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Reaction of SeO_2 with Aromatic Ditellurides. Synthesis and Characterization of Bis(benzenetellurenyl) and Mixed Benzenetellurenyl Benzenetellurinyl Selenides

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The reaction between diaryl ditellurides and selenium dioxide results in the insertion of selenium between the tellurium atoms. The products are identified as benzenetellurenyl benzenetellurinyl selenides, Ar-Te—Se—Te(O)Ar. When a carbonyl group is present ortho to the tellurium atom, a bis(benzenetellurenyl) selenide is formed. The stability of the latter is attributed to Te···O=C interaction. The structures are corroborated by ^1H, ^{13}C, ^{125}Te, and ^{77}Se NMR studies and confirmed crystallographically. The fate of the oxygen from the SeO_2 has not been unequivocally determined, but highly oxygenated insoluble products are formed. These are probably ditellurones or tellurinic acid anhydrides. The tellurium-selenium-tellurium bond is quite stable, much more so, for example, than the sulfur-selenium-sulfur bond.

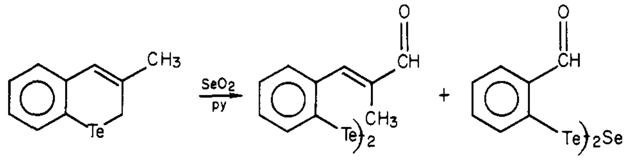
Introduction

The reaction of SeO_2 or $SeOCl_2$ with organic thiols or selenols to form disulfenyl or diselenenyl selenides has been previously reported (eq 1).[1] Aliphatic tellurols are very

$$4RXH + SeO_2 \rightarrow (RX)_2Se + RXXR + 2H_2O$$
$$X = S, Se$$

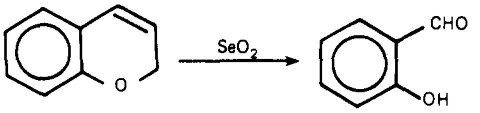
unstable compounds, and aromatic tellurols are not yet characterized. Consequently, a corresponding reaction with tellurols has not been reported. However, bis(benzenetellurenyl) selenide (**1a**) was synthesized by Hauge and Vikane[2] from diphenyl ditelluride (**1**) by using a different synthetic route. This work served to confirm the stability of this type of compound. In an earlier investigation,[3] bis(2-formylbenzenetellurenyl) selenide (**2a**) was obtained as an unexpected byproduct when 3-methyltellurochromene (**3**) was subjected to oxidation by SeO_2. Chromene (**4**) has been shown to yield salicylaldehyde (**5**) when oxidized by SeO_2.[4] Hence, **2a** might be formed by the oxidation of the tellurium analogue of **5**, which in the oxidized form would by **2**. In fact, **2** was found to undergo reaction with SeO_2 to yield **2a**.[3] The reaction was quite unexpected in view of the fact that SeO_2 does not undergo any reaction with either disulfides or diselenides. In this paper the reaction between SeO_2 and a series of aromatic ditellurides is described.

$$\underset{\mathbf{1}}{(C_6H_5)_2Te_2} + KSeCN + Br_2 \rightarrow \underset{\mathbf{1a}}{(C_6H_5Te)_2Se}$$



3

2a



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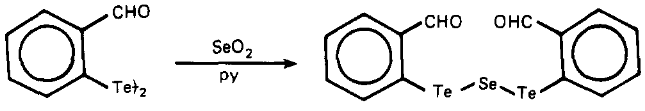
5



2

2a

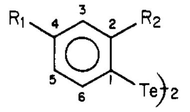
A general equation which describes the reaction studied can be written as

$$ArTe\text{-}TeAr \xrightarrow{SeO_2} \underset{\mathbf{a}}{Ar\text{-}Te\text{-}Se\text{-}Te\text{-}Ar} + \underset{\mathbf{b}}{Ar\text{-}Te\text{-}Se\text{-}Te(O)Ar} + \text{oxygenated products}$$

Results and Discussion

Throughout this paper the absence of a lower case letter following the digit indicates the ditelluride except for **3**, **4**, and **5**. The digit followed by a lower case **a** indicates a bis(tellurenyl) selenide and **b** indicates a mixed tellurenyl tellurinyl selenide. The designation **c**, **d**, and **e** will be used to indicate the presence of two or more oxygen atoms bonded to the chalcogens.

The ditellurides used in this investigation are identified.



1, $R_1 = R_2 = H$
2, $R_1 = H, R_2 = CHO$
6, $R_1 = CH_3, R_2 = H$
7, $R_1 = OCH_3, R_2 = H$
8, $R_1 = F, R_2 = H$
9, $R_1 = H, R_2 = OCH_3$
10, $R_1 = H, R_2 = C(O)OC_2H_5$

Pyridine was the solvent most often used, but ethanol or acetic acid was also employed without altering the nature of the end products formed.

The reaction between SeO_2 and ditellurides is not a simple one. Reaction time, temperature, and especially the $[SeO_2]$:[ditelluride] ratio strongly influence the composition of the products formed. The formation of a single reaction product was not observed in any of the experi-

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(1) Klayman, D. L.; Günther, W. H. H. "Organic Selenium Compounds: Their Chemistry and Biology"; Wiley-Interscience: New York, 1973; Chapter IV.
(2) Hauge, S.; Vikane, O. *Acta Chem. Scand.* **1973**, *27*, 3596-3599.
(3) Dereu, N. L. M. Thesis, University of Liège, Belgium, 1974.
(4) Van Coppenolle, J. Thesis, University of Liège, Belgium, 1974.

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Table I. ^{1}H NMR Shifts (Ppm) in $(ArTe)_2Se$ Compounds

	$\delta(H_3)$	$\delta(H_4)$	$\delta(H_5)$	$\delta(H_6)$	$\delta(CH_2)$	$\delta(CH_3)$	$\delta(CH_2\text{-}CH_3)$
10 $[(o\text{-}COOC_2H_5)C_6H_4Te]_2$	~8.1	~7.25	~7.25	~8.1	4.47	1.46	7.1
10a $[(o\text{-}COOC_2H_5)C_6H_4Te]_2Se$	8.05	7.48	7.27	8.43	4.40	1.40	7.1

Table II. ^{13}C NMR Shifts (Ppm) in $(ArTe)_2Se$ Compounds

	$\delta(C_1)$	$\delta(C_2)$	$\delta(C_3)$	$\delta(C_4)$	$\delta(C_5)$	$\delta(C_6)$	$\delta(C{=}O)$	$\delta(CH_2)$	$\delta(CH_3)$
2 $[(o\text{-}CHO)C_6H_4Te]_2$	112.9	*a*	136.7	127.0	134.4	140.5	193.0		
2a $[(o\text{-}CHO)C_6H_4Te]_2Se$	125.2	*a*	136.2	126.5	134.4	135.5	193.0		
10 $[(o\text{-}COOC_2H_5)C_6H_4Te]_2$	113.7	130.5	130.9	126.8	133.3	139.3	167.7	61.9	14.3
10a $[(o\text{-}COOC_2H_5)C_6H_4Te]_2Se$	123.6	129.3	130.8	126.4	133.2	134.9	168.9	62.3	14.3

[a] Not observed.

Table III. ^{125}Te and ^{77}Se NMR Shifts (Ppm) in ArTeTeAr and $(ArTe)_2Se$ Compounds

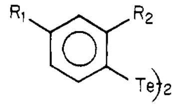
	$\delta(Te)$	$\delta(Se)$
2 $[(o\text{-}CHO)C_6H_4Te]_2$	423	
2a $[(o\text{-}CHO)C_6H_4Te]_2Se$	1120	353
10 $[(o\text{-}COOC_2H_5)C_6H_4Te]_2$	411	
10a $[(o\text{-}COOC_2H_5)C_6H_4Te]_2Se$	907	332
a	834	260
b		462

[a] $C_6H_5TeSeC_6H_5$ from mixture of $(C_6H_5Te\text{-})_2$ and $(C_6H_5Se\text{-})_2$. [b] $(C_6H_5Se\text{-})_2$.

ments performed. However, conditions could be adjusted so as to favor the formation of a particular compound and its subsequent isolation. If conditions were such that an appreciable amount of the starting ditelluride remained unreacted, isolation and purification of product(s) were difficult. On the other hand, if the reaction conditions were adjusted so that reaction proceeded to an advanced stage, highly oxygenated tellurium derivatives (multiple Te–O bonds) were formed. The latter are exceedingly difficult to purify. Hence, only "intermediate" conditions yielded compounds which were positively characterized. It was possible to identify two types of compounds containing the sequences, –Te–Se–Te– and –Te–Se–Te(O)–. In the case of the ditellurides **1**, **6**, **7**, **8**, and **9** only compounds containing the –Te–Se–Te(O)– sequences were easily isolated. Ditellurides bearing a carbonyl substituent in the ortho position (**2** and **10**) yielded only –Te–Se–Te– bonded compounds.

Derivatives Bearing an *o*-Carbonyl Substituent. Using conditions described in the experimental part, compounds **2a** and **10a** were easily isolated. The chemical shifts observed for **2a** and **10a** are similar to those of the respective ditellurides, **2** and **10**. Except for the ring carbons attached directly to tellurium, the resonances generally differ by less than 1.2 ppm. In the case of C_1, the downfield shift, comparing the ditelluride with the tellurenyl selenide, is 12.3 ppm for **2a** and 9.9 ppm for **10a**. For C_6, the corresponding upfield differs by 5.0 ppm for **2a** and 4.4 ppm for **10a**. However, these shifts are not observed for the tellurenyl portions of compounds **1b**, **6b**, **7b**, **8b**, and **10b**. The shifts are probably due to a particular configuration similar to that reported for the *o*-carbonyl tellurenyl halides.[5] In these compounds the carbonyl oxygen is involved in some type of interaction with tellurium, and this is discussed in the section dealing with crystallographic results. A similar effect on the ^{13}C NMR resonance is noted on C_1 in the tellurinyl portion of compounds **1b**, **6b**, **7b**, **8b**, and **9b** where evidence for the presence of a Te–O bond exists. Compared with the corresponding ditellurides, the tellurium atoms of **2a** and **10a** are appreciably deshielded. The downfield shift, relative to the ditelluride, is 697 ppm for **2a** and 493 ppm for **10a**. This effect is greater than that brought about by the replacement of tellurium by selenium as observed for $C_6H_5SeTeC_6H_5$ for which $\Delta\delta = 411$ ppm. In **2a** and **10a**, the selenium atoms are shielded by 109 and 130 ppm, respectively, when compared with the Se atom in $(C_6H_5\text{-}Se\text{-})_2$.

Tellurenyl Tellurinyl Derivatives. Utilizing conditions described in the Experimental Section, we isolated compounds **1b**, **6b**, **7b**, **8b**, and **9b**.



1b,[a] $R_1 = R_2 = H$
6b, $R_1 = CH_3$, $R_2 = H$
7b, $R_1 = OCH_3$, $R_2 = H$
8b, $R_1 = F$, $R_2 = H$
9b, $R_1 = H$, $R_2 = OCH_3$

[a] **1b** was obtained in a sufficiently pure state only when Se_2Cl_2 was substituted for SeO_2.

Two distinct resonances are observed for H_2 and H_3. One of these resonances is virtually unchanged as compared to the parent ditelluride, while the other is found further upfield, up to 4 Hz. The magnetic nonequivalence is due to the presence of one Te–O bond.

The ^{13}C NMR data are listed in Table V. Resonances have been previously assigned for ditelluride **1**.[6] Assignments for the ditellurides **1**, **6**, **7**, **8**, and **9** and for compounds **1b**, **6b**, **7b**, **8b**, and **9b** were fairly straightforward by using empirical parameters for the calculation of chemical shifts in substituted benzenes.[7] The resonance attributed to the carbon attached to the tellurium was always smaller than that commonly observed for a "normal" quaternary carbon. This is probably due to an unusually long relaxation time for such carbon atoms. An asymmetry corresponding to that observed in the ^{1}H NMR shifts was observed also for the ^{13}C NMR. The spectra of the mixed tellurenyl tellurinyl selenides differ from those of the corresponding ditellurides by the presence of two distinct C_1 resonances. One chemical shift is virtually identical with the corresponding resonance in the ditelluride, but the second is shifted downfield by 5.6–6.3 ppm. The other pairs of corresponding carbon resonances differ by less than 0.5 ppm.

In Table VI, the presence of two types of tellurium atoms is clearly indicated by the presence of two widely

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[5] (a) Baiwir, M.; Llabres, G.; Didenberg, O.; DuPont, L.; Piette, J. L. *Acta Crystallogr., Sect. B* **1974**, *B30*, 139. (b) Baiwir, M.; Llabres, G. *J. Appl. Crystallogr.* **1975**, *8*, 397. (c) DuPont, L.; Didenberg, O.; La Motte, J.; Piette, J. L. *Acta Crystallogr., Sect. B* **1979**, *B35*, 849–852.

[6] Forchioni, A.; Irgolic, K. J.; Pappalardo, G. C. *J. Organomet. Chem.* **1977**, *135*, 327–331.

[7] Wehrli, F. W.; Wirthlin, T. "Interpretation of Carbon-13 NMR Spectra"; Heyden and Sons, Ltd.: London, 1978.

Table IV. ^1H NMR Shifts (Ppm) and Coupling Constants (Hz) in ArTeSeTe(O)Ar Compounds

	$\delta(H_2)$ $\delta(H_2')$	$\delta(H_3)$ $\delta(H_3')$	$\delta(CH_3)$	J_{2-3}	J_{2-F}	J_{3-F}	$\Delta\delta_{H_2,H_2'}$, Hz	$\Delta\delta_{H_3,H_3'}$, Hz
6 $[p\text{-}CH_3C_6H_4Te]_2$	7.60	6.91	2.34	8.0				
6b $[p\text{-}CH_3C_6H_4Te]Se\text{-}[p\text{-}CH_3C_6H_4Te(O)]$	7.58/7.62	~6.93[a]	2.34	8.0			4.0	
7 $[p\text{-}CH_3OC_6H_4Te]_2$	7.63	6.66	3.76	8.8				
7b $[p\text{-}CH_3OC_6H_4Te]Se\text{-}[p\text{-}CH_3OC_6H_4Te(O)]$	7.63/7.60	6.66/6.62	3.76	8.7			1.8	3.3
8 $[p\text{-}FC_6H_4Te]_2$	7.66	6.83		8.6	5.4	8.6		
8b $[p\text{-}FC_6H_4Te(O)]Se\text{-}[p\text{-}FC_6H_4Te]$	7.66/7.62	6.83/6.81		8.9	5.6	8.9	3.2	3.2

[a] Broadening.

Table V. ^{13}C NMR Shifts (Ppm) in ArTeSeTe(O)Ar Compounds

	$\delta(C_1)$	$\delta(C_1')$	$\delta(C_2)$	$\delta(C_2')$	$\delta(C_3)$	$\delta(C_3')$	$\delta(C_4)$	$\delta(C_4')$	$\delta(C_5)$	$\delta(C_5')$	$\delta(C_6)$	$\delta(C_6')$	$\delta(CH_3)$	$\delta(CH_3')$
1	108.2		137.5		129.1		127.8							
1b	108.2	114.0	137.5	137.8	129.2	129.2	128.0	128.5						
6	104.2		137.9		130.0		*a*						21.0	
6b	104.2	110.4	138.0	138.2	130.1	130.1	*a*	*a*					21.0	21.2
7	97.6		140.2		115.0		160.1						55.1	
7b	97.6	103.9	140.2	140.3	115.1	115.2	160.2	160.4					55.1	55.1
8[b]	101.6		140.1		116.6		163.3							
8b[b]	101.5	107.5	140.1	140.3	116.6	116.6	163.3	163.3						
9	97.6		158.7		109.2		129.0		122.6		137.7		55.9	
9b	97.7	103.8	158.9	158.9	109.2	109.4	129.1	129.1	122.6	122.6	137.7	137.7	56.1	56.1

[a] Not observed. [b] For 8 and 8b $J_{F-C_4} = 163.3$ Hz, $J_{F-C_3} = 20.6$ Hz, $J_{F-C_2} = 7.3$ Hz, and $J_{F-C_1} < 2$ Hz.

Table VI. ^{125}Te and ^{77}Se Shifts (Ppm) in ArTeSeTe(O)Ar Compounds

	Te	Te-O	Se	J_{TeSe},[a] Hz
1 $(C_6H_5Te)_2$	420	...	...	
1b $[C_6H_5Te]Se[Te(O)C_6H_5]$	431	1014	273	167
6 $[p\text{-}CH_3C_6H_4Te]_2$	433	...	...	
6b $[p\text{-}CH_3C_6H_4Te]Se[p\text{-}CH_3C_6H_4Te(O)]$	424	1010/950	280/567	
7 $[p\text{-}CH_3OC_6H_4Te]_2$	460	...	...	
7b $[p\text{-}CH_3OC_6H_4Te]Se[p\text{-}CH_3OC_6H_4Te(O)]$	455	1012	291	174
8 $[p\text{-}FC_6H_4Te]_2$	457	...	...	
8b $[p\text{-}FC_6H_4Te(O)]Se[p\text{-}FC_6H_4Te]$	456	1027	285	
9 $(o\text{-}CH_3OC_6H_4Te)_2$	168	...	...	
9b $[o\text{-}CH_3OC_6H_4Te]Se[o\text{-}CH_3OC_6H_4Te(O)]$	159	931	438	

[a] Observed on the Se resonance.

separated ^{125}Te NMR shifts. One resonance is the same as that observed for the corresponding ditelluride. A second resonance of equal intensity is observed at 550–660 ppm further downfield. The magnitude of the deshielding effect would be expected for a Te–O bond. The selenium resonance in diphenyl diselenide occurs at 462 ppm[8] while in the compounds which are currently under discussion it is observed at about 280 ppm. This corresponds to a shielding of about 180 ppm. In an analogous situation, when a selenium atom in diphenyl diselenide is replaced by tellurium, the selenium resonance is shifted upfield by 202 ppm. In the case of **9b**, the tellurium resonance is observed at 159 ppm in the starting ditelluride. The methoxy group serves to shield both tellurium resonances while deshielding the central selenium atom.

In the case of **6b**, two resonances were observed in the region attributed to Te–O. The intense one is very close to that observed for Te–O in the case of **1b**, **7b**, and **8b**. The one of weak intensity, situated at 950 ppm, is close to that observed in **9b** in which a methoxy group is located β to the tellurinyl tellurium. In **6b**, two Se resonances are also observed. The major one, at 280 ppm, is again very close to that observed for **1b**, **7b**, and **8b**. The minor one, at 567 ppm, is more deshielded than the Se resonance for **9b** in which a δ-methoxy group is present. The presence of other reaction products, similar in structure and close in chemical stoichiometry, may explain this observation. Such products could include $[ArTe(O)-]_2Se$ and/or ArTe(O)Se(O)TeAr.

In the case of both compounds, **8** and **8b**, coupling between both tellurium atoms and the p-fluorine atom was observed. For compound **8**, $^5J_{Te_1-F_1} = 10.1$ Hz while $^6J_{Te_1-F_2} = 2$ Hz. In the case of **8b**, $^5J_{Te_1-F_1}$ is 10.8 Hz and $^5J_{Te(O)-F_2} = 10.6$ Hz. No ^6J coupling was observed, and $^7J_{Te-F}$ was not resolved. Coupling between ^{77}Se and ^{125}Te was observed on ^{77}Se for **1b** and **7b** (167 and 174 Hz, respectively). These values are consistent with those reported by Pfisterer and Dreeskamp[9] and Granger.[10]

Equilibria between Tellurenyl Tellurinyl Selenides. When a solution consisting of two aryltellurenyl aryltellurinyl selenides is examined (^{125}Te NMR), there appears to occur rapid exchange of the type

$$RTeSeTe(O)R + R'TeSeTe(O)R' \rightleftharpoons RTeSeTe(O)R' + RTe(O)SeTeR'$$

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(9) Pfisterer, G.; Dreeskamp, H. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 654–661.

(10) Granger, P. "Proceedings of the Third International Symposium on Organic Selenium and Tellurium Compounds"; Cagniant, D., Kirsch, G., Eds.; Université de Metz: Metz, France, 1979; p 305.

This is similar to the exchange reaction which has been reported to occur between two diaryl ditellurides.[11] For example, in a solution containing an equimolecular mixture of **6b** and **8b**, eight ^{125}Te resonances are observed. Four can be assigned to the symmetrical species and the other four to the nonsymmetrical ones. The assignments were simplified by the fact that a tellurium attached to a *p*-fluorobenzene group shows a $^5J_{\mathrm{Te-F}}$ coupling. The sharpness of the tellurium resonances indicates that the redistribution reaction is quite slow on the NMR time scale. Thus, in the ^{125}Te region, in a mixture of **6b** and **8b**, the following resonances were observed: δ 418 (**6b**), 448 (**8b**), 430, and 436 (unsymmetrical species). The resonance at δ 430 can be attributed to the F-containing ring because of observed F coupling. In the ^{125}Te(O) region, the same mixture showed the following resonances: δ 1012 (**6b**), 1020 (**8b**), 1016 (shows F coupling), and 1020.5 (unsymmetrical species).

Crystallographic Data. The crystal structures of compounds **10a** and **7a** have been determined.[12] The following fundamental features serve to confirm the proposed structures and establish the fact that selenium is inserted between two tellurium atoms.

In compound **7a** the Se–Te bond distances are 2.525 and 2.562 Å while both of these distances are equal to 2.536 Å in **10a**. The bond angles, Te–Se–Te, are 102.4° in **7a** and 102.9° in **10a**. Because of the implications of the Te→O coordination on the ^{125}Te NMR resonance and the resistance of the *o*-carbonyl-substituted derivatives toward oxidation, i.e., their failure to produce mixed derivatives of type **b**, the Te–O distance is of some interest. In **10a**, the Te···O distance is 2.658 Å. While this is considerably larger than the calculated covalent single-bond distance, 2.04 Å, it is appreciably less than the sum of the van der Waal's radii, 3.60 Å. This indicates appreciable Te···O interaction and offers some explanation of the stability of the *o*-carbonyl derivatives.

Stoichiometric Interpretation. The isolation of the compounds just described leaves unanswered the question of the fate of the oxygen from the SeO_2. From the reaction of compound **6** with SeO_2 or H_2SeO_3 an oxygen-rich organotellurium derivative free of selenium was isolated (see Experimental Section). This white solid had a poorly defined melting point (~200 °C) and was insoluble in water and most organic solvents. It possessed some solubility in hot methanol from which is separated on cooling as a gel. It was moderately soluble in cold acetic acid, but recrystallization from this solvent was difficult. From the elemental analysis it was difficult to choose between **6c** and **6d**. The synthesis of compound **6c** was attempted

$[p\text{-MeC}_6\text{H}_4\text{Te(O)–}]_2\text{O}$ $\qquad$ $[p\text{-MeC}_6\text{H}_4\text{–Te(O)}_2\text{–}]$

6c $\qquad$ **6d**

according to previously published methods[13] in order to aid in the identification of the oxidized tellurium derivatives, but a satisfactory characterization of **6c** was not obtained. With the assumption, as is suggested by the stoichiometric values, that the oxygen is utilized in the formation of ditellurones and/or tellurinic acid anhydrides, the reaction can follow the stoichiometries shown in eq 1–3.

$$4(\text{ArTe–})_2 + 3\text{SeO}_2 \rightarrow 3\text{ArTeSeTe(O)R} + [\text{Ar}_2\text{Te(O)–}]_2\text{O} \quad (1)$$

$$5(\text{ArTe–})_2 + 3\text{SeO}_2 \rightarrow 3\text{ArTeSeTeAr} + 2[\text{ArTe(O)–}]_2\text{O} \quad (2)$$

$$3(\text{ArTe–})_2 + 2\text{SeO}_2 \rightarrow 2\text{ArTeSeTeAr} + \text{ArTe(O)}_2\text{Te(O}_2\text{)Ar} \quad (3)$$

Additional evidence for the formation of the ditellurone **6d**, or a closely related compound, was found in the ^{13}C and ^{125}Te NMR resonances measured in acetic-d_3 acid-*d*. It can be seen that both compounds exhibit very similar patterns.

	^{13}C resonances, ppm			
	C_1	C_2	C_3	C_4
6,[a] unknown oxidation product	143.8	130.7	131.7	143.4
6c,[b] synth	144.2	130.7	131.7	143.3

[a] White precipitate from reaction of H_2SeO_3 with **6**. [b] $[CH_3C_6H_4Te(O)_2\text{–}]_2O$ prepared according to ref 14.

The only real difference is in C_1 which is bonded directly to tellurium. The quality of the spectra was excellent so that the differences in both C_1 and C_4 were easily resolved. The ^{125}Te NMR spectrum of the unknown precipitate, also measured in acetic-d_3 acid-*d*, showed a broadened peak at 1380 ppm having a width of 280 Hz at half-peak height at room temperature. Previously, all Te resonances observed in this investigation displayed widths ranging from 5 to 10 Hz. Compound **6c**, despite its higher concentration, did not reveal an observable ^{125}Te resonance at room temperature. At 90 °C, a broadened peak was observed at 1330 ppm which had bandwidth of 800 Hz at half-peak height. It is to be noted that bis(*p*-tolyl) ditelluride itself in acetic-d_3 acid-*d* displays a resonance at 415 ppm with half-peak bandwidth of ~250 Hz. These data suggest that the white oxidation product is the ditellurone.

Other Oxidation Products. When the [SeO_2]:[ditelluride] ratio is greater than 1, other types of oxidation products are formed. These compounds are difficult to isolate and purify. The basic difference between this group of compounds and those just discussed is that these retain selenium as a component.

The oxidation of **6** by 2 equiv of SeO_2 yields a mixture which, based on analytical data, is made up of **6e** and **6d**.

$p\text{-MeC}_6\text{H}_4\text{Te(O)}_2\text{Se(O)Te(O)}_2\text{–C}_6\text{H}_4\text{–Me-}p$

6d

$p\text{-MeC}_6\text{H}_4\text{Te(O)}_2\text{SeTe(O)}_2\text{–C}_6\text{H}_4\text{–Me-}p$

6e

Anal. Calcd for **6d**: C, 28.18; H, 2.35; Te, 42.80; O, 13.41. Calcd for **6e**: C, 28.95; H, 2.41; Te, 43.98; O, 11.03. Found: C, 28.86; H, 2.55; Te, 41.77; O, 12.14. In the case of **10**, with the same reaction conditions, a similar compound was obtained, viz., $o\text{-C(O)OEtC}_6\text{H}_4\text{–Te(O)}_2\text{–Se–Te(O)}_2\text{C}_6\text{H}_4\text{C(O)OEt}$. Anal. Calcd: C, 31.25; H, 2.74; O, 17.45. Found: C, 31.03; H, 2.58; O, 18.38.

Experimental Section

Melting points were determined by using a Büchi SMP-20 melting point apparatus (capillary method) and are uncorrected. The ^{1}H NMR spectra were recorded on a Varian EM-390 90 MHz spectrometer; the ^{13}C NMR spectra were measured on a JEOL PFT-100 spectrometer. The ^{125}Te and ^{77}Se spectra were obtained by using a Varian FT-80 or a Varian XL-200 spectrometer equipped with a synthesizer and Fourier transform equipment. Solutions were about 0.1 M or saturated, and temperature was maintained around 29 °C, unless otherwise indicated. The solvent was $CDCl_3$ unless otherwise indicated. Chemical shifts are reported in parts per million and are expressed relative to CH_3TeCH_3 for ^{125}Te and CH_3SeCH_3 for ^{77}Se. Microanalyses were performed by the Galbraith Laboratories, Inc., Knoxville, TN. Unless otherwise indicated, or if analytical data were needed for

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Table VII. Analytical Data For New Compounds

	C		H		Te		Se		O	
	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
2a $[(o\text{-CHO})C_6H_4Te]_2Se$	30.89	31.07	1.85	1.97	46.87	46.64				
6a $[p\text{-}CH_3C_6H_4Te]_2Se$	32.56	32.27	2.73	2.75						
10a $[(o\text{-}COOC_2H_5)C_6H_4Te]_2Se$	34.18	33.96	2.84	2.89	40.37	40.60	12.49	12.32		
7b $[p\text{-}CH_3OC_6H_4Te]Se[p\text{-}CH_3OC_6H_4Te(O)]$	29.79	29.56	2.52	2.50					8.50	8.21
1b $[C_6H_5Te]Se[Te(O)C_6H_5]$	28.56	28.38	1.98	2.02	50.62	50.70	15.66	15.29	3.17	2.98
8b $[p\text{-}FC_6H_4Te(O)]Se[p\text{-}FC_6H_4Te]$	26.67	26.89	1.49	1.60					2.96	2.74
9b $[o\text{-}CH_3OC_6H_4Te]Se[o\text{-}CH_3OC_6H_4Te(O)]$					45.22	45.90	14.00	14.30	8.50	8.79
6b $[p\text{-}CH_3C_6H_4Te]Se[p\text{-}CH_3C_6H_4Te(O)]$					47.93	48.19	14.83	15.11	3.00	2.89

other purposes, the analyses agreed well with calculated values and are not reported.

Ditellurides were synthesized according to published preparations.[14]

Syntheses of Tellurenyl Selenides 2a and 10a. To a solution of 2.0 mmol of ditelluride **2** or **10** in 50 mL of pyridine was added 0.2 g (1.8 mmol) of finely powdered SeO_2. The stirred mixture was heated at 80 °C for 30 min. After being cooled, the mixture was hydrolyzed in 250 mL of an ice–water mixture. The mixture was extracted with two 50-mL portions of chloroform. The combined chloroform extracts were washed with three 100-mL portions of water. The chloroform extract was dried over anhydrous $MgSO_4$. After filtration the solvent was removed by distillation. Purification was accomplished by recrystallization from hexane/benzene **10a** or column chromatography using benzene as an eluant followed by recrystallization in hexane/benzene **2a**. The color of compounds **2a** and **10a** was orange as compared with the yellow color of **2** and **10**. The yield of **2a** was 460 mg (42.3%), mp 147–148 °C, and of **10a** was 570 mg (45%), mp 147 °C. TLC data, silica gel (CCl_4):R_f 0.38 (**2**), 0.29 (**2a**), 0.32 (**10**), 0.34 (**10a**).

Synthesis of mixed Tellurenyl Tellurinyl Selenides 6b, 7b, 8b, and 9b. To a solution of 4.0 mmol of the ditelluride **6**, **7**, **8** or **9** in 100 mL of pyridine was added 0.45 g (4.0 mmol) of finely powdered SeO_2. The stirred mixture was heated at 80–90 °C for 45 min. After being cooled, the mixture was hydrolyzed in 500 mL of ice–water. After the mixture was left standing for at least 6 h, the solid material was removed by filtration, washed with water, and dried. The solid material was extracted with hot chloroform. The chloroform was removed by distillation, and the residue consisting mainly of the mixed tellurenyl tellurinyl selenide, some starting ditelluride, and probably some bis(tellurenyl) selenide was recrystallized from a mixture of hexane/benzene to yield pure mixed tellurenyl tellurinyl selenide. The chloroform-insoluble residue, gray-white in color, is a selenium-free, oxygen-rich byproduct which is obtained in a purer state by using H_2SeO_3 in place of SeO_2. Yield: for **6b**, 450 mg (21.1%), mp 66 °C; for **7b**, 700 mg (31.0%), mp 118 °C; for **8b**, 500 mg (23.1%), mp 99 °C; for **9b**, 450 mg (20%), mp 109 °C.

TLC data, silica gel (CCl_4): R_f 0.82 (**1**, **1b**, **6**, **6b**), 0.54 (**7**), 0.50 (**7b**), 0.83 (**8**, **8b**).

Synthesis of Benzenetellurenyl Benzenetellurinyl Selenide (1b). To a stirred solution of 4.1 g (10 mmol) of diphenyl ditelluride **1** in 100 mL of dry pyridine was added dropwise 0.7 g of Se_2Cl_2. The solution was then heated at 80 °C for 30 min. After being cooled, the mixture was hydrolyzed in 500 mL of ice–water. Following the same workup as for **2a** and **10a**, 800 mg of pure **1b** (yield 15.9%, mp 57 °C) was obtained. In a similar way, **6b** and **7b** were obtained from **6** and **7**.

Analytical data for the new compounds prepared are given in Table VII.

The Reaction of H_2SeO_3 with Ditelluride 6. Efficient Synthesis of Selenium-Free and Oxygen-Rich Byproduct. A 2-g (4.57-mmol) sample of **6**, 0.55 g (4.26 mmol) of H_2SeO_3, 100 mL of pyridine, and 20 mL of ethanol were heated at 70 °C for 3 h. After being cooled, the mixture was poured into ice water. After at least 3 h, the solid was removed by filtration and dried. Extraction with hot chloroform yields 1.75 g, consisting of a mixture of **6b** and **6**. The insoluble part (0.25 g) is a white solid melting at ~200 °C. Anal. Calcd for $C_{14}H_{14}O_3Te_2$: C, 33.53; H, 2.79; O, 12.77; Te, 50.92. Found: C, 33.34; H, 2.85; O, 11.10; Te, 49.70; Se, 0.06.

Reaction of Ditellurides with Two Equivalents of SeO_2. Both **6** and **10** were heated with 2 equiv of SeO_2 under the same conditions as described before. The solid collected after hydrolysis was washed with H_2O, dried, and analyzed. These data have already been listed.

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Registry No. **1**, 32294-60-3; **1b**, 79313-58-9; **2**, 28192-55-4; **2a**, 79313-59-0; **6**, 32294-57-8; **6a**, 79313-60-3; **6b**, 79313-61-4; **6c**, 79313-62-5; **6d**, 79313-63-6; **6e**, 79313-64-7; **7**, 35684-37-8; **7b**, 79313-65-8; **8**, 36829-95-5; **8b**, 79313-66-9; **9**, 56821-76-2; **9b**, 79313-67-0; **10**, 67915-87-1; **10a**, 79313-68-1; SeO_2, 7446-08-4; $o\text{-}C(O)OEtC_6H_4\text{-}Te(O)_2\text{-}Se\text{-}Te(O)_2C_6H_4C(O)OEt$, 79313-69-2.

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(14) 1 and 6 were synthesized according to: Piette, J. L.; Renson, M. *Bull. Soc. Chim. Belg.* **1970**, *79*, 353–365. 2 was sythesized according to: Piette, J. L.; Renson, M. *Ibid.* **1970**, *79*, 367–382. 7 according to: Morgan, G. T.; Drew, H. D. K. *J. Chem. Soc.* **1925**, 2307–2315. 8 according to: Haller, W. S.; Irgolic, K. J. *J. Organomet. Chem.* **1972**, *38*, 97–103. 9 according to: Dereu, N.; Piette, J. L.; Van Coppenolle, J.; Renson, M. *J. Heterocycl. Chem.* **1975**, 423–426. 10 according to: Piette, J. L.; Thibaut, P.; Renson, M. *Tetrahedron* **1978**, *34*, 655–659. The melting of 10 reported as 118 °C but observed in this work at 134 °C.