number of compounds of the formula $4\text{-}RC_6H_4Te\text{-}M(C_6H_5)_3$ were prepared from aryl sodium tellurides and $(C_6H_5)_3MCl$ [55] (eqn. 28).

(28)



R, M, yield %, mp.°C: H, Ge, 61%, 105-7°; H, Sn, 76%, 95-7°; H, Pb, 75%, 90-2°; CH_3, Ge, -, 88-90°; CH_3,Sn, -, 78-80°; CH_3, Pb, -, 87-9°; CH_3O, Ge, -, 89-91°; CH_3O, Sn -, 78-80°; CH_3O, Pb, -, 71-3°; Br, Pb, -, 80-2°.

The reaction of R_2SnCl_2 with sodium telluride and of $(R_2Sn)_4$ and tellurium yielded the dimeric dialkyl tin telluride 32 [14]. The four-numbered ring is planar.



32

The compounds RTe-MR'$_3$ have been claimed as components of heat-developable photoimaging materials [55,P-13].

The reactions of $(C_6H_5)_3Sn\text{-}TeR$ with copper(I) chloride to give RTeCu are discussed in section X-F.

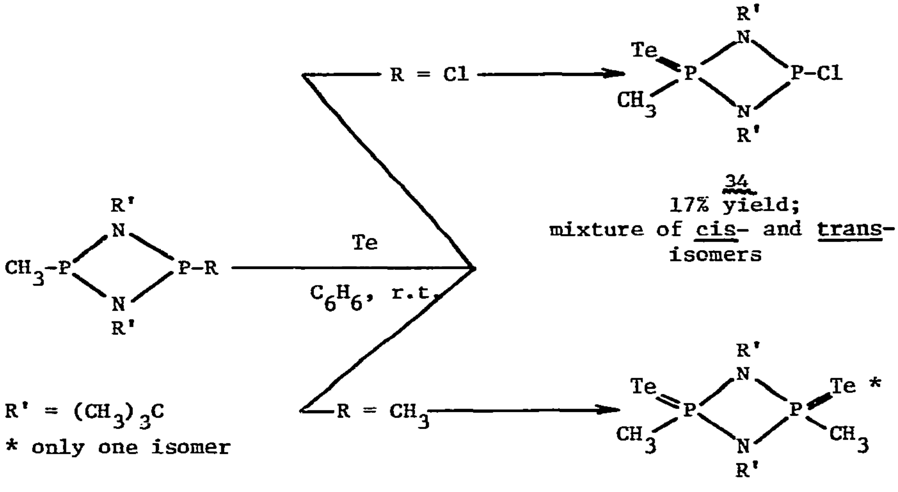
C. Organic Compounds of Tellurium with a Tellurium-Phosphorus or a Tellurium-Nitrogen Bond

The phosphoric acid ester $(C_2H_5O)_2P(O)TeCH_3$, prepared from

$(C_2H_5O)_2P(O)TeNa$ and methyl iodide in absolute ethanol was too unstable for isolation in pure form [16]. The white crystalline, air sensitive tellurophosphate $(C_2H_5O)_2P(O)TeNa$, which was obtained from tellurium and $(C_2H_5O)_2PONa$, reacted regiospecifically in ethanol below room temperature with terminal epoxides to give terminal olefins in good yields. Non-terminal epoxides reacted slowly [16].

The phosphine tellurides 34 and 35 were isolated as yellow crystals from a reaction mixture containing tellurium and the nitrogen-phosphorus heterocycle 33 (eqn. 29).

(29)



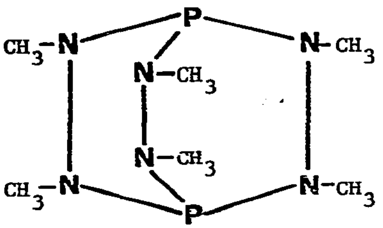
R' = $(CH_3)_3C$
* only one isomer

34
17% yield;
mixture of cis- and trans-isomers

35
8% yield;

Whereas solutions of the phosphine telluride 34 decompose rapidly above 6° precipitating elemental tellurium, solutions of the telluride 35 can be stored for some time at room temperature. The yellow crystals of both compounds are stable in a closed flask at room temperature [15].

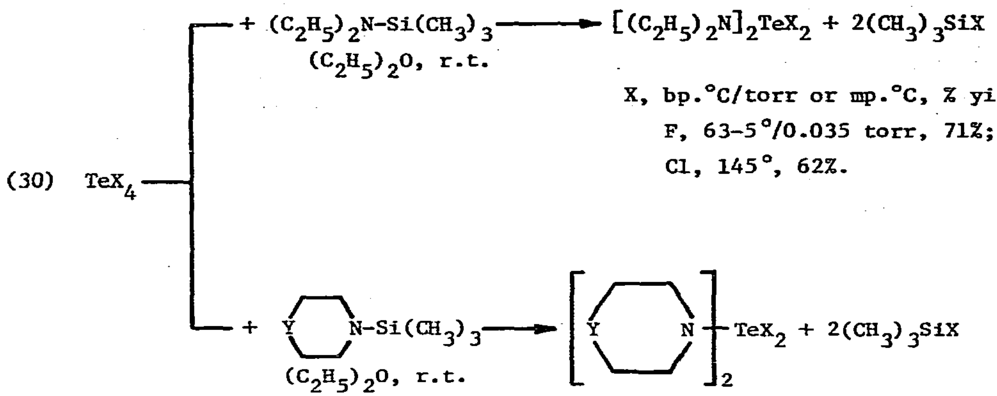
Tellurium did not react with the bicyclic hydrazinodiphosphine 36 [80].



36

Tellurium tetrafluoride and tellurium tetrachloride reacted with trimethylsilylamines [39] to produce diamino tellurium dihalides (eqn. 30).

(30)



$$TeX_4 + (C_2H_5)_2N\text{-}Si(CH_3)_3 \xrightarrow[(C_2H_5)_2O,\ r.t.]{} [(C_2H_5)_2N]_2TeX_2 + 2(CH_3)_3SiX$$

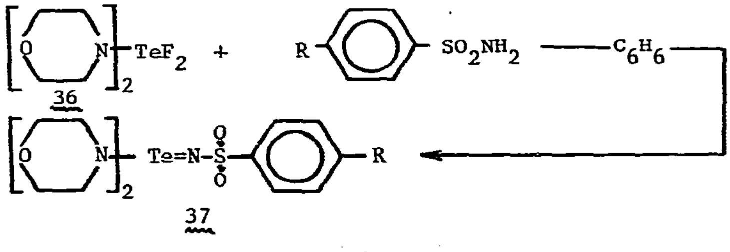
X, bp.°C/torr or mp.°C, % yield:
F, 63-5°/0.035 torr, 71%;
Cl, 145°, 62%.

X, Y, mp.°C, % yield:
F, CH_2, 102-4°(dec), 94%;
Cl, CH_2, 148-9°(dec), 46%;
F, O, 110-2°(dec), 60%;
Cl, O, 128-30 (dec), 84%.

Based on ^{19}F-nmr data a trigonal bipyramidal structure was suggested for the diamino tellurium difluorides with the two amino groups occupying the apical positions. The diamino tellurium difluorides hydrolyze easily, but do not react with trimethylsilyldialkylamines to produce $(R_2N)_4Te$.

The diamino tellurium dichlorides are brownish-grey, amorphous solids, which are insoluble in organic solvents. Dimorpholino tellurium difluoride 36 in benzene suspension condensed with arylsulfonamides to give in quantitative yields the previously reported [5] sulfonimides 37 [39] (eqn. 31).

(31)



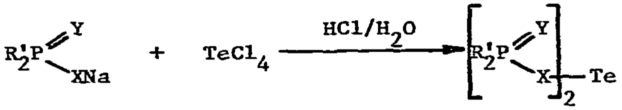
R, mp.°C: H, 114°; CH_3, 112°.

2-Azabenzotellurophene, a heterocyclic compound containing a tellurium-nitrogen bond is described in section XI-F.

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

Tellurium tetrachloride [81] (or TeO_2/HCl[37]) reacted with R_2PS_2Na, [81] $(RO)_2PS_2Na$ [81] or $(RO)_2POXNa$ (X = S, Se) [37] to give the tellurium derivatives 38 (eqn. 32).

(32)



R', Y, X, mp.°C, % yield: C_2H_5, S, S, 117°(dec), 79% [81];
CH_3O, S, S, 91°(dec), 80% [81];
C_2H_5O, S, S, 66°(dec), 76% [81];
i-C_3H_7O, O, S, -, - [37];
i-C_3H_7O, O, Se, -, - [37].

The deep red tellurium selenophosphate $[(\text{i-}C_3H_7O)_2P(O)Se]_2Te$, loses tellurium readily in the dark. The magnitude of the observed J_{P-Se} coupling constant suggests that the tellurium atom is bonded to the selenium atom. The corresponding thiophosphate exists in $CDCl_3$ solution in two forms; in one form the tellurium is bonded only to sulfur, whereas in the other the tellurium is coordinated to the sulfur and the oxygen atoms [37].

The reaction of bis(4-methoxyphenyl) selenide telluride with 2-phenyliodoniobenzoate [38] is described in section VI-A4.

E. Organic Tellurium Compounds as Ligands in Transition Metal Complexes

Copper(I) halide complexes with diorganyl ditellurides as ligands of the composition $R_2Te_2\cdot CuX$ were prepared by mixing copper(I) chloride or copper(I) bromide dissolved in acetonitrile with solutions of diorganyl ditellurides in diethyl ether [19,57] (Table 5). Upon cooling the red to orange complexes precipitated. They are non-electrolytes in acetonitrile. According to Moessbauer spectral data the complexes contain intact ditellurides with both tellurium atoms weakly coordinated to copper atoms. The tellurium atoms' use their 5p orbitals for complexation with little change in their hybridization. The polymeric structure 39 was proposed for these complexes [19].

(Continued on p. 105)

TABLE 5

ORGANIC TELLURIUM COMPOUNDS AS LIGANDS IN TRANSITION METAL COMPLEXES

Compound	Reactants	mp. °C
$(C_2H_5)_2Te_2 \cdot CuCl$	$Cu_2Cl_2/CH_3CN + R_2Te_2/(C_2H_5)_2O$	-
$(C_2H_5)_2Te_2 \cdot CuBr$	$Cu_2Br_2/CH_3CN + R_2Te_2/(C_2H_5)_2O$	-
$(C_4H_9)_2Te_2 \cdot CuCl$	$Cu_2Cl_2/CH_3CN + R_2Te_2/(C_2H_5)_2O$	-
$(C_4H_9)_2Te_2 \cdot CuBr$	$Cu_2Br_2/CH_3CN + R_2Te_2/(C_2H_5)_2O$	-
$(C_5H_{11})_2Te_2 \cdot CuCl$	$Cu_2Cl_2/CH_3CN + R_2Te_2/(C_2H_5)_2O$	-
$(C_5H_{11})_2Te_2 \cdot CuBr$	$Cu_2Br_2/CH_3CN + R_2Te_2/(C_2H_5)_2O$	-
$(C_6H_5)_2Te_2 \cdot CuCl$	$Cu_2Cl_2/CH_3CN + R_2Te_2/(C_2H_5)_2O$	-
$(C_6H_5)_2Te_2 \cdot CuBr$	$Cu_2Br_2/CH_3CN + R_2Te_2/(C_2H_5)_2O$	-
$(4\text{-}C_2H_5OC_6H_4)_2Te_2 \cdot CuCl$	$Cu_2Cl_2/CH_3CN + R_2Te_2/(C_2H_5)_2O$	-
$(4\text{-}C_2H_5OC_6H_4)_2Te_2 \cdot CuBr$	$Cu_2Br_2/CH_3CN + R_2Te_2/(C_2H_5)_2O$	-
trans(?)-$[(C_6H_5)_2Te]_2PdCl_2$	$(C_6H_5CN)_2PdCl_2 + R_2Te$/benzene	164°
trans(?)-$[(C_6H_5)_2Te]_2PdBr_2$	$[(C_6H_5)_2Te]_2PdCl_2 + NaBr$	180°
trans(?)-$[(4\text{-}C_2H_5OC_6H_4)_2Te]_2PdCl_2$	$(C_6H_5CN)_2PdCl_2 + R_2Te$/benzene	125°
trans(?)-$[(4\text{-}C_2H_5OC_6H_4)_2Te]_2PdBr_2$	$[(4\text{-}C_2H_5OC_6H_4)_2Te]_2PdCl_2 + NaBr$	105°
$[(4\text{-}C_2H_5OC_6H_4Te)_2Pd \cdot P(C_6H_5)_3]_2$	$[(C_6H_5)_3P]_4Pd + R_2Te_2$/benzene	117°
[( Te$)_2Pd \cdot P(C_6H_5)_3]_2$	$[(C_6H_5)_3P]_4Pd + R_2Te_2$/benzene	145°

TABLE 5 (CONT'D)

ORGANIC TELLURIUM COMPOUNDS AS LIGANDS IN TRANSITION METAL COMPLEXES

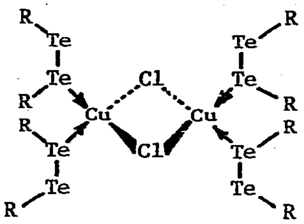
Compound	Reactants	mp. °C
$(C_4H_9)_2Te\cdot 2AgBr$	$R_2Te/(CH_3)_2CO$ + $AgBr/KBr/H_2O$	-
$C_6H_5(C_2H_5)Te\cdot 2AgBr$	$R_2Te/(CH_3)_2CO$ + $AgBr/KBr/H_2O$	-
$C_6H_5(C_6H_5CH_2)Te\cdot 2AgBr$	$R_2Te/(CH_3)_2CO$ + $AgBr/KBr/H_2O$	-
$(C_6H_5)_2Te\cdot 2AgCl$	$R_2Te/(CH_3)_2CO$ + $AgCl/KCl/H_2O$	-
$(C_6H_5)_2Te\cdot 2AgI$	$R_2Te/(CH_3)_2CO$ + $AgI/KI/H_2O$	-
$(4\text{-}CH_3OC_6H_4)_2Te\cdot 2AgBr$	$R_2Te/(CH_3)_2CO$ + $AgBr/KBr/H_2O$	-
$(2\text{-}C_{10}H_7)_2Te\cdot 2AgBr$	$R_2Te/(CH_3)_2CO$ + $AgBr/KBr/H_2O$	-
$[(C_2H_5)_2Te]_2Pt_2I_4^{\dagger}$	R_2Te + $K_2PtCl_4/LiI/H_2O$	160-3°
cis(?)-$(4\text{-}CH_3C_6H_4)_2Pt\cdot[Te(C_2H_5)_2]_2$	trans-$[(C_2H_5)_2Te]_2PtI_2$ + $RLi/(C_2H_5)_2O$	114-6°
trans(?)-$(4\text{-}CH_3C_6H_4)_2Pt\cdot[Te(C_2H_5)_2]_2$	recrystallization of cis-compound from water	65°
trans(?)-$[(4\text{-}C_2H_5OC_6H_4)_2Te]_2PtCl_2$	$(C_6H_5CN)_2PtCl_2$ + R_2Te/benzene	134°
trans(?)-$[(4\text{-}C_2H_5OC_6H_4)_2Te]_2PtBr_2$	$(C_6H_5CN)_2PtCl_2$ + R_2Te/benzene + NaBr	150°
$(CH_3)_2TeI_2\cdot HgCl$	R_2TeI_2 + $HgCl_2$/abs. ethanol	-
$(CH_3)_2TeBr_2\cdot HgI_2$	R_2TeI_2 + $HgBr_2$/abs. ethanol	128°
	R_2TeBr_2 + HgI_2/abs. ethanol	-

TABLE 5 (CONT'D)

ORGANIC TELLURIUM COMPOUNDS AS LIGANDS IN TRANSITION METAL COMPLEXES

Compound	Reactants	mp.°C
$2(CH_3)_2TeI_2\cdot Hg(C_6H_5)_2$		128°
$(C_6H_5)_2Te\cdot HgCl_2$[†]	-	158-60°
$(C_6H_5)_2Te\cdot HgBr_2$[†]	-	150-2°
$(C_6H_5)_2Te\cdot HgI_2$[†]	-	150-1°
$(4\text{-}C_2H_5OC_6H_4)_2Te\cdot HgCl_2$[†]	-	158°
$(4\text{-}C_2H_5OC_6H_4)_2Te\cdot HgBr_2$[†]	-	158°
$(4\text{-}C_2H_5OC_6H_4)_2Te\cdot HgI_2$[†]	-	130°
$(4\text{-}CH_3OC_6H_4)_2Te_2\cdot 2HgCl_2$	$R_2Te_2 + 2HgCl_2$/hot ethanol	115°
$(4\text{-}C_2H_5OC_6H_4)_2Te_2\cdot 2HgCl_2$	$R_2Te_2 + 2HgCl_2$/hot ethanol	110-2°
$(4\text{-}C_2H_5OC_6H_4)_2Te_2\cdot HgBr_2$	R_2Te_2 + HgBr/hot ethanol	120-2°
$(4\text{-}C_2H_5OC_6H_4)_2Te_2\cdot HgI_2$	$R_2Te_2 + HgI_2$/hot ethanol	202-4°

[†] Prepared previously [1].



39

Several new palladium complexes of the type $(R_2Te)_2PdX_2$ were prepared from $(C_6H_5CN)_2PdCl_2$ and diorganyl tellurides. The reactions of tetrakis(triphenylphosphine) palladium with diorganyl ditellurides yielded complexes of the formula $[(RTe)_2Pd \cdot P(C_6H_5)_3]_2$ [34] (Table 5).

The temperature dependences of the CH_2—proton nmr signals of trans-$[(C_2H_5)_2Te]_2MX_2$ (M = Pd, Pt; X = Cl, Br, I) in chlorobenzene were investigated [63,82]. The following coalescence temperatures were obtained (M, X, coalesc. temp. given): Pd, Cl, 30°; Pt, Cl, 107°; Pd, Br, 51°; Pt, Br, 110°; Pd, I, 18°; Pt, I, 105° [82]. Below the coalescence temperature the methylene protons are diastereotropic becoming equivalent at and above this temperature. The inversion of configuration at tellurium is facile and an intramolecular process. However, a dissociative mechanism could not be rigorously excluded [82]. The barriers to inversion are lower in the Pd than in the Pt complexes, decrease in the order Te>Se>S and are sensitive to the trans-influence of the opposite ligands [63].

The complexes $[(RTe)_2Pd \cdot P(C_6H_5)_3]_2$ (R = 2-thienyl, 4-ethoxyphenyl) were decomposed by carbon monoxide to give R_2Te_2, palladium and triphenylphosphine [34].

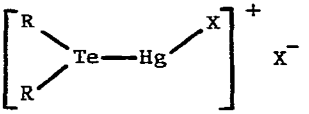
Data about diorganyl telluride-platinum complexes [34,63] and diaryl telluride-silver halide complexes [P-12] are summarized in Table 5. The silver halide complexes are claimed to be useful as image-forming materials in photography [P-12].

The complexes $(CH_3)_2TeX_2 \cdot HgY_2$ were obtained by mixing ethanolic or methanolic solutions of the components [83] (Table 5). Upon boiling of these solutions or upon prolonged storage exchange of the halogen atoms between HgY_2 and $(CH_3)_2TeX_2$ may take place (section VI-B1). According to Moessbauer spectral data the tellurium atom is in a trigonal-bipyramidal environment in these complexes. The ν(TeBr) bands of $(CH_3)_2TeBr_2 \cdot HgI_2$ are complex suggesting that there exists an interaction between the mercury and the bromine atoms, but not between the mercury and the tellurium atom.

In benzene solution the complex is completely dissociated to HgI_2 and $(CH_3)_2TeBr_2$ [83].

The complex $2(CH_3)_2TeI_2 \cdot Hg(C_6H_5)_2$ behaves as a 2:1 electrolyte in DMF. The tellurium atom is in a trigonal environment according to Moessbauer spectral data. Mass spectral evidence indicates that a phenyl group is bonded to the tellurium atom. A Te-C(phenyl) coupling was observed in the ^{13}C nmr spectrum and a ν(Te-phenyl) vibration was present in the infrared and Raman spectra. Therefore, the complex was suggested to be a telluronium salt formulated as $[C_6H_5Te(CH_3)_2]_2^+HgI_4^{--}$ or $[C_6H_5Te(CH_3)_2]^+I^- \cdot HgI_2$ [83].

The low solubility of the complexes $R_2Te \cdot HgX_2$ (Table 5) indicates a polymeric structure for these compounds. Moessbauer spectral data suggest an $[R_3Te]^+$ environment for the tellurium atom. The complexes $R_2Te \cdot HgX_2$ might have the structure 40 [83].



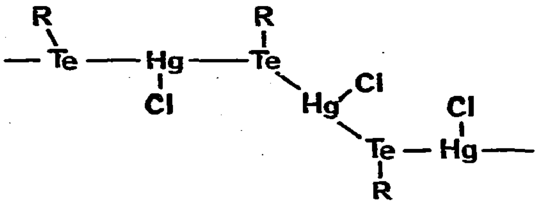
40

Diorganyl ditellurides form two types of complexes with mercury(II) halides of the stoichiometric composition $R_2Te_2 \cdot HgX_2$ and $R_2Te_2 \cdot 2HgX_2$ (Table 5). The Te-Te bond was probably not cleaved upon complexation [83].

F. Organic Tellurium Compounds with a Tellurium-Mercury or Tellurium Copper Bond

In this section only those tellurium-mercury and tellurium-copper compounds are discussed which contain a covalent tellurium-metal bond. When X-ray structures of complexes of the type $R_2Te \cdot HgX_2$ and similar compounds, which are now considered to be held together by coordinate-covalent bonds (section X-E), become available, they might turn out also to have covalent tellurium-metal bonds.

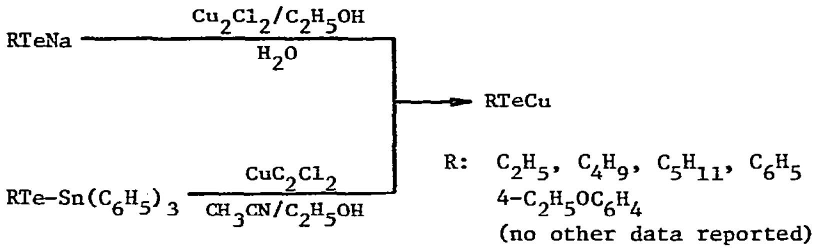
The tellurium-mercury compound $(4\text{-}C_2H_5OC_6H_4Te)_2Hg$, a red powder, melting at 110-2°, was obtained in 57 percent yield by shaking the diaryl ditelluride in dry benzene with mercury. When $(4\text{-}C_2H_5OC_6H_4Te)_2Hg$ was refluxed in ethanol with mercury(II) chloride an extremely insoluble, yellow powder melting at 161° was obtained. The ν(Te-Hg) was found in the Raman spectrum at 119 cm^{-1}. The Te-Te vibration was absent. The insolubility of this compound suggests a polymeric structure such as 41 [83].



41

A series of tellurium-copper compounds, RTeCu, was prepared according to eqn. (33). The reactions with organyl triphenylstannyl tellurides and copper(I) halides gave higher yields of purer products than obtainable from reactions with organyl sodium tellurides. It is likely that a tellurium atom bridges two copper atoms in the structure of these molecules. The bonds involve primarily tellurium p-orbitals [19,57].

(33)



$$\mathrm{RTeNa} \xrightarrow[H_2O]{Cu_2Cl_2/C_2H_5OH} \mathrm{RTeCu} \xleftarrow[CH_3CN/C_2H_5OH]{CuC_2Cl_2} \mathrm{RTe{-}Sn(C_6H_5)_3}$$

R: C_2H_5, C_4H_9, C_5H_{11}, C_6H_5
$4\text{-}C_2H_5OC_6H_4$
(no other data reported)

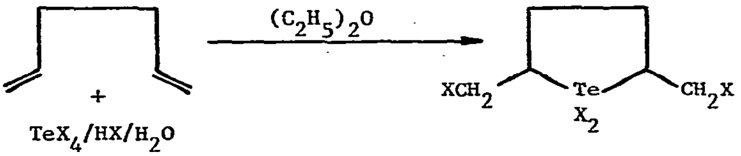
XI. Heterocyclic Tellurium Compounds

Telluracyclopentane, benzodihydrotellurophenes, tellurophenes, [4,5-d]-fused tellurophenes, 2-azabenzotellurophene, dibenzotellurophene, heterocycles with tellurium and tin atoms as ring members, 1-M-4-telluracyclohexanes (M=O,S, NR), 1-thia-4-telluracyclohexa-2,5-diene 1,1-dioxides and phenoxtellurine were investigated.

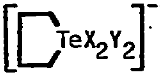
A. Tellurocyclopentane

The ability of tellurium tetrahalides to add to carbon-carbon double bonds was employed to prepare 2,5-dihalomethyl-1-telluracyclopentane from 1,5-hexadiene [36] (eqn. 34).

(34)



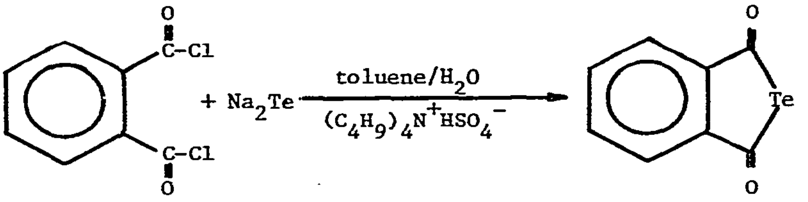
X, mp.°C, % yield: Cl, 135°(dec), 6%;
Br, 119°, 34%.

Salts of the type $[R_4M]_2^+$  were prepared by the interaction of 1-telluracyclopentane 1,1-diiodide with tetraorganylonium salts in refluxing chloroform or by halogen exchange between the anions and silver or alkali metal halides. Information about these reactions and their products is summarized in Table 6. The salts behave as 2:1 electrolytes in acetonitrile. The derivatives containing NCO or NCS groups have these pseudohalides bonded to the tellurium atom <u>via</u> the nitrogen atom. An octahedral configuration has been suggested for the tetrahalotellurate(IV) anions [84].

B. [3,4-c]-Benzo-2,5-dioxo-2,5-dihydrotellurophene

The [3,4-c]-benzo-2,5-dioxo-2,5-dihydrotellurophene was synthesized from phthaloyl dichloride dissolved in toluene and sodium telluride in aqueous solution (eqn. 35). Tetrabutylammonium hydrogen sulfate served as phase transfer reagent [20].

(35)

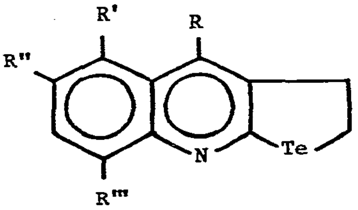


mp. 127°; 40% yield

C. [4,5-d]-Fused 2,3-Dihydrotellurophenes

[4,5-d]-Benzo-3-oxo-2,4-dihydrotellurophene was obtained when 2-acetylphenyl tellurium bromide dissolved in benzene was treated with ammonia [46]. A similar reaction was carried out earlier using ethanol and potassium hydroxide instead of benzene and ammonia [4].

The [4,5-d]-quinolino-2,3-dihydrotellurophenes 42 were converted to



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the tellurium dibromides by N-bromosuccinimide and to the diiodides by iodine in carbon tetrachloride. The crude dihalides were treated with 1,5-diazabicyclo[5,4,0]undec-7-ene to yield tellurophenes [85] (section XI-E).

TABLE 6

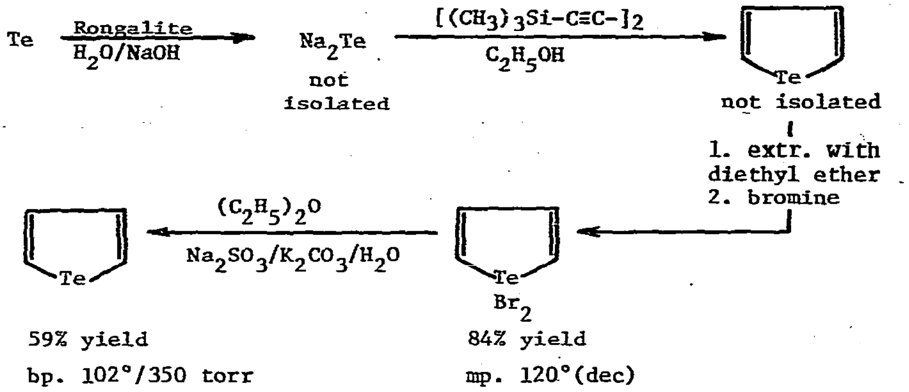
COMPOUNDS OF THE GENERAL FORMULA $[R_4M]^+_2$ $\Big[$$TeX_2Y_2\Big]^{--}$ [84]

X	Y	R	M	Method	mp.°C	Yield %
F	F	C_6H_{13}	N	$(R_4N)_2$ TeI_4 + Ag_2O, then HF	235°	100
I	I	C_2H_5	N	TeI_2 + $2R_4NI/CHCl_3$	153-5°	90
		C_3H_7	N	TeI_2 + $2R_4NI/CHCl_3$	113°	90
		C_4H_9	N	TeI_2 + $2R_4NI/CHCl_3$	99°	90
		C_6H_{13}	N	TeI_2 + $2R_4NI$	64°	90
		C_7H_{15}	N	TeI_2 + $2R_4NI$	80-2°	90
		C_6H_5	P	$(R_4P)_2$ $TeI_2Br_2/HCl/KI$	200°(dec)	100
		C_6H_5	As	$(R_4As)_2$ $TeI_2Cl_2/HCl/KI$	210°	100
I	Cl	CH_3	N	TeI_2 + $2R_4NCl/CHCl_3$	140°(dec)	90
		C_2H_5	N	TeI_2 + $2R_4NCl/CHCl_3$	210°	90
		C_6H_5	P	TeI_2 + $2R_4PCl$	116°(dec)	90
		C_6H_5	As	TeI_2 + $2R_4AsCl$	131°(dec)	90
		C_6H_5	Sb	TeI_2 + $2R_4SbCl$	185°(dec)	90
I	Br	C_2H_5	N	TeI_2 + $2R_4NBr$	88-90°(dec)	90
		C_4H_9	N	TeI_2 + $2R_4NBr$	83°	90
		C_6H_5	P	TeI_2 + $2R_4PBr$	104-7°(dec)	90
I	-NCO	C_6H_5	P	$(R_4P)_2$ TeI_2Cl_2 + $KNCO/CHCl_3$	172°(dec)	100
	-NCS	C_6H_5	As	$(R_4As)_2$ TeI_2Cl_2 + $KNCS/CHCl_3$	148°(dec)	98
-NCO	-NCO	C_2H_5	N	$(R_4N)_2$ TeI_4 + $KNCO/CHCl_3$	164°	100
N_3	N_3	C_4H_9	N	$(R_4N)_2$ TeI_4 + $KN_3/CHCl_3$	162°	100

D. Tellurophene

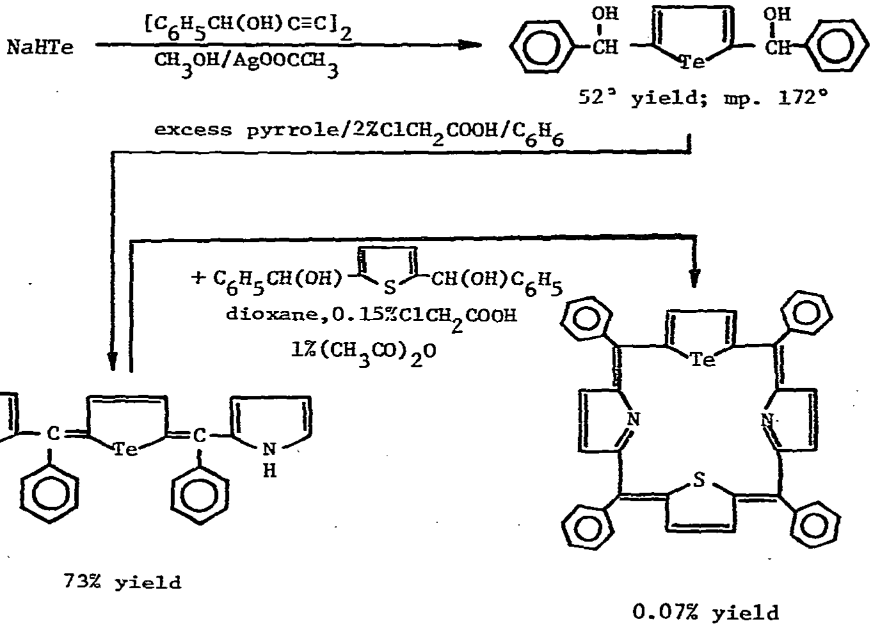
Tellurophene was prepared in 59 percent yield (based on tellurium) by an improved method employing sodium telluride solutions, obtained from tellurium and Rongalite in aqueous alkaline medium, and 1,4-bis(trimethylsilyl)butadiene. Upon addition of bromine to the reaction mixture the rather insoluble tellurophene 1,1-dibromide was isolated, which was then reduced to tellurophene [17] (eqn. 36).

(36)



Tetraphenyl-21-tellura-23-thiaporphyrin [26] was synthesized as described in eqn. (37).

(37)



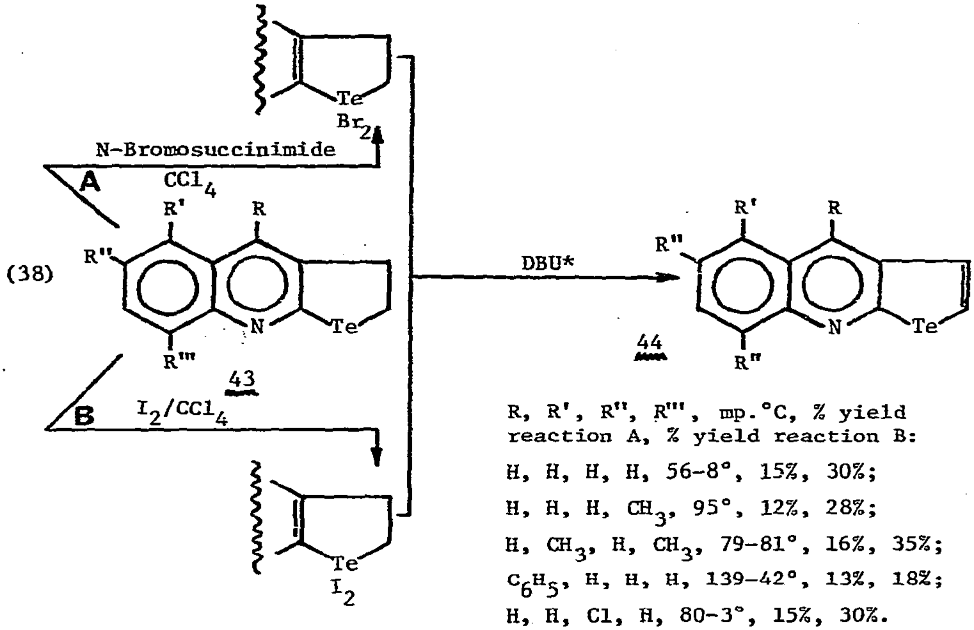
2,5-Diphenyltellurophene irradiated with the light from a medium-pressure mercury arc lamp (Pyrex filter) in tetrahydrofuran/diethyl ether solution did not dimerize [86]. The compound was recovered quantitatively.

The magnetic circular dichroism (MCD) spectrum of tellurophene in hexane solution was studied. The tellurophene spectrum displays more details than the spectrum of thiophene. Oscillator strengths, energies, transition moment directions and MCD terms were calculated from semi-empirical quantum mechanical calculations in the π-electron approximation [87].

E. [4,5-d]-Fused Tellurophenes

The quinolinotellurophenes **44** were synthesized from the dihydrotellurophenes **43** applying a halogenation-dehalogenation reaction sequence (eqn. 38) [85].

(38)



R, R', R'', R''', mp.°C, % yield reaction A, % yield reaction B:

H, H, H, H, 56-8°, 15%, 30%;

H, H, H, CH_3, 95°, 12%, 28%;

H, CH_3, H, CH_3, 79-81°, 16%, 35%;

C_6H_5, H, H, H, 139-42°, 13%, 18%;

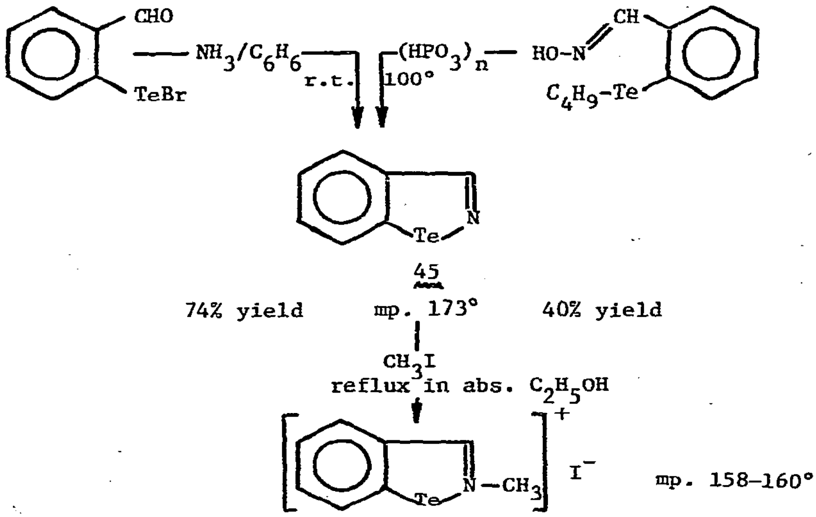
H, H, Cl, H, 80-3°, 15%, 30%.

*DBU is 1,5-diazabicyclo-[5,4,0]undec-7-ene.

F. 2-Azabenzotellurophene

2-Azabenzotellurophene **45** was synthesized from 2-formylphenyl tellurium bromide and ammonia or by heating the oxime of 2-formylphenyl butyl telluride with polyphosphoric acid at 100° [46] (eqn. 39).

(39)



G. Dibenzotellurophene

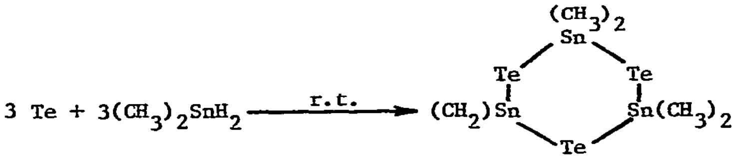
McCullough [88] prepared dibenzotellurophene 5,5-diiodide by grinding the dichloride with potassium iodide under methyl ethyl ketone.

Moessbauer spectral data for the picric acid adduct of dibenzotellurophene are identical to those for dibenzotellurophene. Picric acid is, therefore, not coordinated to tellurium. A charge-transfer interaction probably exists between the aromatic rings [35].

H. 1,3,5-Tristanna-2,4,6-tritelluracyclohexane

Stirring a mixture of dimethylstannane with excess tellurium (eqn. 40) at room temperature under a nitrogen atmosphere for three days gave a 58 percent yield of 1,1,3,3,5,5,-hexamethyl-1,3,5-tristanna-2,4-6-tritelluracyclohexane. The yellow needles melted at 78.5°.

(40)



The four-membered heterocyclic compound, 1,1,3,3-tetra(*tert*-butyl)-1,3-distanna-2,4-ditelluracyclobutane is described in section X-B (structure **32**).

I. 1-M-4-Telluracyclohexanes (M = O, S, NR)

Tellurium tetrahalides prepared from tellurium dioxide and aqueous hydrohalic acids reacted with diallyl ether, sulfide or amines (eqn. 41) to produce the heterocycles **46**. All of the compounds **46** may consist of a mixture of isomers. Only 3,5-bis(bromomethyl)-1-oxa-4-telluracyclohexane 4,4-dibromide was successfully resolved into *cis*- and *trans*-isomers by fractional recrystallization. The reaction between tellurium tetrabromide and allyl formate gave the *cis*-isomer of compound **46** (X=Br, Y=O) [36].

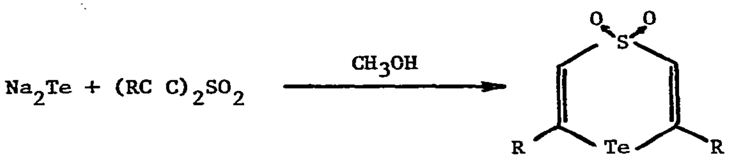
(41)


46

Y, X, mp.°C, % yield: O, Cl, 143°, 55%;
O, Br, 128°(cis), 108°(trans), 69%;
S, Cl, 109°(dec), 50%;
S, Br, 137°, 41%;
NH, Br, 175°(dec), 35%;
NCH_3, Cl, 91°, 39%;
NCH_3, Br, 170°(dec), 79%.

J. 3,5-Dialkyl-1-thia-4-telluracyclohexa-2,5-diene 1,1-Dioxide

Dialkinyl sulfones reacted readily with sodium telluride in methanol (eqn. 42) to give the heterocycles 47 [25].

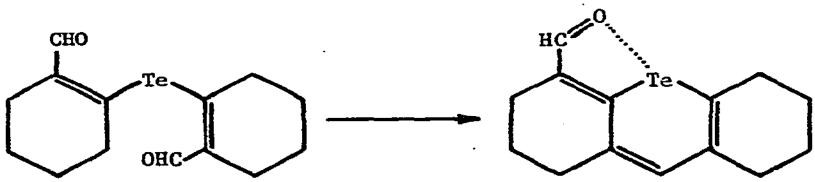
(42)


47

R, mp.°C, % yield: CH_3, 158°, 65%;
$(CH_3)_3C$, 144-6°, 80%.

K. 1-Formyl-3,4,5,6,7,8-hexahydro-2H-9-telluraanthracene

The heterocyclic compound 48, which melted at 86°, was synthesized from bis(2-formylcyclohex-1-enyl) telluride (eqn. 43). Infrared data indicate that the carbonyl group is strongly interacting with the tellurium atom [93].

(43)


48

L. Phenoxtellurine

The first excited singlet state and the first triplet state relaxation processes of phenoxtellurine and related compounds were studied. Phosphorescence spectra were obtained. Calculations showed that the heavy atom effect is preponderant for a singlet-triplet radiative transition, whereas for a singlet-triplet nonradiative transition the folded configuration of the molecules is of major importance [89].

XII. Physicochemical Investigations of Organic Tellurium Compounds

Infrared, Raman, ultraviolet-visible, ^{1}H-, ^{11}B-, ^{13}C-, ^{19}F-, ^{31}P- and ^{125}Te-nuclear magnetic resonance, electron, Moessbauer and mass spectroscopy, X-ray structure analysis and dipole moment measurements were employed 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 in this section. Frequencies (cm^{-1}) are listed only for modes involving the tellurium atom.

$[(C_6H_5)_4P]^+TeCN^-$ [90]: ir(Nujol),R(solid); TeCN vibrations, force constants; $Te^{13}CN$ spectra.
$[(C_6H_5)_4As]^+TeCN^-$ [90]: ir(Nujol),R(solid); TeCN vibrations, force constants; $Te^{13}CN$ spectra; previous assignment of ν_3 to 360 cm^{-1} incorrect [2].
$[(C_6H_5)_3P]_2NTeCN$ [90]: ir(Nujol), R(solid,CH_3CN soln.); TeCN vibrations, force constants.

2-$RC(O)C_6H_4TeX$ (X=Br; R=HO,CH_3O,C_2H_5O; X=Cl; R=C_6H_5) [45]; ir($CHCl_3$), ν(CO).

$(C_6H_5)_2Te_2$ [19,57]: ir, R; $\nu_{as}(Te\text{-}C_6H_5)$ 255, ν(TeTe) 167.
[91]: ir(KI), R; ring, CH-bending, Te-sensitive vibrations.
(2-$C_2H_5OOCC_6H_4)_2Te_2$ [45]: ir(KBr); ν(CO).

$(CH_3)_2Te$ [64]: ir(gas), R; ν_{as}(CXC) 843; δ(CXC) 531; detailed assignments.
2-$R'C(O)C_6H_4TeR$ (R=CH_3,R'=C_6H_5; R=C_6H_5,R'=HO,CH_3O,Cl) [45]: ir(KBr,CCl_4); ν(CO).
$(C_6H_5)_2Te$ [91]: ir, R; ring, CH-bending, Te-sensitive vibrations.
1,2-(4'-$RC_6H_4Te)C_6H_4$ [38]: ir(KBr); bands listed.
1-(4-$CH_3OC_6H_4Te$)-2-(4-$CH_3OC_6H_4Se)C_6H_3R'$[38]: ir(KBr); bands listed.

$4\text{-}RC_6H_4TeC(O)C_6H_4R'$ (see eqn. 16, section VI-A3) [12,52,70]: ir($CHCl_3$ or CCl_4); ν(CO).

$2\text{-}(2'\text{-}RC_6H_3CO)\text{-}4\text{-}CH_3C_6H_3TeC_6H_4CH_3$ (see eqn. 15, formula 13, section VI-A2) [52]: ir(CCl_4); ν(CO).

$1,4\text{-}(4'\text{-}CH_3C_6H_4TeCO)_2C_6H_4$ [70]: ir(KBr); ν(CO).

$(CH_3)_2TeBr_2$ [83]: R; ν(TeC) 533; ν(TeBr) 188, 158.

$2\text{-}CH_3OOCC_6H_4(C_6H_5)TeCl_2$ [45]: ir(KBr); ν(CO).

$(4\text{-}RC_6H_4)_2Te(NC)_2$ [6]; ir(Nujol); ν(CN).

$(4\text{-}RC_6H_4)_2Te(NCX)_2$ (X=O, S, Se) [61,62]: ir(Nujol or solid); ν(CN), ν(CX), δ(NCX).

$(4\text{-}RC_6H_4)_2TeIX'$ (X'=NC, NCO, NCS) [62]: ir(Nujol); ν(CN), ν(CX), δ(NCX).

$(4\text{-}RC_6H_4)_2TeBr(NC)$ [62]: ir(Nujol); ν(CN).

$(C_6H_5)_2Te(NC)(NCX)$ (X=O, S) [62]: ir(Nujol); ν(CN), ν(CX), δ(NCX).

$[CH_3(C_6H_5)_2Te]^+X^-$ (X=NCS, BF_4, PF_6) [61]: ir($CHCl_3$, solid); ν($Te\text{-}CH_3$) 520-536; ν(X).

$B_{10}H_{12}Te$ [79]: ir(KBr); bands listed.

$[(CH_3)_4N](B_{10}H_{10}Te)_2M$ (M=Fe, Co) [79]: ir(KBr); bands listed.

$C_5H_5Co(B_{10}H_{10}Te)$ [79]: ir(KBr); bands listed.

$[(CH_3)_2SnTe]_3$ [13]: ir(polyethylene); ν(ring, SnTe) 203, 198, 183, 178, 173; δ(ring, SnTe) 59, 51, 40.

RTeCu (see section X-F) [19]: ir; ν(CuTe) 185 (?).

$R_2Te_2\cdot CuCl$ (see section X-E) [19,57]: ir; $\nu_{as}(TeC_6H_5)$ 250; ν(TeTe) 170-180; ν(CuCl), phenyl X, X'.

$[(4\text{-}RC_6H_4)_2Te]_2\cdot MX_2$ (M=Pd, Pt; X=Cl, Br) [34]: ir(Nujol); ν_{as}(PdTe) 200, ν(MX), ν(phenyl).

$(4\text{-}RC_6H_4)_2Te\cdot HgX_2$ [83]: ir, R; ν(TeC) 261-295; ν(TeHg) 101-133; ν(HgX), ν(phenyl).

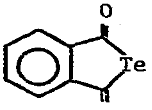
$(CH_3)_2TeI_2\cdot HgBr_2$ [83]: R; ν(TeC) 533, ν(TeBr) 168, 147, ν(HgX).

$2(CH_3)_2TeI_2\cdot(C_6H_5)_2Hg$ [83]: R; ν(TeC) 533, ν(TeC_6H_5) 262, 248, ν(HgI).

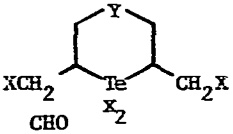
Tetrahydrotellurophene [92]: ir, R; ν(CTeC) 564, 544; detailed assignments.

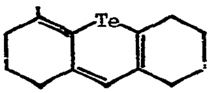
2,5-bis(bromomethyl)tetrahydrotellurophene 1,1-dibromide [36]: ir(KBr); bands listed.


(see Table 6, section XI-A) [84]: ir(KBr or Nujol); ν(TeC) 520-550, ν(X or Y).


[20]: ir(KBr); bands listed.

tellurophene [17]: ir(CCl_4); bands listed.
2-azabenzotellurophene [46]: ir(KBr).


(Y=O, S, NR; X=C, Br) [36]: ir(KBr); bands listed.


[93]: ir(C_2Cl_4); $\nu(C^{16}O,\ C^{18}O)$.

B. Ultraviolet-Visible Spectroscopy

Ultraviolet-visible spectral data were reported for $4\text{-}CH_3OC_6H_4\cdot$ [53], bis(2-thienyl) ditelluride [34], dibenzyl telluride [18], telluroethinyl ethers [94], $[(CH_3)_4N](B_{10}H_{10}Te)_2M$ (M=Co, Fe) [79], $C_5H_5Co(B_{10}H_{10}Te)$ [79], $[(4\text{-}RC_6H_4)_2Te]_2MCl_2$ (M=Pd, Pt) [34], $[(RTe)_2Pd\cdot P(C_6H_5)_3]_2$ ($R=4\text{-}C_2H_5C_6H_4$, 2-thienyl) [34], $(4\text{-}C_2H_5OC_6H_4Te)_2Hg$ [83] 2-azabenzotellurophene [46] and a tellurophene containing porphyrin (eqn. 37, section XI-D) [26].

C. Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectroscopy employing the nuclei ^1H, ^{11}B, ^{13}C, ^{19}F, ^{31}P and ^{125}Te was used to characterize organic tellurium compounds.

1. ^1H-NMR Spectroscopy

^1H-nmr data were reported for the following compounds:
$2\text{-}RC(O)C_6H_4TeX$ (R, X: C_6H_5, Cl; CH_3O, Br; C_2H_5O, Br; C_6H_5, CN) [45].

$4\text{-}RC_6H_5TeX_3$ ($R=CH_3$, CH_3O, Cl, Br; X=Cl, Br) [47].

R_2Te_2($R=CH_3$, C_2H_5) [21,95]: no rotational isomers detected [95].

$(C_6H_5CH_2)_2Te_2$ [18]; $(4\text{-}C_5H_{11}C_6H_4)_2Te_2$ [12]; $(2\text{-}C_6H_5COC_6H_4)_2Te$ [45].

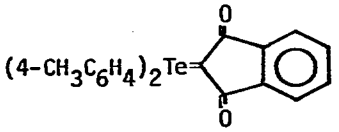
$(CH_3)_2Te$ [64,96,97]: comparison with other chalcogenides [97]; spectra in nematic phase of liquid crystal; ^{123}Te, ^{125}Te satellites; $J_{^{123}Te\text{-}H}$; structural parameters, intermethyl indirect coupling [96]; internal rotation [64].

$(C_2H_5)_2Te$ [21]; $(C_6H_5CH_2)_2Te$ [18].
$RTe{-}C{\equiv}C{-}CH{=}CH_2$ ($R{=}CH_3$, C_2H_5) [98]: comparison with S, Se derivatives.
$4{-}RC_6H_4TeCH_3$ (R=H, CH_3, Cl, Br) [97]; coupling constants, comparison with O, S, Se derivatives.
$2{-}C_6H_5COC_6H_4TeCH_3$ [45]: $J_{^{125}Te-CH_3}$ 16 Hz.
$2{-}RCOC_6H_4TeC_6H_5$ [45]; $4{-}(CH_3)_2NC_6H_4TeC_6H_4R$ (4-R=H, CH_3, CH_3O, C_2H_5O, C_6H_5O, Cl) [49]; coupling constants.
$2{-}(2'{-}CH_3XC_6H_4){-}4{-}CH_3C_6H_3Te{-}C_6H_4CH_3$ (see eqn. 15, formula **13**, section VI-A2) [52].
$4{-}CH_3C_6H_4TeCOC_6H_4R$ (R=H, $2{-}CH_3O$, $4{-}CH_3O$, $2{-}CH_3S$, $2{-}CH_3SO_2$, 2-Cl) [52].
$4{-}C_5H_{11}C_6H_4(4{-}C_8H_{17}OC_6H_4CO)Te$ [12].
$1{-}(4'{-}RC_6H_4Te){-}2{-}(4{-}CH_3OC_6H_4X)C_6H_3R'$ (X=Te, Se; $R'{=}CH_3$; $R{=}CH_3$ CH_3O, C_2H_5O) [38].

$(C_6H_5CH_2)_2TeBr_2$ [18]; $(4{-}CH_3OC_6H_4)_2TeCl_2$ [32]; $C_6H_5COCH_2(4{-}ROC_6H_4)TeCl_2$ [33]; $4{-}(CH_3)_2NC_6H_4(4{-}RC_6H_4)TeX_2$ (see Table 2, section VI-B2) [50].

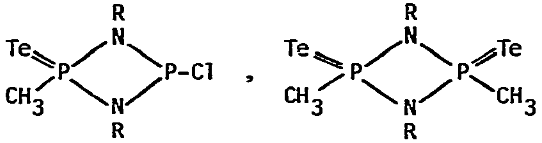
$[CH_3(C_6H_5)_2Te]^+X^-$ ($X{=}NCS, BF_4, PF_6$) [61]: $J_{^{125}Te-H}$ 25 Hz.

$(4{-}CH_3C_6H_4)_2Te{=}C(COOC_2H_5)X$ ($X{=}COOC_2H_5$, NO_2) [78].



[78].

$[(CH_3)_4N](B_{10}H_{11}Te)$ [79]; $C_5H_5Co(B_{10}H_{10}Te)$ [79];
$[(CH_3)_2N]_3PTe$ [80]; $(C_2H_5O)_2P(O)TeCH_3$ [16];



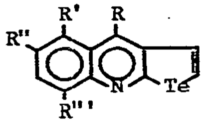
[R = $(CH_3)_3C$]

trans-$[(C_2H_5)_2Te]_2MX_2$ (M=Pd, Pt; X=Cl, Br, I) [63,82]: variable temperature nmr; coalescence temperature.
cis-$(4{-}CH_3C_6H_4)_2Pt[Te(C_2H_5)_2]_2$ [63]: variable temperature nmr; coalescence temperature.

2,5-Dihalomethyltetrahydrotellurophene 1,1-dihalide (Cl, Br) [36].

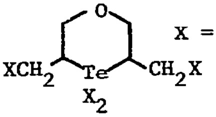

(X=I, Cl) [84];
tellurophene [17]; $2{,}5{-}[C_6H_5CH(OH)]_2$-tellurophene [26];

tellurophene-containing porphyrin (eqn. 37, section XI-D) [26].
2-azabenzotellurophene, N-methyl-2-azabenzotellurophene iodide [46].

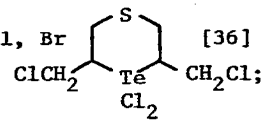


(see formula 44, eqn.37, section XI-E) [85].

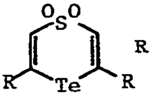
1,3,5-hexamethyl-1,3,5-tristanna-2,4,6-tritelluracyclohexane [13].



X = Cl, Br ;



[36]



R = CH_3, $(CH_3)_3C$ [25]

2. ^{11}B-NMR Spectroscopy

The ^{11}B nmr spectra of $[B_{10}H_{11}Te]^-$ [79], $B_{11}H_{11}Te$ [28], $B_{10}H_{12}Te$, $[(CH_3)_4N](B_{10}H_{10}Te)_2M$ (M=Fe, Co) and $C_5H_5Co(B_{10}H_{10}Te)$ [79] were reported.

3. ^{13}C-NMR Spectroscopy

^{13}C-Nmr data were reported for the following compounds:
$(C_6H_5CH_2)_2Te_2$ [18]; $CH_3TeC_6H_5$ [97]: comparison with O, S, Se derivatives.
R-TeC_6H_5 (R=CH_3, C_2H_5, $\underline{i}$-C_3H_7) [54]: TeR groups exert almost no inductive effect, some donation of π-electrons into phenyl ring.
RTe-C≡C-CH=CH_2 [98]: correlations for the S, Se, Te series of compounds, Te influences only C≡C group through an inductive mechanism.
$(CH_3)_2TeI_2 \cdot Hg(C_6H_5)_2$ [83]: spectrum of ^{125}Te enriched compound;

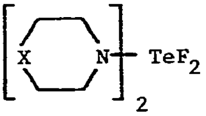
$$J_{^{125}Te-^{13}C} \quad 171.6 \text{ Hz.}$$

tellurophene [17]; 2-azabenzotellurophene [46].

4. ^{19}F-NMR Spectroscopy

^{19}F-Nmr data were reported for the following compounds:
4-$FC_6H_4TeX_3$ and 3-$FC_6H_4TeX_3$ (X=Cl, Br) [47].
3-or 4-FC_6H_4TeR (R=CH_3, C_6H_5) [47].
4-$FC_6H_4(CH_3)TeX_2$ and 3-$FC_6H_4(CH_3)TeX_2$ (X=F [69]; X=Cl, Br, I [47]).
4-$FC_6H_4(C_6H_5)TeX_2$ and 3-$FC_6H_4(C_6H_5)TeX_2$ (X=F, NCS [69]; X=Cl, Br [47].

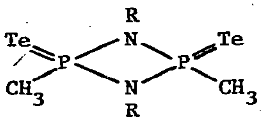
$[(C_2H_5)_2N]_2TeF_2$,



(X = CH_2, O) [39].

5. ^{31}P-NMR Spectroscopy

^{31}P-Nmr spectral data were reported for $[(CH_3)_2N]_3PTe$ [80].

$[(C_6H_5)_4P]^+[C_6H_5Te]^-$ [56], $(C_2H_5O)_2P(O)TeNa$ (J_{PTe} 2114.9 Hz) [16], $(C_2H_5)_2P(O)TeCH_3$ [16], $[(\textit{i}\text{-}C_3H_7O)_2P(O)Se]_2Te$ ($^2J_{PTe}$ 61.1 Hz) [37], $[(\textit{i}\text{-}C_3H_7O)_2P(O)S]_2Te$ (two forms, $^2J_{PTe}$ 50.7 Hz, 48.2 Hz) [37], and for  (R = *tert*-C_4H_9) [15].

6. ^{125}Te-NMR Spectroscopy

^{125}Te-Nmr measurements were carried out on liquid and solid tellurium and the Knight shifts [99,100] and the spin-lattice relaxation [100] determined.

^{125}Te-Chemical shifts were reported for $4\text{-}RC_6H_4CO\,(4\text{-}R'C_6H_4)Te$ [relative to bis(4-methylphenyl) ditelluride] (R,R': H, CH_3; CH_3O, CH_3; $C_8H_{17}O$, C_5H_{11}) [12] and for 2-R-tellurophenes (R=CH_2OH, CHO, CH_3CO, COOH, CH_3OOC, Cl, Br) relative to external tellurophene [101].

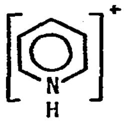
D. Electron Spectroscopy

The He(I) photoelectron spectrum of tetrahydrotellurophene was measured, interpreted and compared with the spectra of furan, thiophen and selenophen [102].

E. ^{125}Te-Moessbauer Spectroscopy

Quite a large number of organic tellurium compounds have been studied by ^{125}Te-Moessbauer spectroscopy. These compounds are listed below. Summaries of earlier work in this area are given in reference [3] and [4].

$C_6H_5TeBr_3$ [103], $4\text{-}CH_3OC_6H_4TeF_3$ [105], $4\text{-}CH_3OC_6H_4TeCl_3$ [35], $4\text{-}CH_3OC_6H_4TeCl_3\cdot L$ (L=tetramethylthiourea, pyridine) [103], $4\text{-}C_2H_5OC_6H_4TeF_3$ [105], $4\text{-}C_2H_5OC_6H_4TeCl_3$ [103], $2\text{-}C_6H_5C_6H_4TeX_3$ (X=Cl, Br, I) [35].

$[4\text{-}C_2H_5OC_6H_4TeCl_4]^-$  ; $4\text{-}C_2H_5OC_6H_4Te(O)Cl$ [103].

$(HOOCCH_2)_2Te_2$ [35]; $(4\text{-}RC_6H_4)_2Te_2$ (R=H, CH_3O, C_2H_5O, C_6H_5O) [103]; $(2\text{-}C_6H_5C_6H_4)_2Te_2$ [35].

$(CH_3)_2Te$, $(C_6H_5)_2Te$ [103]; $(4\text{-}C_2H_5OC_6H_4)_2Te$ [104]; $(2\text{-}C_6H_5C_6H_4)_2Te$ [35].

$(CH_3)_2TeX_2$ (X=Cl, Br, I), $(C_6H_5\text{-}CCl=CH)_2TeCl_2$ [103]; $CH_3(C_6H_5)TeI_2$ [105]; $(C_6H_5)_2TeF_2$ [105]; $(C_6H_5)_2TeBr_2$, $(C_6F_5)_2TeBr_2$ [103]; $(C_6H_5)_2Te(NO_3)_2$ [35]; $(4\text{-}CH_3OC_6H_4)_2TeX_2$ (X=F, Cl, Br, I) [105], (X=Cl) [103]; $(4\text{-}C_2H_5OC_6H_4)_2TeF_2$ [105]; $(4\text{-}C_2H_5OC_6H_4)_2TeBr_2$ [103]; $(2\text{-}C_6H_5C_6H_4)_2TeX_2$ (X=Cl, Br, I) [35].

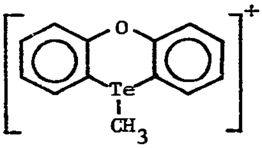
$(C_6H_5)_2Te(OOCR)_2$ (R=CH_3, C_6H_5), $(4\text{-}CH_3C_6H_4)_2Te(OOCCH_3)_2$, $(4\text{-}CH_3OC_6H_4)_2Te(OOCR)_2$(R=$CH_3$, C_6H_5), $(4\text{-}C_2H_5OC_6H_4)_2Te(OOCC_6H_5)_2$ [105].

$(C_6H_5)_2TeO$ [35].

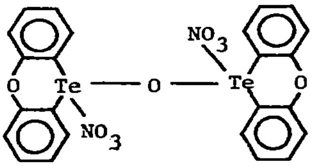
$[(C_6H_5)_3Te]^+Cl^-$ [35,83]; $[C_6H_5(CH_3)_2Te]^+I^-$, $[(C_6H_5)_2CH_3Te]^+I^-$ [105]; $[(4\text{-}CH_3OC_6H_4)_2CH_3Te]^+I^-$ [35].

RTeCu (R=C_2H_5, C_4H_9, C_5H_{11}, C_6H_5, $4\text{-}C_2H_5OC_6H_4$) [19];
$R_2Te_2\cdot CuX$ (R=C_2H_5, C_4H_9, C_5H_{11}, C_6H_5, $4\text{-}C_2H_5OC_6H_4$; X=Cl, Br) [19];
$(4\text{-}C_2H_5OC_6H_4)_2Te\cdot CuX$ (X=Cl, Br, I) [104].
$[(4\text{-}C_2H_5OC_6H_4)_2Te]_2MX_2$ (M=Pd, Pt; X=Cl, Br) [104].
$(4\text{-}C_2H_5OC_6H_4)_2Te_2\cdot HgX_2$ (X=Cl, Br, I) [19,83]; $(4\text{-}C_2H_5OC_6H_4)_2Te_2\cdot 2HgCl_2$ [83];
$(4\text{-}RC_6H_5)_2Te\cdot HgX_2$ (R=H, C_2H_5O; X=Cl, Br, I) [83,104].
$4\text{-}C_2H_5OC_6H_4TeHgCl$, $(4\text{-}C_2H_5OC_6H_4Te)_2Hg$ [83].
$(CH_3)_2TeBr_2\cdot HgX_2$ (X=Br, I) [83]; $2(CH_3)_2TeI_2\cdot Hg(C_6H_5)_2$ [83].

1-telluracyclopentane 1,1-dihalides (X=Br, I) [103];
1-telluracyclohexane-2,5-dione, 1-telluracyclohexane-2,5-dione 1,1-dichloride [35];
dibenzotellurophene, dibenzotellurophene dichloride [35];
phenoxtellurine [35]; phenoxtellurine dichloride [35,103];
phenoxtellurine dinitrate [35];



I^-,



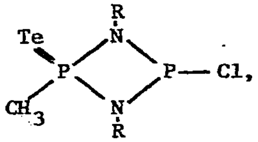
[35].

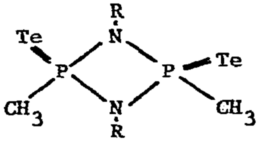
The ^{125}Te isomer shifts increase in the order $R_2Te<R_2Te_2<R_2TeX_2<RTeX_3$ corresponding to an increasing s-electron density on the tellurium nucleus. The bonding in the tellurides and ditellurides is intermediate between pure p and sp^3 [103].

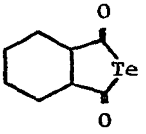
The ^{125}I labelled iodobenzene, benzyl iodide and iodine in benzene were studied by Moessbauer spectroscopy. The ^{125}Te formed by decay of ^{125}I gave spectra indicative of species with Te-I, Te-Te or Te-C bonds. In these different chemical environments ^{125}Te forms a unique stable chemical bond over the lifetime of the Moessbauer transition [106].

F. Mass Spectroscopy

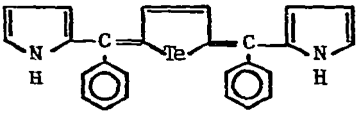
Mass spectral data were reported for 2-$RCOC_6H_4TeX$ (R,X: C_6H_5, Cl; 3-thienyl, Cl; HO, Br) [45];
(4-$C_5H_{11}C_6H_4)_2Te_2$ [12]; [2-(2'-$CH_3SC_6H_4CO$)-4-$CH_3C_6H_3]_2Te_2$ [52];
$(C_6H_5CH_2)_2Te$ [18]; 4-$CH_3C_6H_4$-(RC_6H_4CO)Te (R=H, 2-CH_3O, 4-CH_3O, 2-CH_3S, 2-CH_3SO_2, 2-Cl) [52]; 4-$C_8H_{17}OC_6H_4CO$(4-$C_5H_{11}C_6H_4$)Te [12];
2-(2'RC_6H_4CO)-4-$CH_3C_6H_3$(4-$CH_3C_6H_4$)Te (R=CH_3O, CH_3SO_2) [52];
$(C_6H_5CH_2)_2TeBr_2$ (no $M^{+\cdot}$) [18]; (4-$CH_3OC_6H_4)_2TeCl_2$ (no $M^{+\cdot}$) [32];
(4-$RC_6H_4)_2Te(NCS)_2$ (R=H, C_2H_5O; R=CH_3O, no $M^{+\cdot}$) [61];
$C_5H_5Co(B_{10}H_{10}Te)$ [79]; $B_{11}H_{11}Te$ [28]; $(CH_3)_2TeI_2\cdot Hg(C_6H_5)_2$ (no $M^{+\cdot}$) [83];


,


[15];


[20];

tellurophene [17]; comparison with furan, thiophen, selenophen [107]; tellurophene 1,1-dibromide (no $M^{+\cdot}$) [17]; a tellurophene containing porphyrin (eqn. 37, section IX-D) [26];


[26]; 2-azabenzotellurophene [46];
$[(CH_3)_2SnTe]_3$ [13].

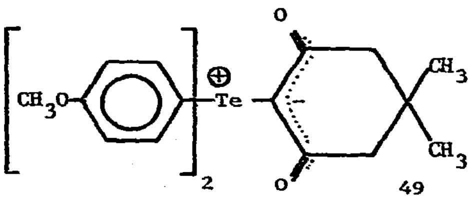
Unless otherwide stated, molecular ions were observed for these compounds.

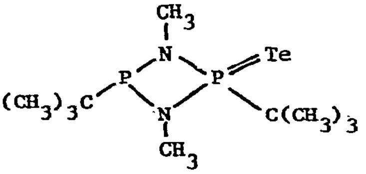
G. X-Ray Structure Analysis

The molecule $(CH_3)_2TeI_4$ consists of $(CH_3)_2TeI_2$ and I_2 and does not contain hexavalent tellurium. The iodine molecules are bound to iodine atoms of $(CH_3)_2TeI_2$ and not to the tellurium atom [108].

The structures of triphenyl telluronium pseudohalides were the subject of a dissertation by J. S. Lee [109]. They have already been published [4,5].

In the tellurium ylide 49 the tellurium atom protrudes above the plane formed by the three carbon atoms bonded to it. The tellurium-carbon bond lengths are 2.08 and 2.15 Å (Te-phenyl) and 2.07 Å. The cyclohexanedione group assumes a half-chair conformation and has the negative


49


50

charge delocalized to the carbonyl groups. The 4-methoxyphenyl moieties, which are equivalent in solution, are slightly non-equivalent in the solid [110].

The molecules of the four-membered phosphorus-nitrogen heterocycle 50 deviate significantly from planarity. In contrast to solutions, in which the tellurium atom in 50 migrates between phosphorus atoms [5], the crystals of 50 contain isolated molecules with fixed P-Te bonds (2.354 Å) [111].

The molecules $[(CH_3O)_2P(S)S]_2Te$ contain a P-S-Te-S-P chain in the trans form with a Te-S bond length of 2.44 Å and a S-Te-S angle of 98.3°. Two weak, intermolecular Te···S bonds provide an almost square-planar coordination for the tellurium atom [112].

2-Azabenzotellurophen crystallizes in the space group $P2_{1/a}$. The length of the Te-N bond is 2.09-2.11 Å. There exist short, intermolecular Te-N contacts of approximately 2.4 Å [113].

Dibenzotellurophene diiodide consists of a nearly planar dibenzotellurophene moiety with a C-Te-C bond angle of 81.8°. The two iodine atoms are bonded axially to the tellurium atom approximately normal to the C-Te-C plane. The I-Te-I bond angle is 178.5° [88].

H. Dipole Moment Measurements

The dipole moments of the alkyl vinylacetylenyl tellurides $RTeC{\equiv}C\text{-}CH{=}CH_2$ ($R{=}CH_3$, C_2H_5, C_3H_7, C_4H_9) were measured at 20° in benzene solutions. In this series of chalcogenides the p-π interaction of the heteroatoms with the triple bond decreased in the sequence S>Se>Te [67].

Dipole moment data and MO calculations indicated that in $4\text{-}RC_6H_5Te\text{-}C{\equiv}CR'$ (R=H, CH_3, Br, Cl, NO_2; R'=H, C_6H_5) both the R group (except NO_2) and the tellurium atom act as electron donors to the benzene ring [114].

The calculated dipole moments for the tellurides $4\text{-}(CH_3)_2NC_6H_4TeC_6H_4R$ (see Table 1, section VI-A2 for specific compounds) were consistently lower than those determined experimentally at 25° in dioxane. The magnitude of the differences depends on the nature of the substituent R. Polar conjugation of the dimethylamino group with the bridging tellurium atom by means of vacant d-orbitals has been suggested as a possible cause for the differences [49]. Similar dipole moment investigations of $[4\text{-}(CH_3)_2NC_6H_4](RC_6H_4)TeX_2$ (see Table 2, section VI-B2 for specific compounds) showed that conductance of electronic effects of substituents through the TeX_2 group occurs less readily than through a tellurium bridge [50].

The dipole moment of 1-formyl-3,4,5,6,7,8-hexahydro-2H-9-telluraanthracene in benzene solution was determined to be 3.31 D [93].

XIII. Analytical Techniques

The separation and determination of tellurium in water, metals, pharmaceuticals, steroids and biological materials was reviewed [115].

The molar responses of heteroaromatic compounds among them tellurophene and 2-acetyltellurophene [116] were determined for flame ionization detectors.

Methods for preparing artificial standards for the spectral analysis of selenium and tellurium were worked out [117].

Hexachlorotellurates were used to precipitate and spectrophotometrically determine eleven medicinal organic bases [118].

Potentiometric, bipotentiometric and biamperometric titrations of tellurate and tellurite with iron(II) in alkaline solutions in the presence of sorbitol were investigated [119]. Morpholinodithiocarbamate was used as a reagent for the gravimetric determination of tellurite [120].

XIV. Biology of Organic Tellurium Compounds

Piette [66] reported 2-carboxyphenyl methyl telluride to be the most active among the chalcogenides of this type in provoking convulsive seizures in rats (DL_{100}i.v. 175 mg/kg, DL_{100}i.p. 375 mg/kg).

The effects on workers of exposure to tellurium in the air was described [10].

Single endotracheal injections of tellurium and tellurium dioxide at dosage levels sufficient to cause observable stress in rats, did not result in a progressive fibrotic tissue response after 180 days. The observation period of 180 days was too short to assess the lack of tumorigenic potential of these substances [121].

Rats treated with injections of 2 mg/kg potassium tellurite for 112 days had cerebral gray matter grossly darkened. Growth of the animals was impaired but not performance of simple memory tasks [122].

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