

## CHEMISTRY OF ORGANO-CHALCOGEN COMPOUNDS

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*(Received 20 June 1988; Accepted 20 October 1988)*

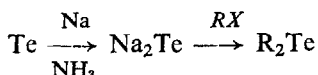
Dialkyl tellurides and ditellurides have been prepared in good yields by the reaction of elemental tellurium with hydrazine hydrate in the presence of sodium hydroxide and or sodium dithionite. Similarly, selenoethers have been prepared by cleaving dialkyl/aryl diselenide with hydrazine hydrate. Alkoxyalkyl organyl selenides/tellurides have been obtained in quantitative yields by the reaction of 1-bromo-2-ethoxyethane or 1-bromo-2-methoxyethane with sodium organyl selenolates/tellurolates. Diorganyl selenium/tellurium(IV) bis(trifluoroacetates) have been obtained from their respective oxides. Unsymmetrical diorganyl tellurium(IV) trifluoroethoxides have been prepared and characterized.

**Key Words :** Organo-chalcogens; Diethyl Tellurides & Ditellurides; Hydrazine Hydrate; Selenoether; Rongalite-C

THE growing importance of organochalcogenides viz., organosulphur, -selenium and -tellurium, as reagents and intermediates in organic synthesis has stimulated a great interest in developing cheap and convenient methods of their preparation. Strategies adopted by various workers in preparation of these compounds are briefly reviewed. Wohler in 1840 prepared the first organotellurium compound by reacting potassium telluride with barium ethyl sulphate and later employed various alkyl sulphates for the synthesis of other aliphatic tellurides. Dialkyl ditellurides are commonly prepared by alkylating inorganic tellurium compounds, such as  $K_2Te$ ,  $Na_2Te$ , elemental tellurium and  $TeCl_4$ . The alkylating agents used have been potassium alkyl sulphate, dialkyl mercury compounds, alkyl halides and Grignard's reagents etc.

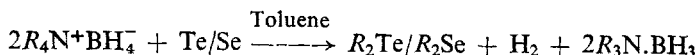
Alkylation of metallic tellurium or sodium telluride with 'Rongalite-C', i.e., sodium formaldehyde sulfoxylate produced predominantly ditelluride.<sup>1</sup> Sodium dithionite in basic solution also reduces elemental tellurium to sodium telluride, however, this reduction is inferior to that of 'Rongalite'.

Elemental sodium and tellurium react together in liquid ammonia to form sodium telluride<sup>2</sup> which on alkylation gives dialkyl tellurides in good yield.

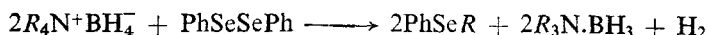


Dialkyl tellurides can conveniently be prepared in reasonable yields by reduction of dialkyltellurium dihalides. The reducing agents being  $Na_2SO_3$ ,  $NaHSO_3$  etc. in a aqueous solution containing  $NaOH$  or  $Na_2CO_3$ .

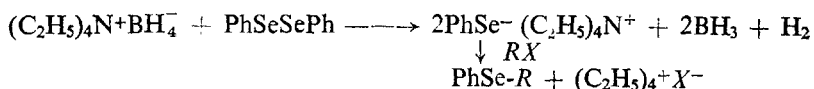
Bergman and Engman<sup>3</sup> have obtained symmetrical tellurides/selenides in excellent yields by the action of elemental tellurium/selenium with tetraalkylammonium borohydride in toluene.



Tetraalkylammonium borohydride functions both as a reducing and an alkylating agent. However, this synthesis is restricted only to the preparation of dibutyl telluride/selenide, as the corresponding ethyl, propyl or hexyl derivatives do not react with elemental tellurium/selenium even under rigorous conditions. Alkyl phenyl selenides could similarly be prepared from tetraalkylammonium borohydride and diphenyl diselenide

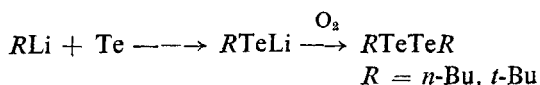


Tetraethyl borohydride reduces diphenyl diselenides to phenyl selenide anion and does not give the expected ethyl phenyl selenide, probably due to low alkylating power of tetraethylammonium ion. The utility of phenyl selenide anion for effecting a wide variety of synthetic transformations has focussed some interest on its synthesis. When an alkyl or an acyl halide is added to the toluene solution of  $PhSe^-$ , the corresponding products can be isolated in good yields.



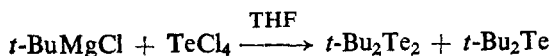
Only recently<sup>4</sup>,  $LiEt_3BH$  (superhydride) has been profitably used for the reduction of elemental sulphur, selenium or tellurium to give  $M^{2-}$  or  $M_2^{2-}$  depending on the mole ratio of the element: super hydride.

Bergman and Cava<sup>5</sup> have described the first synthesis of di-*t*-butyl ditelluride,  $t-Bu_2Te_2$  by the reaction of  $t-BuLi$  with tellurium in dry THF followed by aerial oxidation.



An attempt to prepare above ditellurides in ether as a solvent was unsuccessful.

Jones and Sharma,<sup>6</sup> however, found that elemental tellurium when added to  $t-BuLi$  in THF cooled to  $-78^\circ C$  dissolved on warming to  $-10^\circ C$  to yield a dark red-brown solution which on aerial oxidation produced di(*neo*-hexyl) ditelluride,  $[(CH_3)_3CCH_2CH_2]_2Te_2$ . It was confirmed that  $t-BuLi$  reacts with THF at room temperature to produce  $(CH_3)_3CCH_2CH_2Li$  which on reaction with tellurium yielded the observed product. Jones *et al.* have also prepared ditellurides by the reaction of  $t-BuMgCl$  with  $TeCl_4$  in THF.



It is evident from the above discussion that a number of reducing agents have been employed to prepare the alkali metal tellurides or ditellurides.

The synthetic procedures hitherto reported have either employed expensive materials or involve troublesome manipulations, and have not been, in particular, suitable for large scale preparations. The authors, among others have been pursuing different strategies to find out convenient methods for the preparation of these organochalcogen compounds.

Elements S, Se, Te react readily with hydrazine hydrate at room temperature in the presence of sodium hydroxide resulting in yellowish orange, brown or pink colours respectively with the evolution of nitrogen. Alkylation of these yield quantitatively the disulphides, diselenides and ditellurides, indicating that the species chemically equivalent to  $S_2^{2-}$ ,  $Se_2^{2-}$ ,  $Te_2^{2-}$  have been formed. Attempts to prepare the monoatomic anions  $S^{2-}$ ,  $Se^{2-}$ ,  $Te^{2-}$  using hydrazine hydrate were unsuccessful. However, if to the hydrazine hydrate solution of S, Se, Te (in the presence of NaOH), sodium dithionite is added, species chemically equivalent to  $S^{2-}$ ,  $Se^{2-}$  and  $Te^{2-}$  are formed quantitatively. Using different stoichiometric ratios of  $S/N_2H_4.H_2O$  followed by alkylation, it has been possible to prepare the corresponding trisulphides in excellent yields.

Table I gives the list of ditellurides and tellurides prepared by the method described above along with their proton NMR.

The synthesis<sup>7</sup> of dialkyl tellurides and ditellurides described herein have the following attributes:

- (i) Only a single reaction flask is required, most reactions proceed satisfactorily at room temperature.
- (ii) Starting materials are inexpensive and readily available.
- (iii) No undesirable by-products are formed and the work-up procedures are simple.
- (iv) The yields are excellent.

Although much attention has been focussed on the synthesis of organoselenium compounds, little work has been done on the synthesis of the compounds of the type<sup>8</sup>;  $RSe(CH_2)_nSeR$ . Of late, it has been found that hydrazine hydrate can cleave dimethyl diselenide and diphenyl diselenide in the presence of a strong base in aprotic solvents like THF, benzene or hexane to give methyl selenolate and phenyl selenolate anion respectively. The reaction proceeds at room temperature in the presence of tetrabutylammonium chlorides, which acts as a phase transfer catalyst. The anions thus formed react readily with various alkylating agents to give the selenoethers in excellent yields.

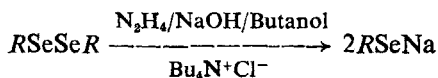


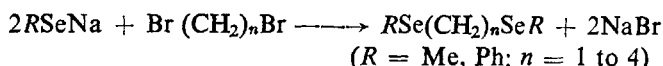
TABLE I  
 Preparative and  $^1\text{H}$  NMR data of ditellurides and tellurides

Compound	% yield <sup>a,b</sup>	Reaction time/hr <sup>c</sup>	$^1\text{H}$ NMR ( $\text{CCl}_4$ )
<i>Dialkyl ditellurides</i>			
$(\text{CH}_3\text{Te})_2$	70	4	2.71 (s)
$(\text{C}_2\text{H}_5\text{Te})_2$	90	3	1.62 (t, 3H) 3.02 (q, 2H)
$(n\text{-C}_3\text{H}_7\text{Te})_2$	90	4	1.03 (t, 3H) 1.77 (m, 2H) 3.12 (t, 2H)
$(n\text{-C}_4\text{H}_9\text{Te})_2$	92	4	0.95 (t, 3H) 1.70-1.90 (m, 4H) 3.13 (t, 2H)
<i>Dialkyl tellurides</i>			
$(\text{CH}_3)_2\text{Te}$	55	10	1.9 (s)
$(\text{C}_2\text{H}_5)_2\text{Te}$	75	11	1.62 (t, 3H)
$(n\text{-C}_3\text{H}_7)_2\text{Te}$	75	10	1.03 (t, 3H) 1.77 (m, 2H) 2.63 (t, 2H)
$(n\text{-C}_4\text{H}_9)_2\text{Te}$	80	12	0.95 (t, 3H) 1.73-1.90 (m, 4H) 2.65 (t, 2H)

<sup>a</sup>products are identified by comparison with authentic samples.

<sup>b</sup>yields are based on starting elemental tellurium.

<sup>c</sup>room temperature.



Similar attempts with tellurium compounds have not so far been successful.

Table II gives the list of selenoethers obtained by this method<sup>9</sup> with their proton NMR and mass spectral data. Mass spectra of the compounds were recorded to confirm their constitution. The presence of six natural isotopes of selenium ( $^7\text{Se} = 0.87$ ,  $^{76}\text{Se} = 9.2$ ,  $^{77}\text{Se} = 7.58$ ,  $^{78}\text{Se} = 23.52$ ,  $^{80}\text{Se} = 49.82$  and  $^{82}\text{Se} = 9.19\%$ ) leads to highly characteristic groups of peaks for selenium containing fragments. All the selenoethers show molecular ion peaks and the fragmentation pattern as expected showed considerable resemblance to those of the corresponding thioethers,  $\text{RS}(\text{CH}_2)_n\text{SR}$ . The values reported are with respect to  $^{80}\text{Se}$  isotope.

The methyl substituted compounds generally show loss of Me, MeSe and MeSeH in the major fragmentation. In case of  $\text{MeSe}(\text{CH}_2)_2\text{SeMe}$ , elimination of the backbone—a process absent in other cases is in keeping with the earlier findings on fluorinated selenoethers.<sup>10</sup>

TABLE II  
Physical characteristics of diselenoethers

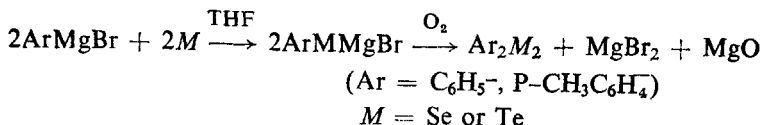
Compound <sup>a</sup>	m.p./b.p.(°C)		Yield <sup>b</sup> %	<sup>1</sup> H N.M.R. (CCl <sub>4</sub> )	<i>m/e</i> (relative intensity)
	Found	Lit.			
CH <sub>3</sub> SeCH <sub>3</sub> SeCH <sub>3</sub>	62°/10mm	76°/12mm	88	2.07 (s, 6H, 2C <sub>6</sub> H <sub>5</sub> Se); 3.62 (s, 2H, CH <sub>3</sub> SeCH <sub>3</sub> )	204 (50), 189 (10) 109 (100), 94 (15) 93 (35)
CH <sub>3</sub> SeCH <sub>2</sub> CH <sub>2</sub> SeCH <sub>3</sub>	86°/10mm	88/8mm	85	2.06 (s, 6H, 2C <sub>6</sub> H <sub>5</sub> Se); 2.82 (s, 4H, 2CH <sub>2</sub> SeCH <sub>3</sub> )	218 (20), 190 (50) 175 (30), 123 (100), 109 (20), 95 (100) 93 (60)
CH <sub>3</sub> SeCH <sub>2</sub> CH <sub>2</sub> SeCH <sub>2</sub>	104°/10mm	102/8mm	85	2.06 (s, 6H, 2C <sub>6</sub> H <sub>5</sub> Se), 2.63 (t, 4H, 2CH <sub>2</sub> SeCH <sub>2</sub> CH <sub>3</sub> ), 1.98 (m, 2H, CH <sub>3</sub> SeCH <sub>2</sub> )	232 (20), 217 (100), 202 (10), 190 (10), 175 (70), 121 (20) 109 (50)
C <sub>4</sub> H <sub>9</sub> SeCH <sub>2</sub> SeC <sub>6</sub> H <sub>5</sub>	35-37	36-38	75	4.20 (s, 2H, C <sub>4</sub> H <sub>9</sub> SeCH <sub>2</sub> ), 7.13-7.68 (m, 10H, 2C <sub>6</sub> H <sub>5</sub> Se)	328 (10), 171 (60) 158 (10), 157 (5) 93 (10)
C <sub>4</sub> H <sub>9</sub> Se(CH <sub>2</sub> ) <sub>2</sub> SeC <sub>6</sub> H <sub>5</sub> <sup>c</sup>	44-45	—	82	3.12 (s, 4H, 2C <sub>6</sub> H <sub>5</sub> SeCH <sub>2</sub> ), 7.17-7.62 (m, 10H, 2C <sub>6</sub> H <sub>5</sub> Se)	342 (10), 314 (10) 185 (80) 158 (10), 157 (100);
C <sub>4</sub> H <sub>9</sub> Se(CH <sub>2</sub> ) <sub>3</sub> SeC <sub>6</sub> H <sub>5</sub> <sup>c</sup>	Yellow oil	—	80	2.94 (t, 4H, 2C <sub>6</sub> H <sub>5</sub> SeCH <sub>2</sub> ), 2.10 (g, 2H, C <sub>4</sub> H <sub>9</sub> SeCH <sub>2</sub> CH <sub>2</sub> ) and 7.12-7.64 (m, 10H, 2C <sub>6</sub> H <sub>5</sub> Se)	356 (25), 314 (20) 279 (10) 234 (10) 199 (80), 171 (35) 158 (15), 157 (100)

<sup>a</sup>Satisfactory C, H and Se analyses were obtained,

<sup>b</sup>Yields are based upon selenium substrates,

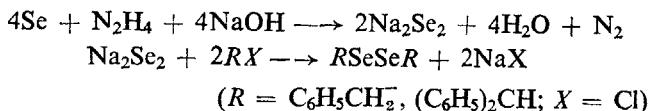
<sup>c</sup>New Compounds.

Diaryl ditellurides/diselenides have been conveniently prepared in one pot synthesis by the reaction of Grignard's reagents with the metal in THF in the presence of oxygen.

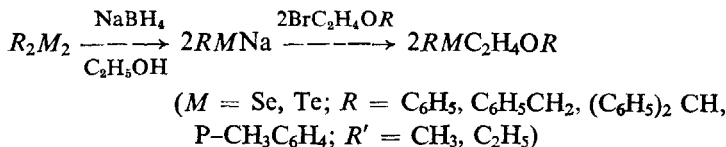


The yield in *p*-tolyl derivatives is lower as compared with that in phenyl derivatives, which may be more due to steric factors.

Dibenzyl- and bis(diphenyl) methyl diselenides were prepared in quantitative yields by dissolving the metal in hydrazine hydrate in the presence of NaOH followed by alkylation.



The ditellurides and the diselenides are readily reduced by sodium borohydride in ethanol to give sodium organyl telluroate or selenoate, highly potential nucleophiles used *in situ*. These nucleophilic anions readily replace the halide ions from alkoxy-alkyl halides.



Some β-alkoxy organyl selenides and tellurides prepared by this method<sup>11</sup> are given in Table III alongwith their b.p.t.s and important IR frequencies. These are

TABLE III  
Boiling points and important IR frequencies (cm<sup>-1</sup>) of compounds

Compound*	B.Pt. (°C) at 4mm	Yield	ν(C-M-C)	ν <sub>s</sub> (C-O-C)	ν <sub>as</sub> (C-O-C)
1 C <sub>6</sub> H <sub>5</sub> SeC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	200	90	520 <sub>s</sub>	940 <sub>s</sub>	1010 <sub>s</sub>
2 C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SeC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	80	87	510 <sub>w</sub>	960 <sub>w</sub>	1100 <sub>s</sub>
3 (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSeC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	200	80	510 <sub>w</sub>	950 <sub>w</sub>	1100 <sub>s</sub>
4 C <sub>6</sub> H <sub>5</sub> SeC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	180	90	520 <sub>s</sub>	940 <sub>s</sub>	1080 <sub>r</sub>
5 C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SeC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	75	88	510 <sub>w</sub>	955 <sub>m</sub>	1100 <sub>s</sub>
6 (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSeC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	200 <sup>d</sup>	80	510 <sub>w</sub>	940 <sub>m</sub>	1100 <sub>s</sub>
7 C <sub>6</sub> H <sub>5</sub> TeC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	120	78	600 <sub>m</sub>	940 <sub>w</sub>	1110 <sub>s</sub>
8 CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> TeC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	124	75	610 <sub>m</sub>	960 <sub>w</sub>	1110 <sub>s</sub>
9 C <sub>6</sub> H <sub>5</sub> TeC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	100	80	585 <sub>m</sub>	960 <sub>w</sub>	1105 <sub>s</sub>
10 CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> TeC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	110	75	580 <sub>m</sub>	960 <sub>w</sub>	1120 <sub>s</sub>

\*Satisfactory analytical results were obtained.

M = Se or Te

yellowish high boiling stable liquids. The telluride derivatives decompose in light probably to diaryl tellurides. These compounds are well characterised by their elemental analysis, IR, NMR and mass spectral data.

A broad band around  $590\text{--}510\text{cm}^{-1}$  in these compounds is assigned to  $\nu_{(\text{C-M-C})}$  and is in excellent agreement with the reported values<sup>12</sup> for other tellurides and selenides.

In case of proton nmr of these compounds (Table IV), the chemical shifts in case of tellurides are comparatively lower than those of corresponding selenide derivatives indicating that tellurium is deshielding the protons more than the selenium atom in the same environment.

TABLE IV

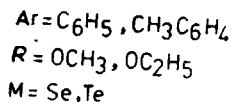
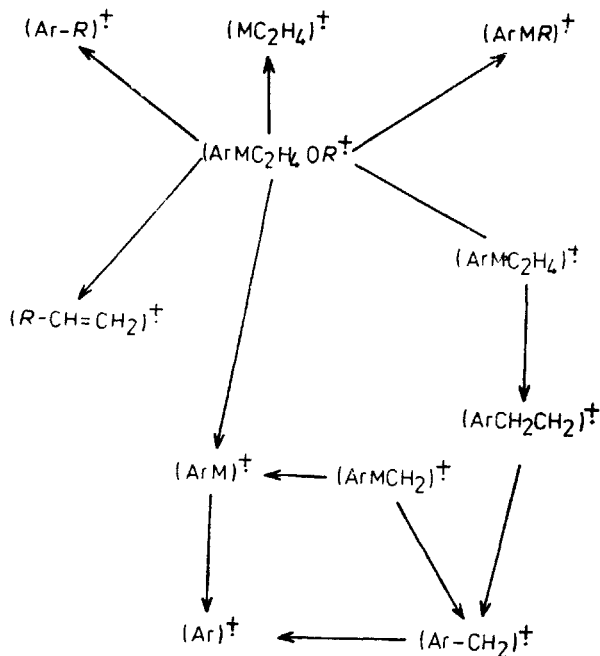
<sup>1</sup>H NMR Data (ppm) of alkoxyalkyl organyl selenides and tellurides

Compound	CH <sub>3</sub> C-	-SeCH <sub>2</sub>	-CH <sub>2</sub> OCH <sub>2</sub> -	C <sub>6</sub> H <sub>5</sub> CH-	C <sub>6</sub> H <sub>y</sub> -	
1 C <sub>6</sub> H <sub>5</sub> SeC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	1.16	3.0	3.50	—	7.33-7.60 (5H)	
2 C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SeC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	1.18	2.56	3.53	3.90 (2H)	7.43 (5H)	
3 (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSeC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	1.16	2.56	3.59	5.56 (1H)	7.50 (10H)	
Compound	-SeCH <sub>2</sub> -	-OCH <sub>3</sub>	-CH <sub>2</sub> O-	-C <sub>6</sub> H <sub>5</sub> CH $\bar{x}$	C <sub>6</sub> H <sub>y</sub>	
4 C <sub>6</sub> H <sub>5</sub> SeC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	3.0	3.36	3.60	—	7.33-7.60 (5H)	
5 C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> SeC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	2.56	3.33	3.50	3.80 (2H)	7.36 (5H)	
6 (C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHSeC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	2.53	3.36	3.53	5.53 (1H)	7.50 (10H)	
Compound	CH <sub>3</sub> C-	-C <sub>6</sub> H <sub>4</sub> . CH <sub>3</sub>	TeCH <sub>2</sub> -	OCH <sub>2</sub> . CH <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> . O-	C <sub>6</sub> H <sub>y</sub>
7 C <sub>6</sub> H <sub>5</sub> TeC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	1.16	—	3.02	3.42	3.76	7.30-7.79 (5H)
8 CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> TeC <sub>2</sub> H <sub>4</sub> OC <sub>2</sub> H <sub>5</sub>	1.13	2.37	2.97	3.43	3.73	7.07-7.76 (4H)
Compound	-C <sub>6</sub> H <sub>4</sub> CH <sub>3</sub>	-TeCH <sub>2</sub> -	-OCH <sub>3</sub>	-CH <sub>2</sub> CH <sub>2</sub> O-	C <sub>6</sub> H <sub>y</sub>	
9 C <sub>6</sub> H <sub>5</sub> TeC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	—	3.05	3.39	3.76	7.36-7.89 (5H)	
10 CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> TeC <sub>2</sub> H <sub>4</sub> OCH <sub>3</sub>	2.39	2.96	3.36	3.69	7.09-7.72 (4H)	

$y = 4$  or  $5$

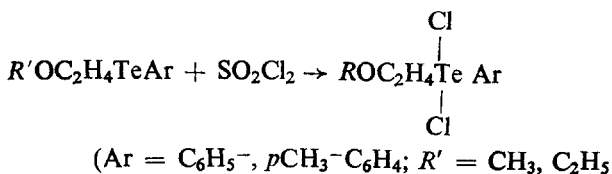
The tellurium and selenium containing ions give group of peaks with internal relative abundance well in agreement with the natural abundance for Te and Se isotopes. The fragmentation pattern for alkoxy alkyl organyl selenides/tellurides is given in Scheme I.

Diorganochalcogenides with halogens give the compounds of the type  $R_2MCl_2$ . We have found<sup>13</sup> that sulphuryl chloride is better suited for the synthesis of dichlorides.

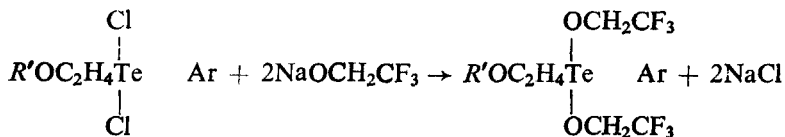


Scheme 1

Fragmentation pattern of alkoxy alkyl organyl selenides and tellurides



These dichlorides react conveniently<sup>13</sup> with sodium trifluoroethoxide in 2,2,2-trifluoroethanol in dry  $N_2$  atmosphere to give the corresponding trifluoroethanolate derivatives :



These compounds are odourless liquids decomposing at higher temperature and have been characterized on the basis of their elemental analysis, IR,  $^1H$  and  $^{19}F$  NMR, and mass spectral data.<sup>13</sup>



$^1\text{H}$  NMR spectra (Table V) of alkoxyethylaryltellurium(IV) bis(trifluoroethoxide) in  $\text{CCl}_4$  show that alkyl as well as aryl protons appear at comparatively lower field than in the present compounds reflecting, thereby, the deshielding effect of electron withdrawing nature of  $-\text{OCH}_2\text{CF}_3$  groups. The protons adjacent to Te are more deshielded. The  $^{19}\text{F}$  nmr spectra of these compounds shows a triplet at  $-76.6\text{ppm}$  upfields w.r.t.  $\text{CCl}_3\text{F}$ .

TABLE V

$^1\text{H}$  NMR data of trifluoroethanolates of unsymmetric diorganyl tellurides

Compound	$-\text{CCH}_3$	$-\text{C}_6\text{H}_4$ $\text{CH}_3$	$-\text{Te}$ $\text{CH}_2$	$\text{OCH}_2$ $\text{CH}_3$	$-\text{CH}_3$ $\text{CH}_2\text{O}-$	$-\text{OCH}_2$ $\text{CF}_3$	$\text{C}_6\text{H}_y$
1 $(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5\text{TeX}_2^*$	1.16	—	3.1	—	—	4.16	7.70–8.20 (5H)
2 $(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5$ $\text{OC}_2\text{H}_4\text{TeX}_2$	1.20	—	3.29	3.53	4.0	4.0	7.56–8.26 (5H)
3 $(\text{CH}_3\text{C}_6\text{H}_4)_2$ $\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{TeX}_2$	1.26	2.52	3.22	3.66	3.99	3.99	7.42–8.12 (4H)

Compound	$-\text{C}_6\text{H}_4$ $\text{CH}_3$	$-\text{TeCH}_2$	$-\text{OCH}_3$	$-\text{CH}_2$ $\text{CH}_2\text{O}$	$-\text{OCH}_2$ $\text{CF}_3$	$\text{C}_6\text{H}_y$
4 $(\text{C}_6\text{H}_5)_2\text{CH}_3$ $\text{OC}_2\text{H}_4\text{TeX}_2$	—	3.26	3.43	3.96	3.96	7.46–8.13 (5H)
5 $(\text{CH}_3\text{C}_6\text{H}_4)_2\text{CH}_3$ $\text{OC}_2\text{H}_4\text{TeX}_2$	2.56	3.30	3.66	4.1	4.1	7.60–8.20 (4H)

\*X =  $\text{OCH}_2\text{CF}_3$

Y = 4 or 5

In IR spectra (Table VI) of these compounds, strong multiplet bands around  $1180\text{cm}^{-1}$  are attributed to  $\nu_{\text{CF}_3}$ . The  $\nu_{\text{C-Te-C}}$  remains unchanged on the formation of these compounds. A trigonal bipyramidal structure (tentatively) is proposed on the basis of spectral studies.<sup>13</sup>

TABLE VI

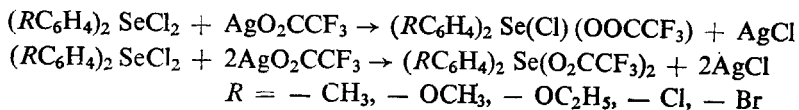
Important IR bands<sup>†</sup> ( $\text{cm}^{-1}$ ) of Trifluoroethanolates of unsymmetric diorganyl telluride

Compound	$\nu_{\text{CF}_3}$	$\nu_{\text{C-Te-C}}$	$\nu_{\text{Te-O}}$
1 $(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5\text{TeX}_2^*$	1210–1110s	600b	265m
2 $(\text{C}_6\text{H}_5)_2\text{CH}_3\text{OC}_2\text{H}_4\text{TeX}_2$	1220–1120s	610b	260m
3 $(\text{C}_6\text{H}_5)_2\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{TeX}_2$	1180–1110s	620b	265m
4 $(\text{CH}_3\text{C}_6\text{H}_4)_2\text{CH}_3\text{OC}_2\text{H}_4\text{TeX}_2$	1220–1120s	600b	260m
5 $(\text{CH}_3\text{C}_6\text{H}_4)_2\text{C}_2\text{H}_5\text{OC}_2\text{H}_4\text{TeX}_2$	1220–1120s	600b	260m

X =  $-\text{OCH}_2\text{CF}_3$ , †s = strong; m = medium; b = broad.

Te-O bonds are weaker as compared to S-O or Se-O bonds. The observation that the mass spectrum of alkoxyethylaryltellurium(IV) bis(trifluoroethoxides) do not show a molecular ion peak but has the highest ion corresponding to  $M-OCH_2CF_3$ , exemplifies this weakness. No metastable peaks are observed. The fragmentation pattern observed<sup>13</sup> probably arise from combination of thermolysis and volatilization of monomeric species in the vapour phase.

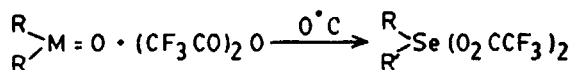
Diorganyl selenium dichlorides react with silver trifluoroacetate to give diorganyl selenium chloro(trifluoroacetates)/bis(trifluoroacetates) depending upon the amount of silver trifluoroacetate used.<sup>14</sup>



Similarly diorganylselenium(IV) bis(trifluoroethoxides) were obtained<sup>15</sup> by reacting corresponding dichlorides with sodium trifluoroethoxide.

Trifluoroethylphenyl selenide reacts with halogens to give<sup>16</sup>  $C_6H_5(CH_2CF_3)SeX_2$ ;  $X = Cl, Br, I$  in yields above 80 per cent.

A convenient synthetic route for the preparation of diorganylselenium/tellurium(IV) bis(trifluoroacetates) is developed<sup>17,18</sup> by reacting corresponding diorganylselenoxide/telluroxide with trifluoroacetic anhydride at low temperatures in the absence of solvent.



where  $R, R' = CH_3C_6H_4, CH_3OC_6H_4, C_2H_5OC_6H_4, ClC_6H_4, BrC_6H_4$  and  $CH_3$

and  $R = C_6H_5; R' = CH_2CF_3$

and  $M = Se$  or  $Te$

The above reaction is being extended to other fluorinated sulphonic anhydrides.<sup>19</sup>

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