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Preparation and NMR Studies of Tetraalkoxyselenuranes and Tetraalkoxytelluranes

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Abstract: A series of tetraalkoxyselenuranes has been prepared. Methanol yielded **5**, ethanol, **6**, 2-propanol, **7**, neopentyl alcohol, **8**, trifluoroethanol, **9**, ethylene glycol, **1**, pinacol, **3**, and neopentyl glycol, **4**. These molecules varied greatly in their thermal stability. Compounds **5** and **6** could be detected by ^{77}Se NMR but they could not be isolated. Compounds **7** and **8** are somewhat more stable and can be isolated as crystalline solids. The remaining selenuranes are reasonably thermally stable. Variable-temperature NMR experiments show that these substances undergo both intermolecular and intramolecular ligand reorganization. The intermolecular process can often be slowed by addition of an acid scavenger, and the intramolecular ligand reorganization process can often be inhibited at low temperatures. Both NMR and X-ray studies show that these molecules adopt structures which are trigonal bipyramidal or very nearly so. Treatment of **9** with trifluoroethoxide ion yielded the pentacoordinated ate complex. A series of tetraalkoxytelluranes has also been prepared. Ethylene glycol yielded **19**, pinacol, **20**, neopentyl glycol, **21**, methanol, **22**, ethanol, **23**, 2-propanol, **24**, neopentyl alcohol, **25**, trifluoroethanol, **26**, and hexafluoro-2-propanol, **27**, which was isolated as a 1:1 complex with tetrahydrofuran. Variable-temperature NMR studies on these substances, except for **19** and **21** which are too insoluble, show that they undergo ligand reorganization. In the case of **20** both NMR and X-ray studies show it has a distorted trigonal-bipyramidal structure. It was not possible to slow the reorganization of the ligands of the remaining telluranes sufficiently to determine their favored structure.

During the past two decades considerable progress has been made in reaching an understanding of the chemistry of pentacoordinated phosphorus compounds.[1] Similar studies of tetracoordinated sulfur compounds, where the lone pair functions as a ligand, have been conducted and at least some of the chemistry of these intriguing molecules has been delineated.[2] Much less is known about the chemistry of tetracoordinated selenium and tellurium compounds. Paetzold and Reichenbacher[3] have reviewed the chemistry of tetraalkoxyselenuranes, and although a number of simple tetraalkoxyselenuranes have been reported, their chemistry has received little attention and they have been found to be extremely unstable. Irgolic and Kudchadker[4] have also reviewed the organic chemistry of selenium. Only two tetraorganylselenium compounds have been prepared, and an attempt to synthesize tetraphenylselenurane[5] led to biphenyl and diphenyl selenide. The chemistry of diorganylselenium dihalides has received considerable study.[4] Reich[6] has prepared several mixed (aryloxy)selenuranes containing five-membered rings, and he has demonstrated that they do not undergo stereochemical inversion about selenium under the conditions studied.

The chemistry of tetracoordinated tellurium is somewhat better developed than that of selenium, and it has been recently reviewed.[7] Tetramethoxytellurane was prepared by Meerwein in 1929.[8] More recently a number of other tetraalkoxytelluranes have been prepared.[9,10] Tetraphenyltellurane is a relatively stable molecule. It does decompose on heating to give biphenyl and diphenyl telluride. Barton and co-workers[11] have studied the mechanism of this decomposition and they have concluded that it occurs by an intramolecular process. Interestingly, Hellwinkel and Fahrbach[12] have shown that tetrabutyltellurane decomposes to give octane and dibutyl telluride.

Despite these studies, really very little is known about the chemistry of selenuranes and telluranes. In particular their structures in solution have received little attention. The role of intramolecular and intermolecular ligand reorganization processes has not been defined. The effect of incorporating the element in a ring has received little attention.

The purpose of the research being reported here was to prepare a number of tetraalkoxyselenuranes and -telluranes and to study their chemistry. Both ^{77}Se and ^{125}Te are NMR active with spin $^{1}/_{2}$, and the absorptions of these nuclei in the molecules under investigation have been obtained. In some cases both T_1 and the nuclear Overhauser effect were measured.

Results and Discussion

Tetraalkoxyselenuranes. It has been found that pentaalkoxyphosphoranes and tetraalkoxysulfuranes are stabilized when the central atom is incorporated in a five-membered ring. A similar effect is apparent with tetraalkoxyselenuranes. Compound **1** has been prepared and it is a relatively stable crystalline solid.[13] The proton NMR spectrum of **1** at room temperature[14] shows a single resonance. When the compound is cooled, the spectrum becomes quite complicated and many lines are evident. Addition of (diethylamino)trimethylsilane, a known acid and water scavenger, led to an extremely complicated but symmetrical ambient spectrum centered at δ 4.07. The ^{13}C NMR spectrum of **1** at room temperature showed only one resonance at δ +65.55. There was no change in the spectrum on cooling to −75 °C.

Compound **3** was also prepared as a crystalline solid. The ^{1}H NMR spectra of several samples of **3** had resonances at δ 1.20 and 1.25 for hydrogens of nonequivalent pairs of methyl groups. On occasion a single resonance was observed; addition of acid scavenger led to separate resonances as described above. At −110 °C a broad absorption was found for the hydrogens of the methyl groups. The ^{13}C NMR spectrum of **3** at room temperature had

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(1) (a) Emsley, J.; Hall, C. D. "The Chemistry of Phosphorus"; Wiley: New York, 1976; Chapter 6. (b) Sheldrick, W. S. *Top. Curr. Chem.* *73*, 1–49. (c) Luckenbach, R. "Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements"; Georg Theime Verlag: Stuttgart, 1973.

(2) (a) Reid, D. H. "Organic Compounds of Sulphur, Selenium and Tellurium"; The Chemical Society: Burlington House, London, WIVOBN; Vol. 1, 1970; Vol. 2, 1973; Vol. 3, 1975; Vol. 4, 1977; Vol. 5, 1979. (b) Martin, J. C., Perozzi, E. F. *Science (Washington, D.C.)* **1976**, *191*, 14. (c) Trost, B. M. *Top. Curr. Chem.* **1973**, *41*, 1–29.

(3) Paetzold, R.; Reichenbacher, M. "Organic Selenium Compounds, Their Chemistry and Biology"; Klayman, D. L., Gunther, W. H. H., Eds.; Wiley: New York, 1973; Chapter IX.

(4) Irgolic, K. J.; Kudchadker, M. V.; "Selenium"; Zingaro, R. A., Cooper, W. C., Eds.; Van Nostrand-Reinhold: New York, 1974; Chapter 8.

(5) Wittig, G.; Fritz, H. *Justus Liebigs Ann. Chem.* **1952**, *577*, 39.

(6) Reich, H. *J. Am. Chem. Soc.* **1973**, *95*, 964.

(7) Irgolic, K. J. "The Organic Chemistry of Tellurium"; Gordon and Breach: New York, 1974.

(8) Meerwein, H.; Bersin, T. *Justus Liebigs Ann. Chem.* **1929**, *476*, 113.

(9) Methrotra, R. C.; Mathur, S. N. *J. Indian Chem. Soc.* **1965**, *42*, 749.

(10) Methrotra, R. C.; Mathur, S. N. *J. Indian Chem. Soc.* **1965**, *42*, 1.

(11) Barton, D. H. R.; Glover, S. A.; Ley, S. V. *J. Chem. Soc., Chem. Commun.* **1977**, 266.

(12) Hellwinkel, D.; Fahrbach, G. *Chem. Ber.* **1968**, *101*, 574.

(13) Paetzold, R.; Reichenbacher, M. *Z. Chem.* **1970**, *10*, 307.

(14) Denney, D. B.; Denney, D. Z.; Hsu, Y. F. *J. Am. Chem. Soc.* **1978**, *100*, 5982.

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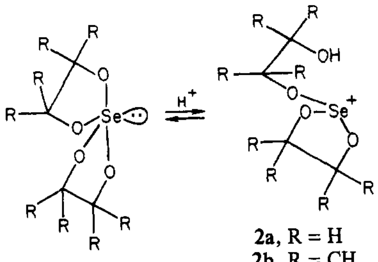


1, R = H
3, R = CH_3

2a, R = H
2b, R = CH_3

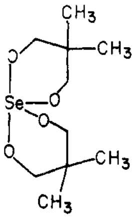
two resonances at δ 24.40 and 24.70 which are assigned to pairs of nonequivalent methyl group carbons. A single resonance for quaternary carbons was found at δ 81.40. At −112 °C, the ^{13}C NMR spectrum of compound **3** exhibited a broad absorption, half-height width of 101 Hz, for methyl group carbons and two absorptions separated by 76 Hz at δ 79.0 and 82.8 for nonequivalent quaternary carbons. The $\Delta G^{\ddagger}$ for the ligand reorganization process is 8 kcal/mol.[15]

The low-temperature ^{13}C NMR spectrum is consistent with a static trigonal-bipyramidal, TBP, or nearly TBP structure. When the compound is warmed, a reorganization process occurs rapidly on the NMR time scale which renders the quaternary carbons equivalent but not the pairs of methyl group carbons. This process most probably involves axial–equatorial switching of the rings with the lone pair remaining in an equatorial position.

The acid-catalyzed process which renders all of the groups equivalent undoubtedly involves **2a** and **2b** in equilibrium with **1** and **3**, respectively. Switching of a,e-positions of the rings by ionization, rotation, and ring closure renders trans groups equivalent. This process coupled with intramolecular ligand reorganization, which renders cis groups equivalent, leads to all of the various groups becoming equivalent.

The crystal structure of **3**[16] reveals it to be a distorted TBP with the distortion away from the lone pair. The apical O–Se bond length is 1.871 Å and the equatorial O–Se bond length is 1.770 Å. The angle O–Se–O in the rings is 85.7° while the O–Se–O angle between the two equatorial oxygens is 109.6°. Schmutzler and co-workers[17] have determined the solid-state structure of a tetraoxysulfurane by X-ray analysis. The material is ca. TBP, with all the bonds bent away from the lone pair with longer axial then equatorial bonds. Their results are similar to those found for **3**.

The selenurane **4** has a ^1H NMR spectrum at room temperature which shows that all of the methylene hydrogens are equivalent as are the hydrogens of the methyl groups. Addition of acid scavenger caused a broadening of the resonance of the methyl group hydrogens and separation of the resonance of the methylene group hydrogens into two broad absorptions. This behavior is of course that expected of an ionization–recombination process. Another ligand reorganization process is also taking place: when the compound is cooled to −90 °C, two resonances were clearly evident in the ^{13}C NMR spectrum for nonequivalent carbons of the methylene groups. The resonance of the carbons of the methyl groups broadened, while that of the quaternary carbons remained sharp. These NMR data are consistent with a TBP or nearly TBP static structure at low temperatures. The $\Delta G^{\ddagger}$ for the ligand reorganization reaction is 10 kcal/mol.



4

$Se(OR)_4$
5, R = CH_3
6, R = C_2H_5
7, R = $(CH_3)_2CH$
8, R = $(CH_3)_3CCH_2$
9, R = CF_3CH_2

Although simple acyclic tetraalkoxyselenuranes have been reported,[3] very little is known about their stability and structure. Two approaches have been used in this work in attempting to prepare these substances. One involved allowing selenium tetrachloride to react with the appropriate alcohol in the presence of triethylamine and the other consisted of condensation of selenium tetrachloride with the appropriate alkoxide.

Attempts to form tetramethoxyselenurane by either method always led to the formation of dimethyl selenite (**10**). When the reaction was conducted in the probe of the NMR spectrometer at −35 °C, a resonance at δ 1176 downfield from dimethyl selenite was observed. This resonance rapidly decayed to give a spectrum which showed that only selenite **10** was present. Similarly formation of tetraethoxyselenurane (**6**) in the probe led to a resonance at δ 1183 which rapidly was replaced by that of diethyl selenite (**11**). It is believed that the initial resonances are those of tetramethoxy- and tetraethoxyselenuranes and that these substances decompose rapidly to the corresponding selenites. These results are somewhat different from those reported, and no explanation for these differences can be offered.

Tetrakis(isopropyloxy)selenurane (**7**) can be prepared and isolated as a crystalline solid. The NMR spectral data for this substance can be found in Table I. The four methine carbons of **7** are found to be equivalent as are the eight methyl group carbons. Variable-temperature ^{13}C NMR measurements down to −100 °C show that these resonances broaden but they never become resolved. Similar results were obtained from variable-temperature ^1H NMR studies. Although no other studies were conducted, it seems safe to conclude that **7** is probably ionizing and also undergoing intramolecular ligand reorganization. A solution of **7** was monitored by ^{77}Se NMR, and it was found that the selenurane decomposed to the corresponding selenite **12** in 48 h.

Tetrakis(neopentyloxy))selenurane (**8**) was prepared and isolated as a crystalline solid which decomposed on attempted sublimation. The ^1H and ^{13}C NMR spectra show that all methylene hydrogens and carbons are equivalent as are the methyl group hydrogens and carbons. The variable-temperature ^{13}C NMR spectra show that there is line broadening on cooling, but no distinct separation of nonequivalent signals could be observed even at −100 °C.

It is well-know that electronegative groups often stabilize hypervalent molecules and as a consequence of this tetrakis(trifluoroethoxy)selenurane (**9**) was prepared and found to be a distillable liquid. The room-temperature ^1H, ^{13}C, and ^{19}F NMR spectra show that all of the potentially equivalent atoms of the trifluoroethyl groups are so. The variable-temperature ^{19}F NMR spectra of **9** show that at −80 °C there are two kinds of trifluoromethyl groups which absorb at δ −80.11 and −81.09. The $\Delta G^{\ddagger}$ for the process that renders them equivalent is 11 kcal/mol; coalescence was found at −34 °C. These results strongly suggest that at low temperatures, **9** exists as a TBP, a result which is in agreement with the proposed structure of selenium tetrafluoride at low temperatures.[18] These findings do not distinguish between inter- and intramolecular ligand reorganization. In view of the stability and volatility of **9** it seems reasonable to conclude that ionization is not taking place and that the reorganization is intramolecular.

Addition of potassium trifluoroethoxide (1 mol) to **9** (1 mol) in the presence of 18-crown-6-ether (1 mol) in benzene caused a change in the ^{77}Se chemical shift from δ 1159 to 1083. When 1.5 mol of salt was added to **9** in the presence of 1.5 moles of 18-crown-6-ether, the ^{77}Se resonance shifted to δ 1021. Further addition up to a 5:1 molar ratio of salt–crown ether to selenurane caused no further change. It is well-known that selenium tetra-

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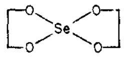
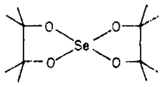
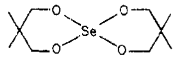
[15] The maximum separation may not have been achieved at −112 °C. A further separation of the two resonances would lead to a slightly lower activation energy.

[16] Private communication from Professor R. R. Holmes.

[17] Hodges, K. C.; Schomberg, D.; Weiss, J.-V.; Schmutzler, R. *J. Am. Chem. Soc.* **1977**, *99*, 6096.

[18] Seppelt, Von K. *Z. Anorg. Allg. Chem.* **1975**, *416*, 12.

Table I[a-c]

compd	^{77}Se NMR	^{1}H NMR			^{13}C NMR			^{19}F NMR	T_1, s
		α	β	γ	α	β	γ		
 **1**	1261	4.07			65.6				
 **3**	1200		1.20 1.25		81.4	24.4 24.7			10.8
 **4**	1053	3.87		0.97	75.0	33.2	23.1		
$Se(OCH_3)_4$ **5**	1176								
$Se(OCH_2CH_3)_4$ **6**	1183								
$Se(OCH(CH_3)_2)_4$ **7**	1287	5.41 (6.0)	1.42 (6.0)		76.5	24.7			
$Se(OCH_2C(CH_3)_3)_4$ **8**	1256	4.27		0.96	79.1	33.3	26.5		
$Se(OCH_2CF_3)_4$ **9**	1159	4.40 (8.5)			63.5 (36)	124.2 (278)		−80.6 (8.5)	
$Se(OCH(CF_3)_2)_4$ **18**	1158							−79.1[d] −77.2[d]	

[a] The numbering system is as follows: Se–O–C_α–C_β–C_γ. Coupling constants are given in hertz and chemical shifts are given in δ. The coupling constants listed in parentheses are $^3J_{HCCH}$, $^3J_{HCCF}$, $^2J_{CCF}$, and $^1J_{CF}$. All ^{1}H NMR spectra integrated areas are correct to better than 10%. [b] T_1 and NOE data are accurate to ±5%. [c] ^{77}Se chemical shifts to low field of Me_2Se are given positive values. [d] Broad.

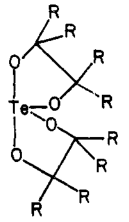
fluoride forms pentafluoroselenates, $MSeF_5$, on reaction with alkali metal fluorides.[19] Other selenium–halogeno complex anions have been shown to favor hexacoordination, SeX_6^{2-}.[20] In the reaction of **9** with trifluoroethoxide ion only a 1.5 mole ratio of salt to selenurane is required to produce the maximum equilibrium displacement as monitored by ^{77}Se NMR. Since formation of a hexacoordinated species would require at least 2 mol of salt, it seems reasonable to conclude that **9** reacts with trifluoroethoxide ion to yield a pentacoordinated (trifluoroethoxy) selenate. The upfield shift of the ^{77}Se resonance is expected of the more highly shielded selenium in the ate complex. The ^{1}H, ^{13}C, ^{19}F, and ^{77}Se NMR spectra of these reaction mixtures indicate that there is a rapid equilibrium between **9**, trifluoroethoxide ion, and the ate complex; i.e. multiple resonances are not found which would be the case if the rate of equilibration were slow.

When hexafluoro-2-propanol was allowed to react with selenium tetrachloride in the presence of triethylamine at −50 °C, a solution was obtained which had a ^{77}Se resonance at δ 1158. The ^{19}F NMR spectrum showed two broad doublets. When the compound is warmed, these resonances disappeared as did the ^{77}Se absorption. Two ^{19}F resonances replaced the original two. One of the new resonances is due to hexafluoro-2-propanol, and the other is most likely due to hexafluoroacetone. The latter evaporated from solution on standing. An interpretation of these results is that tetrakis((hexafluoroisopropyl)oxy)selenurane (**18**) was formed at −50 °C where it was found as a rigid TBP on the NMR time scale and that is decomposed on warming to give selenium, hexafluoroacetone, and hexafluoro-2-propanol.

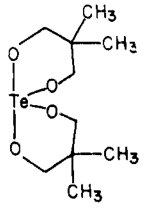
Although it has been possible to prepare a number of phosphoranes[1] and sulfuranes[21] derived from catechol, attempts to prepare such a selenurane by reaction of selenium tetrachloride with dilithio catecholate always led to selenium metal and organic materials which appear to be derived from *o*-quinone.

During the course of this work selenites were often found as byproducts of these reactions, authentic samples of these materials were prepared and their NMR parameters are collected in Table II.

Tetraalkoxytelluranes. Three cyclic tetraalkoxytelluranes, **19–21**, have been prepared. Compound **20** shows in both its ^{1}H and ^{13}C NMR spectra that there are two kinds of methyl groups present at room temperature. In one experiment the proton NMR spectrum showed only one broad resonance at room temperature; addition of acid scavenger produced two resonances for hydrogens of nonequivalent methyl groups. The ^{13}C NMR spectrum shows equivalent quaternary carbons. Variable-temperature ^{13}C NMR studies in one instance led to a spectrum with separate resonances for the quaternary carbons. The temperature was not recorded but it was below −110 °C. In another series broad resonances for methyl group carbons and quaternary carbons were found at −107 °C. These data favor a rearranging TBP structure in solution. The crystal structure has been determined.[16] The molecule exists as a distorted TBP with apical Te–O bond lengths of 2.005 Å, and the equatorial bond lengths are 1.936 Å. The O–Te–O bond angle in the rings is 80.3°, and the O–Te–O angle between the two equatorial oxygens is 105.9°. There is some evidence for intermolecular association.



19, R = H
20, R = CH_3



21

Compounds **19** and **21** were found to be too insoluble for variable-temperature NMR studies. They probably associate in the crystalline state, and this contributes to their insolubility. The ^{1}H and ^{13}C NMR spectra of **21** at room temperature show that all the methylene groups are equivalent as are all of the methyl groups. Dissociation is probably the means by which they become equivalent.

Tetramethoxytellurane (**22**), tetraethoxytellurane (**23**), tetrakis(isopropyloxy)tellurane (**24**), tetrakis(neopentyloxy)tellurane (**25**), tetrakis(trifluoroethoxy)tellurane (**26**), and a 1:1 complex of tetrakis((hexafluoroisopropyl)oxy)tellurane (**27**), with tetra-

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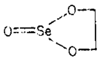
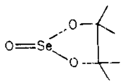
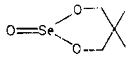
[19] Aynsley, E. E.; Peacock, R. D.; Robinson, P. L. *J. Chem. Soc. A* **1952**, 1231.

[20] Greenwood, N. N.; Straughan, B. P. *J. Chem. Soc. A* **1966**, 962.

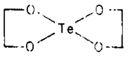
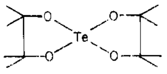
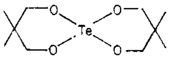
[21] Wilson, G. E., Jr.; Belkind, B. A. *J. Org. Chem.* **1977**, *42*, 765.

Table II[a]

compd	^{77}Se NMR	^{1}H NMR α	^{1}H NMR β	^{1}H NMR γ	^{13}C NMR α	^{13}C NMR β	^{13}C NMR γ	^{19}F NMR	T_1, s	NOE
 15	1430	4.52[c]			70.6					
 16	1409		1.37 1.53		90.8	24.5 24.6			6.7	
 17	1284	4.12[c]		0.82 1.32	68.3	33.0	22.6 21.9		7.4	0.06
$O{=}Se(OCH_3)_2$ 10	1332	3.73			48.8					
$O{=}Se(OCH_2CH_3)_2$ 11	1340	4.17[c]	1.29 (7.0)		57.9	16.6				
$O{=}Se(OCH[CH_3]_2)_2$ 12	1342	4.82[b]	1.29 (6.0) 1.33 (6.0)		66.3	24.6 24.8			11.9	0.19
$O{=}Se(OCH_2C[CH_3]_3)_2$ 13	1341	3.72[c]		0.95	71.2	32.3	26.4			
$O{=}Se(OCH_2CF_3)_2$ 14	1337	4.35[c]			58.1 (37)	124.1 (277)		−79.4 (8.4)	13.1	0.09
$O{=}Se(OCH[CF_3]_2)_2$ 34	1355	5.12[b]			66.7 (36)	121.4 (283)		−77.9[d] −79.0[d]		

[a] The numbering system is as follows: Se-O-C_α-C_β-C_γ. The notation for coupling constants, the convention for ^{77}Se chemical shifts, and the accuracy of data are all as outlined in the footnotes to Table I. [b] Broadened septet. [c] The chemical shift given is the center of a centrosymmetric multiplet. The methylene protons of the compounds are nonequivalent. Second-order effects are observed. The spectrum of each compound could be simulated by using the following values for coupling constants and chemical shifts: **15**, under study; **17**, ABX_3, $^2J_{AB}$ = 12 Hz, $^3J_{AX}$ = 0.5 Hz, $^3J_{BX}$ = 0Hz, δ_A 4.88, δ_B 3.36; **11**, ABX_3, $^2J_{AB}$ = 10 Hz, $^3J_{AX}$ = 7 Hz, $^3J_{BX}$ = 7 Hz, δ_A 4.23, δ_B = 4.11; **13**, AB, $^2J_{AB}$ = 10 Hz, δ_A 3.92, δ_B 3.52; **14**, ABX_3, $^2J_{AB}$ = 12 Hz, $^3J_{AX}$ = 8.4 Hz, $^3J_{BX}$ = 8.4 Hz, δ_A 4.41, δ_B 4.29. [d] Broad.

Table III

compd	^{125}Te NMR	^{1}H NMR α	^{1}H NMR β	^{1}H NMR γ	^{13}C NMR α	^{13}C NMR β	^{13}C NMR γ	^{19}F NMR	T_1, s	NOE
 19	1601									
 20	1526		1.24 1.32		80.1	25.6 25.9			2.99	zero
 21	1355	0.95		3.92	74.5	35.5	22.5			
$Te(OCH_3)_4$ 22	1510	3.83			51.8					
$Te(OCH_2CH_3)_4$ 23	1503	4.09 (7.0)	1.26 (7.0)		59.8	18.9				
$Te(OCH(CH_3)_2)_4$ 24	1523	4.62 (6.0)	1.22 (6.0)		66.1	26.4			2.23	zero
$Te(OCH_2C(CH_3)_3)_4$ 25	1525	3.72		0.93	74.4	33.5	26.7			
$Te(OCH_2CF_3)_4$ 26	1463	4.47 (8.5)			62.6 (36)	124.8 (278)		−80.2 (8.5)	1.57	zero
$Te[OCH(CF_3)_2]_4$·THF 27	1394	4.90[c]	1.91[d] 3.76[d]		70.9 (33)	123.0 (285)	25.9 69.0	−79.4[c]		

[a] The numbering system is as follows: Te-O-C_α-C_β-C_γ. The coupling constants listed in parentheses are $^3J_{HCCH}$, $^3J_{HCCF}$, $^2J_{CCF}$, and $^1J_{CF}$. The accuracy of other data is that outlined in footnotes to Table I. [b] ^{125}Te chemical shifts downfield relative to Me_2Te are given positive values. [c] Broad. [d] Multiplet.

hydrofuran have been prepared, and pertinent spectral data are collected in Table III.

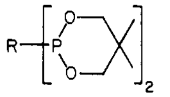
Variable-temperature ^{13}C NMR studies on **22**–**25** showed that all of the lines broadened between −50 and −100 °C. In no case were separate resonances observed for nonequivalent groups. The ^{19}F NMR spectrum of **26** at −90 °C showed a single triplet.

Both **26** and **27** behave as Lewis acids. Addition of triethylamine to a solution of **26** caused a shift in the ^{125}Te resonance from δ 1462 to 1413. The 1:1 complex of **27** with tetrahydrofuran was stable enough to be distilled.

Reaction of tetrakis(trifluoroethoxy)tellurane with potassium trifluoroethoxide ion in the presence of 18-crown-6-ether followed a pattern similar to that found for the analogous selenurane. Initially the ^{125}Te resonance was found at δ 1447; after the addition of 1 mol of base it shifted to δ 1352, and, after 1.5 mol was added, it was found at 1251. Further addition up to 5:1 ratio of base to **26** led to no further change in the ^{125}Te NMR absorption. The preparation and study of the pentafluorotellurate ion, TeF_5^- are widely documented.[22,23] Other tellurium–halogeno complexes are known to prefer hexacoordination,[20] TeX_6^{2-}, although pentachlorotellurates have been identified in a few instances.[24] The explanation preferred for the reaction of **26** with trifluoroethoxide ion follows that outlined for the reaction of the analogous selenurane **9**. It is suggested that the tellurane reacts with trifluoroethoxide ion to give a pentacoordinated trifluoroethoxy tellurate species. Both the ^{1}H and ^{13}C NMR spectra show broad almost featureless lines which indicates that the exchange process is relatively slow at the higher molar ratios of salt to tellurane.

Recently Holmes[25] has reviewed the current understanding of the structures and ligand reorganizations of cyclic pentacoordinated molecules of main-group elements. The evidence indicates that the barriers to intramolecular ligand reorganizations are somewhat higher for five-membered rings containing tetraalkoxysulfuranes analogous to **1** and **3** than for related phosphoranes. In fact it has not been possible to determine the barriers to e–a switching in phosphoranes structurally similar to **1** and **3**. The activation energy, 8 kcal/mol, found for the intramolecular ligand reorganization of **3** is very similar to values reported for a number of tetraalkoxysulfuranes containing two five-membered rings.[25]

Sulfuranes similar to **4** are unknown. The pentaalkoxyphosphorane, **28**, and the tetraalkoxyphosphoranes, **29** and **30**,



28, R = OC_2H_5
29, R = C_6H_5
30, R = CH_3

$M(OR)_n$

31, M = S, R = $OC(CF_3)_3$, $n = 4$
32, M = P, R = $OC(CF_3)_3$, $n = 5$
33, M = P, R = OCH_2CF_3, $n = 5$

have been prepared, and their variable-temperature ^{1}H NMR spectra have been recorded.[26] In the case of **28**, there was no change in the ^{1}H NMR spectrum from −65 °C to ambient. It was concluded that intramolecular reorganization was rapid over the temperature range and that the rings continued to adopt diequatorial dispositions. Compounds **29** and **30** had variable-temperature ^{1}H NMR spectra which indicated the phenyl and methyl groups adopted a favored equatorial position with continued e–a switching of the rings. It should be noted that a static square or rectangular pyramid with phenyl or methyl apical also satisfies these data. It seems probable that the activation energy for ligand reorganization of **4** is higher than that of **28**. Very similar δ values for protons of **28** could invalidate this conclusion.

Very little is known about activation energies for ligand rearrangements in simple acyclic alkoxysulfuranes, selenuranes, telluranes, and phosphoranes. Shreeve and co-workers[27,28] have prepared **31** and **32**. They report that the "^{19}F NMR spectrum is composed of two broad resonances of equal area at δ 68.5 and 70.8". One might conclude that **31** is rigid at room temperature. On the other hand, compound **32** has a single resonance in its ^{19}F NMR spectrum and it is concluded that rapid ligand exchange is occurring. No variable-temperature NMR measurements were reported.

Recently, **33**[29] has been prepared and its ^{19}F NMR spectrum has been shown to not change over the temperature range investigated. This result should be compared to that found for **9**, $\Delta G^{\ddagger} = 11$ kcal/mol.

The results of this work and those cited support the suggestion that structurally similar tetraalkoxysulfuranes and -selenuranes have similar energy barriers toward intramolecular ligand reorganization and that these may be slightly higher than those of telluranes, whereas pentaalkoxyphosphoranes have significantly lower barriers than any of the others. It is tempting to conclude that the presence or absence of the nonbonding electron pair on the central atom not only influences structures but also affects the rates of ligand reorganization. This latter behavior may be due to an interaction between the lone pair on the central atom and the lone pairs on oxygen as the transition state for ligand reorganization is approached. Such an interaction does not occur during pentaalkoxyphosphorane rearrangement.

Selenium and Tellurium NMR. Studies in the field of ^{77}Se NMR have to date been relatively few.[30] Two problems associated with observation of this nucleus are its low abundance (7.5%) and its low NMR sensitivity (6.97×10^{-3} relative to the proton). ^{77}Se chemical shifts have been recorded by using double resonance[31,32] and direct observation techniques.[33-35] These shifts cover a wide range of at least 2200 ppm. More recently, with the advent of improved Fourier transform techniques attention has turned to the optimization of the ^{77}Se NMR experiment. To this end several workers have determined the spin–lattice relaxation time (T_1) and the nuclear Overhauser enhancement (NOE) of the ^{77}Se nucleus in some simple molecules.[36,37] Typically T_1's were found to be of the order of 10 s and any NOE was negligibly small. Spin rotation and chemical shift anisotropy were identified as the most important mechanisms of spin–lattice relaxation for the ^{77}Se nucleus in small molecules. The current work measured ^{77}Se NMR chemical shifts for a range of variously substituted selenuranes and selenites. These shifts are recorded in Tables I and II along with spin–lattice relaxation times and NOE's for selected compounds. The results show that among selenuranes and among selenites the ^{77}Se NMR chemical shift is measurably influenced by variations in ligand properties. The accumulated data do not permit any clear correlation between changes in chemical shift and factors such as ligand electronegativity or ring size. However, the results of this and of other studies demonstrate that ^{77}Se NMR is potentially a valuable diagnostic technique. For example, by monitoring the ^{77}Se NMR at −30 °C it was possible to observe formation of tetramethoxyselenurane and subsequent decomposition of this to give dimethyl selenite.

As seen in Tables I and II the ^{77}Se spin–lattice relaxation times determined for four selenites and a single selenurane fall in the range 6.7–13.1 s. These values are of the same order as those found by Ellis[36b] for other small selenium-containing molecules. The very small nuclear Overhauser effects follow the same pattern that has so far been determined for other selenium compounds. A potentially large NOE of 3.61 exists. The almost negligible enhancements indicate that dipole–dipole interactions contribute little to spin–lattice relaxation of the selenium nucleus in selenites. The low efficiency of the dipole–dipole mechanism is probably a consequence of the relatively long Se–H distances which are dictated in part by the size of the selenium atom. In these compounds it is expected that, as elsewhere, spin-rotation and chemical shift anisotropy are the principle contributory mechanisms to ^{77}Se spin–lattice relaxation.

The field of ^{125}Te NMR is less well developed than that of ^{77}Se

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NMR.[30] There have been few reports of observation of the ^{125}Te nucleus by either direct[38,39] or indirect means.[40,41] The ^{125}Te isotope has $I = {}^1/_2$, a natural abundance of 7%, and a sensitivity of 3.16×10^{-2} relative to that of the proton. This sensitivity is an order of magnitude larger than that of ^{77}Se. These factors appear to make ^{125}Te a favorable nuclide for NMR study. One problem, however, is that where nuclear Overhauser effects become important the negative gyromagnetic ratio of the ^{125}Te nucleus may attenuate sensitivity.

Literature reports have documented ^{125}Te NMR shifts covering a range of 4000 ppm. Only one report of a ^{125}Te spin–lattice relaxation time has been found, and no details of experimentally determined NOE's have been found.

The current work measured ^{125}Te NMR chemical shifts of a series of variously substituted telluranes. These shifts are presented in Table III together with ^{125}Te spin–lattice relaxation times and NOE's of three compounds. The results show that the ^{125}Te NMR chemical shifts of telluranes are influenced to a measurable degree by variation of the ligands. There appears to be no obvious correlation between changes in chemical shift and change in ligand properties.

The three T_1's found for the telluranes fall in the range 1.5–3.0 s. These values are of the same order as the previously reported ^{125}Te T_1 of 1.1 s for diethyl telluride.[38] Despite a potentially large negative NOE of −2.58 for this nucleus, no Overhauser effects were observed in any of the telluranes studied. The very short T_1's of these compounds are indicative of efficient spin–lattice relaxation processes. The absence of any NOE precludes the involvement of dipole–dipole interactions in the relaxation. This is probably due to the size of the tellurium atom and the long Te–H distances involved.

The accumulated data on ^{125}Te relaxation times are not yet sufficient to permit broad conclusions. Early indications are that short T_1's permit fast recycle times and that potentially adverse NOE's present little or no problem.

Experimental Section

^{1}H NMR spectra were recorded with a Varian Model T-60 spectrometer. Chemical shift values are reported in parts per million relative to internal tetramethylsilane. ^{13}C, ^{19}F, ^{77}Se, and ^{125}Te NMR spectra were recorded with a Varian Model FT-80 spectrometer equipped with a variable-temperature broad-band probe. In all cases nuclei which are deshielded relative to their respective standard are assigned a positive chemical shift. ^{13}C NMR spectra were obtained by using full proton decoupling, a 45° flip angle, and a 2-s repetition rate with no pulse delay. All ^{13}C chemical shifts are reported in parts per million relative to internal tetramethylsilane. ^{19}F NMR spectra were acquired by using a 90° flip angle, a 5-s repetition rate with no pulse delay, and full proton coupling. Chemical shifts are reported in parts per million relative to external trichlorofluoromethane.

^{77}Se NMR spectra were recorded with the broad-band probe tuned to 15.168 MHz. Approximate shifts of previously unknown selenurane absorptions were located by employing a 24-KHz spectral width,[42] a 45° flip angle, and a repetition time of 0.35 s. Once the position of a resonance had been estimated then the exact chemical shift was determined by using a 8-KHz spectral width, a 45° flip angle, full proton decoupling, and a repetition rate of 1 s. These parameters were also employed for the ^{77}Se NMR spectra of the various selenites. All reported chemical shifts are referenced to external dimethyl selenide. Large shift values prevented standard methods of internal and external referencing. A sealed 2 M solution of dimethyl selenide in benzene-d_6 was prepared, and the resonance frequency of this was established as 15 170 121 Hz. Chemical shift values were then calculated by frequency difference.

^{125}Te NMR spectra were recorded with the probe tuned to 25.129 MHz. The positions of previously unknown tellurane resonances were located by using a 24-KHz spectral width and then positively identified by using an 8-KHz spectral width, a pulse width of 45°, full proton decoupling, and a recycle time of 1 s. The chemical shift values are referenced to dimethyl telluride. A sealed 2 M solution of dimethyl telluride in benzene-d_6 was found to resonate at 24 095 324 Hz, and all tellurane shifts were subsequently calculated by frequency difference from this standard.

^{77}Se and ^{125}Te spin–lattice relaxation times were measured by using the inversion–recovery pulse sequence, $(180°–\tau–90° - T)_n$. For both nuclei the experiments employed a spectral width of 1 KHz, a 90° pulse width of 12 μs, and a recycle time of six T_1's. Samples were degassed by bubbling with argon. Nuclear Overhauser effects were determined by comparison of integrated spectral intensities obtained from experiments by using different decoupling techniques. First, with the decoupler on throughout, a fully proton-decoupled spectrum was recorded by using a spectral width of 1 KHz, a 90° pulse width of 12 μs, an acquisition time of 1 s, and a pulse delay of 10 T_1's. A second experiment employed identical spectral parameters but gated the decoupler off during the pulse delay. The difference in integrated spectral intensities between these two modes of decoupler operation is a measure of the NOE enhancement factor (η). Values of the NOE itself are reported as $1 + \eta$.

Materials. All alcohols and diols were obtained from commercial sources and then dried and purified by literature methods prior to use. All solvents were also rigorously dried. Tellurium tetrachloride and selenium tetrachloride were obtained commercially. Selenium tetrachloride required purification by vacuum sublimation prior to use.

Preparation of 1. Compound **1** was prepared as previously reported.[13] To a solution containing selenium tetrachloride (2.20 g, 0.01 mol) and 1,2-ethanediol (1.24 g, 0.02 mol) in tetrahydrofuran (50 mL) at −40 °C was added dropwise a solution of triethylamine (4.05 g, 0.04 mol) in tetrahydrofuran (20 mL). After removal of solids by filtration, the mixture was stored at −45 °C. The white crystals which formed were washed twice with tetrahydrofuran at −45 °C and then dried in vacuo: mp 100–103 °C (lit.[13] 102 °C]; mass spectrum, *m/e* 199 (molecular ion).

Preparation of 3. The method of preparation of **3** was exactly that described for **1**. Using 2,3-dimethyl-2,3-butanediol, selenium tetrachloride, and triethylamine, a white crystalline product was obtained. This was purified by sublimation at 60–70 °C (0.03 mm); mp 89–91 °C.

Anal. Calcd for $C_{12}H_{24}O_4Se$: C, 46.30; H, 7.77. Found: C, 46.57; H, 7.75.

Preparation of 4. Dropwise addition of triethylamine (6.01 g, 0.06 mol) in tetrahydrofuran (20 mL) to a solution of selenium tetrachloride (3.27 g, 0.015 mol) and 2,2-dimethyl-1,3-propanediol (3.09 g, 0.03 mol) in tetrahydrofuran (50 mL) at −40 °C gave a mixture from which the solids were removed by filtration. The solution was concentrated and stored at −40 °C. The supernatant liquid was removed, and the pink crystalline product was washed three times with tetrahydrofuran at −45 °C before being dried in vacuo. Attempted purification by sublimation led to extensive decomposition to give selenite **17**. Variable-temperature ^{13}C NMR studies were conducted without further purification after ^{1}H, ^{13}C, and ^{77}Se NMR spectra showed the compound to be of high if not analytical purity.

Preparation of Tetrakis(isopropyloxy)selenurane (7). Selenium tetrachloride (4.46 g, 0.02 mol) was dissolved in tetrahydrofuran (30 mL), and to this was added propan-2-ol (4.85 g, 0.081 mol). To this solution at −30 °C was added dropwise triethylamine (8.17 g, 0.081 mol) in tetrahydrofuran (30 mL). When the addition was completed, the mixture was allowed to warm to room temperature, and it was then filtered immediately. The filtrate was concentrated and stored at −40 °C for 16 h. The white crystalline product was then washed twice with cold tetrahydrofuran and dried in vacuo. The compound was extremely hygroscopic and decomposed before melting.

Preparation of Tetrakis(neopentyloxy)selenurane (8). Compound **8** was obtained by the preparative method described for **7**. A pink crystalline material was obtained which ^{77}Se, ^{13}C, and ^{1}H NMR confirmed to be a mixture of selenurane **8** (95%) and the corresponding selenite **13**, (5%). Attempted purification of the selenurane by either sublimation or distillation resulted in total decomposition to the selenite.

Preparation of Tetrakis(2,2,2-trifluoroethoxy)selenurane (9). To a solution containing selenium tetrachloride (2.98 g, 0.0134 mol) and 2,2,2-trifluoroethanol (5.40 g, 0.054 mol) in tetrahydrofuran (30 mL) at −40 °C was added dropwise triethylamine (5.46 g, 0.054 mol) in tetrahydrofuran (20 mL). Solids were removed by filtration, the solution was concentrated, and the selenurane was distilled as a colorless liquid, bp 114–115 °C (20 mm).

Attempted Preparation of Tetrakis((hexafluoroisopropyl)oxy)selenurane (18). To a stirred solution of selenium tetrachloride (2.79 g, 0.0125 mol) and hexafluoroisopropanol (8.49 g, 0.05 mol) in tetrahydrofuran (40 mL) at −50 °C was added dropwise triethylamine (5.11 g, 0.05 mol) in tetrahydrofuran (20 mL). For removal of solids an aliquot of the mixture was centrifuged for short intervals under nitrogen. The temperature of

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the sample was maintained below −30 °C by periodic immersion in a dry ice/acetone bath. The ^{77}Se NMR spectrum of the supernatant liquid at −30 °C showed an absorption at δ 1158. The ^{19}F NMR spectrum at −30 °C consisted of two broad absorptions separated by 131 Hz. When the temperature of the probe was raised to 0 °C and the ^{19}F NMR spectrum was monitored for 1 h, it showed a gradual decomposition of the selenurane **18** to give two doublets. No ^{77}Se resonance could be detected for the decomposition products. On removal from the probe a red precipitate was observed. After the precipitate was left standing at room temperature for 1 h, the ^{19}F NMR spectrum showed one doublet at δ 80.8 (J_{HCCF} =v 6.5 Hz).

Attempted Preparation of Tetramethoxyselenurane (5). Selenium tetrachloride (3.24 g, 0.015 mol) was dissolved in scrupulously dried tetrahydrofuran (25 mL), and to this was added methanol (1.88 g, 0.059 mol) in tetrahydrofuran (25 mL). To this solution at −60 °C was added dropwise triethylamine (5.94 g, 0.059 mol) in tetrahydrofuran (30 mL). When the addition was completed, a sample of the reaction mixture was centrifuged under nitrogen. The temperature was maintained below −35 °C by periodic immersion in a dry ice/acetone bath. The ^{77}Se NMR spectrum showed a resonance at δ 1170. The NMR spectrum of the same sample monitored at ambient temperature over 10 h showed emergence of a resonance at δ 1332.

In a similar reaction, immediately after the addition of triethylamine the solids were removed by filtration under nitrogen and the solution was concentrated. The ^{77}Se NMR recorded immediately showed a single resonance at δ 1332.

Synthesis of **5** was also attempted by dropwise addition of a solution of sodium methoxide prepared from sodium (1.69 g, 0.074 mol) in methanol/tetrahydrofuran (30 mL, 50:50) to a solution of selenium tetrachloride (3.98 g, 0.018 mol) in tetrahydrofuran (30 mL). The ^{77}Se NMR spectrum was recorded immediately at −35 °C. It invariably showed a major resonance at δ 1332 and occasionally a small peak at δ 1219.

Attempted Preparation of Tetraethoxyselenurane (6). The methods employed were directly analogous to those used for the attempted preparation of **5**. Crude reaction mixtures were monitored by ^{77}Se NMR at temperatures between −35 and −70 °C immediately after the additions were completed. Invariably the major absorption (> 95%) was found at δ 1341, and on one occasion only was a second small resonance observed at δ 1183.

Preparation of 15. Selenium dioxide (5.10 g, 0.046 mol) was added to 1,2-ethanediol (2.87 g, 0.046 mol) in benzene (100 mL), and the mixture was heated under reflux for 16 h at 95 °C by using a Dean–Stark apparatus. After filtration, the solvents were removed in vacuo to give the selenite as a white solid which was purified by sublimation at 55 °C (0.03 mm); mp 64–66 °C (lit.[43] 64–65 °C).

Preparation of 16. Selenium dioxide (4.15 g, 0.037 mol) was suspended in benzene (90 mL), and to this was added 2,3-dimethyl-1,2-butanediol (4.42 g, 0.037 mol). Azeotropic distillation for 60 h at 95 °C yielded a brown solution which was then filtered, and the solvent was removed to give a yellow-brown solid. This material was recrystallized from tetrahydrofuran at −40 °C and then purified by sublimation at 65 °C (0.08 mm); mp 115.5–116.5 °C.

Anal. Calcd for $C_6H_{12}O_3Se$: C, 34.13; H, 5.73. Found: C, 34.15; H, 5.84.

Preparation of 17. 2,3-Dimethyl-1,3-propanediol (4.21 g, 0.04 mol) was added to selenium dioxide (4.49 g, 0.04 mol) suspended in benzene (90 mL). Heating under reflux for 60 h at 95 °C gave a pale yellow solution. After removal of the benzene, tetrahydrofuran was added. The solution was then filtered and allowed to stand at −45 °C. Pink crystals were isolated and purified by sublimation at 60 °C (0.08 mm) to give a white solid, mp 84.5–86 °C.

Anal. Calcd for $C_5H_{10}O_3Se$: C, 29.88; H, 5.09. Found: C, 30.47; H, 5.11.

Preparation of Bis(2,2,2-trifluoroethyl) Selenite (14). Dropwise addition of 2,2,2-trifluoroethanol (10 g, excess) to sodium in tetrahydrofuran (10 mL) gave the corresponding alkoxide. This solution was then added dropwise to a solution of selenium dichloride oxide (2.45 g, 0.015 mol) in tetrahydrofuran (10 mL) at 0 °C. The solids were separated by centrifugation. The solvents were then removed in vacuo, and the selenite was isolated by distillation at 115 °C (39 mm).

Anal. Calcd for $C_4H_4F_6O_3Se$: C, 16.39; H, 1.37. Found: C, 16.32; H, 1.36.

Preparation of Bis(hexafluoroisopropyl) Selenite (34). Hexafluoro-2-propanol (6.78 g excess) was added dropwise to sodium (0.79 g, 0.034 mol) in tetrahydrofuran (10 mL); this solution was then added to a stirred solution of selenium dichloride oxide (2.85 g, 0.017 mol) in tetrahydrofuran (10 mL). When the addition was completed, the reaction mixture was centrifuged under nitrogen and the solids were removed. The solvents were removed in vacuo, and the selenite was isolated as a white solid by distillation at 84 °C (38 mm); mp 40–42 °C. The compound was hydrolytically unstable and produced white fumes when exposed to air.

Preparation of Other Acyclic Dialkyl Selenites. Dimethyl selenite (**10**) was invariably isolated as the lone selenium-containing product from the attempted preparations of tetramethoxyselenurane (**5**). The compound was identified by its ^{77}Se NMR absorption at δ 1332. It is a colorless liquid, bp 62 °C (8 mm) (lit.[44] 67 °C (10 mm)).

Diethyl selenite (**11**) was isolated as the lone selenium-containing product from attempted preparations of tetraethoxyselenurane (**6**). Distillation gave a colorless liquid, bp 60 °C (9 mm) (lit.[44] 76 °C (10 mm)).

Diisopropyl selenite (**12**) was isolated in a number of instances in attempted preparations of the corresponding selenurane. The selenite **12** distilled as a colorless liquid, bp 120 °C (41 mm) (lit.[44] 88 °C (4.5 mm)).

Dineopentyl selenite (**13**) was obtained after both attempted sublimation and distillation of tetrakis(neopentyloxy)selenurane (**8**) had led to decomposition of that material. The selenite distilled as a colorless liquid, bp 74–76 °C (0.3 mm).

Preparation of 19. Tellurium dioxide (6.0 g, 0.038 mol) was suspended in 1,2-ethanediol (20 mL, excess), and the mixture was heated under reflux at 90 °C under slight vacuum for 16 h. The mixture was filtered while hot and yielded a white crystalline product on cooling. This material was separated by filtration, dried, and then purified by sublimation at 150 °C (0.25 mm); mp 207–210 °C (lit.[43] 209–210 °C).

Anal. Calcd for $C_4H_8O_4Te$: C, 19.39; H, 3.26. Found: C, 19.32; H, 3.35.

Preparation of 20. Dropwise addition of triethylamine (5.01 g, 0.05 mol) to a stirred solution of 2,3-dimethyl-2,3-butanediol (2.92 g, 0.025 mol) and tellurium tetrachloride (3.33 g, 0.0125 mol) in tetrahydrofuran (60 mL) at 40 °C gave a white precipitate of triethylamine hydrochloride which was removed by filtration. The filtrate was concentrated, and white crystals were obtained on standing at −45 °C. These were washed twice with tetrahydrofuran at −45 °C, dried, and then purified by sublimation at 90 °C (0.25 mm) (lit.[9] 110 °C (0.5 mm)); mp 129.5–130 °C.

Anal. Calcd for $C_{12}H_{24}O_4Te$: C, 40.04; H, 6.72. Found: C, 40.01; H, 6.80.

Preparation of 21. To a stirred solution of tellurium tetrachloride (4.0 g, 0.015 mol) and 2,2-dimethyl-1,3-propanediol (3.10 g, 0.03 mol) in tetrahydrofuran (70 mL) at −40 °C was added dropwise triethylamine (6.01 g, 0.06 mol) in tetrahydrofuran (30 mL). Removal of the solids gave a clear yellow filtrate which on concentration at room temperature precipitated a small amount of white solid. This material was isolated by filtration but further purification proved impossible due to its extremely low solubility in the solvents tested. They were tetrahydrofuran, benzene, dimethyl sulfoxide, pyridine, pentane, ether, and chloroform. Spectra were obtained by using a dilute solution of **21** in methylene chloride. The material did not sublime.

Preparation of **21** was also attempted by exchange of tetraethoxytellurane (**23**) (0.88 g, 0.003 mol) with 2,2-dimethyl-1,3-propanediol (0.61 g, 0.006 mol). After azeotropic distillation with benzene (15 mL) for 48 h, the crude reaction mixture showed a ^{125}Te NMR absorption at δ 1352. This indicated a successful exchange. Addition of pentane precipitated a gray-white material which, as before, could not be purified further. Reaction of the diol with tellurium dioxide gave no indication of reaction.

Preparation of Tetramethoxytellurane (22). A solution of triethylamine (7.55 g, 0.075 mol) in tetrahydrofuran (30 mL) was added dropwise to a stirred solution of tellurium tetrachloride (5.03 g, 0.0185 mol) and methanol (2.38 g, 0.075 mol) in tetrahydrofuran (40 mL) at −40 °C. After the mixture was allowed to warm to room temperature, the solids were removed by filtration. The volume of the filtrate was then reduced, and the solution was allowed to stand at −45 °C. A white crystalline product was obtained. It was washed twice with tetrahydrofuran, dried, and then purified by sublimation at 53–55 °C (0.03 mm) (lit.[10] bp 115 °C (9 mm)).

Preparation of Tetraethoxytellurane (23). To a stirred, ice-water-cooled solution of tellurium tetrachloride (8.79 g, 0.033 mol) in tetrahydrofuran/benzene (100 mL, 50:50) was added dropwise a solution of sodium ethoxide prepared by adding sodium (3.0 g, 0.13 mol) to ethanol (50 mL). Following difficult removal of sodium chloride by filtration, the solution was concentrated and the residue was distilled (bp 100 °C (0.25 mm) (lit.[10] 107–107.5 °C (5 mm)) to yield **23** as a colorless liquid.

Preparation of Tetrakis(isopropyloxy)tellurane (24). The method of preparation of **24** was analogous to that described for **23**. Replacing

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ethanol with propan-2-ol yielded **24** as colorless liquid which distilled; bp 73–74 °C (0.5 mm) (lit.[10] 76 °C (0.5 mm)).

Preparation of Tetrakis(neopentyloxy)tellurane (25). To a stirred solution of tellurium tetrachloride (5.42 g, 0.02 mol) and neopentyl alcohol (6.93 g, 0.08 mol) in tetrahydrofuran (50 mL) at 0 °C was added dropwise triethylamine (7.98 g, 0.08 mol) in tetrahydrofuran (20 mL). The precipitate which formed was removed by filtration to give a pale brown solution which was then reduced in volume. Attempts to precipitate **25** from solution found little success although addition of pentane and storage at −45 °C gave a small amount of white solid. The solution was then evaporated to dryness to give an off-white colorless powder. This material proved soluble in most common organic solvents, and this precluded recrystallization. Dissolution in acetonitrile followed by cooling gave only cloudy suspensions. Attempted sublimation of the crude solid material at 0.03 mm resulted only in melting with probable decomposition at 70 °C. A crude sample of **25** was shown by ^{125}Te, ^{13}C, and ^{1}H NMR to be of high if not analytical purity and was therefore studied in solution without further purification.

Preparation of Tetrakis(2,2,2-trifluoroethoxy)tellurane (26). 2,2,2-Trifluoroethanol (14 g, 0.14 mol) was added dropwise to sodium (2.36 g, 0.10 mol) suspended in tetrahydrofuran (40 mL). This solution was then added to a solution of tellurium tetrachloride (6.89 g, 0.025 mol) in tetrahydrofuran (30 mL) at −40 °C. When the addition was completed, the reaction mixture was centrifuged under nitrogen and the solids were removed. The solvents were then removed, and the residue was distilled to yield **26** as a colorless liquid, bp 79–80 °C (0.7 mm).

Anal. Calcd for $C_8H_8F_{12}O_4Te$: C, 18.34; H, 1.54. Found: C, 18.19; H, 1.58.

Preparation of Tetrakis((hexafluoroisopropyl)oxy)tellurane–THF Adduct (27). Hexafluoro-2-propanol (15 g, excess) was added dropwise to sodium (1.0 g, 0.044 mol) suspended in ice-water-cooled tetrahydrofuran (40 mL). This solution was then added dropwise to a solution of tellurium tetrachloride (2.93 g, 0.011 mol) in tetrahydrofuran (20 mL) at ambient temperature. The mixture was allowed to stand for 20 h, and it was then centrifuged to remove solids. After removal of solvents, distillation of the residue gave a colorless liquid, bp 60–62 °C (0.07 mm). Attempts to redistill this material resulted in partial breakdown of the complex.

Reaction of 9 with Potassium Trifluoroethoxide. The reactants were mixed initially in a unimolar ratio. Tetrakis(2,2,2-trifluoroethoxy)selenurane (**9**) (0.394 g, 0.83 mmol) was dissolved in benzene (1.5 mL). The ^{77}Se NMR spectrum showed an absorption at δ 1159. To this solution at 0 °C was added dropwise a solution of potassium 2,2,2-trifluoroethoxide (0.114 g, 0.83 mmol) and 18-crown-6-ether (0.219 g, 0.83 mmol) in benzene (2 mL). This mixture showed a ^{77}Se resonance at δ 1083.

The reaction was then repeated in an identical manner but using a 1.5:1 molar ratio of trifluoroethoxide/18-crown-6-ether to selenurane. The resulting solution showed a broad ^{77}Se NMR signal at δ 1021. Further addition of trifluoroethoxide/18-crown-6-ether to this solution gave a 5:1 molar excess over the selenurane. This caused no further change in the ^{77}Se chemical shift which remained at δ 1021. No further purification of any reaction mixtures was attempted.

Reaction of 26 with Potassium Trifluoroethoxide. The reactants were mixed initially in a equimolar ratio. Tetrakis(2,2,2-trifluoroethoxy)tellurane (**26**) (0.374 g, 0.715 mmol) was dissolved in benzene (1.5 mL). The ^{125}Te NMR spectrum showed a resonance at δ 1463. To this solution was added dropwise a solution of potassium 2,2,2-trifluoroethoxide (0.100 g, 0.715 mmol) and 18-crown-6-ether (0.190 g, 0.715 mmol) in benzene (2 mL). This mixture showed a ^{125}Te NMR absorption at 1352 ppm.

In a similar reaction using a 1.5:1 mole ratio of trifluoroethoxide/18-crown-6-ether to tellurane, a mixture with a broad ^{125}Te NMR signal at δ 1251 was obtained. Further addition of trifluoroethoxide to the mixture resulted in a 5:1 molar excess over the tellurane. This caused no change in the ^{125}Te chemical shift.

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Isolation and Characterization of Pyrimidine–Psoralen Photoadducts from DNA

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Abstract: We have examined the photoadducts of 4′-hydroxymethyl-4,5′,8-trimethylpsoralen (HMT) and native DNA. Five nucleoside–HMT monoaddition products have been isolated and characterized, corresponding to three deoxythymidine–HMT and two deoxyuridine (derived from deoxycytidine)–HMT adducts. Structural assignments are based on high resolution mass spectrometry and ^{1}H NMR studies, including homonuclear spin decoupling and nuclear Overhauser effect (NOE) experiments. The results of this study indicate that (1) a limited number of nucleoside–psoralen adducts are formed with native, double-stranded DNA, and (2) the stereochemistry of the adducts is apparently determined by the geometry of the noncovalent intercalative complex formed by HMT and DNA prior to irradiation.

Introduction

The family of furocoumarin derivatives known as psoralens has been actively investigated both with regard to their ability to act as dermal photosensitizing agents and as probes of nucleic acid structure and function.[1,2] The biological activity of psoralens is primarily the result of the covalent bonding they undergo with nucleic acids, especially DNA. This process is believed to involve three distinct steps: (1) noncovalent, intercalative binding to the DNA helix; (2) upon irradiation at 365 nm, formation of a monoaddition product between the psoralen and a DNA base, probably, but not necessarily exclusively, a pyrimidine residue; and (3) absorption of a second photon by some monoadducts to form diadducts, which results in interstrand cross-linking.[1,3] Model studies, for the most part carried out with nucleosides or pyrimidine bases, have suggested that the mono- and diadducts result from a cyclophotoaddition between the 5,6 bond of the pyrimidine and the 3,4 (pyrone) or 4′,5′ (furan) bond of the psoralen.[4-6] For diadducts to be formed with 365-nm irradiation,

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