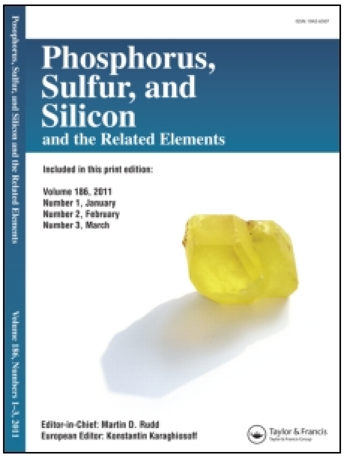


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

SYNTHESIS, CHARACTERIZATION AND SPECTRAL BEHAVIOR OF DIORGANOTELLURIUM(IV) SPECIES HAVING A (Te—S) BOND

T. N. Srivastava[a]; Jai Deo Singh[b]; Sanjay Kumar Srivastava[c]
[a] Chemistry Department, Lucknow University, Lucknow, (India) [b] Partly abstracted from the Ph.D. Thesis of JDS. University of Lucknow, [c] School of Studies in Chemistry, Jiwaji University, Gwalior, (M.P.), (India)

To cite this Article Srivastava, T. N. , Singh, Jai Deo and Srivastava, Sanjay Kumar(1991) 'SYNTHESIS, CHARACTERIZATION AND SPECTRAL BEHAVIOR OF DIORGANOTELLURIUM(IV) SPECIES HAVING A (Te—S) BOND', Phosphorus, Sulfur, and Silicon and the Related Elements, 55: 1, 117 — 124

To link to this Article: DOI: 10.1080/10426509108045930

URL: http://dx.doi.org/10.1080/10426509108045930

Phosphorus, Sulfur, and Silicon, 1991, Vol. 55, pp. 117–124
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS, CHARACTERIZATION AND SPECTRAL BEHAVIOR OF DIORGANOTELLURIUM(IV) SPECIES HAVING A (Te—S) BOND

T. N. SRIVASTAVA* AND JAI DEO SINGH†
Chemistry Department, Lucknow University, Lucknow-226007 (India)

and

SANJAY KUMAR SRIVASTAVA
School of Studies in Chemistry, Jiwaji University,
Gwalior-474011, (M.P.), (India)

(Received January 19, 1990; in final form May 11, 1990)

(Te—S) bonded compounds of the general formula $[R_2Te\{S_2P(OR')_2\}_2]$ [R = CH_3, C_6H_5, *p*-$MeOC_6H_4$; R′ = CH_3, C_2H_5, $CH(CH_3)_2(CH_2)_2CH_3$ and $CH_2CH(CH_3)_2$] have been synthesized by the reaction of R_2TeCl_2 with the ammonium salt of O,O′-dialkyldithiophosphoric acid in anhydrous toluene at ambient temperature or by the reaction of $R_2Te(OR')_2$ ($R'{=}CH_3$ or C_2H_5) with corresponding acids. The compounds are monomeric and non-electrolytes in nature. They decompose ($Te^{IV} \rightarrow Te^{II} \rightarrow Te^{0}$) slowly in solvents such as CH_2Cl_2, $CHCl_3$ or CCl_4 at ambient temperature. The decomposition products have been characterized. The interaction of $[R_2Te\{S_2P(OR')_2\}_2]$ with phosphine donor bases results in their complete decomposition yielding tellurium metal. The newly synthesized derivatives have been characterized on the basis of analytical and spectral (IR, ^{1}H, ^{13}C, ^{31}P and ^{125}Te NMR) data. A possible geometry around the central tellurium atom has been proposed.

Key words: Diorganotellurium(IV); dithiophosphate; synthesis; characterization, spectra IR; NMR

INTRODUCTION

(Te—S) bonded compounds continue to find applications as accelerators in rubber vulcanization thereby showing great promise in rubber technology.[1–3] It has also been pointed out that organotellurium derivatives are of biological interest and ^{123m}Te-labelled agents find potential use in diagnostic applications involving nuclear medicines.[4,5] In recent years serious attention has been paid to the structure and modes of bonding of these ligands to metal atoms.[6–13] In view of the above and an increasing interest in (Te—S) bonded compounds,[14–19] we report herein the synthesis, characterization and spectral behavior of some new organotellurium (IV) species having Te—S bonds. Their behavior in solution accounts for their potential use in rubber vulcanization.

---

*Author to whom correspondence should be addressed.

†Partly abstracted from the Ph.D. Thesis of JDS, University of Lucknow (1985).

RESULTS AND DISCUSSION

The formation of diorganotellurium(IV) species having (Te—S) bonds may be represented as shown below.

$$\begin{tikzcd} R_2Te(OR')_2 + 2(R'O)_2PS_2H \arrow[r, "-2R'OH"] & {[R_2Te\{S_2P(OR')_2\}_2]} \\ R_2TeCl_2 + 2NH_4S_2P(OR')_2 \arrow[ur, "-2NH_4Cl"'] & \end{tikzcd} \qquad (1)$$

$$\begin{tikzcd} R_2TeO + 2(R'O)_2PS_2H \arrow[r, "2R'OH"] & {[\{R_2TeS_2\,P(OR')_2\}_2O]_2\cdot H_2O} \arrow[d, "-\ H_2O"] \\ & {2[R_2Te\{S_2P(OR')_2\}_2O]} \end{tikzcd} \qquad (2)$$

[R = CH_3, C_6H_5, *p*$MeOC_6H_4$; R' = CH_3, C_2H_5, $CH(CH_3)_2$, $(CH_2)_2CH_3$ and $CH_2CH(CH_3)_2$]

The compounds $[R_2Te\{S_2P(OR')_2\}_2]$ may be synthesized by refluxing $R_2Te(OR')_2$ with $(R'O)_2PS_2H$ in anhydrous toluene and removing alcohols azeotropically or by the stirring of R_2TeCl_2 with $NH_4S_2P(OR')_2$ in toluene for about 30 min. in (1:2) molar ratio. They are also prepared by the reaction of R_2TeO with corresponding acids but the reaction depends upon the nature of the solvent (i) when 2,2'-dimethoxy propane is used as solvent the yield of $[R_2Te\{S_2P(OR')_2\}_2]$ is about 20% (ii) while in anhydrous methanol the product obtained is $[\{R_2TeS_2P(OR')_2\}_2O]_2H_2O$ and (iii) in case of benzene as solvent the composition of the product corresponds to $[R_2Te\{S_2P(OR')_2\}]_2O$. The product (II), when placed under vacuum over P_2O_5 for 16 to 20 hrs. yields (iii). Reactions represented by (eq. 1) are facile in anhydrous toluene and the yield is greater than 70%. The interaction of R_2TeCl_2 with $NH_4S_2P(OR')_2$ when carried out in solvents such as C_2H_5OH, CH_3CN, CCl_4, CH_2Cl_2 and C_6H_6 proceeds smoothly. However, due to rapid decomposition the yield of the main product is never greater than 10–15%.

The newly synthesized compounds are yellow crystalline sharp melting solids, soluble in common organic solvents such as MeOH, EtOH, Pr^nOH, Pr^iOH, Bu^iOH, C_6H_6, CCl_4, $CHCl_3$, CH_2Cl_2, CH_3CN, Me_2CO, Me_2SO and $C_6H_5NO_2$. The isolated crystalline materials are stable in air, even after long standing. However, when they are dissolved in low boiling solvents such as CH_2Cl_2, MeCN, MeOH, $CHCl_3$ etc., they undergo a redox decomposition to R_2Te and $[(R'O)_2P(S)S—S(S)P(OR')_2]$, on standing for a few hours. They are thermally unstable in solution and when refluxed deposit the free metal. On interaction with phosphine bases such as Ph_3P, $Ph_2P(CH_2)_2PPh_2$ and $(C_6H_{11})_3P$, molecular adducts of definite stoichiometry could not be isolated. Instead complete decomposition occurred with deposition of tellurium metal and the product isolated from the mother liquor was found sulfide derivatives of respective phosphines such as Ph_3PS, $(C_6H_{11})_3PS$ and $Ph_2P(S)(CH_2)_2(S)PPh_2$.

$[R_2Te\{(S_2P(OR')_2\}_2]$ when heated above 100°C disproportionated irreversibly as follows:

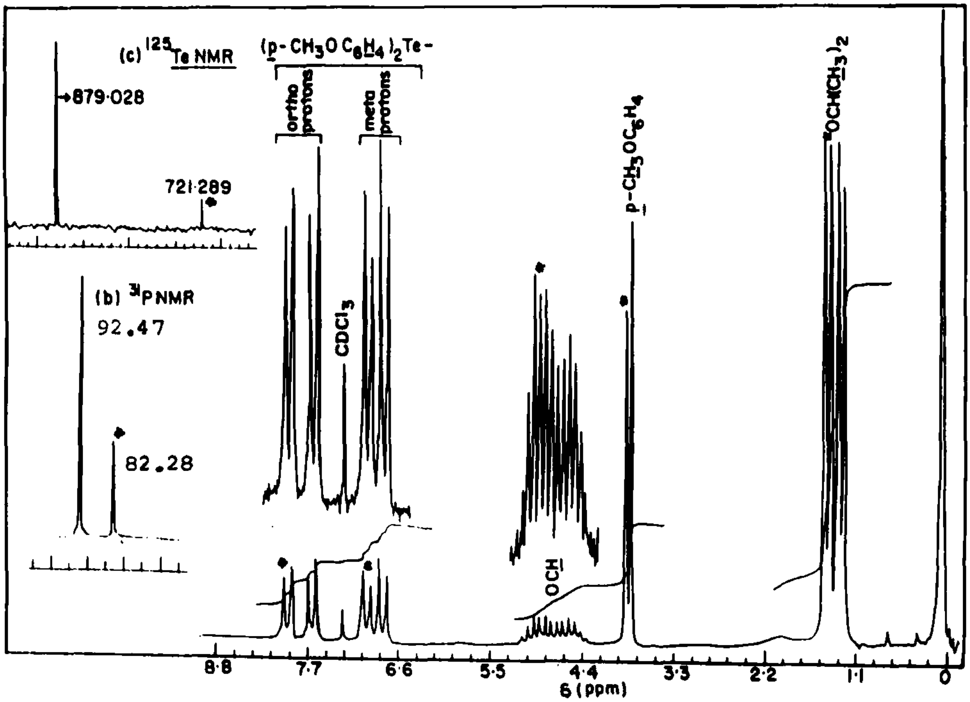


FIGURE 1 (a) ^{1}H NMR($CDCl_3$), (b) ^{31}P NMR($CHCl_3$) and (c) ^{125}Te NMR($CHCl_3$) chemical shifts for $[(p\text{-}MeOC_6H_4)_2Te\{S_2P(OCHMe_2)_2\}_2]$. (*Peaks appearing due to Redox reactions in solution).

$$[R_2Te\{S_2P(OR')_2\}_2] \rightarrow [R_2Te] + 2[(R'O)_2P(S){-}S{-}S{-}(S)P(OR')_2]$$

The analytical data correspond to (1:2) (Metal:Ligand) stoichiometry. Their purity was ascertained by thin layer chromotography in toluene. Molar conductance in non-polar solvents (C_6H_6 and $CHCl_3$) indicate that they are non-electrolytes. However, the molar conductance in acetone or acetonitrile (0–5°C), correspond to (1:2) electrolyte.

Their molecular weight in chloroform or benzene was determined by vapor phase osmometry at 40°C. In solution the molecular weight data indicate dissociation which increases smoothly and becomes constant after 4 to 6 hrs. Due to their abnormal behavior actual molecular weight could not be determined. In toluene they correspond to a monomer. The molecular weight data were also determined cryscopically in freezing nitrobenzene and the values obtained are higher than expected for a monomer indicating their associated nature. Most of the work was carried out in the laboratory condition with fluorescent light.[5] Due to lack of facilities the photolytic behavior could not be ascertained. It has been suggested that organotellurium compounds eliminate organic halides from organotellurium (IV) halides oxidatively, photolytically or thermally.[20] The photosensitivity of organotellurium compounds is well recognized.[21]

IR Spectra

In spectra were recorded in CSI, KBr and CS_2 solution in the region 4000–200 cm^{-1} and 4000–400 cm^{-1}. Vibrations associated with O,O'-dialkyldithiophosphate group and their assignments were made on the basis of previous reports.[8,9] The ϑ_{asym} (PS_2) and ϑ_{sym} (PS_2) vibrations appear in the range 690–630 and 540–480 cm^{-1} respectively. The ϑ_{asym} (PS_2) absorptions in the solid state spectra of these compounds are invariably splitted with a strong band in the range 645–630 cm^{-1}. The absorptions in CS_2 solution spectra are significantly sharp indicating that interaction occurs in the solid state. ϑ (P)—O—C and ϑ P—O—(C) vibrations are usually strong and broad in the range 1080–950 and 830–730 cm^{-1} respectively. The IR spectra of the products are almost identical to those of parent acids and their ammonium salts and do not yield significant information about the nature of coordination of the O,O′-dialkyldithiophosphate ligand to tellurium atom. The two bands due to ϑ (TeS_2, asym) and ϑ (TeS_2sym) are identified at 370 ± 5 cm^{-1} and 295 ± 5 cm^{-1} respectively. The Te—S stretching modes are consistant with those reported for tellurium dithiocarbamates.[19]

^1H NMR Spectra

^1H NMR spectra of a few compounds were screened in $CDCl_3$ using 5–10 scans. In $(R'O)_2PS_2H$, the chemical shift value for the protons (S—H) ranges between δ 3.60–3.40. The signals disappear in the spectra of the newly synthesized compounds indicating deprotonation of the ligand. The characteristic proton resonance for alkoxy groups [R′ = CH_3, C_2H_5, $CH(CH_3)_2$, $(CH_2)_2CH_3$ or $CH_2CH(CH_3)_2$] are in accordance with the proposed formulae. The peaks for protons of α-carbon of P—O—C chains get doubled due to coupling with ^{31}P nucleus. The signals and their integration in the compounds $[R_2Te\{S_2\text{-}P(OR')_2\}_2]$ indicate (1:2) (Metal:Ligand) stoichiometry. When the spectra were screened at higher scans another set of signals appear for each proton besides that for the compounds. The additional signal became more dominant when solution stayed for several hours. It is proposed that in solution three species viz, R_2Te, $[(R'O)_2PS_2]_2$ and $[R_2Te\{S_2P(OR')_2\}_2]$ are present resulting from a redox type reaction in solution.

^{13}C, ^{31}P and ^{125}Te NMR spectra

^{13}C NMR spectra of $[R_2Te\{S_2P(OR')_2\}_2]$ have been screened in CCl_4 and ^{31}P NMR spectra of the compounds were recorded in CH_2Cl_2, $CHCl_3$, CCl_4, CH_3CN, Me_2SO and Me_2CO and are listed in Table I. ^{125}Te chemical shifts for a few compounds were examined in THF and $CHCl_3$. To observe (^{125}Te-^1H), (^{125}Te-^{13}C) and (^{125}Te-^{31}P) coupling constant by ^1H, ^{13}C, ^{31}P and ^{125}Te NMR spectra at higher scans, at the time of NMR observation, the slow redox process was observed and multiplicity of each hydrogen, carbon, phosphorus and tellurium signals in $[R_2Te\{S_2P(OR')_2\}_2]$ were found double than that expected for the derivatives. It was found that an extra peak developed at $\delta < 86$ ppm (in ^{31}P NMR) and another extra peak at $\delta \sim$ 718–721 ppm (in ^{125}Te NMR) in addition to those of $[R_2Te\{S_2P(OR')_2\}_2]$. The signals and their positions are entirely related and corresponds to signals of $[R_2Te\{S_2P(OR')_2\}_2]$, $[R_2Te]$ and $[(R'O)_2P(S)SS(S)P(OR')_2]$ in their ^1H, ^{13}C, ^{31}P and ^{125}Te NMR spectra. Coupling was not observed at higher scans 100 to 1000 scans (^1H, ^{31}P) or 1000 to 10000 scans (^{13}C, ^{125}Te). A typical spectrum of $[(p\text{-}MeOC_6H_4)_2Te\{S_2P(OCHMe_2)_2\}_2]$ (operating 1 to 10 hrs for their ^1H, ^{31}P and ^{125}Te

TABLE I

^{13}C, ^{31}P and ^{125}Te NMR Shifts for $[R_2Te\{S_2P(OR')_2\}_2]$

Compound	Chemical Shift (δ) (in ppm) (Solvent)		
	^{13}C NMR	^{31}P NMR	^{125}Te NMR
1	19.51(H_3C—Te); 73.90, 73.63(OCH_2); 24.60, 24.39(CH_3)(*A*)	93.70(A) 111.4(*G*)	—
7	123.4(1), 128.7(2), 115.2(3), 160.8(4), 57.7(5) (Aryl), 53.2(CH_3O—P)(*B*)	—	—
8	122.8(1), 136.8(2), 115(3), 159.4(4) 54.9(5) (aryl); 62.77, 62.71(OCH_3); 15.55, 15.54(CH_3)($CDCl_3$)	95.10(*C*), 108.75(*I*) 111.20(F), 111.55(*H*), 113.39(*E*), 114.61(*G*)	—
9	128.2(1), 139.6(2), 115.23(3) 161.2(4), 55.04(5), (Aryl); 72.71, 71.94(CH), 23.45, 23.67(CH_3)(*B*)	92.47(*B*), 92.47(*C*) 110.32(*G*)	879.02 (171.28) *(*B*)
10	123.5(1), 137.4(2), 115.4(3) 161.8(4), 54.5(5) (aryl); 68.74, 68.47(OCH_2); 23.65, 23.37(CH_2); 10.04(CH_3)(*A*)	95.71(*A*), 95.62(*C*), 112.8(*G*)	881.40(721.58) *(*B*) 885.17(721.54) *(*D*)
11	124.43(1), 137.30(2), 114.95(3), 160.94(4), 54.60(5) (aryl); 78.49, 78.17, 76.0, 75.67 (OCH); 30.28, 30.17, 30.01(CH_2); 20.91, 20.74(CH_3)(*G*)	92.56(*A*), 92.20(*B*) 113.9(*G*)	882.45(718.27) *(*B*); 885.68(721.56) *(*D*)

*Peaks corresponds to (p-$MeOC_6H_4$) Te; Solvent denoted as (*A*) CH_2Cl_2, (*B*) $CHCl_3$, (*C*) CCl_4, (*D*) THF (*E*) MeOH, (*F*) MeCN (*G*) Me_2SO, (*H*) C_5H_5N and (*I*) Me_2CO.

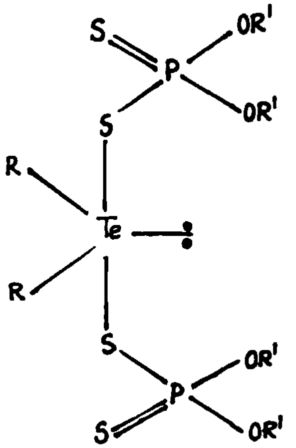
NMR spectral observations) showing decomposition in solution and peaks assigned, are shown in graph.

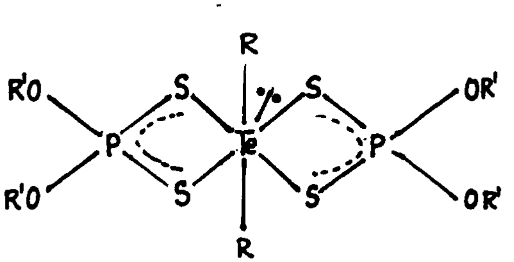
STRUCTURE AND BONDING

The 0,0′-dialkyldithiophosphate ligand can bind a metal atom in several ways (ionic, unidentate and bidentate bridging or chelating).[22] The ^{31}P NMR chemical shift may be helpful to suggest a tentative structure for the newly synthesized compounds. Experimentally observed chemical shift values fall in the general range (δ 87–101 ppm) proposed by Glidwell[23] for chelating or bridging -$S_2P(OR')_2$ ligands. The ^{31}P NMR chemical shift for the $(R'O)_2PS_2$-ligand in the compounds $[R_2Te\{S_2P(OR')_2\}_2]$ merely corresponds to bidentate nature. Coordination of the ligand $(R'O)_2PS_2$ via non-bonded sulphur atoms is thus supported and its in accord with the soft acid nature of tellurium.[1,24] However, the possibility of intramolecular or intermolecular secondardy interaction could not be ruled out. In the present complexes, the bidentate nature of the ligand in solution may be due to either a weak coordination between non-bonded sulphur and tellurium or due to inter or intramolecular secondary interaction between tellurium and sulphur. The associating nature of molecules in nitrobenzene in their molecular weight determination and monomeric nature in toluene show distinct secondary interaction in solution. The two bands in the IR spectra assigned to $\vartheta_{as}TeS_2$ and $\vartheta_{sy}TeS_2$ appear at 370 ± 5 and 290 ± 5 cm^{-1}. The significantly large separation between ϑ_{as} and ϑ_{sy} modes of vibration suggest that the S—Te—S angle may be near 180° rather than 90° and it is expected a monodentate attachment of the ligand in these compounds.[14]

A pseudotrigonal bipyramidal geometry around central tellurium atom may be suggested in the solid state, where the positions are occupied by R and -$S_2P(OR')_2$ group and a lone pair of electrons. However, in solution a weak coordination from the non-bonded sulphur to tellurium atom or an inter or intramolecular secondary interaction between non-bonded sulphur of the ligand and metal may be expected.

The two structure in solid and solution may be proposed as shown below:





[R=Me, Ph, p-$MeOC_6H_4$; R'=Me, Et, $(CH_2)_2CH_3$, $CHMe_2$, CH_2CHMe_2]

EXPERIMENTAL

All manipulations were carried out under dry nitrogen atmosphere $TeCl_4$ (BDH), Te (200 mesh) were used as such. Me_2TeI_2 (ref. 25) Ph_2TeCl_2 (ref. 26) $(p\text{-}MeOC_6H_4)_2TeCl_2$ (ref. 27), 0,0-dithiophosphoric acids and their ammonium salts were prepared according to established procedure. NMR spectra were recorded on JEOL FX-90 Q FT NMR spectrometer. ^{125}Te NMR was observed at 28.25 MHz with an external D_2O capillary lock and referenced against external Me_2Te solution. ^{31}P spectra were measured at 36.23 MHz and referenced against external 85% H_3PO_4. ^{13}C spectra was measured at 22.49 MHz and referenced against internal Me_4Si. Other physicochemical studies were made as described earlier.[28,29]

Some representative reactions for the preparation of $[R_2Te\{S_2P(OR')_2\}_2]$ are described below:

(a) *Reaction of* $(p\text{-}MeOC_6H_4)_2TeCl_2$ *with* $NH_4S_2P(OC_2H_5)_2$. To a suspension of the ammonium salt of 0,0'-diethyldithiophosphoric acid (4.06 g; 20 mmol) in anhydrous toluene (25 ml) was added a solution of $(p\text{-}MeOC_6H_4)_2TeCl_2$ (4.12 g; 10 mmol) in toluene (25 ml). The reaction mixture was stirred for 1 hr. Filtration followed by distillation of the solvent under reduced pressure gave a viscous mass, which was recrystallized from toluene/n-pentane (1:10) mixture.

(b) *Reaction of* $R_2Te(OR')_2$ *with* $(R'O)PS_2H$. $R_2Te(OR')_2$ were prepared *in situ* by the reaction of NaOR' and R_2TeCl_2 in corresponding alcohols. Lower alcohols, CH_3OH, C_2H_5OH, $(CH_3)_2CHOH$ were used as reactant as well as solvent while $CH_3(CH_2)_2OH$ and $(CH_3)_2CHCH_2OH$ were used as reactant in (1:2) molar ratio, using toluene or benzene as a solvent. The prepared alcoxide was isolated and used as follows:

In a representative reaction, $Ph_2Te(OC_2H_5)_2$ (3.5 g; 10 mmol) in toluene (10 ml) was added, O,O'-diethyldithiophosphoric acid (3.70 g; 20 mmol) in toluene (10 ml). The reaction mixture was refluxed for 1 hr. and alcohol was removed azeotropically, followed by distillation under reduced pressure. The yellow viscous mass thus obtained was recrystallized from toluene/n-pentane (1:10) mixture. Other derivatives were prepared similarly.

Analytical data for $[R_2Te\{S_2P(OR')_2\}_2]$: Anal. found (%) (calcd.), (R=Me, R'=Et) (**1**) m.p. 89°C; Te, 23.86 (24.16); C, 22.52 (22.74); H, 4.43 (4.96); S, 24.01 (24.28). (R=Ph, R'=Me) (**2**) m.p. 112°C; Te, 21.31 (21.40); C, 32.07 (32.23); H, 3.53 (3.72); S, 21.29 (21.51). (R=Ph, R'=Et) (**3**) m.p. 94°C;

Te, 19.03 (19.56); C, 36.16 (36.83); H, 4.42 (4.63); S, 19.17 (19.66). ($\mathrm{R{=}Ph, R'{=}CHMe_2}$) (**4**) m.p. 120°C; Te, 17.86 (18.01); C, 40.13 (40.69); H 5.31 (5.40); S, 18.01 (18.10). [$\mathrm{R{=}Ph, R'{=}(CH_2)_2Me}$] (**5**) m.p. 103°C; Te, 17.78 (18.01); C, 40.26 (40.69); H, 5.17 (5.40); S, 17.87 (18.10). ($\mathrm{R{=}Ph, R'{=}Ch_2CHMe_2}$) (**6**) m.p. 131°C; Te, 16.33 (16.69); C, 43.58 (43.99); H, 5.67 (6.06); S, 16.20 (16.77). ($\mathrm{R{=}}p\text{-}\mathrm{MeOC_6H_4, R'{=}Me}$) (**7**) m.p. 102°C; Te, 19.11 (19.44), C, 32.47 (32.95); H, 3.56 (3.99); S, 19.18 (19.54). ($\mathrm{R{=}}p\text{-}\mathrm{MeOC_6H_4, R'{=}Et}$) (**8**) m.p. 70°C, Te, 17.35 (17.91); C, 36.69 (37.10); H, 4.23 (4.81); S, 17.71 (18.00). ($\mathrm{R{=}}p\text{-}\mathrm{MeOC_6H_4, R'{=}CHMe_2}$) (**9**) m.p. 100°C; Te, 16.12 (16.60); C, 40.23 (40.64); H, 5.26 (5.51); S, 16.25 (16.69). ($\mathrm{R{=}}p\text{-}\mathrm{MeOC_6H_4, R'{=}(CH_2)Me}$ (**10**) m.p. 114°C; Te, 16.28 (16.60); C, 40.07 (40.64); H, 5.19 (5.51); S, 16.34 (16.69). ($\mathrm{R{=}}p\text{-}\mathrm{MeOC_6H_4, R'{=}CH_2CHMe_2}$) (**11**) m.p. 115°C; Te, 15.20 (15.47); C 43.26 (43.70); H, 5.93 (6.11); S, 15.17 (15.55).

(c) *Reaction of R_2TeO with $(R'O)_2PS_2H$.* (p-$\mathrm{MeOC_6H_4)_2TeO}$ (3.57 g; 10 mmol) and $\mathrm{[\{(CH_3)_2CH_2CHO\}_2\text{-}PS_2H]}$ (4.84 g; 20 mmol) were refluxed together in anhydrous toluene (50 ml) and water removed azeotropically. The yellow product thus obtained was washed with solvent ether and identified as $\mathrm{[(}p\text{-}\mathrm{MeOC_6H_4)_2TeS_2P(OCHCH_2Me_2)_2]_2O}$. Similar reaction was carried out in methanol. The solution was filtered and allowed to evaporate slowly to give yellow crystals of $\mathrm{[\{(}p\text{-}\mathrm{MeOC_6H_4)_2TeS_2P\text{-}(OCHCH_2Me_2)\}_2O]_2 \cdot H_2O}$.

Analytical data: found (%) (calcd.) ($\mathrm{R{=}}p\text{-}\mathrm{MeOC_6H_4}$, in all compounds). $\mathrm{[R_2TeS_2P(OCH_2CHMe_2)_2]_2O}$; Te, 21.50 (21.60); C. 44.65 (44.70); H, 5.39 (5.41); S, 10.76 (10.83); ^{31}P NMR (δ) 92.44 ($\mathrm{CHCl_3}$). $\mathrm{[R_2TeS_2P(OEt)_2]_2O}$; Te, 23.67 (23.90); C, 44.27 (44.40); H, 4.36 (4.48); S, 11.80 (11.97); ^{31}P NMR (δ) 93.65 ($\mathrm{C_6H_6}$). $\mathrm{[R_2TeS_2P(OCHMe_2)_2]_2O}$; Te 22.64 (22.68); C, 42.56 (42.65); H, 4.86 (4.97); S, 11.34 (11.37); ^{31}P NMR (δ) 92.26 ppm ($\mathrm{CCl_4}$). $\mathrm{[\{R_2TeS_2P(OCH_2CHMe_2)_2\}_2O]_2 \cdot H_2O}$; Te, 21.41 (21.44); C, 44.25 (44.36); H, 5.33 (5.46); S, 10.70 (10.75); ^{31}P NMR (δ) 92.17 ppm ($\mathrm{CHCl_3}$). $\mathrm{[\{R_2TeS_2P(OEt)_2\}_2O]_2 \cdot H_2O}$; Te, 23.51 (23.66); C, 39.96 (40.66); H, 4.34 (4.54), S, 11.83 (11.87); ^{31}P NMR (δ) 93.36 ppm ($\mathrm{CCl_4}$). $\mathrm{[\{R_2TeS_2P(OCHMe_2)_2\}_2O]_2 \cdot H_2O}$; Te, 22.46 (22.50); C, 42.28 (42.43); H, 4.49 (5.02); S, 11.20 (11.28); ^{31}P NMR (δ) 92.22 ppm ($\mathrm{CHCl_3}$).

(d) *Thermogravimetric analysis.* TG analysis of the compounds $\mathrm{[R_2Te\{S_2P(OR')_2\}_2]}$ [$\mathrm{R{=}Ph}$, and p-$\mathrm{MeOC_6H_4}$ and $\mathrm{R'{=}Me}$ or $\mathrm{C_2H_5}$] were carried out. The compounds (200 mg) when heated at 5°C min^{-1} in a self produced atmosphere, decompose without step-wise loss in weight at (140°–180°C) leaving behind $\mathrm{R_2TeS}$. On further heating (180–280°C) a residue corresponding to $\mathrm{TeS_2}$ was obtained.

(e) *Solution study.* When the compound $\mathrm{[R_2Te\{S_2P(OR')_2\}_2]}$ were kept in $\mathrm{CH_2Cl_2}$, $\mathrm{CHCl_3}$ or $\mathrm{CCl_4}$ for 24 hr. at room temperature, more than 50% of the compound decomposed during this period according to eq.

$$2[\mathrm{R_2Te\{S_2P(OR')_2\}_2}] \rightarrow [\mathrm{R_2Te}] + [\mathrm{(R'O)_2P(S)SS(S)P(OR')_2}] + [\mathrm{R_2Te\{S_2P(OR')_2\}_2}]$$

Removal of the solvent to complete dryness and addition of solvent ether to the mixture of the products resulted in the separation of $\mathrm{R_2Te}$ derivatives. A fractional crystallization of the mixture with toluene and n-pentane (1:10) mixture separates $\mathrm{[R_2Te\{S_2P(OR')_2\}_2]}$ from the ligand $\mathrm{[(R'O)_2P(S)SS(S)P(OR')_2]}$. Reaction of $\mathrm{R_2Te}$ with $\mathrm{[(R'O)_2PS_2]_2}$ ligand does not produce $\mathrm{[R_2Te\{S_2P(OR')_2\}_2]}$ oxidatively. Refluxing of $\mathrm{[R_2Te\{S_2P(OR')_2\}_2]}$ species in $\mathrm{CH_2Cl_2}$ or $\mathrm{CHCl_3}$ for 24 hr. gave 100% decomposition and tellurium metal was obtained.

(f) (i) *Reaction of $[R_2Te\{S_2P(OR')_2\}_2]$ with bases.* Reaction of neat DMSO, DMF or $\mathrm{C_5H_5N}$ with $\mathrm{[R_2Te\{S_2P(OR')_2\}_2]}$ gave Te° metal and $\mathrm{[(R'O)_2PS_2]_2}$. The other products of the reaction could not be identified. A photochemical or thermochemical reaction may be possible.

(ii) *Reaction of $[R_2Te\{S_2P(OR')_2\}_2]$ with phosphines.* $\mathrm{Ph_3P}$ and $\mathrm{Ph_2P(CH_2)_2PPh_2}$ gave corresponding phosphine sulphides and another unidentified product. The presence of phosphine sulphides was confirmed by ^{31}P NMR spectra [δ 42.5($\mathrm{CHCl_3}$)$\mathrm{Ph_3PS}$ and δ 45.21($\mathrm{CHCl_3}$)$\mathrm{Ph_2P(S)(CH_2)_2(S)PPh_2}$].

ACKNOWLEDGEMENT

One of the us (JDS) wishes to express his gratitude to Mr. Sumar Kumar Gupta, who carried out some of the NMR measurements with enthusiasm. We are also thankful to (CSIR) for financial assistance and (DST) for awarding a young scientist fellowship to (SKS).

REFERENCES

1. K. G. K. De Silva, W. R. McWhinnie and J. E. Stuckey, *Inorg. Chim. Acta.*, **122,** 153 (1986).
2. W. C. Cooper (ed.) 'Tellurium' Van Nostrand and Reinhold, (1971).
3. W. R. McWhinnie and J. E. Stuckey, *The Use of Selenium and Tellurium in Rubber Technology*, Selenium and Tellurium Development Assoc. Inc. (1983).
4. F. F. Knapp Jr., K. R. Ambrose, A. P. Callahan, L. A. Ferren, R. A. Grigsby and K. J. Irgolic, "*Radiopharmaceuticals II*"; Society of Nuclear Medicine: New York, (1979).
5. F. F. Knapp Jr., T. A. Butler, K. R. Amorose, A. P. Callahan, C. E. Guyer, J. A. Roberts, L. A. Ferren, H. A. Grigsby and K. J. Irgolic, "*Practical Applications of Nuclear and Radiochemistry*" Pergaman Press, New York, **28,** 343 (1982).
6. S. Husebye, *Phosphorus and Sulfur*, **38,** (1988) 271.
7. R. C. Mehrotra, G. Srivastava and B. P. S. Chauhan, *Coord. Chem. Rev.*, **55,** 207 (1984).
8. J. L. Lefferts, K. C. Molloy, J. J. Zuckerman, I. Haiduc, C. Guta and D. Ruce, *Inorg. Chem.*; **19,** 1662, 2861 (1980).
9. R. K. Chadha, J. E. Drake and A. B. Sarkar, *Inorg. Chem.*, **24,** 3156 (1985).
10. P. G. Harrison and T. Kikabhai, *J. Chem. Soc. Dalton Trans.*, 807 (1987).
11. M. G. B. Drew, M. Hasan, R. J. Hobson and D. A. Rice, *J. Chem. Soc. Dalton Trans.*, 1161 (1986).
12. R. K. Chadha, J. E. Drake and A. B. Sarkar, *Inorg. Chem.*, **26,** 2885 (1987).
13. R. K. Chadha, J. E. Drake and A. B. Sarkar, *J. Organometal. Chem.*, **323,** 27 (1987).
14. R. K. Chadha, J. E. Drake, N. T. McManus, B. A. Quinlan and A. B. Sarkar, *Organometallics*, **6,** 813 (1987).
15. D. Dakternieks, R. D. Giacomo, R. W. Gable and B. F. Hoskins, *J. Am. Chem. Soc.*, **110,** 6541, 6753, 6762 (1988).
16. D. Dakternieks, R. D. Giacomo, R. W. Gable and B. F. Hoskins, *J. Organometal. Chem.*, **349,** 305 (1988); **353,** 35 (1988).
17. A. J. Casey and A. M. Vecchio, *Inorg. Chim. Acta.*, **131,** 191 (1987).
18. S. Husebye, *In proceedings of the fourth International conference on the organic chemistry of Selenium and Tellurium* (edited by F. J. Berry and W. R. McWhinnie) pp 298–369, University of Aston in Birmingham (1983).
19. M. A. K. Ahmed, W. R. McWhinnie and P. Granger, *Polyhedron*, **5,** 859 (1986).
20. S. Uemura and S. I. Fukuzawa, *J. Organometal. Chem.*, **268,** 223 (1984).
21. D. J. L. Clive, G. J. Chittattu, V. Farina, W. A. Kiel, S. M. Menchem, C. G. Russell, A. Singh, Chi Kwong Wong and N. J. Curtis, *J. Am. Chem. Soc.*, **102,** 4438 (1980).
22. I. Haiduc, *Rev. Inorg. Chem.*, **3,** 353 (1981).
23. C. Glidwell, *Inorg. Chim. Acta.*, **25,** 159 (1977).
24. J. E. Huheey, "*Inorganic Chemistry.*" *Principles of Structure and Reactivity*, Harper International SI ed. N.Y. IIIrd ed. 314 (1983).
25. R. H. Vernon, *J. Chem. Soc.*, **117,** 86 (1920).
26. R. C. Paul, K. K. Bhasin and R. K. Chadha, *J. Inorg. Nucl. Chem.*, **37,** 2337 (1975).
27. J. Bergman, *Tetrahedron*, **28,** 3323 (1972).
28. T. N. Srivastava, Jai Deo Singh and Sanjay Kumar Srivastava, *Polyhedron*, **6,** 219 (1987).
29. T. N. Srivastava, Jai Deo Singh and Sanjay Kumar Srivastava, *Polyhedron*, **9,** 943 (1990).