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12-Te-5 Pertelluranes from 1,2-Oxatellurolyl-1-ium Halides. Synthesis, Structure, and Reactivity. The Quest for Delocalization in 10-Te-3 Telluranes and 12-Te-5 Pertelluranes of Thiathiophthene Structure

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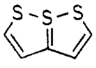
The oxidative addition of chlorine or bromine to 1,2-oxatellurolyl-1-ium chlorides or bromides, respectively, at 0 °C occurs rapidly to give 12-Te-5 pertelluranes. The structure of 3,5-diphenyl-1,2-oxatellurolylium tribromide (**9**) was determined unambiguously by single-crystal X-ray crystallographic analysis. Pertelluranes were neutral in solution (CH_2Cl_2), as determined by conductance studies. The pertelluranes were easily reduced electrochemically to halide ions and the oxatellurolylium halide and were susceptible to nucleophilic attack by Michael addition on the enone segment. Spectroscopic and crystallographic comparison of the pertelluranes with the corresponding oxatellurolylium halides and of dioxatellurapentalenes with the corresponding pertellurane analogues suggested ionic bonding between Te and the halides or O for all four of these systems. Theoretical treatment with CNDO/2 calculations by the program GEOMORV suggested ionic bonding of O and halides to the Te with little π-delocalization involving Te–O and Te–C bonds in both the tellurane and pertellurane systems. A low-lying π^* LUMO in the pertelluranes was predicted, consistent with the susceptibility to nucleophilic attack, as observed experimentally.

The structure and bonding in thiathiophthenes **1** and related dioxapentalene structures **2** have intrigued chemists since first proposals of their aromaticity.[1] These compounds formally represent heteroaromatic structures with 10 π electrons. Structural studies have shown that the bonds between heteroatoms are long and, in the diazadioxapentalenes **3**, the bonds between heteroatoms become increasingly more ionic as the central heteroatom becomes larger.[2] However, aromatic stabilization has been presumed in all of the structures **1**–**3** through $p\pi$–$p\pi$ or $p\pi$–$d\pi$ multiple bonding.[1,2] Electrophilic substitution reactions on the pentalene ring have been observed for compounds of structure **2**.[3]



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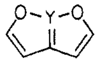
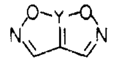
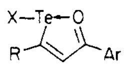


2, Y= S,Se



3, Y= S,Se,Te

We recently reported the preparation and properties of 10-Te-3 telluranes with general structures **4**[4] and **5**.[5] The dioxatellurapentalenes **5** complete the series for general structures **2**, whereas the oxatellurolylium halides **4** and the corresponding oxaselenolylium halides[4b] offer the first monocyclic, 6π-electron analogues of thiathiophthene-related compounds in which bonding to the central heteroatom should be similar in both monocyclic and bicyclic structures.



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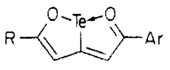

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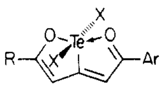

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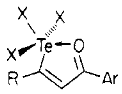

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Dioxathia- and dioxaselenapentalenes undergo electrophilic substitution at C when treated with halogens,[3] but dioxatellurapentalenes **5** undergo oxidative addition of chlorine or bromine at Te to give 12-Te-5 pertelluranes **6**.[5] The pertelluranes can then undergo substitution reactions to give C halogenation. This difference in reactivity of the dioxatellurapentalenes relative to the dioxathia- and dioxaselenapentalenes may reflect differences in the electronic structure and π delocalization (if any) among the systems. In particular, the increased size of Te may eliminate $p\pi$–$d\pi$ or $p\pi$–$p\pi$ multiple bonding between Te and O.

The oxidative addition of halogens to the oxatellurolylium halides would lead to 12-Te-5 pertelluranes of structure **7**. Such compounds would complete the series **4**–**7** and allow the comparison of structurally related systems with different electronic structure at Te. In the 12-Te-5 pertelluranes, the orbitals of Te capable of π bonding with O or C have been utilized in bonding to the Te ligands. In the 10-Te-3 telluranes, π bonding of the Te $5p_z$ or $4d_{z^2}$ orbitals with O or C is still possible.

We report here the oxidative addition of halogens to oxatellurolylium halides **4** to give 12-Te-5 pertelluranes **7**. Interestingly, oxaselenolylium chlorides undergo oxidative addition of chlorine as well to give 12-Se-5 perselenuranes. The 10-Te-3 telluranes **4** and **5** are compared with their 12-Te-5 pertellurane counterparts **6** and **7** by using spectroscopic, crystallographic, and theoretical techniques.

Results

X-ray Structural Data. The addition of 1 equiv of bromine to a 0 °C solution of oxatellurolylium bromide **8**[4] in CH_2Cl_2 at 0 °C gave a pale yellow solution that yielded bright orange crystals of **9** upon concentration and recrystallization from CH_3CN. The structure of **9** was determined unambiguously by single-crystal X-ray diffraction (Figure 1).[6]

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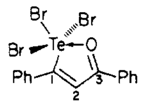

9

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(1) (1) Reid, D. H., "Organic Compounds of Sulphur, Selenium, and Tellurium"; The Chemical Society: London, 1970; Vol. I, pp 321–335.

(2) Saethre, L. J.; Martensson, N.; Svensson, S.; Malmquist, P. A.; Gelius, U.; Siegbahn, K. *J. Am. Chem. Soc.* **1980**, *102*, 1783.

(3) Reid, D. H.; Webster, R. G. *J. Chem. Soc., Chem. Commun.* **1972**, *1283*.

(4) (a) Detty, M. R.; Murray, B. J.; Smith, D. L.; Zumbulyadis, N. *J. Am. Chem. Soc.* **1983**, *105*, 875. (b) Detty, M. R.; Murray, B. J. *J. Am. Chem. Soc.* **1983**, *105*, 883.

(5) Detty, M. R.; Luss, H. R. *J. Org. Chem.* **1983**, *48*, 5149.

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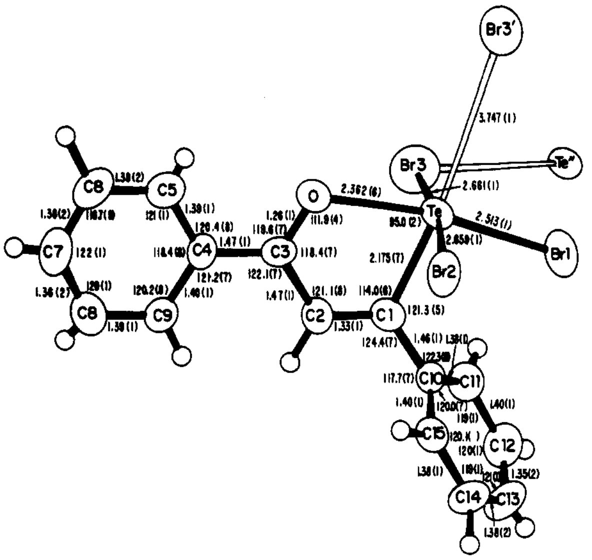
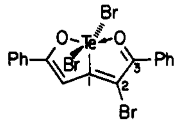


Figure 1. Plot of **9** with 50% probability thermal ellipsoids. Hydrogen atoms (unlabeled) were given arbitrary radii. The intermolecular interactions, designated by the open bonds, are to molecules related by symmetry x, −y, 1/2 + z (Br3′) and x, −y, −1/2 + z (Te″).

The bonding in **9** appears to be somewhat different from that found for **10**,[5] **11**,[5] and **12**,[4] which were all characterized by a linear three-center system with two long bonds of "fractional" bond character attributed to three-center four-electron bonding. The Te–O bonds are 2.19 Å (**12**), 2.127 Å (**11**), and 2.135 and 2.171 Å (**10**), all longer than a single-bond value (2.00 Å).[7] The Te–C bonds in these same compounds were 2.08 Å (**12**), 2.043 Å (**11**), and 2.11 Å (**10**), all near the single-bond value (2.08 Å).[7]



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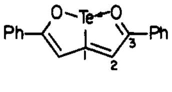

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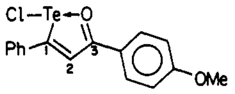

12

In the present structure, the linear O–Te–Br1 system also contains a long Te–O bond (2.362 Å). The Te–Br1 bond (2.513 Å), trans to O, appears to be a good single bond (sum of covalent radii = 2.50 Å).[7] In addition, the Te-C bond (2.175 Å) is significantly longer than expected. The two long bonds then are not trans, but cis like those in compound **13**.[8] In **13**, the Te–O bond (2.49 Å) is trans to the shortest Te–Br bond (2.50 Å) and cis to a long Te-C bond (2.26 Å) (distances averaged over two equivalent molecules). In **9**, Pauling's formula for fractional bond numbers gives 0.25 and 0.75 for the Te–O and Te–C bonds, respectively, a good indication of the relative fractional bond character of these bonds. The C–O bond (1.26 Å) in **9** is comparable to that in carboxylate ions[9] (0.5 double-bond character), and the heterocyclic carbon bonds C1–C2 (1.33 Å) and C2–C3 (1.47 Å) are near good double-bond (1.34 Å) and single-bond (1.48 Å)[10] values, respectively. The axial Te–Br bond lengths (2.659, 2.661 Å) are close to those in **10** (2.620, 2.668 Å),[2] in **13** (2.652–2.678 Å),[8] and in $TeBr_6^{2-}$ ions (2.681–2.695 Å).[11] Table I summarizes the Te–C, Te–O, C–O, C1–C2, and C2–C3 bond lengths for **9**–**12**.

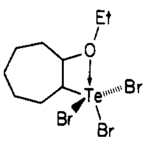

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Table I. Comparison of Selected Bond Lengths for 10-Te-3 Telluranes 11 and 12 and 12-Te-5 Pertelluranes 9 and 10

compd	bond length, Å Te–C	Te–O	C–O	C1–C2	C2–C3
9	2.175	2.362	1.26	1.33	1.47
10[a]	2.11	2.135, 2.171	1.27, 1.33	1.42, 1.29	1.43
11[a]	2.043	2.127	1.314	1.395	1.397
12[b]	2.08	2.19	1.27	1.354	1.426

[a] Reference 5. [b] Reference 4a.

Table II. Preparation of 12-Te-5 Pertelluranes of Structure 7

compd	X	R	Ar	yield,[a] %	mp, °C
9	Br	Ph	Ph	89	161–162.5
15	Cl	Ph	Ph	66	166–168
18	Cl	Me	Ph	74	139–141
19	Br	Me	Ph	70	144–145.5
23	Cl	H	Ph	70	96–98
24	Br	H	Ph	52	115.5–117
25	Cl	Me	4-FC_6H_4	92	152–154
26	Cl	Me	4-$Me_2NC_6H_4$	39	162–162.5
27	Cl	Ph	3-FC_6H_4	88	150–151
28	Cl	Ph	4-FC_6H_4	88	147–149
29	Cl	Ph	4-$MeOC_6H_4$	55	177–179.5
30	Cl	Ph	2-MeC_6H_4	82	154–155
31	Cl	4-$MeOC_6H_4$	Ph	85	178–179
32	Cl	4-*t*-BuC_6H_4	Ph	79	128–130

[a] Isolated yield after recrystallization from CH_3CN.

The intermolecular bonding to tellurium in the crystal structure of pertellurane **9** is interesting as well. Trans to the Te–C bond and completing the octahedral geometry about Te is a long Te···Br3 intermolecular interaction (3.757 Å) similar but longer than that found in the dioxatellurapentalene pertellurane **10** (3.555 Å). This intermolecular secondary bonding[12] results in the formation of "polymeric" chains of molecules along the c axis.

Preparative Studies. The addition of chlorine gas to a 0 °C solution of 3,5-diphenyl-1,2-oxatellurolyl-1-ium chloride (**14**)[4a] in CH_2Cl_2 resulted in a rapid disappearance of the gold color of the solution to give a pale yellow solution. Concentration of the reaction mixture and recrystallization of the residue gave bright yellow needles of 12-Te-5 pertellurane **15**. The chlorine addition to ox-

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[6] Crystals of **5** form in the monoclinic space group *Cc* with *a* = 18.654 (4) Å, *b* = 10.725 (3) Å, *c* = 8.572 (4) Å, *β* = 95.56 (3)°, *V* = 1707 (2) Å^3, and *Z* = 4. The intensities of 1500 independent reflections were measured (2*θ* < 60°), and all were included in the refinement of the structure. The locations of the tellurium and bromine atoms were obtained from a Patterson map. Subsequent difference electron-density maps gave all of the light atoms including hydrogens. Least-squares refinement of the complete structure converged with *R* = 0.0252 and R_w = 0.0316.

[7] Pauling, L. "The Nature of the Chemical Bond", 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

[8] Cameron, T. S.; Amero, R. B.; Chan, C.; Cordes, R. E. *Cryst. Struct. Commun.* **1980**, *9*, 543.

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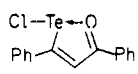
[10] Burke-Laing, M.; Laing, M. *Acta Crystallogr. Sect. B* **1976**, *32*, 3216.

[11] Foss, O. "Selected Topics in Structure Chemistry"; Anderson, P., Bastiansen, O., Furberg, S., Eds.; Universitatsforlaget: Oslo, 1967; p 145.

[12] Alcock, N. W. *Adv. Inorg. Chem. Radiochem.* **1972**, *15*, 1.

atellurolylium chlorides is a general reaction as is the addition of bromine to oxatellurolylium bromides, as shown in Table II, to produce a variety of 12-Te-5 pertelluranes. Oxatellurolylium iodide **16**[4a] did not react with iodine; only unreacted **16** was isolated.



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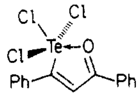

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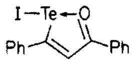
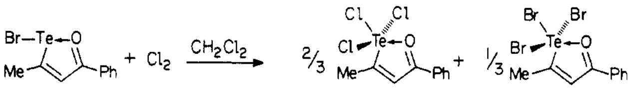
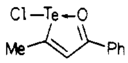


16

We attempted the preparation of mixed halides by the addition of chlorine to an oxatellurolylium bromide. Two products in a 2:1 ratio were detected by ^{1}H NMR and field-desorption mass spectroscopy (FDMS) after chlorine gas was added to a CH_2Cl_2 solution of oxatellurolylium bromide **17**. The major product was trichloride **18**, and the minor product was tribromide **19** (eq 1). Similarly, the addition of bromine to oxatellurolylium chloride **20** gave a 2:1 mixture of **19** and **18**.



17 **18** **19**



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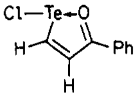
The most surprising reaction in our attempts to prepare mixed halides was the reaction of oxatellurolylium iodide **16** with bromine. Tribromide **9** and iodine were the only observed products. Similarly, oxatellurolylium bromide **8** gave no detectable reaction with iodine.

These reactions suggest that the observed pertellurane products prefer to have three identical halogen atoms attached to Te. Since no mixed halides are observed, a fast halogen-exchange mechanism must exist in the pertelluranes.

The addition of chlorine to **21** and bromine to **22** gave pertelluranes **23** and **24**, respectively, in 70 and 52% yields.



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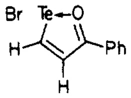

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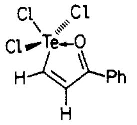

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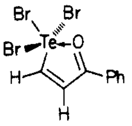
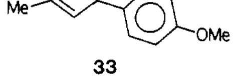


24

These compounds were thermally unstable, with mild heating giving the oxatellurolylium halide and halogen.

Dioxatellurapentalenes **5** undergo oxidative addition of halogens to give 12-Te-5 pertelluranes, but the dioxaselenapentalenes undergo electrophilic substitution reactions at carbon—not oxidative addition of halogen at selenium. In contrast, oxaselenolylium chloride **33** added chlorine in CH_2Cl_2 at 0 °C to give 12-Se-5 perselenurane **34** in 75% yield as a yellow crystalline solid. However, the molecule was prone to reductive elimination of chlorine upon heating or storage in a vacuum oven. Attempts to prepare the 12-Se-5 perselenurane tribromide were unsuccessful.



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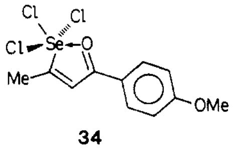
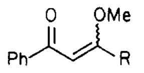
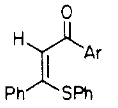


34

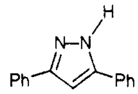
Reactions of 12-Te-5 Pertelluranes. The reactions of 12-Te-5 pertellurane trihalides with a variety of nucleophiles were examined. Acetonitrile solutions of pertelluranes **15** and **18** reacted with aqueous ammonium hydroxide to give 1,3-diphenyl-1,3-propanedione and 1-phenyl-1,3-butanedione in 63 and 56% yields, respectively. Oxatellurolylium chlorides **14** and **20** were also isolated in 36 and 13% yields, respectively. The addition of triethylamine to solutions of **18** and **15** in 1:1 (v/v) methanol/methylene chloride gave the methyl ethers **35** and **36** as mixtures of stereoisomers in 56 and 80% yields, respectively. 1-Phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione were also isolated in 38 and 15% yields, respectively, as well as trace amounts of **20** and **14**. Tellurium metal was also produced in these reactions. The corresponding oxatellurolylium halides were stable to the reaction conditions mentioned above.



35, R = Me
36, R = Ph



37, Ar = Ph
38, Ar = *m*-FC$_6$H$_4$



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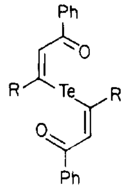
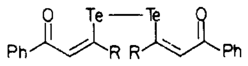
Non-oxygen nucleophiles gave similar results. The addition of sodium thiophenoxide to pertelluranes **15** and **27** gave exclusively the *Z* isomers **37** and **38**, respectively, in 74 and 82% yields. The addition of hydrazine to a CH_2Cl_2 solution of pertellurane **15** gave pyrazole **39** in 44% yield and oxatellurolylium chloride **14** in 22% yield.

The 12-Te-5 pertelluranes were reduced quantitatively to the oxatellurolylium halides with hypophosphorous acid. Thus, pertellurane **9** was reduced to **8** and **15** to **14** upon treatment with the acid.

Other reducing agents were tried with the 12-Te-5 pertelluranes. One of the more interesting reagents used was lithium triethylborohydride. When used in excess with **15** and **23**, this reagent gave small amounts of the expected oxatellurolylium chlorides **14** and **21** and a new product in each case identified as **40** and **41**, respectively. The structures of **40** and **41** were assigned on the basis of their field-desorption mass spectra (strong parent ion clusters), elemental analyses, IR spectra, and ^{1}H and ^{13}C NMR spectra (see below).



40, R = Ph
41, R = H



42, R = Ph
43, R = H

The addition of 1.1 equiv of lithium triethylborohydride to oxatellurolylium halides **14** and **21** gave >80% yields of **40** and **41**, respectively. Analysis of these crystalline solids by FDMS showed, in addition to large parent ion clusters for **40** and **41**, weaker parent ion clusters for the corresponding ditellurides **42** and **43**. Stirring the product mixtures with Cu powder gave only **40** and **41**.

In spectroscopic comparisons of the 12-Te-5 pertelluranes and their oxatellurolylium halide counterparts, **40** and **41** serve as useful model compounds. These compounds show the effect of a Te octet in an 8-Te-2 telluride

Table III. Oxidation-Reduction Potentials of Oxatellurolylium Halides and Corresponding 12-Te-5 Pertelluranes by Cyclic Voltammetry[a]

	Ep_c, V			Ep_a, V	
compd	1	2	3	1	2
8	−0.87	−1.36		+0.58	+1.28
9	+0.11	−0.93	−1.44	+0.54	+0.81
14	−0.98	−1.46		+0.74	
15	−0.07	−0.99	−1.44	+0.69	+0.98
17	−1.04			+0.46	+1.24
18	−0.21	−1.19		+0.51	+0.97
19	+0.01	−1.15		+0.46	+0.84
20	−1.11			+0.55	+1.41
21	−1.04			+0.42	+1.45
22	−1.05			+0.41	+1.42
23	−0.12	−1.03		+0.37	+1.17
24	+0.11	−1.04		+0.46	+1.28
10	−0.18	−1.50		+0.95	+1.14
11	−1.50			+1.36	

[a] Potentials are vs. a saturated calomel reference electrode (saturated aqueous NaCl) at a platinum disk with a scan rate of 100 mV/s. Sample concentration was ~5 × 10^{-4} M with 0.1 M tetrabutylammonium fluoroborate as supporting electrolyte in dichloromethane.

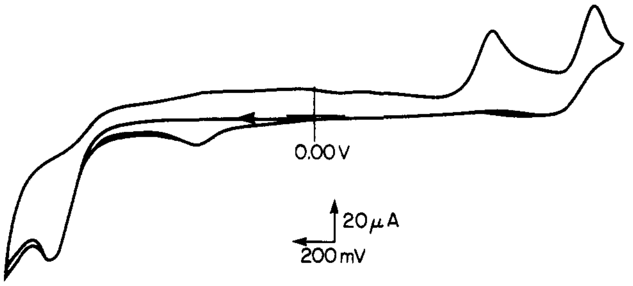


Figure 2. CV scan of oxatellurolylium bromide **8** in CH_2Cl_2 with 0.1 M TBAF as supporting electrolyte; Pt working electrode; scan speed 100 mV/s. Anodic direction is to the left.

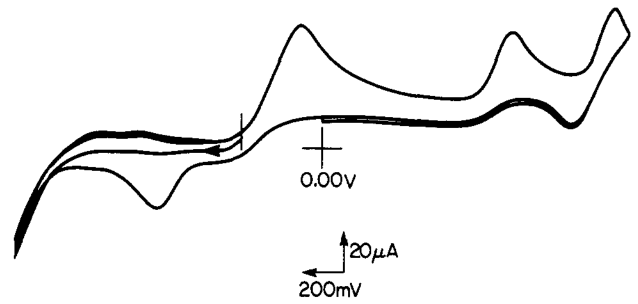


Figure 3. CV scan of 12-Te-5 pertellurane **9** in CH_2Cl_2 with 0.1 M TBAF as supporting electrolyte; Pt working electrode; scan speed 100 mV/s. Anodic direction is to the left.

Table IV. Spectroscopic Data for 10-Te-3 Telluranes

	^1H NMR δ, ppm			^{13}C NMR δ, ppm			IR νCO, cm^{-1}
compd	H_α	H_β	CH_3	C=O	C_α	C_β	
8	8.38						1540
14	8.43			192.8	125.5	188.5	1520
17	8.35		3.00				1530
20	8.40		2.97	193.2	125.1	189.1	1530
21	8.67	11.15		191.4	124.3	178.5	1520
22	8.60	11.22					1525
11	8.20			181.0	107.7	180.5	1500

Table V. Spectroscopic Data for 12-Te-5 Pertelluranes and Model Systems

	^1H NMR δ, ppm			^{13}C NMR δ, ppm			IR ν_{CO}, cm^{-1}
compd	H_α	H_β	CH_3	C=O	C_α	C_β	
9	8.00			195.6	137.9	172.0	1595
15	8.22			197.2	138.5	179.0	1595
18	8.13		2.97	196.6	138.0	180.0	1590
19	7.90		2.97				1590
23	8.45	9.25					1590
24	8.50	9.86					1590
40	7.70						1615
41	8.30	9.00		190.7	133.0	151.3	1610
46[a]	7.38	8.61		185.5	134.3	134.6	
10	7.83						1550

[a] Reference [14].

interacting with two carbonyl units as well as the effect of a Te substituent at the β-position of an enone system without involving hypervalent oxidation states.

Conductance Studies. The specific conductances of solutions of **9** from 1.0 × 10^{-5} to 1.0 × 10^{-2} M (solubility limited) in CH_2Cl_2 were all less than 0.5 $\mu\Omega^{-1}$ cm^{-1}, indicative of a nonconductive, nonionized structure. The values for pertellurane **9** were identical with those obtained for bicyclic pertellurane **10**.[5] In contrast, a 1.0 × 10^{-4} M solution of *n*-Bu_4NBr gave a specific conductance of 37 $\mu\Omega^{-1}$ cm^{-1}.

Electrochemical Studies. Pertelluranes **9**, **15**, **18**, **19**, **23**, and **24** and the corresponding oxatellurolylium halides were examined by cyclic voltammetry (CV) (see Table III). Typical CV scans are shown for an oxatellurolylium halide in Figure 2 for **8** and for a 12-Te-5 pertellurane in Figure 3 for **9**.

CV scans of the 12-Te-5 pertelluranes in the cathodic direction show an irreversible two-electron reduction followed by one-electron reductions associated with the oxatellurolylium halides. The initial two-electron reduction presumably corresponds to reductive loss of two halides to regenerate the oxatellurolylium halide. Coulometric reduction of **9** at −0.1 V (vs. SCE) gave 1.95 faraday/mol. In the anodic direction, an irreversible oxidation is observed in the +0.81–1.28 V range, at the appropriate potential for the oxidation of halide to halogen; however, the corresponding reduction of halogen is not observed. Thus the CV scans of tetrabutylammonium bromide gave Ep_a = +0.88 V vs. SCE and of tetraethylammonium chloride gave Ep_a = +1.16 V vs. SCE. The oxatellurolylium halide oxidation wave found in the range +1.28–1.50 V (vs. SCE) is not observed. This implies that under CV conditions the halogen formed adds oxidatively to the oxatellurolylium halide to regenerate the pertellurane in a fast reaction. In CV scans of the pertelluranes begun in the anodic direction, the oxidation waves due to halide and the oxatellurolylium halide are absent until the second scan, after reduction has occurred. The 12-Te-5 pertellurane **10** undergoes a two-electron reduction (2.1 faraday/mol at −0.25 V vs. SCE) to give the corresponding dioxatellurapentalene (Table III). The suggestion that electrochemically generated halogen from halide oxidation could react rapidly with electrochemically generated 10-Te-3 telluranes was tested by the following reactions. CV scans of solutions of oxatellurolylium halides in the presence of tetraalkylammonium halides were begun at +0.10 V (vs. SCE) in both the anodic and cathodic directions. First waves begun in the cathodic direction showed only reduction of the oxatellurolylium halide. In scans begun in the anodic direction, reduction waves associated with the 12-Te-5 pertelluranes were observed after oxidation of halide to halogen. Reduction of halogen was not observed.

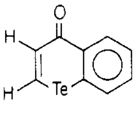
Spectroscopic Studies. The ^1H NMR, ^{13}C NMR, and IR spectral data for various 12-Te-5 pertelluranes, their oxatellurolylium halide counterparts, and the model compounds **40** and **41** can be compared from the data in Tables

IV and V. Spectral data for the dioxatellurapentalene **11** and its 12-Te-5 pertellurane counterpart **10** are included as well.

The carbonyl stretching frequency in the IR spectra of these compounds should be sensitive to the Te–O bond order and the C–O double-bond character. With chalcone as a model enone system with $\nu_{C=O}$ at 1661 cm^{-1}, the introduction of a tellurium at the β carbon reduces the frequency to 1615 cm^{-1} for **40** and 1610 cm^{-1} for **41**, showing significant interaction of Te with the carbonyl. Interestingly, a β-methoxy substituent as in **36** shows little interaction with the carbonyl ($\nu_{C=O}$ 1660 cm^{-1}), whereas a β-phenylthio substituent as in **37** is intermediate between O and Te interactions ($\nu_{C=O}$ 1630 cm^{-1}). The enone carbonyl stretching frequency in both the 12-Te-5 pertelluranes ($\nu_{C=O}$ 1590–1595 cm^{-1}) and the oxatellurolylium halides ($\nu_{C=O}$ 1520–1540 cm^{-1}) is substantially lower than in chalcone or the model enones **40** and **41**, showing less C–O double-bond character and a stronger Te–O interaction. The dioxatellurapentalene **11** gives what is assumed to be a C–O stretching band at 1500 cm^{-1}. In the 12-Te-5 pertellurane **10**, this band appears at 1550 cm^{-1}.

By ^{1}H NMR, the ring protons in the 10-Te-3 telluranes would be expected to be at lower field than the ring protons of the 12-Te-5 pertelluranes if the former species were aromatic due to a diamagnetic ring current.[13] The protons in the telluranes on the carbon α to the carbonyl are at slightly lower field (0.1–0.38 ppm) than corresponding protons in the pertelluranes. In oxatellurolylium halides **21** and **22** and pertelluranes **23** and **24**, with protons at both the α and β positions relative to the carbonyl, significant chemical shift differences are noted between the telluranes and the pertelluranes for the β proton. Thus, the β proton in **21** is at 1.9 ppm lower field than in pertellurane **23**, and the β proton in **22** is at 1.36 ppm lower field than in pertellurane **24**. The tellurane and pertellurane ring protons are at lower field than the α and β protons of **40** and **41**, but the pertellurane values are at only slightly lower field. Attempts to oxidize **40** and **41** to 10-Te-4 compounds by oxidative addition of halogens failed.

The ^{13}C chemical shifts are much more sensitive to charge density in the ring than the corresponding ^{1}H NMR chemical shifts. The ring carbons in both the oxatellurolylium halides **4** and the 12-Te-5 pertelluranes **7** have similar ^{13}C NMR chemical shifts (Tables IV and V). These are quite different from the values observed for **41** or tellurachromone **46** (C=O, δ 185.5; C$_\alpha$, δ 134.3; C$_\beta$, δ 134.6).[14]



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In tellurachromone **46**, the Te cannot interact with the carbonyl O. However, in **41** the Te and carbonyl O atoms can interact, removing electron density from the carbonyl C. A large downfield shift is observed for the chemical shift of C$_\beta$ (δ 151.3). In the 10-Te-3 telluranes and 12-Te-5 pertelluranes, the Te–O interaction is expected to be stronger than in **41** (formal Te–O bonding), and the ^{13}C NMR chemical shifts in these systems are even farther downfield (C$_\beta$, δ 172.0–180.0 for 12-Te-5 pertelluranes and δ 178.5–189.1 for 10-Te-3 telluranes).

The chemical shifts of the carbonyl carbons are similar in both the 10-Te-3 telluranes of structure **4** (δ 191.4–193.2) and the 12-Te-5 pertelluranes of structure **7** (δ 195.6–197.2). These values are slightly downfield of those chemical shifts observed for the carbonyl carbon of **41** (δ 190.7) and **46** (δ 185.5).

The most interesting changes between the ^{13}C NMR spectra of the 10-Te-3 telluranes and the 12-Te-5 pertelluranes occur in the chemical shift differences at C$_\alpha$. In model enone **41** and tellurachromone **46**, the chemical shifts of C$_\alpha$ are δ 133.0 and 134.3, respectively. In the 10-Te-3 telluranes, the chemical shift of C$_\alpha$ is upfield between δ 124.3 and 125.5 for compounds of structure **4** and δ 107.7 for **11**. In the 12-Te-5 pertelluranes, the chemical shift of C$_\alpha$ is downfield (δ 137.9–138.5) relative to **41** and **46**.

Discussion

For oxatellurolylium halides **4** and dioxatellurapentalenes **5** to be aromatic, significant π bonding must exist between Te and O. The X-ray structural data (Table I) show only fractional covalent bonding between Te and O in telluranes **11** and **12**, with Pauling bond numbers of 0.61 and 0.45, respectively,[7,15] and in the 12-Te-5 pertelluranes **9** and **10** with Pauling bond orders of 0.25 and 0.56, respectively. Covalent bonding in all of these compounds can be described in terms of electron-rich three-center bonds between X–Te–O and O–Te–O similar to that proposed for the various Te(II)[16] and Te(IV)[16,17] species.

The stereochemistry of Te(II) and Te(IV) complexes has been discussed on the basis of linear three-center, four-electron bonds and the trans effect in which one ligand is strongly bonded and has a more weakly bonded ligand in the trans position.[11,18] The limit of this effect is no-bond trans to a strongly bound ligand and a T-shaped configuration. Using this model and from observed bond lengths, Foss has assigned "half-p-bond" and no-bond radii of 1.64[11] and 1.91 Å,[19] respectively, to Te(II) and a half-p-bond radius of 1.54–1.56 Å[11] for Te(IV). Expected Te–O fractional bond distances would be 2.30 and 2.21 Å for Te(II) and Te(IV), respectively. The monocyclic pertellurane **9** approaches the limit of the trans effect, with a strong Te–Br bond and a weaker Te–O bond. In bicyclic pertellurane **10**, two nearly identical O ligands are trans, and bonding is essentially identical with each. Thus, the Te–O bonds in **10** are stronger than the Te–O bond of **9**, with the bond order in **10** at the limit of 0.5, owing to symmetry.

We examined the four tellurane and pertellurane ring systems with computational methods to evaluate bonding between atoms and electron densities on atoms. We chose CNDO/2[20] calculations using the program GEOMORV[21] since calculations of this type have already been partially parametrized for this collection of atoms.[2,22] No d functions were included with Te in these calculations.

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(15) The bond orders to Te were computed from the equation $D(n) = D(1) - 0.60 \log n$, where $D(1)$ is the single-bond distance (Te–O, 2.00 Å), n is the Pauling bond number, and $D(n)$ is the observed bond distance.

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(22) The parameters for Te were taken from ref 2: orbital exponent = 2.15; $1/2(I_s + A_s) = 17.35$; $1/2(I_p + A_p) = 6.3$.

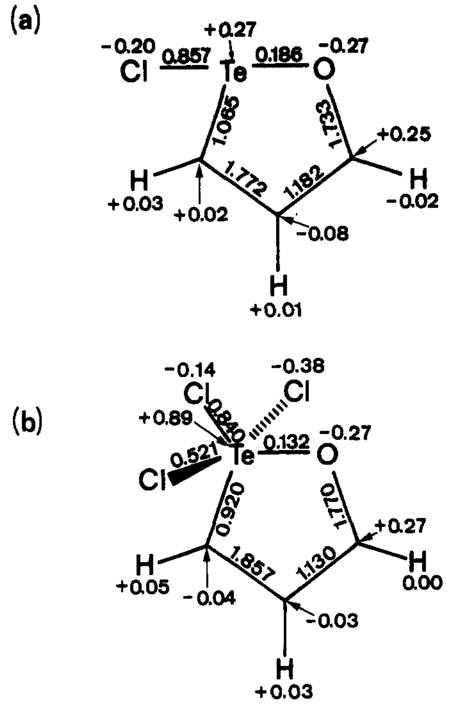


Figure 4. Net charge and Wiberg indices for (a) oxatellurolylium chloride and (b) oxatellurolylium trichloride.

The structures examined by CNDO/2 are shown in Figures 4 and 5 along with net charge on individual atoms and Wiberg indices between atoms. The geometries used in the calculations were taken from X-ray structural data for **9**, **10**,[5] **11**,[5] and **12**.[4a] Table VI contains the calculated HOMO and LUMO energy levels for these systems as well as Fukui indices at Te.[23] In the 12-Te-5 pertelluranes, the LUMO is a low-lying π^* orbital with a large coefficient at (C_β) and the LUMO + 1 and LUMO + 2 σ^* orbitals that are close in energy but heavily weighted on Te. In the 10-Te-3 telluranes, the LUMO is a higher energy π^* orbital with LUMO + 1 and LUMO + 2 σ^* orbitals again heavily Te weighted.

The calculations suggest fractional covalent bonding between Te and O in both the 10-Te-3 telluranes and the 12-Te-5 pertelluranes. The bonding is primarily ionic with a negatively charged O and positively charged Te, which would seemingly preclude p-type π delocalization in these systems. The calculations agree with experiment in that covalent bonding is stronger between Te and O in the dioxatellurapentalene structures than in the monocyclic oxatellurolylium structures, as indicated by the Pauling bond orders and the Wiberg indices for experiment and theory, respectively. Furthermore, the change in Pauling bond order and Wiberg indices between Te and O is small in going from the 10-Te-3 tellurane to the 12-Te-5 pertellurane in the dioxatellurapentalene system, giving about a 10% decrease in covalent bonding. This is presumably due to identical ligands being trans to one another. The change in Pauling bond order and Wiberg indices between Te and O in going from the 10-Te-3 tellurane to the 12-Te-5 pertellurane in the oxatellurolylium system is much larger, giving a 30–40% decrease in covalent bonding.

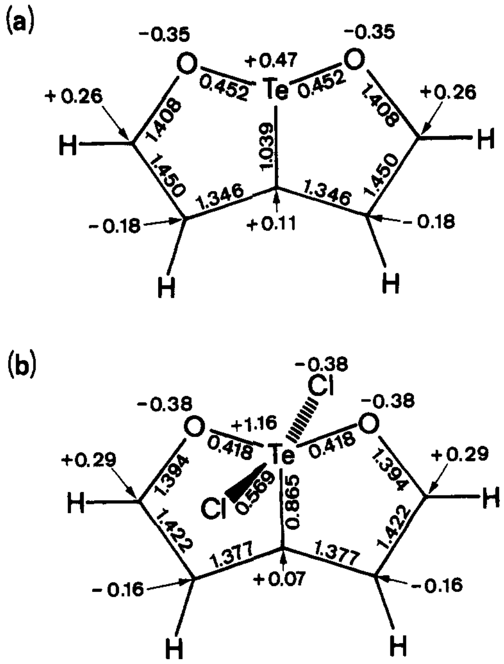
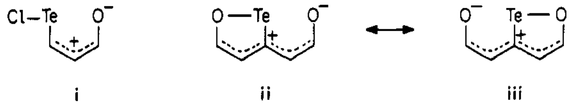


Figure 5. Net charge and Wiberg indices for (a) dioxatellurapentalene and (b) dioxatellurapentalene dichloride.

The X-ray structural data argue against extensive delocalization in pertelluranes **9** and **12**, where distinct, alternating single and double bonds occur in the enone segment, and argue for a large ionic contribution to bonding between Te and O. The observed lengthening of double bonds and shortening of single bonds in **12** can be attributed to a larger ionic character in the enone fragment from resonance form i. The ^{13}C NMR chemical shifts of the oxatellurolylium halide ring carbons also suggest the allyl cation resonance from i by their alternating nature.[4a]



In the dioxatellurapentalenes **10** and **11**, the observed averaging of C–C single and double bonds in both the crystal structure and the CNDO/2 calculations may be aided by symmetry as shown in canonical forms ii and iii. Such delocalization would not be unexpected and is, furthermore, consistent with the observed bond order of $\sim$0.5 for the Te–O bond in these systems. In comparing the carbonyl stretching frequencies in the dioxatellurapentalene and oxatellurolylium systems, the greater Te–O covalent bonding in the dioxatellurapentalenes as well as contributions from canonical forms ii and iii contribute to the lower carbonyl stretching frequency when compared with the appropriate structure in the oxatellurolylium halides in both the 10-Te-3 telluranes and the 12-Te-5 pertelluranes.

The CNDO/2 calculations predict the observed changes in chemical shift in both the ^{13}C and ^{1}H NMR spectra from tellurane to pertellurane. These predictions are based on the net charge at C and H in these systems for equivalent positions, as shown in Figures 4 and 5. Although qualitatively correct, the magnitude of the difference in the chemical shift of H_β between telluranes and pertelluranes is not predicted by charge densities in the CNDO/2 calculations. One cannot rigorously exclude the presence of a diamagnetic ring current to account for the observed chemical shifts of H_β in the oxatellurolylium halides on the basis of ^{1}H NMR data alone, although this large shift is not observed for H_α. A greater positive charge on Te or C_β as well as the utilization of Te d functions could remove electron density and deshield H_β, thus accounting for the magnitude of the deshielding.

The X-ray structural data (bond length) and the calculations (Wiberg indices) show decreased covalent

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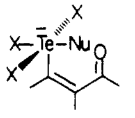
(23) Fujimoto, H.; Fujui, K. In "Advances in Quantum Chemistry"; Lowdin, P.-O., Ed.; Academic Press: New York, 1972; Vol. 6, p 177.

Table VI. CNDO/2 Calculated HOMO and LUMO Energy Levels for 10-Te-3 Telluranes and 12-Te-5 Pertelluranes of Structures 4–7 (R = Ar = H) with Fukui Indices at Te in Parentheses

compd	HOMO, eV	LUMO, eV	LUMO + 1, eV	LUMO + 2, eV
oxatellurolylium chloride	−8.36	+1.59 (0.039)	+2.52 (0.20)	+4.20 (0.11)
oxatellurolylium trichloride	−5.79	+0.10 (0.44)	+1.12 (0.43)	+2.16 (0.21)
dioxatellurapentalene	−10.45	+1.71 (0.033)	+2.85 (0.22)	+5.39 (0.085)
dioxatellurapentalene dichloride	−7.32	+0.01 (2.9)	+1.32 (0.46)	+3.15 (0.13)

bonding between Te and C in the 12-Te-5 pertelluranes relative to the 10-Te-3 telluranes. This is consistent with the higher valency and increased positive charge on Te in the pertelluranes and increased ionic bonding to all ligands in the Te octahedron including C. More electronegative ligands would stabilize this bonding array, whereas less electronegative ligands such as iodide would destabilize it.

The HOMO–LUMO energy levels listed in Table VI predict that the 12-Te-5 pertelluranes should be more readily reduced than the 10-Te-3 telluranes, as observed (Table III). Because the LUMO is significantly lower in energy and is π^* in character with a large coefficient at C_β, nucleophilic attack might be expected to be more facile in the 12-Te-5 pertelluranes at C_β in the enone as well. Furthermore, the LUMO + 1 and LUMO + 2 orbitals are σ^* orbitals on Te in the 12-Te-5 pertelluranes. Nucleophilic attack at Te could occur to give structures such as pertellurane 47 in which Te-O bonding has been eliminated. The propensity for nucleophilic attack at Te in the 12-Te-5 pertelluranes is suggested by the Fukui indices in Table IV. Intermediates similar to 47 have been isolated as in 48.[24] The resulting enone would be "normal", since Te–O interactions are precluded and susceptible to Michael addition by a nucleophile. The pertellurane group could function as a leaving group to give the observed substitution products. The 10-Te-3 telluranes have higher-energy LUMO's and are not as susceptible to nucleophilic attack. Aromatic stabilization need not be invoked to account for the difference in reactivity.



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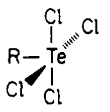

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The attributed aromaticity of the thiathiophthenes 1 and related dioxachalcogenapentalenes 2 has been based in part on the observed electrophilic aromatic substitution of halogens on the ring carbons. The CNDO/2 calculations predict that electrophiles would attack C2 in both the 10-Te-3 telluranes and 12-Te-5 pertelluranes of dioxatellurapentalene, since significant negative charge density is found on these carbons in the ionic bonding model. For pertelluranes 6, this is observed experimentally.[5] Similarly, extension to the dioxathia- and dioxaselenapentalenes would rationalize the observed substitution reactions without invoking aromatic substitution.

There is little evidence that oxatellurolylium halides 4 and dioxatellurapentalenes 5 display any Te–O π bonding, either pπ–dπ or pπ–pπ. The Te–O bonds are part of linear three-center bonds in which two highly electronegative atoms act as donating ligands for a more electropositive Te atom. The maximum amount of covalent bonding in these systems is a total bond order of 1.0 for the sum of the two bonds. The importance of the ionic contribution to bonding in these systems can be inferred from the observed chemistry.

In summary, the 10-Te-3 telluranes and the 12-Te-5 pertelluranes 4–7 are unusual heterocyclic molecules in which bonding is a hybrid of traditional organic and inorganic bonding concepts. There is little evidence of pπ–dπ or pπ–pπ bonding between Te and its ligands, which precludes aromaticity in these heterocyclic systems although there is some covalent character to all bonds to Te. The bonding of Te to the more electronegative elements is best described in terms of three-center, four-electron bonds.

The electronegativities of the atoms in the X–Te–X three-center four-electron bonds appear to be important in determining the reactivity of the Te atom toward oxidative addition of halogens, nucleophilic attack, and ligand exchange.

The spectroscopic properties of these systems resemble those of enones for the monocyclic systems and enolized pentene-1,5-diones for the bicyclic system. The tellurium perturbations in these systems are similar to those observed upon protonation of enones or pentenediones.[27] Carbonyl stretching frequencies are weakened, and allyl and pentadienyl cation segments are observed by NMR for the carbon frameworks.

Finally, CNDO/2 calculations appear to give a good qualitative description of the observed bonding and reactivity of the telluranes and pertelluranes of this study. However, the quantitative comparisons of charge densities between theory and experiment are not parallel and require further refinement of theory.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. ^1H NMR spectra were recorded on a Varian EM-390 instrument. ^{13}C NMR spectra were recorded on a Varian CFT-20 or an IBM WP270SY spectrometer. Carbon assignments were made with SFORD and proton double-resonance techniques. IR spectra were recorded on a Beckman IR 4250 instrument. UV-visible spectra were recorded on a Cary 17 spectrophotometer. Solvents (Kodak Laboratory Chemicals) were dried over 3-Å molecular sieves before use or were used as received. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl. A Perkin-Elmer C, H, and N analyzer was used for microanalyses, and tellurium and selenium were determined by atomic absorption spectroscopy with ±1% accuracy.

Electrochemical Procedures. A Princeton Applied Research Model 173 potentiostat/galvanostat and a Model 175 Universal programmer were used for the electrochemical measurements. The working electrode for cyclic voltammetry was a platinum disk obtained from Princeton Applied Research. All samples were run in J. T. Baker HPLC-grade methylene chloride, which had been stored over Kodak 3-Å molecular sieves. Electrometric-grade tetrabutylammonium fluoroborate (Southwestern Analytical Chemicals, Inc.) was recrystallized from ethyl acetate/pentane and dried at 80 °C under vacuum for 72 h. This material was used as supporting electrolyte at 0.1 M concentration. Argon was used for sample deaeration.

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Preparation of Oxatellurolylium Halides. Oxatellurolylium halides **8**, **12**, **14**, **16**, **17**, **20**, and **21**, were prepared by literature procedures,[1] as was oxaselenolylium chloride **33**.[4] The other oxatellurolylium halides were prepared analogously.

5-Phenyl-1,2-oxatellurolyl-1-ium Bromide (22): mp 108–109.5 °C. Anal. Calcd for C_9H_7BrOTe: C, 32.2; H, 2.1; Te, 37.7. Found: C, 32.1; H, 2.1; Te, 38.3.

3-Methyl-5-(*p*-(*N*,*N*-dimethylamino)phenyl)-1,2-oxatellurolyl-1-ium Chloride: mp 208–210 °C; λ_{max} (CH_2Cl_2) (log ϵ) 460 nm (4.61); FDMS, *m/e* 353 ($C_{12}H_{14}{}^{35}ClON^{130}Te$).

3-Phenyl-5-(*σ*-methylphenyl)-1,2-oxatellurolyl-1-ium Chloride: mp 127.5–128 °C. Anal. Calcd for $C_{16}H_{13}ClOTe$: C, 50.0; H, 3.4; Cl, 9.2; Te, 33.2. Found: C, 49.9; H, 3.5; Cl, 9.3; Te, 33.6.

3-(*p*-Methoxyphenyl)-5-phenyl-1,2-oxatellurolyl-1-ium Chloride: mp 123.5–125 °C. Anal. Calcd for $C_{16}H_{13}ClTeO_2$: C, 48.0; H, 3.3; Cl, 8.9; Te, 31.9. Found: C, 47.9; H, 3.4; Cl, 8.6; Te, 31.4.

3-(*p*-*tert*-Butylphenyl)-5-phenyl-1,2-oxatellurolyl-1-ium Chloride: mp 132–134 °C. Anal. Calcd for $C_{19}H_{19}ClTeO$: C, 53.5; H, 4.5; Cl, 8.3; Te, 29.9. Found: C, 53.6; H, 4.7; Cl, 8.2; Te, 30.0.

General Procedure for Preparation of Pertellurane Trichlorides. Preparation of 3,5-Diphenyl-1,2-oxatellurolyl-1-ium Trichloride (15). A solution of 1.00 g (2.7 mmol) of **14** in 10 mL of CH_2Cl_2 was chilled to 0 °C. Chlorine gas was bubbled into the solution until the initial gold color faded to pale yellow. The reaction mixture was concentrated, and the residue was recrystallized from CH_3CN to give 0.79 g (66%) of **15** as bright yellow needles: mp 166–168 °C, ^1H NMR (CD_2Cl_2) δ 8.30 (dd, 2 H), 8.22 (s, 1 H), 8.0–7.5 (m, 8 H); IR (KBr) 1595, 1580, 1315, 760, 693 cm^{-1}; FDMS, *m/e* 442 ($C_{15}H_{11}{}^{35}Cl_3O^{130}Te$), 407 (M – Cl), 372 (M – 2 Cl); λ_{max} (CH_2Cl_2) (log ϵ) 311 nm (4.28). Anal. Calcd for $C_{15}H_{11}Cl_3OTe$: C, 40.8; H, 2.5; Te, 28.9. Found: C, 40.9; H, 2.6; Te, 29.0.

18: ^1H NMR (CD_2Cl_2) δ 8.30 (dd, 2 H), 8.13 (q, 1 H, J = 1.5 Hz), 7.70 (m, 3 H), 2.97 (d, 3 H, J = 1.5 Hz); IR (KBr) 1590 cm^{-1}; λ_{max} (CH_2Cl_2) (log ϵ) 308 nm (4.26); FDMS, *m/e* 380 ($C_{10}H_9{}^{35}Cl_3O^{130}Te$), 345 (M – Cl). Anal. Calcd for $C_{10}H_9Cl_3OTe$: C, 31.7; H, 2.4; Te, 33.7. Found: C, 31.7; H, 2.4; Te, 33.1.

25: IR (KBr) 1590 cm^{-1}; FDMS, *m/e* 398 ($C_{10}H_8{}^{35}Cl_3FO^{130}Te$), 363 (M – Cl), 328 (M – 2Cl). Anal. Calcd for $C_{10}H_8Cl_3FOTe$: C, 30.2; H, 2.2; Te, 32.1. Found: C, 30.6; H, 2.2; Te, 31.1.

26: IR (KBr) 1595 cm^{-1}; FDMS, *m/e* 357 (M – 2Cl). The material was very insoluble.

27: IR (KBr) 1590 cm^{-1}; FDMS, *m/e* 460 ($C_{15}H_{10}Cl_3FO^{130}Te$), 425 (M – Cl), 390 (M – 2Cl). Anal. Calcd for $C_{15}H_{10}Cl_3FOTe$: C, 39.2; H, 2.2; Te, 27.8. Found: C, 39.4; H, 2.4; Te, 27.5.

28: ^1H NMR (CD_2Cl_2) δ 8.33 (m, 2 H), 8.07 (s, 1 H), 7.53 (m, 5 H), 7.30 (m, 2 H); IR (KBr) 1595 cm^{-1}. Anal. Calcd for $C_{15}H_{10}Cl_3FOTe$: C, 39.1; H, 2.2; Te, 27.8. Found: C, 39.1; H, 2.2; Te, 27.9.

29: ^1H NMR ($CDCl_3$) δ 8.23 (m, 2 H), 8.00 (s, 1 H), 7.57 (m, 5 H), 7.20 (m, 2 H), 3.90 (s, 3 H); IR (KBr) 1570 cm^{-1}. Anal. Calcd for $C_{16}H_{13}Cl_3O_2Te$: C, 40.8; H, 2.8; Te, 27.1. Found: C, 40.7; H, 2.8; Te, 26.6.

30: ^1H NMR ($CDCl_3$) δ 8.07 (s, 1 H), 8.00 (d, 1 H), 7.50 (m, 8 H), 2.80 (s, 3 H); IR (KBr) 1600, 1560 cm^{-1}. Anal. Calcd for $C_{16}H_{13}Cl_3OTe$: C, 42.2; H, 2.9; Te, 28.0. Found: C, 42.1; H, 2.8; Te, 26.7.

31: ^1H NMR ($CDCl_3$) δ 8.27 (dd, 2 H), 8.07 (s, 1 H), 7.53 (m, 5 H), 7.12 (dd, 2 H), 3.98 (s, 3 H); IR (KBr) 1605, 1590 cm^{-1}. Anal. Calcd for $C_{16}H_{13}Cl_3O_2Te$: C, 40.8; H, 2.8; Te, 27.1. Found: C, 40.7; H, 2.8; Te, 26.4.

32: ^1H NMR ($CDCl_3$) δ 8.20 (dd, 2 H), 8.05 (s, 1 H), 7.58 (dd, 2 H), 7.50 (m, 5 H), 1.30 (s, 9 H); IR (KBr) 1595 cm^{-1}. Anal. Calcd for $C_{19}H_{19}Cl_3OTe$: C, 45.9; H, 3.9. Found: C, 45.8; H, 4.0.

Preparation of Oxaselenolylium Trichloride 34. A solution of oxaselenolylium chloride **33** (0.29 g, 1.0 mmol) in 10 mL of CH_2Cl_2 was cooled to 0 °C. Chlorine gas was bubbled through the solution, giving a pale yellow solution. The reaction mixture was concentrated, and the residue was recrystallized from CH_3CN to give 0.27 g (75%) of a pale yellow solid: mp 127–129 °C dec; ^1H NMR ($CDCl_3$) the sample lost chlorine to show only oxaselenolylium chloride **33**; IR (KBr) 1595, 1500, 1251, 1020, 838 cm^{-1}; FDMS, *m/e* 360 ($C_{11}H_{11}Cl_3O_2Se$), 326 (M – Cl). Anal. Calcd for $C_{11}H_{11}Cl_3O_2Se$: C, 36.6; H, 3.1; Se, 21.9. Found: C, 37.2; H, 3.2; Se, 22.9.

General Procedure for the Preparation of Pertellurane Tribromides. Preparation of 3,5-Diphenyl-1,2-oxatellurolyl-1-ium Tribromide (9). A solution of 0.42 g (1.0 mmol) of **8** in 10 mL of CH_2Cl_2 was chilled to 0 °C. A solution of 0.19 g (1.2 mmol) of bromine in 2.5 mL of CH_2Cl_2 was added, giving a pale yellow solution. The reaction mixture was concentrated, and the residue was recrystallized from CH_3CN to give 0.51 g (89%) of **9** as orange crystals: mp 161–162.5 °C; ^1H NMR (CD_2Cl_2) δ 8.30 (dd, 2 H), 8.00 (s, 1 H), 7.9–7.4 (m, 8 H); IR (KBr) 1590, 1580, 1340, 1245, 755, 690 cm^{-1}; λ_{max} (CH_2Cl_2) (log ϵ) 310 nm (4.23); FDMS, *m/e* 574 ($C_{15}H_{11}Br_3O^{130}Te$), 495 (M – Br), 416 (M – 2Br). Anal. Calcd for $C_{15}H_{11}Br_3OTe$: C, 31.4; H, 1.9; Te, 22.2. Found: C, 31.5; H, 1.9; Te, 22.5.

19: ^1H NMR (CD_2Cl_2) δ 8.23 (dd, 2 H), 7.90 (q, 1 H, J = 1.5 Hz), 7.85–7.45 (m, 3 H), 2.97 (d, 3 H, J = 1.5 Hz); IR (KBr) 1590 cm^{-1}; λ_{max} (CH_2Cl_2) (log ϵ) 305 nm (4.32); FDMS, *m/e* 512 ($C_{10}H_9Br_3O^{130}Te$), 433 (M – Br), 354 (M – 2Br). Anal. Calcd for $C_{10}H_9Br_3OTe$: C, 23.4; H, 1.8; Te, 24.9. Found: C, 23.3; H, 1.7; Te, 24.8.

24: FDMS, *m/e* 419 (M – Br), 340 (M – 2Br). Anal. Calcd for $C_9H_7Br_3OTe$: C, 21.7; H, 1.4. Found: C, 21.7; H, 1.4.

Addition of Bromine to 20. Bromine (0.16 g, 1.0 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a solution of **20** (0.31 g, 1.0 mmol) in 10 mL of CH_2Cl_2 cooled to 0 °C. The bromine color disappeared instantly. The reaction mixture was concentrated at 0 °C under vacuum. ^1H NMR analysis of the residue showed two products, **18** and **19**, in a 1:2 ratio. FDMS showed only these products as well.

Addition of Chlorine to 17. A solution of **17** (0.35 g, 1.0 mmol) in 15 mL of CH_2Cl_2 was cooled to 0 °C. Chlorine gas was slowly bubbled into the solution just to the point where the gold color faded to pale yellow. The reaction mixture was concentrated, and the residue was examined by ^1H NMR. Two products, **18** and **19**, were detected in a 2:1 ratio. FDMS confirmed these assignments.

Addition of Iodine to 16. Iodine (0.28 g, 1.1 mmol) was added to a solution of **16** (0.46 g, 1.0 mmol) in 15 mL of CH_2Cl_2. The resulting solution was stirred at ambient temperature for 15 h and at reflux for 10 h. The reaction mixture was concentrated. The residue was recrystallized from CH_3CN to give 0.40 g (87%) of recovered **16**.

Addition of Bromine to 16. Bromine (0.43 g, 1.5 mmol) in 5 mL of CH_2Cl_2 was added dropwise to a 0 °C solution of **16** (0.46 g, 1.0 mmol) in 15 mL of CH_2Cl_2. The reaction mixture initially became pale yellow and then turned muddy red. The reaction mixture was concentrated. The residue contained iodine, which sublimed. Recrystallization from CH_3CN gave 0.51 g (90%) of **9**: mp 161–163 °C.

Ammonium Hydroxide Hydrolysis of 15. Ammonium hydroxide solution (0.5 mL) was added dropwise to a stirred solution of **15** (0.40 g, 0.90 mmol) in 5 mL of CH_3CN. Tellurium metal precipitated. The reaction mixture was diluted with ether (50 mL) and water (50 mL). The organic phase was dried over sodium sulfate and concentrated. The residue was purified by chromatography on silica gel (3% MeOH–CH_2Cl_2) to give 0.10 g (48%) of 1,3-diphenyl-1,3-propanedione and 0.12 g (36%) of **14**.

Ammonium Hydroxide Hydrolysis of 18. The procedure described for **15** was followed with 0.38 g (1.0 mmol) of **18**. 1-Phenyl-1,3-butanedione and **20** were isolated in 63% and 13% yields, respectively.

Methanolysis of 15. A solution of **15** (0.44 g, 1.0 mmol) in 5 mL of CH_2Cl_2 was diluted with 1 mL of methanol. Triethylamine (0.2 g, 2 mmol) was added, giving an exothermic reaction. The reaction mixture was concentrated and purified by chromatography on silica gel (3% MeOH–CH_2Cl_2) to give 0.20 g (80%) of **36**, 0.040 g (15%) of 1,3-diphenyl-1,3-propanedione, and a trace of **14**.

36: ^1H NMR ($CDCl_3$) δ 7.85 (m, 4 H), 7.40 (m, 6 H), 6.45, 6.17 (s, 1 H), 3.72, 3.70 (s, 3 H); IR (film) 1650, 1550 cm^{-1}; FDMS, *m/e* 238 ($C_{16}H_{14}O_2$).

Methanolysis of 18. The procedure described for **15** was repeated with 0.19 g (0.50 mmol) of **18**. Chromatography gave 0.051 g (56%) of **35**, 0.030 g (38%) of 1-phenyl-1,3-butanedione, and a trace of **20**.

35: ^{1}H NMR (CDCl$_3$) δ 7.83 (m, 2 H), 7.40 (m, 3 H), 6.36, 6.06 (s, 1 H), 3.70 (s, 3 H), 2.33 (s, 3 H); IR (KBr) 1660 cm^{-1}; FDMS, *m/e* 176 ($C_{11}H_{12}O_2$).

Addition of Sodium Thiophenoxide to 9. Thiophenol (0.17 g, 1.5 mmol) was added to 5 mL of 1 M sodium methoxide in methanol. The resulting solution was added to a solution of **9** (0.35 g, 0.61 mmol) in 10 mL of CH_2Cl_2, giving an exothermic reaction that precipitated Te metal. The reaction mixture was diluted with ether (75 mL). The resulting solution was washed with water (2 × 50 mL), filtered through Celite, dried over sodium sulfate, and concentrated. Recrystallization from hexanes gave 0.14 g (74%) of **37**: mp 106.5–108.5 °C; ^{1}H NMR (CDCl$_3$) δ 8.10 (m, 2 H), 7.53 (s, 1 H), 7.50 (m, 2 H), 7.17 (m, 6 H); IR (KBr) 1640, 1510, 1493, 1240, 950 cm^{-1}; FDMS, *m/e* 316 ($C_{21}H_{16}OS$). Anal. Calcd for $C_{21}H_{16}OS$: C, 79.7; H, 5.1; S, 10.1. Found: C, 79.4; H, 5.2; S, 10.6.

Addition of Sodium Thiophenoxide to 27. The procedure described for **9** was repeated with 0.30 g (0.50 mmol) of **27**. Crude **38** was recrystallized from hexanes to give 0.14 g (82%) of **38**: mp 95–97 °C; ^{1}H NMR (CDCl$_3$) δ 7.85 (m, 3 H), 7.6–7.0 (m, 11 H), 7.35 (s, 1 H); IR (KBr) 1640 cm^{-1}; FDMS, *m/e* 334 ($C_{21}H_{15}OS$).

Lithium Triethylborohydride Reduction of 21. Oxatellurolylium chloride **21** (0.293 g, 1.00 mmol) was dissolved in 5 mL of dry THF. Lithium triethylborohydride (1.10 mL, 1 M in THF) was added via syringe. The resulting solution was stirred for 2.0 h at ambient temperature. The reaction mixture was concentrated. The residue was purified by chromatography on silica gel to give 0.18 g (92%) of **41**: mp 215–216 °C; ^{1}H NMR (CDCl$_3$) δ 9.00 (d, 2 H, *J* = 9 Hz), 8.30 (d, 2 H, *J* = 9 Hz), 8.10 (m, 4 H), 7.53 (m, 6 H); IR (KBr) 1610, 1500, 1240, 1010, 742 cm^{-1}; λ_{max} (CH$_2$Cl$_2$) (log ϵ) 425 nm (4.77); FDMS, *m/e* 392 ($C_{18}H_{14}O_2{}^{130}Te$). Anal. Calcd for $C_{18}H_{14}O_2Te$: C, 55.4; H, 3.6; Te, 32.7. Found: C, 55.3; H, 3.6; Te, 33.3.

Lithium Triethylborohydride Reduction of 14. The procedure described for **21** was repeated with 0.29 g (0.78 mmol) of **14**, giving 0.11 g (53%) of **40** as an orange solid: mp 160–163 °C; ^{1}H NMR (CDCl$_3$) δ 8.10 (m, 4 H), 7.77 (s, 2 H), 7.52 (m, 6 H), 7.4–6.8 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 190.7, 151.3, 137.6, 133.0, 128.8, 128.4, 127.3; IR (KBr) 1610, 1595, 1570, 1500, 1480, 1225, 745, 685 cm^{-1}; λ_{max} (CH$_2$Cl$_2$) (log ϵ) 452 nm (4.36); FDMS, *m/e* 544 ($C_{30}H_{22}O_2{}^{130}Te$). Anal. Calcd for $C_{30}H_{22}O_2Te$: C, 66.5; H, 4.1; Te, 23.6. Found: C, 66.6; H, 4.1; Te, 23.9.

Registry No. **8**, 99654-55-4; **9**, 99654-54-3; **10**, 87761-70-4; **11**, 87761-67-9; **14**, 99654-54-3; **15**, 99654-53-2; **16**, 82531-87-1; **17**, 82531-84-8; **18**, 99654-57-6; **19**, 99654-58-7; **20**, 82531-97-3; **21**, 82531-88-2; **22**, 100993-57-5; **23**, 99654-61-2; **24**, 99654-62-3; **25**, 99654-59-8; **26**, 99654-56-5; **27**, 99654-60-1; **28**, 100993-53-1; **29**, 100993-54-2; **30**, 100993-55-3; **31**, 100993-56-4; **32**, 101009-43-2; **33**, 100993-60-0; **34**, 99654-63-4; (*E*)-**35**, 50487-01-9; (*Z*)-**35**, 50515-43-0; (*E*)-**36**, 101009-45-4; (*Z*)-**36**, 101009-48-7; **37**, 53656-87-4; **38**, 101009-46-5; **40**, 101009-44-3; **41**, 100993-58-6; 3-(*p*-methoxyphenyl)-5-phenyl-1,2-oxatellurolyl-1-ium chloride, 84280-84-2; 3-(*p*-*tert*-butylphenyl)-5-phenyl-1,2-oxatellurolyl-1-ium chloride, 100993-59-7; 3-methyl-5-(*p*-(*N*,*N*-dimethylamino)phenyl)-1,2-oxatellurolyl-1-ium chloride, 101009-47-6; 3-phenyl-5-(α-methylphenyl)-1,2-oxatellurolyl-1-ium chloride, 84281-07-2.

Supplementary Material Available: Tables VII–X, showing crystal data for **9**, positional and thermal parameters, general temperature factor expressions, and bond angles involving Te (3 pages). Ordering information is given on any current masthead page.

Synthesis of 2-Substituted 5,7,8-Trimethyl-6-hydroxythiochromans and Purported Syntheses of Sulfur-Containing Analogues of Vitamin E[1]

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The syntheses of 5,7,8-trimethyl-, 2,5,7,8-tetramethyl-, and 2,2,5,7,8-pentamethyl-6-hydroxythiochromans have been achieved by a Michael-type condensation of methyl acrylate and related methyl esters with 2,3,5-trimethyl-4-hydroxythiochromans followed by cyclization of the free acid and reduction. These three previously unknown compounds can serve as simple models for the still unknown 1-thia-α-tocopherol (**1**), which could not be prepared by this route. Indeed, two purported syntheses of **1**[8,9] have been shown to yield an essentially identical mixture of five isomers of the desired compound. For three components in this mixture, including the two major products, it is highly probable that the initial condensation at sulfur has not been followed by ring closure.

Vitamin E is the major lipid-soluble, chain-breaking antioxidant present in human blood.[3,4] α-Tocopherol, the main component of vitamin E, and other alkylated 6-hydroxychromans are excellent antioxidants in vitro.[5] Detailed structure–activity studies led us to synthesize alkylated 5-hydroxydihydrobenzofurans which were found, as predicted, to be even better antioxidants than the 6-hydroxychromans.[6,7] We wished to extend these studies to the sulfur-containing analogue of α-tocopherol, **1**, since this compound would also be expected to be an excellent antioxidant. The purported synthesis of **1** and related compounds was first reported in 1944[8] and again in 1982.[9] We repeated both syntheses and found that they do not yield **1** in significant amounts (vide infra). We therefore developed, and report herein, a short synthesis of three model 6-hydroxythiochromans **2** (R_1 and R_2 = H or CH$_3$).

Although there are various potential synthetic approaches to **1** and **2**[10–14] reagents containing a free phenolic

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