bonds about the central nitrogen atom. Because of the general tendency of increased planarity of the amino group in the presence of para electron-withdrawing substituents,[20] the planar geometry is most appropriate in the benzoyl cations.

Acknowledgment. We thank the La Trobe University Computer Centre for a generous allocation of computer time and facilities. D.C. gratefully acknowledges support in part from a CSIRO postdoctoral studentship and a Monash postdoctoral fellowship.

Registry No. 2 ($X = NH_2$), 84132-25-2; **2** (X = OH), 56176-50-2; **2** (X = F), 39981-36-7; **2** ($X = CH_3$), 20122-40-1; **2** (X = H), 19270-10-1; **2** ($X = CF_3$), 46061-29-4; **2** (X = CN), 56176-49-9; **2** ($X = NO_2$), 45945-94-6.

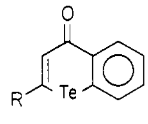
Cyclization of 3-(Arylchalcogeno)propenoyl Chlorides. 1. 1,2-Oxatellurol-1-ium Halides via "Ipso" Acylation

Michael R. Detty,* Bruce J. Murray, Douglas L. Smith, and Nicholas Zumbulyadis

Contribution from the Research Laboratories, Eastman Kodak Company, Rochester, New York 14650. *Received March 29, 1982*

Abstract: 3-(Aryltelluro)propenoyl chlorides react thermally and with Lewis acids to give products of rearrangement that are identified as new tellurium heterocycles, 1,2-oxatellurol-1-ium chlorides. The heterocyclic nature of the compounds was confirmed by single-crystal X-ray crystallography, which also showed a chlorine–tellurium bond with a nearly linear (170°) Cl–Te–O array containing fractional bonds. A bonding picture utilizing a three-center, four-electron bond is described. ^{125}Te NMR spectroscopy suggests that Te(IV) may be the correct oxidation state for tellurium in these compounds. The chlorine in these molecules is easily exchanged for other halogens as well as trifluoroacetate. The rearrangement appears to involve "ipso" acylation followed by aryl migration to give the observed products. The rates of rearrangement, both thermal and Lewis acid catalyzed, are sensitive to substituent effects.

Interest in the preparation of tellurium analogues of various heterocyclic systems has been increasing. Two systems that have been successfully prepared are tellurochromones (**1**)[1] and telluroxanthone (**2**).[2] Although the cyclizations of β-(arylthio)- and β-(arylseleno)acrylic acids (**3**) have been useful for the preparation of 4*H*-(benzo[*b*]thio)pyrones and 4*H*-(benzo[*b*]seleno)pyrones,[3] the extension of the reaction to include the cyclization of β-(aryltelluro)acrylic acids and derivatives has not been described.



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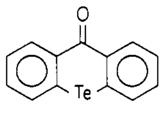

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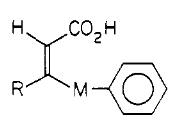
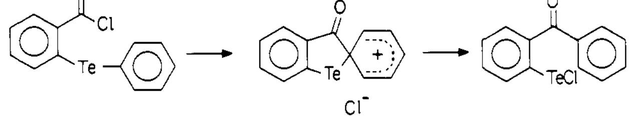


3

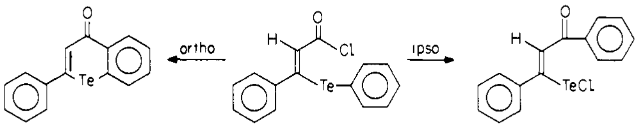
M = S, Se, Te

The reaction of *o*-(phenyltelluro)benzoyl chloride (**4**) with zinc chloride has been reported to give not **2** but a rearrangement product, *o*-(chlorotellurenyl)benzophenone (**5**).[4] This product presumably arises by attack of an acylium species or its equivalent on the carbon bearing tellurium to give a spirocyclic intermediate followed by fission of the carbon–tellurium bond to give an aryl migration and the observed product.[4,5]



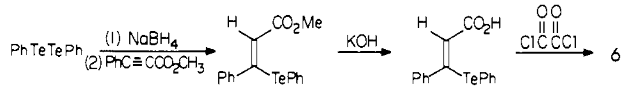
4 **5**

Scheme I



7 **6** **8**

Scheme II



9 **10**

The rearrangement product **5** displayed some interesting spectral features.[4] The IR carbonyl stretching frequency was 1580 cm^{-1}. This lowering of the stretching frequency was attributed to an interaction between the carbonyl oxygen and the tellurium atom.

We were interested in the fate of β-(aryltelluro)acryloyl and -cinnamoyl chlorides when treated with Lewis acids. The questions of whether ortho or ipso acylation would predominate and what would be the properties of the products were of particular interest. Herein, we report the Lewis acid and thermally induced rearrangements of β-(aryltelluro)acryloyl and -cinnamoyl chlorides, which proceed by ipso acylation. The rearrangement products show strong tellurium–oxygen interactions and represent a new class of tellurium heterocycles, 1,2-oxatellurol-1-ium chlorides.

Results and Discussion

Although tellurochromones have been prepared (**1**, R = H, CH_3),[1] telluroflavones (**1**, R = Ph) have yet to be described. With this fact in mind, we first examined the reaction of β-(phenyltelluro)cinnamoyl chloride (**6**) with aluminum chloride. If ortho acylation were observed, telluroflavone (**7**) would be the expected product, whereas ipso acylation should lead to the vinyltellurenyl chloride **8** (Scheme I).

The synthesis of **6** was straightforward, as indicated in Scheme II. The reduction of diphenyl ditelluride with sodium borohydride in ethanolic tetrahydrofuran (THF) gave a colorless solution of sodium phenyltelluride.[6] Methyl phenylpropionate was then

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(2) Lohner, W.; Praefcke, K. *Chem.-Ztg.* **1979**, *103*, 265.

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(4) Piette, J.-L.; Thibaur, P.; Renson, M. *Tetrahedron* **1978**, *34*, 655.

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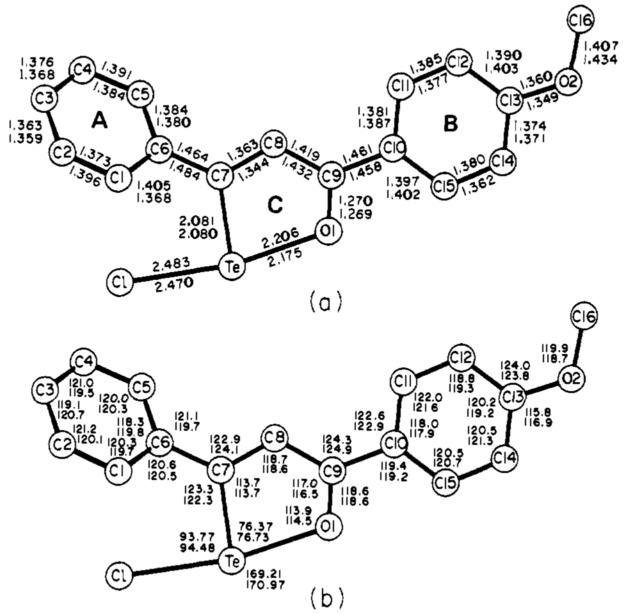


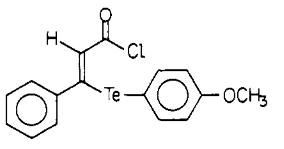
Figure 1. Bond lengths and angles. The upper figures are for the A molecule, the lower for B. Estimated standard deviations for distances average 0.0043 Å (range 0.0032–0.0057 Å) for C–C and C–O, 0.0011 Å for Te–Cl, and 0.0024 Å for Te–O and Te–C. The esd's average 0.08° (range 0.06–0.10°) for angles around Te, 0.19° for Te–O1–C9, and 0.27° (range 0.23–0.35°) for all other angles.

added, giving a mildly exothermic reaction with formation of a cinnamate ester.[7] Only one ester was detected, methyl (*Z*)-3-phenyl-3-(phenyltelluro)propenoate (**9**). The stereochemistry was assigned on the basis of the ^{1}H NMR chemical shift of the olefinic proton at δ 6.67.[3d] Saponification with aqueous potassium hydroxide in ethanol followed by acidification gave cinnamic acid **10**. The acid chloride **6** was generated quantitatively when **9** was treated with oxalyl chloride at room temperature.

Reaction of a methylene chloride solution of **6** with aluminum chloride gave an orange, crystalline solid in excellent yield. The isolated material was isomeric with the starting acid chloride, as shown by both elemental analysis and its field desorption mass spectrum. This showed that ortho acylation had not occurred. This compound had an IR carbonyl stretching frequency at 1520 cm^{-1}, much lower than expected for a structure such as **8**. The ^{1}H NMR spectrum of the product consisted of 10 aromatic protons and a one-proton singlet at δ 8.42. The ^{13}C NMR spectrum displayed 11 signals, indicative of two phenyl groups. Finally, the visible absorption spectrum of the molecule showed a maximum at 428 nm with a molar extinction coefficient of 17000.

Although the NMR spectral data fit structure **8**, the IR and visible absorption spectra as well as the chemical shift of the enone singlet suggested that representation as **8** might be an oversimplification. A single-crystal X-ray structural analysis was used to assign the structure unambiguously.

Suitable crystals were obtained from a closely related compound. This molecule was obtained by rearrangement of (*Z*)-β-(*p*-(methoxyphenyl)telluro)cinnamoyl chloride, **11**. Spectroscopically, this product was similar to that obtained by rearrangement of **6**. The IR carbonyl stretching frequency was 1530 cm^{-1}, and the visible absorption spectrum gave a λ_{max} at 435 nm with a molar extinction coefficient of 30200.



11

The final atomic parameters and structure factors are given in Tables I–IV of the supplementary information. Bond lengths and angles, uncorrected for thermal motion, are given in Figure 1.

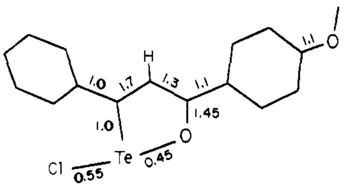


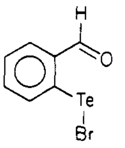
Figure 2. Smoothed Pauling bond numbers.

The coordination at tellurium is T-shaped with a strong equatorial bond to carbon [2.081 (3), 2.080 (3) Å] and weaker axial bonds of order $^1/_2$ to chlorine [2.483 (1), 2.470 (1) Å] and oxygen [2.206 (2), 2.175 (2) Å]. Furthermore, the Cl–Te–O bonds are nearly linear, with an angle of 170° formed by the three atoms.

Tellurium is well-known for its variety of coordination interactions. A search for intermolecular contacts that would indicate weak "secondary interactions"[8] showed that all contacts are consistent with the van der Waals radii of Bondi,[9] who assigns Te a radius of 2.06 Å. The most significant contacts are TeA···TeB ($\bar{x}$, $1-y$, $1-z$) = 4.289 (1) Å, a distance to which Dewan and Silver[10] have attached some significance in terms of very weak electronic interactions that produce color, and TeB–C(4)A ($1-x$, $1-y$, $1-z$) = 3.654 (4) Å. Thus, "secondary interactions" are insignificant, and the Te atom in both molecules is three-coordinate of the type AX_3E_2. For one to account for more than eight electrons around a central atom, either d orbitals must be used, as in the valence-shell electron-pair repulsion (VSEPR) treatment,[11] or delocalized three-center four-electron bonds must be used.[12]

Both of the above approaches are qualitative explanations of the observed structure where the coordination at Te is T-shaped with a normal Te–C equatorial bond and elongated Te–Cl and Te–O axial bonds. The Te lone pairs of electrons occupy the other equatorial positions in the trigonal bipyramid. Both approaches probably grossly misrepresent the contributions of d orbitals to the bonding. Nevertheless, ^{125}Te Mössbauer spectra of a number of Te(II) and Te(IV) compounds have been interpreted in terms of three-center bonds by using the Te 5p orbitals.[13] The stereochemistry of Te(IV) has also been reviewed with respect to these approaches.[14]

Crystal structures have been reported for three other Te(II) compounds in which the bonding configuration is very similar to that of the present compound. In (*o*-formylphenyl)tellurenyl bromide (**12**)[15] and in 2-(bromotelluro)benzamide (**13**) and 2-(chlorotelluro)-*N*-methylbenzamide (**14**),[16] Te bonds with a strong single bond to carbon and with weaker, fractional, axial bonds



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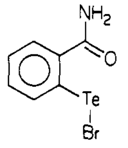

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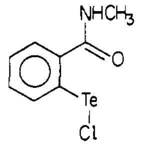

14

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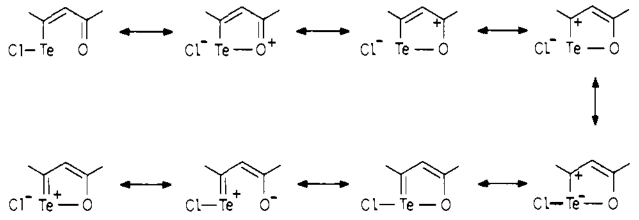
Scheme III



to oxygen and a halogen. The Te–O bonds are 2.31, 2.250 (7), and 2.237 (8) Å, respectively, and therefore are all somewhat weaker than in the present compound.

The degree of bonding between atoms, i.e., the bond numbers,[17] would be useful to facilitate the interpretation of the bonding in the present compound. For the organic ligand, the bond numbers were obtained from published bond-length–bond-number curves.[18] For the bonds to Te, eq 1[17] was used, where $D(1)$ is the single

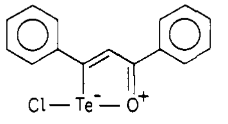
$$D(n) = D(1) - 0.60 \log n \qquad (1)$$

bond distance, n is the Pauling bond number, and $D(n)$ is the observed bond distance. The bond numbers for the present compound are given in Figure 2. They are based on bond lengths averaged for the two independent molecules and have been smoothed to leave atoms Te and C(8) with no net charge.

The observed bond lengths and the calculated bond numbers both suggest considerable σ character in the Te–O bond, approximately equal in magnitude to the σ character of the Te–Cl bond. In this example, the Te–O bond is much stronger than in the other literature examples.[15,16] The compound examined should be legitimately considered as a five-membered heterocycle in the crystalline state.

The bond numbers of the organic ligand suggest that resonance forms in which the enone unit is not discrete are important in the overall structure. The C–C and C–O double bonds have less than double-bond character, and the C–C single bond has more than single-bond character. Various resonance forms are shown in Scheme III. Interestingly, contributions from both Te(II) and Te(IV) oxidation states are possible.

The naming of such compounds can be taken from protonation studies of 1,6-dioxa-6a-thia- and 1,6-dioxa-6a-selenapentalenes to give 1,2-oxathiolium and 1,2-oxaselenolium cations.[19] By analogy, the rearrangement products of **6** and **11** would be represented as oxatellurolium species **15** and **16**. Structure **15** would be named 3,5-diphenyl-1,2-oxatellurol-1-ium chloride, and **16** would be named 3-phenyl-5-(4-methoxyphenyl)-1,2-oxatellurol-1-ium chloride.



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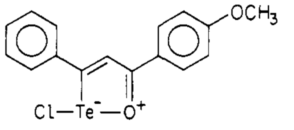
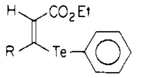
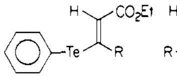


16

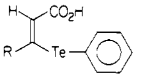
The rearrangement was also observed for various β-(aryltelluro)acryloyl chlorides. The addition of ethyl propiolate to sodium phenyltelluride in ethanolic THF gave a 13:1 mixture of cis and trans esters **17** and **18**, respectively. The stereochemistries of **17** and **18** were established by ^{1}H NMR, which showed a cis olefinic coupling constant of 10 Hz for **17** and a trans olefinic coupling constant of 16.5 Hz for **18**.[20] Saponification with potassium hydroxide in aqueous ethanol gave **19**. Treatment of **19** with oxalyl chloride gave the corresponding acid chloride, which, upon treatment with aluminum chloride, gave 5-phenyl-1,2-oxatellurol-1-ium chloride (**20**).



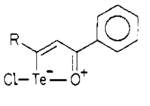
17, R = H
21, R = CH_3



18, R = H
22, R = CH_3



19, R = H
23, R = CH_3



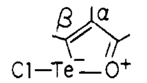
20, R = H
24, R = CH_3

Similarly, the addition of ethyl tetrolate to sodium phenyltelluride gave *Z* ester **21**. None of the *E* isomer **22** was detected. Saponification of **21** gave **23**, which was converted to the acid chloride. Treatment of the acid chloride with aluminum chloride gave 3-methyl-5-phenyl-1,2-oxatellurol-1-ium chloride (**24**).

Table I. Spectral Parameters of 1,2-Oxatellurol-1-ium Chlorides[a]

compd	^{1}H NMR, δ			^{13}C NMR, δ		
	H_α	H_β	CH_3	C=O	C_α	C_β
15	8.42			192.8	125.5	188.5
16	8.34			189.8	125.3	187.8
20	8.67	11.15		191.4	124.3	178.5
24	8.40		2.97	193.2	125.1	189.1

[a] The following representation is used:

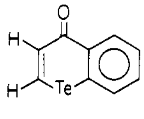


The spectral parameters of **15**, **20**, and **24** were quite revealing (Table I). All three compounds display very low carbonyl stretching frequencies (1520–1530 cm^{-1}), indicating a strong tellurium–oxygen interaction. The α proton of the enone segment is extremely deshielded, falling in the range δ 8.40–8.67. What is even more surprising is the appearance of the β proton of **20** at δ 11.15. These chemical shifts show that a considerable amount of positive charge is delocalized into the ring carbons. The chemical shift of the methyl group of **24** is also at lower field than would be expected for simple attachment to the β-carbon of an enone system.

The ^{13}C NMR spectra are also consistent with significant positive charge delocalization into the ring. The chemical shifts of the enone carbons are quite similar to those observed for protonated enones (which bear a full positive charge) in strong acid solution.[21]

Attempts to ionize the chloride in the oxatellurolium chlorides with silver tetrafluoroborate in deuterioacetonitrile gave unexpected results. Signals for the free oxatellurolium cation with a tetrafluoroborate anion could not be detected. From these reactions, the corresponding oxatellurolium fluorides could be isolated (see below).

The ^{1}H and ^{13}C NMR spectra of **15**, **20**, and **24** can be compared with those of tellurochromone (**25**),[22] an enone bearing an aryl telluro group at the β-carbon. The α and β protons in **25** appear at δ 7.38 and 8.61, respectively. This is at much higher field than the protons of **15**, **20**, and **24**. Similarly, the ^{13}C NMR spectrum of **25** is markedly different. The α- and β-carbons resonate at δ 134.3 and 134.6, and the carbonyl carbon appears at δ 185.5. These values show that the ^{13}C NMR spectra of **15**, **20**, and **24** do not merely reflect the effect of a tellurium substituent on the β-carbon of an enone.



25

The formation of the oxatellurolium chlorides should be mechanistically similar to the rearrangement of **4**.[4,5] Attack of an acylium cation on the aromatic carbon bearing tellurium (ipso

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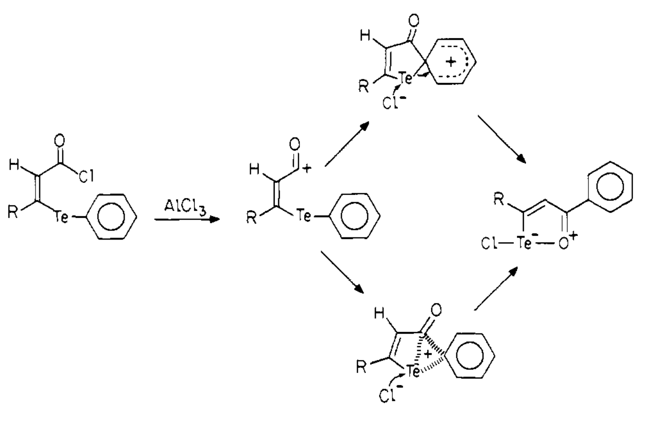
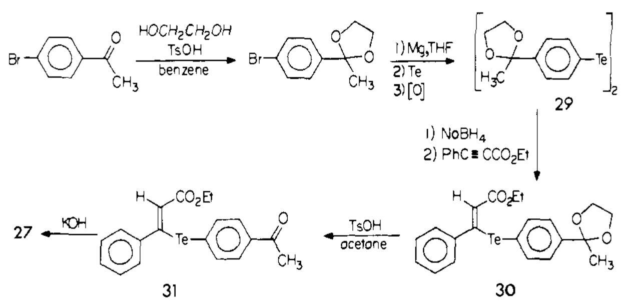
Scheme IV



Scheme V



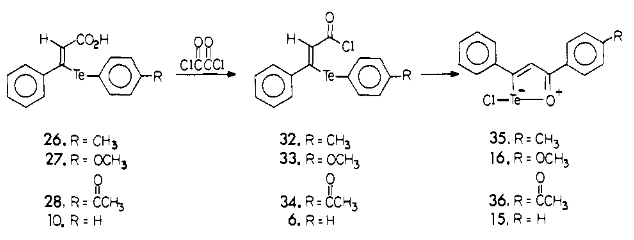
acylation) would lead to the formation of a σ intermediate spirocyclic complex. Nucleophilic attack of chloride at tellurium would generate the oxatellurolium species as well as complete the aryl migration. Alternatively, the acylium cation could attack the carbon–tellurium bond directly without formation of a spirocyclic intermediate. The cleavage of tellurium esters by hydrohalic acids (protodetelluration) to form tellurenyl halides is believed to involve direct attack of a carbon–tellurium bond by a proton.[4] These two possibilities for aryl migration are shown in Scheme IV.

The possibilities for aryl migration should be easily distinguished on the basis of substituent effects if attack of the aromatic ring is rate determining. If ipso acylation is involved, the rate of rearrangement should be sensitive to substituent effects in the para position, since a fully developed positive charge would be present in the ring in the spirocyclic intermediate that could be delocalized to the para carbon. If direct electrophilic attack of the carbon–tellurium bond or reductive elimination from a tellurocyclobutenone occurred, the substituent effect would be limited to an inductive effect with no mesomeric contributions. As a result, the substituent effects should be small.

We prepared the (*Z*)-3-(aryltelluro)cinnamic acids **26**–**28** to investigate substituent effects of the rearrangement of the corresponding acid chlorides. Acids **26** and **27** were prepared by allowing the appropriate aryltelluride anion to react with ethyl phenylpropionate followed by saponification of the resultant esters. The aryltelluride anions were prepared as before. The diaryl ditellurides were prepared by the action of tellurium metal on the aryl Grignard reagents prepared from 4-bromotoluene and 4-bromoanisole.[23]

The preparation of **28** was somewhat more elaborate, as shown in Scheme V. *p*-Bromoacetophenone was converted to its ethylene ketal in 94% yield with ethylene glycol and a catalytic amount of *p*-toluenesulfonic acid in benzene with azeotropic removal of water. Treatment of the ketal with magnesium turnings in THF gave the appropriate Grignard reagent, which reacted with tellurium metal to give ditelluride **29** in 32% yield. Sodium borohydride reduction of **29** followed by the addition of ethyl phenylpropiolate gave the *Z* ester **30** in 77% yield. Acid-catalyzed ketal exchange gave keto ester **31** in 96% yield, which was then saponified in 93% yield with ethanolic potassium hydroxide to give keto acid **28**.

Scheme VI



Attempted conversion of **27** to acid chloride **33** gave an interesting result. None of the acid chloride could be detected or isolated. Oxatellurolium chloride **16** was produced in quantitative yield at room temperature. This suggested a thermal route to oxatellurolium chlorides, as shown in Scheme VI, which would allow *easy kinetic monitoring of the rearrangement. In fact*, heating a solution of **32** in refluxing deuteriochloroform produced **35** by a first-order reaction with a half-life of 1 h. Similarly, heating a solution of **6** in refluxing deuteriochloroform produced **15** by a first-order reaction with a half-life of 30 h. Acid chloride **34** showed no detectable reaction after 72 h in refluxing chloroform.

Although two points make a crude Hammett plot, a ρ value of -6 is obtained by using σ^+ substituent constants.[24] With a ρ value of -6, the *p*-methoxy derivative **33** would be expected to have a half-life of a few seconds at most at 25 °C, and the *p*-acetyl derivative **34** should show less than 1% reaction after 72 h in refluxing deuteriochloroform. Qualitatively, the experimental observations are consistent with a ρ value of -6.

The crude ρ value obtained for this reaction is essentially the same as the value obtained for aromatic nitration (-5.97), which is thought to involve a σ-complex intermediate.[25] The rearrangement of the acid chlorides to the oxatellurolium chlorides apparently involves ipso acylation. Direct electrophilic attack of the carbon–tellurium bond is seemingly precluded.

Acid chloride **32** gave **35** after a few minutes upon treatment with aluminum chloride at -78 °C. The reaction of acid chloride **34** with aluminum chloride was sluggish. Conversion of **36** was realized only after heating **34** with 3 equiv of aluminum chloride for 6 h in refluxing methylene chloride. These results show that the Lewis acid and the thermal routes give identical products and that the rate of the Lewis acid catalyzed rearrangement is sensitive to substituent effects.

The para orientation of the substituents in **32**, **33**, and **34** was maintained during the aryl transfer to form the oxatellurolium halides. We were curious whether ortho substituents in the aromatic ring or other aromatic nuclei would divert the ipso acylation pathway to give substituent scrambling.

The acid chlorides **37** and **38** were prepared from dinaphthyl ditelluride and di-*o*-tolyl ditelluride, respectively, as described above. Treatment of these compounds with aluminum chloride gave **39** and **40** as the only products. Ipso acylation with aryl migration was observed in both rings.

Although aryl migration occurs presumably through ipso acylation, several mechanistic details are unresolved. The extent to which tellurium participates in the acylium cation generation is unclear. One could envision an oxidative addition of the acid chloride function to tellurium to give a Te(IV) species or initial complexation of the acylium cation to Te. The mechanistic picture is incomplete.

The bonding model for oxatellurolium chlorides in the crystalline state predicts that chlorine should bear considerable negative charge and that the Te–Cl bond should have considerable ionic

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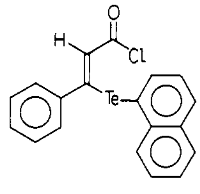
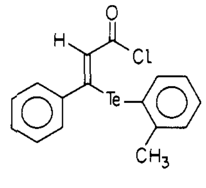
[23] Piette, J.-L.; Renson, M. *Bull. Soc. Chim. Belg.* **1970**, *79*, 353.

[24] Hammett, L. P. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1970. Wells, P. R. *Chem. Rev.* **1963**, *63*, 171. Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

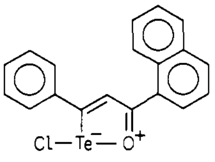
[25] Gordon, A. J.; Ford, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 148.



37



38



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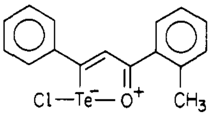


40

character. This suggests that chlorine should be easily exchanged for other ionic groups. Tellurenyl halide functions have been manipulated in various ways, including treatment with silver salts[4,26] and dialkyl cadmium reagents.[4,27] The oxatellurolium chlorides were converted to other oxatellurolium halides and trifluoroacetates via the procedures shown in Scheme VII. No other products other than halogen exchange were observed. Some of the physical properties for the oxatellurolium halides are given in Table II.

The oxatellurolium halides and trifluoroacetates are stable to air and to light in the solid phase and in solution. Thermolysis at temperatures up to 300 °C and irradiation with an unfiltered Hanovia 450-W lamp failed to deposit tellurium metal.

The oxidation state of tellurium in these compounds remains undefined. As discussed above, resonance forms incorporating both Te(II) and Te(IV) can be drawn for the oxatellurolium compounds. The chemical shift of ^{125}Te is a sensitive probe for the oxidation state of tellurium.[28,29] The ^{125}Te chemical shifts for 3-methyl-5-phenyl-1,2-oxatellurol-1-ium chloride (**24**), bromide (**45**), and iodide (**46**) are summarized in Table III together with the chemical shifts of other representative tellurium compounds.[28,29] The chemical shift of the chloro derivative is farther downfield than any tellurium shifts observed to date in a survey by one of us (N.Z.) of more than 50 tellurium-containing compounds. The shielding of the tellurium nucleus increases (upfield shift) in going from the chloro to the bromo and iodo derivatives. Such behavior has been reported for the dihalo oxidation products of 1,3-dihydrobenzo[*c*]tellurophene.[28] The chemical shifts of all three compounds fall in the range expected for Te(IV) compounds.

No decoupling was used in acquiring the spectra because ^{125}Te has a negative gyromagnetic ratio and has never shown full NOE enhancement. A small, long-range coupling to the sole proton in the ring system was observed. The magnitude of the coupling constant depends on the halogen atom attached to tellurium. It is <2, 18, and 14 Hz for Cl, Br, and I, respectively.

The X-ray crystallographic data described above are also consistent for a Te(IV) structure. The sum of the average Te–Cl and Te–O distances is 4.67 Å. If the covalent radii of Cl (0.99 Å) and O (0.66 Å)[17] are subtracted from this, a radius of 1.51 Å for Te is obtained. Foss has reported radii for Te in three-center bonds to be 1.64 Å for Te(II) and 1.54–1.56 Å for Te(IV).[30] Thus, the tellurium radius for the oxatellurolium chlorides is in the range expected for Te(IV).

Scheme VII

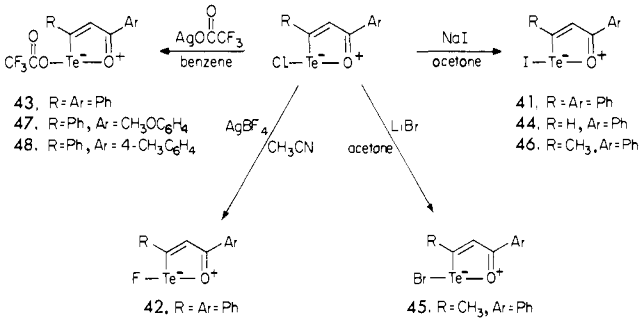
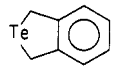
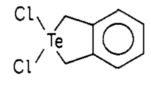


Table II. Physical Properties of Oxatellurolium Halides and Trifluoroacetates

compd	yield,[a] %	mp, °C	ν_{CO}, cm^{-1}	λ_{max} (CH_2Cl_2), nm	log ε
15	81[b]	104-105	1520	428	4.28
16	96[b]	123.5-125.5	1531	435	4.48
20	82[b]	96-98	1520	427	4.30
24	76[b]	104-106	1530	418	4.25
35	92[b]	127.5-128	1532	427	4.34
36	50[b]	175-177	1528	436	4.40
39	82[b]	134-135.5	1522	431	4.28
40	75	oil	1560	430	4.20
41	89[c]	136-136.5	1540	459	4.30
42	33[c]	88-90	1535		
43	86[c]	140.5-142.5	1530	425	4.26
44	75[c]	109-110	1525	450	4.27
45	78[c]	121-122	1540	424	4.28
46	83[c]	98-99	1540	440	4.30
47	50[c]	125-127	1520	432	4.45
48	63[c]	130-132	1532	425	4.30

[a] Isolated yield. [b] From acid chloride. [c] From oxatellurolium chloride.

Table III. ^{125}Te Chemical Shifts for Oxatellurolium Halides and Other Representative Compounds

compd	chemical shift[a]
24	+911.0
45	+858.0
46	+677.0
TeO_3^{2-}	+892.0
Ph_2Te	−145.0
$(C_{16}H_{33})_2Te$	−602.0
	−564.6[b]
	+160.1[b]

[a] Chemical shifts reported in ppm from bis(diethyldithiocarbamato)tellurium(II). Positive values indicate a downfield shift. [b] Reference 28.

Summary and Conclusions

The new tellurium heterocycles 1,2-oxatellurol-1-ium chlorides are easily prepared by Lewis acid or thermally catalyzed rearrangement of β-(aryltelluro)acryloyl or -cinnamoyl chlorides. The rearrangement proceeds via ipso acylation at the aromatic carbon bearing tellurium, resulting in an aryl migration.

An X-ray crystal structure of **16** showed strong, nearly equal fractional bonds from tellurium to both chlorine and oxygen. The observed bond lengths and bond orders are best explained by a three-center, four-electron bond among chlorine, tellurium, and oxygen. This bonding theory predicts considerable negative charge density at the more electronegative atoms in this bond, chlorine and oxygen, and suggests considerable ionic character to the bond.

Chemically, the chlorine atom in these compounds is easily exchanged for other halides and trifluoroacetate. This fact is consistent with the bonding picture.

Spectroscopically, both ^{13}C and ^{1}H NMR spectra show that the ring carbons appear to delocalize a considerable amount of positive charge, which would be consistent with negative charge

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(26) Piette, J.-L.; Renson, M. *Bull. Soc. Chim. Belg.* **1971**, *80*, 669.

(27) Piette, J.-L.; Talbot, J.-M.; Genard, J.-C.; Renson, M. *Bull. Soc. Chim. Fr.* **1973**, 2468.

(28) Zumbulyadis, N.; Gysling, H. J. *J. Organomet. Chem.* **1980**, *192*, 183.

(29) Taken from a compilation of new ^{125}Te NMR data: Zumbulyadis, N.; Gysling, H. J., manuscript in preparation.

(30) Foss, O. In "Selected Topics in Structural Chemistry"; Andersen, P., Bastiansen, O., Furberg, S., Eds.; Universitetsforlaget: Oslo, 1967; pp 145–173.

being localized at chlorine and oxygen; positive charge would have to be borne by tellurium and the ring carbons. The ^{125}Te spectra of some of the oxatellurolium halides suggest that Te(IV) may be the appropriate oxidation state in these compounds. The low-field shifts observed in the ^{1}H and ^{13}C NMR spectra may be explained by the presence of an electron-deficient Te(IV). Alternatively, these low-field shifts may be explained by an aromatic ring current from a 6π-electron ring system.

The system proposed by Perkins et al. can be used[31] to avoid the ambiguity of assigning an oxidation state to Te in these compounds. By their definition, the oxatellurolium halides would be described as 10-Te-3 compounds with 10 electrons in the valence shell of Te having 3 ligands.

The chemical properties as well as other spectral properties of these compounds are being examined.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are corrected. ^{1}H NMR spectra were recorded on a Varian EM-390 instrument. Infrared spectra were recorded on a Beckman IR 4250 instrument. UV-visible spectra were recorded on a Cary 17 spectrophotometer. Tellurium powder and tellurium shot were purchased from Ventron. Ethyl phenylpropiolate was purchased from Aldrich. Solvents were obtained from Kodak Laboratory Chemicals and were used as received. Microanalyses were performed by Galbraith Laboratories or at Kodak on a Perkin-Elmer C, H, and N analyzer. Tellurium analyses were performed by atomic absorption spectroscopy. All reactions were conducted under normal laboratory lighting.

General Procedure for Ditelluride Preparation. Di-*p*-anisyl Ditelluride. *p*-Bromoanisole (5.82 g, 0.311 mol) was dissolved in 20 mL of dry THF. Part of this solution (2 mL) was added to magnesium turnings (1.0 g, 0.042 mol) under an argon atmosphere. A small crystal of iodine (~25 mg) was added to initiate the reaction. After the mixture was stirred for several minutes, the iodine color faded. The rest of the *p*-bromoanisole solution was added dropwise fast enough to sustain gentle reflux. After addition was complete, reflux was maintained for 0.5 h. The reaction mixture was cooled to room temperature, and tellurium shot (3.81 g, 0.0300 mol) was added. The resulting mixture was stirred at reflux for 3 h and then cooled to 0 °C; 20 mL of saturated ammonium chloride solution was added (vigorous evolution of gas). The reaction mixture was filtered through a pad of Celite. The filtered solids were washed with saturated ammonium chloride (100 mL) and ether (3 × 50 mL). The ether phase was separated, washed with brine, and dried over sodium sulfate. Concentration and recrystallization of the residue from methanol gave 5.16 g (74%) of di-*p*-anisyl ditelluride as a red-brown solid, mp 57–59 °C.

Bis(*p*-acetylphenyl) Ditelluride Bis(ethylene ketal) (29). *p*-Bromoacetophenone ethylene ketal (12.2 g, 0.0500 mol) was treated as described with magnesium (1.8 g, 0.075 mol) and tellurium shot (6.4 g, 0.050 mol) to give 4.7 g (32%) of bis(*p*-acetylphenyl) ditelluride bis(ethylene ketal) as a red solid, mp 140–143 °C.

Di-*p*-tolyl Ditelluride. This material, mp 52–53 °C, was generously provided by Dr. H. Gysling.

Di-1-naphthyl Ditelluride. 1-Bromonaphthalene (42.0 g, 0.203 mol) was treated with magnesium (5.6 g, 0.23 mol) and tellurium shot (25.5 g, 0.200 mol) as described to give 20.5 g (40%) of di-1-naphthyl ditelluride as a dark red solid, mp 116.5–120 °C.

Di-o-tolyl Ditelluride. *o*-Bromotoluene (6.0 g, 0.035 mol) was treated with magnesium (1.13 g, 0.0465 mol) and tellurium shot (4.47 g, 0.035 mol) as described to give 7.0 g (91%) of di-*o*-tolyl ditelluride as a dark red oil.

Preparation of *p*-Bromoacetophenone Ethylene Ketal. *p*-Bromoacetophenone (27.5 g, 0.138 mol), ethylene glycol (30 mL), and *p*-toluenesulfonic acid (1.0 g) were dissolved in 200 mL of benzene. The resulting solution was warmed at reflux for 15 h with azeotropic removal of water via a Dean–Stark trap (2.5 mL theoretical, 2.8 mL collected). The benzene solution was washed with saturated sodium bicarbonate solution (100 mL) and brine (2 × 100 mL), dried over sodium sulfate, and concentrated. The solid residue was recrystallized from petroleum ether (bp 30–60 °C) to give 31.5 g (94%) of the ketal as a white crystalline solid, mp 44–46 °C: ^{1}H NMR (CDCl$_3$) δ 7.40 (m, 4 H), 4.1–3.5 (m, 4 H), 1.63 (s, 3 H).

General Procedure for the Addition of Sodium Aryltellurides to Methyl and Ethyl Acetylenic Esters. The diaryl ditelluride was dissolved in 1/1 (v/v) THF/ethanol (1 mmol/10 mL) under an argon atmosphere. Sodium borohydride powder was added in 0.1-g portions every 2 min until the characteristic dark-red color of the ditelluride faded. The ethyl phenylpropiolate (methyl phenylpropiolate for **8** and **10**), ethyl tetrolate, or ethyl propiolate in ethanol (2 mmol/mL) was added in one portion. The resulting solution was stirred for 0.5 h at room temperature. The excess sodium borohydride was quenched with acetic acid, and the reaction mixture was concentrated in vacuo. The residue was partitioned between methylene chloride and 1 N hydrochloric acid. The methylene chloride layer was dried over sodium sulfate and concentrated. The 3-(aryltelluro)propenoates were recrystallized from methanol. Table IV gives appropriate physical data for the esters.

Table IV. Preparation of R(ArTe)C$\overset{Z}{=}$CHCO$_2$R'

compd	R	Ar	R'	yield,[a] %	mp, °C	^{1}H NMR[b]	IR[c]
9	Ph	Ph	CH$_3$	95	92–95	6.67	1670
17	H	Ph	C$_2$H$_5$	95	oil		
21	CH$_3$	Ph	C$_2$H$_5$	83	oil		
26	Ph	4-CH$_3$-C$_6$H$_4$	C$_2$H$_5$	87	95–96.5	6.66	1671
			Ethyl Ester				
27	Ph	4-CH$_3$-OC$_6$H$_4$	C$_2$H$_5$	71	100-102	6.70	1670
30	Ph	4-CH$_3$-COC$_6$H$_4$	C$_2$H$_5$	77	66–66.5	6.73	1670
37	Ph	1-C$_{10}$H$_7$	CH$_3$	84	129-133	6.73	1670
			Methyl Ester				
38	Ph	2-CH$_3$-C$_6$H$_4$	C$_2$H$_5$	58	83–86		

[a] Isolated yield. [b] Chemical shift (δ) in ppm of α proton in α,β-unsaturated ester. [c] Ester carbonyl stretching frequency in cm^{-1}.

For **9**: mass spectrum, *m/e* 382 (C$_{17}$H$_{16}$O$_2$Te). Anal. Calcd for C$_{17}$H$_{16}$O$_2$Te: C, 53.7; H, 4.2; Te, 33.6. Found: C, 53.7; H, 4.4; Te, 33.8.

For **26** (ethyl ester): mass spectrum, *m/e* 396 (C$_{18}$H$_{18}$O$_2$Te). Anal. Calcd for C$_{18}$H$_{18}$O$_2$Te: C, 54.9; H, 4.6; Te, 32.4. Found: C, 54.6; H, 4.6; Te, 32.6.

For **27** (ethyl ester): mass spectrum, *m/e* 412 (C$_{18}$H$_{18}$O$_3$Te). Anal. Calcd for C$_{18}$H$_{18}$O$_3$Te: C, 52.7; H, 4.4; Te, 31.1. Found: C, 52.6; H, 4.6; Te, 30.6.

For **30**: mass spectrum, *m/e* 468 (C$_{21}$H$_{22}$O$_4$Te). Anal. Calcd for C$_{21}$H$_{22}$O$_4$Te: C, 54.1; H, 4.8; Te, 27.4. Found: C, 53.6; H, 4.7; Te, 27.4.

For **37** (methyl ester): mass spectrum, *m/e* 418 (C$_{20}$H$_{16}$O$_2$Te).

For **38** (ethyl ester): mass spectrum, *m/e* 396 (C$_{18}$H$_{18}$O$_2$Te).

Hydrolysis of Ester 30. Preparation of Keto Ester 31. The ketal ester **30** (3.00 g, 6.45 mmol) was dissolved in 25 mL of acetone and 5 mL of water. *p*-Toluenesulfonic acid (0.5 g) was added. The resulting solution was warmed at 50 °C until TLC analysis (silica gel, 10/1 (v/v) CH$_2$Cl$_2$/acetone) showed complete consumption of starting material. The reaction mixture was diluted with water (200 mL), and the products were extracted with ether (3 × 50 mL). The combined ether extracts were dried over sodium sulfate and concentrated to give 2.60 g (96%) of a yellow solid that was used without further purification: ^{1}H NMR (CDCl$_3$) δ 7.50 (s, 4 H), 7.00 (s, 5 H), 6.75 (s, 1 H), 4.33 (q, 2 H, J = 7 Hz), 2.50 (s, 3 H), 1.37 (t, 3 H, J = 7 Hz).

General Procedure for Saponification of (*Z*)-3-(Aryltelluro)propenoate Esters. The ester was dissolved in hot (50 °C) ethanol (1 g of ester/20 mL of ethanol). To this solution was added aqueous potassium hydroxide (2.0 g of KOH/5 mL of water per gram of ester). The resulting solution was stirred at 50 °C for 1 h and then diluted with 50 mL of water per gram of ester. After cooling to room temperature, the aqueous solution was extracted with carbon tetrachloride and acidified with 10% chloric acid. The acidified solution was extracted with methylene chloride (4 × 50 mL). The combined methylene chloride extracts were dried over sodium sulfate and concentrated to give the crude acid. Recrystallization (usually from acetonitrile) gave pure acid. Table V gives physical properties for the tellurium-containing acids.

For **10**: Anal. Calcd for C$_{15}$H$_{12}$O$_2$Te: C, 51.2; H, 3.4; Te, 36.3. Found: C, 51.0; H, 3.5; Te, 35.6.

For **19**: ^{1}H NMR (CDCl$_3$) δ 8.72 (d, 1 H, J = 10 Hz), 7.80 (m, 2 H), 7.30 (m, 3 H), 7.03 (d, 1 H, J = 10 Hz); mass spectrum, *m/e* 278 (C$_9$H$_8$O$_2$Te). Anal. Calcd for C$_9$H$_8$O$_2$Te: C, 39.2; H, 2.9; Te, 46.3. Found: C, 39.1; H, 2.9; Te, 45.4.

For **23**: ^{1}H NMR (Me$_2$SO-d_6) δ 7.90 (m, 2 H), 7.40 (m, 3 H), 6.83 (quartet, 1 H, J = 1.2 Hz), 2.05 (d, 3 H, J = 1.2 Hz); mass spectrum, *m/e* 292 (C$_{10}$H$_{10}$O$_2$Te). Anal. Calcd for C$_{10}$H$_{10}$O$_2$Te: C, 41.4; H, 3.5; Te, 44.0. Found: C, 41.4; H, 3.5; Te, 44.6.

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(31) Perkins, C. W.; Martin, J. C.; Arduengo, A. J.; Lau, W.; Alegria, A.; Kochi, J. K. *J. Am. Chem. Soc.* **1980**, *102*, 7753.

Table V. Preparation of R(ArTe)C=CHCO$_2$H

compd	R	Ar	yield,[a] %	mp, °C	^{1}H NMR[b]	IR[c]
10	Ph	Ph	92	174–176	6.67	1650
19	H	Ph	82	150–153	7.03	1650
23	CH$_3$	Ph	79	175–178	6.83	1650
26	Ph	4-CH$_3$-C$_6$H$_4$	95	187–189	6.73	1651
27	Ph	4-CH$_3$-OC$_6$H$_4$	89	182.5–185.5	6.71	1650
28	Ph	4-CH$_3$-COC$_6$H$_4$	93	188–192	6.77	1676, 1655
37	Ph	1-C$_{10}$H$_7$	90	205–208	6.67	1651
38	Ph	2-CH$_3$-C$_6$H$_4$	68	193–196	6.70	1650

[a] Isolated yield. [b] Chemical shift (δ) in ppm of α proton in α,β-unsaturated acid. [c] Acid carbonyl stretching frequency in cm^{-1}.

Table VI. Preparation of R(ArTe)C$\overset{Z}{=}$CHCOCl

compd	R	Ar	^{1}H NMR[a]
6	Ph	Ph	7.11
32	Ph	4-CH$_3$C$_6$H$_4$	7.05
34	Ph	4-CH$_3$COC$_6$H$_4$	7.13
37	Ph	1-C$_{10}$H$_7$	7.10

[a] Chemical shift (δ) in ppm of α proton in α,β-unsaturated acid chloride.

For **26**: mass spectrum, *m/e* 368 (C$_{16}$H$_{14}$O$_2$Te). Anal. Calcd for C$_{16}$H$_{14}$O$_2$Te: C, 52.5; H, 3.9; Te, 34.9. Found: C, 52.6; H, 4.0; Te, 34.7.

For **27**: mass spectrum, *m/e* 384 (C$_{16}$H$_{14}$O$_3$Te). Anal. Calcd for C$_{16}$H$_{14}$O$_3$Te: C, 50.3; H, 3.7; Te, 33.4. Found: C, 50.6; H, 3.7; Te, 32.6.

For **28**: mass spectrum, *m/e* 396 (C$_{17}$H$_{14}$O$_3$Te). Anal. Calcd for C$_{17}$H$_{14}$O$_3$Te: C, 51.8; H, 3.6; Te, 32.4. Found: C, 51.5; H, 3.7; Te, 32.2.

For **37** (carboxylic acid): Anal. Calcd for C$_{19}$H$_{14}$O$_2$Te: C, 56.8; H, 3.5; Te, 31.7. Found: C, 56.7; H, 3.6; Te, 32.4.

For **38** (carboxylic acid): mass spectrum, *m/e* 368 (C$_{16}$H$_{14}$O$_2$Te). Anal. Calcd for C$_{16}$H$_{14}$O$_2$Te: C, 52.5; H, 3.9; Te, 34.9. Found: C, 52.3; H, 3.9; Te, 34.2.

General Procedure for Preparation of 3-(Aryltelluro)propenoyl Chlorides. Under a nitrogen atmosphere, the 3-(aryltelluro)propenoic acids were added to oxalyl chloride (1 g acid/5 mL oxalyl chloride). The resulting mixtures were stirred for 30–60 min at room temperature. The progress of reaction was followed by ^{1}H NMR spectroscopy. If reaction was not complete, the reaction mixture was then stirred at 40 °C until the acid was consumed. The excess oxalyl chloride was removed by evaporation at reduced pressure to give the acid chlorides as red waxy solids. The acid chlorides were used without further purification. Table VI gives ^{1}H NMR data.

General Procedure for the Preparation of 1,2-Oxatellurol-1-ium Chlorides. The 3-(aryltelluro)propenoyl chloride derivatives were dissolved in methylene chloride (1 g/10 mL) under a nitrogen atmosphere. The resulting solution was cooled to −78 °C, and 1.1 equiv of aluminum chloride was added. The cooling bath was removed, and the reaction was allowed to warm to room temperature. The reaction mixture was poured into ice water (200 mL), and the products were extracted with methylene chloride (3 × 50 mL). The combined methylene chloride extracts were dried over sodium sulfate and concentrated. The (usually) solid residue was conveniently recrystallized from methanol.

For **15**: ^{1}H NMR (CDCl$_3$) δ 8.43 (s, 1 H), 8.08 (m, 2 H), 7.50 (m, 3 H), 7.45 (s, 5 H); IR (KBr) 1595, 1520, 1455, 1391, 1235, 780, 688 cm^{-1}; mass spectrum, *m/e* 372 (C$_{15}$H$_{11}$ClOTe). Anal. Calcd for C$_{15}$H$_{11}$ClOTe: C, 48.7; H, 3.0; Cl, 9.6; Te, 34.5. Found: C, 48.7; H, 3.0; Cl, 9.9; Te, 34.3.

For **16**: ^{1}H NMR (CDCl$_3$) δ 8.25 (s, 1 H), 7.90 (d, 2 H, *J* = 9 Hz), 7.27 (s, 5 H), 6.83 (d, 2 H, *J* = 9 Hz), 3.70 (s, 3 H); IR (KBr) 1631, 1600, 1235, 1185, 835, 763, 695 cm^{-1}; mass spectrum, *m/e* 402 (C$_{16}$H$_{13}$ClO$_2$Te). Anal. Calcd for C$_{16}$H$_{13}$ClO$_2$Te: 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.

For **20**: ^{1}H NMR (CDCl$_3$) δ 11.15 (d, 1 H, *J* = 7.5 Hz), 8.67 (d, 1 H, *J* = 7.5 Hz), 8.05 (m, 2 H), 7.55 (m, 3 H); IR (KBr) 1595, 1520, 1450, 1373, 1250, 730 cm^{-1}; ^{13}C NMR (CDCl$_3$) δ 191.39, 178.47, 135.41, 134.05, 129.31, 128.92, 124.30; mass spectrum, *m/e* 296 (C$_9$H$_7$ClOTe). Anal. Calcd for C$_9$H$_7$ClOTe: C, 36.7; H, 2.4; Cl, 12.1; Te, 43.4. Found: C, 36.6; H, 2.2; Cl, 11.9; Te, 42.7.

For **24**: ^{1}H NMR (CDCl$_3$) δ 8.43 (q, 1 H, *J* = 1 Hz), 8.15 (m, 2 H), 7.55 (m, 3 H), 2.97 (d, 3 H, *J* = 1 Hz); IR (KBr) 1595, 1530, 1450, 1390, 1250, 830, 775 cm^{-1}; mass spectrum, *m/e* 310 (C$_{10}$H$_9$ClOTe). Anal. Calcd for C$_{10}$H$_9$ClOTe: C, 39.0; H, 2.9; Cl, 11.5; Te, 41.4. Found: C, 38.9; H, 2.9; Cl, 11.6; Te, 41.3.

For **35**: ^{1}H NMR (CDCl$_3$) δ 8.33 (s, 1 H), 7.93 (d, 2 H, *J* = 8 Hz), 7.40 (s, 5 H), 7.25 (d, 2 H, *J* = 8 Hz), 2.40 (s, 3 H); IR (KBr) 1605, 1532, 1365, 858, 822, 759, 693 cm^{-1}; mass spectrum, *m/e* 386 (C$_{16}$H$_{13}$ClOTe). 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.

For **36**: ^{1}H NMR (CDCl$_3$) δ 8.47 (s, 1 H), 8.18 (d, 2 H, *J* = 8 Hz), 8.04 (d, 2 H, *J* = 8 Hz), 7.45 (s, 5 H), 2.65 (s, 3 H); IR (KBr) 1681, 1528, 1428, 1260, 690 cm^{-1}; mass spectrum, *m/e* 414 (C$_{17}$H$_{13}$ClO$_2$Te). Anal. Calcd for C$_{17}$H$_{13}$ClO$_2$Te: C, 49.5; H, 3.2. Found: C, 49.4; H, 3.1.

For **39**: ^{1}H NMR (CDCl$_3$) δ 8.60 (m, 1 H), 8.27 (s, 1 H), 7.87 (m, 3 H), 7.50 (m, 3 H), 7.36 (s, 5 H); IR (KBr) 1605, 1570, 1522, 1231, 803, 770, 758, 694 cm^{-1}; mass spectrum, *m/e* 422 (C$_{19}$H$_{13}$ClTeO). Anal. Calcd for C$_{19}$H$_{13}$ClTeO: C, 54.3; H, 3.1; Cl, 8.4; Te, 30.3. Found: C, 54.2; H, 3.2; Cl, 8.5; Te, 30.3.

For **40**: ^{1}H NMR (CDCl$_3$) δ 8.27 (s, 1 H), 7.80 (m, 1 H), 7.45 (s, 5 H), 7.3 (m, 3 H), 2.65 (s, 3 H). Anal. Calcd for C$_{16}$H$_{13}$ClOTe: C, 50.0; H, 3.4; Te, 33.2. Found: C, 49.8; H, 3.5; Te, 33.4.

General Procedure for Conversion of Oxatellurolium Chlorides to Trifluoroacetates. Silver trifluoroacetate was dissolved in dry benzene (1 mmol/20 mL). The oxatellurolium chloride (1 equiv) was added gradually as a powder over 3 min. After the addition was complete, the reaction mixture was stirred for 1 h at room temperature. The reaction mixture was filtered through a pad of Celite. The filtrate was washed with brine, dried over sodium sulfate, and concentrated. The residue was recrystallized from absolute ethanol to give the oxatellurolium trifluoroacetates.

For **43**: ^{1}H NMR (CDCl$_3$) δ 8.50 (s, 1 H), 8.07 (d × d, 2 H, *J* = 2, 8 Hz), 7.53 (m, 3 H), 7.40 (s, 5 H); IR (KBr) 1710, 1600, 1530, 1460, 1389, 1374, 1195, 1170, 1162, 1150, 755, 722, 691 cm^{-1}; mass spectrum, *m/e* 450 (C$_{17}$H$_{11}$F$_3$O$_3$Te). Anal. Calcd for C$_{17}$H$_{11}$F$_3$O$_3$Te: C, 45.6; H, 2.5; F, 12.7; Te, 28.5. Found: C, 45.3; H, 2.5; F, 12.8; Te, 28.2.

For **47**: ^{1}H NMR (CDCl$_3$) δ 8.47 (s, 1 H), 8.03 (d, 2 H, *J* = 9 Hz), 7.38 (s, 5 H), 6.97 (d, 2 H, *J* = 9 Hz), 3.87 (s, 3 H); IR (KBr) 1710, 1685, 1605, 1540, 1520, 1491, 1440, 1374, 1270, 1175, 1022, 835, 762, 697 cm^{-1}; mass spectrum, *m/e* 480 (C$_{18}$H$_{13}$F$_3$O$_4$Te). Anal. Calcd for C$_{18}$H$_{13}$F$_3$O$_4$Te: C, 45.2; H, 2.7; Te, 26.7. Found: C, 45.2; H, 2.8; Te, 26.7.

For **48**: ^{1}H NMR (CDCl$_3$) δ 8.47 (s, 1 H), 7.90 (d, 2 H, *J* = 9 Hz), 7.33 (s, 5 H), 7.27 (d, 2 H, *J* = 9 Hz), 2.34 (s, 3 H); IR (KBr) 1712, 1610, 1532, 1490, 1375, 1170, 828, 762, 698 cm^{-1}; mass spectrum, *m/e* 464 (C$_{18}$H$_{13}$F$_3$O$_3$Te). Anal. Calcd for C$_{18}$H$_{13}$F$_3$O$_3$Te: C, 46.8; H, 2.8; Te, 27.6. Found: C, 46.8; H, 2.8; Te, 26.7.

General Procedure for Conversion of Oxatellurolium Chlorides to Iodides. Sodium iodide was dissolved in acetone (1 mmol/5 mL/3 equiv). The oxatellurolium chloride (1 equiv) was added. The resulting solution was stirred for 15 min at 50 °C. The reaction mixture was concentrated in vacuo. The residue was partitioned between methylene chloride (50 mL/mmol) and water (50 mL/mmol). The organic phase was dried over sodium sulfate and concentrated. The residue was recrystallized from acetonitrile.

For **41**: ^{1}H NMR (CDCl$_3$) δ 8.23 (s, 1 H), 8.13 (d × d, 2 H, *J* = 2, 8 Hz), 7.8–7.2 (m, 8 H); IR (KBr) 1600, 1540, 1450, 1240, 755 cm^{-1}; mass spectrum, *m/e* 464 (C$_{15}$H$_{11}$IOTe). Anal. Calcd for C$_{15}$H$_{11}$IOTe: C, 39.0; H, 2.4; Te, 27.6. Found: C, 39.0, H, 2.1; Te, 28.0.

For **44**: ^{1}H NMR (CDCl$_3$) δ 11.3 (d, 1 H, *J* = 7.5 Hz), 8.47 (d, 1 H, *J* = 7.5 Hz), 8.10 (d × d, 2 H, *J* = 2, 8 Hz), 7.60 (m, 3 H); IR (KBr) 1595, 1525, 1450, 1355, 1250, 735 cm^{-1}; mass spectrum, *m/e* 388 (C$_9$H$_7$IOTe). Anal. Calcd for C$_9$H$_7$IOTe: C, 28.0; H, 2.0; Te, 33.1. Found: C, 28.0; H, 1.9; Te, 32.0.

For **46**: ^{1}H NMR (CDCl$_3$) δ 8.30 (q, 1 H, *J* = 1.0 Hz), 8.10 (m, 2 H), 7.60 (m, 3 H), 3.05 (d, 3 H, *J* = 1.0 Hz); IR (KBr) 1595, 1540, 1455, 1250, 826, 774 cm^{-1}; mass spectrum, *m/e* 402 (C$_{10}$H$_9$IOTe). Anal. Calcd for C$_{10}$H$_9$IOTe: C, 30.0; H, 2.3; Te, 31.9. Found: C, 30.3; H, 2.3; Te, 31.5.

Preparation of 3,5-Diphenyl-1,2-oxatellurol-2-ium Fluoride (42). Silver tetrafluoroborate (0.252 g, 1.34 mmol) was dissolved in 20 mL of dry acetonitrile. Oxatellurolium chloride **15** (0.50 g, 1.3 mmol) was added as a powder. The resulting solution was stirred under nitrogen for 3 h at room temperature. The reaction mixture was filtered through a pad of Celite, and the filtrate was concentrated. The residue was taken up in 50 mL of methylene chloride. The resulting solution was washed with brine, dried over sodium sulfate, and concentrated to give 0.16 g (33%) of **42** as a fluffy, yellow solid: ^{1}H NMR (CDCl$_3$) δ 8.53 (s, 1 H), 8.10 (d × d, 2 H, *J* = 2, 8 Hz), 7.57 (m, 8 H); IR (KBr) 1600, 1540, 1450, 1240, 755 cm^{-1}; mass spectrum, *m/e* 356 (C$_{15}$H$_{11}$FOTe). Anal. Calcd for C$_{15}$H$_{11}$FOTe: C, 51.0; H, 3.1. Found: C, 50.8; H, 3.0.

Preparation of 3-Methyl-5-phenyl-1,2-oxatellurol-1-ium Bromide (45). Anhydrous lithium bromide (0.87 g, 10 mmol) was dissolved in 20 mL of acetone. Oxatellurolium chloride **24** (0.61 g, 2.0 mmol) was added as a powder. The resulting mixture was warmed at reflux for 10 min and then concentrated in vacuo. The residue was partitioned between 40 mL of methylene chloride and 40 mL of water. The organic phase was dried over sodium sulfate and concentrated. The residue was recrystallized from acetonitrile to give 0.54 g (78%) of **45**: ^{1}H NMR ($CDCl_3$) δ 8.35 (q, 1 H, J = 1.0 Hz), 8.04 (m, 2 H), 7.50 (m, 3 H), 3.00 (d, 3 H, J = 1.0 Hz); IR (KBr) 1595, 1530, 1455, 1430, 1398, 1353, 1250, 830, 775 cm^{-1}; mass spectrum, m/e 354 ($C_{10}H_9BrOTe$). Anal. Calcd for $C_{10}H_9BrOTe$: C, 34.1; H, 2.6; Te, 36.2. Found: C, 34.5; H, 2.6; Te, 35.6.

Thermal Rearrangements of 3-(Aryltelluro)propenoyl Chlorides. Approximately 1 M solutions of 3-(aryltelluro)propenoyl chlorides **6**, **32**, and **34** in 10 mL of deuteriochloroform were prepared. The solutions were placed in 25-mL two-necked flasks each equipped with a rubber septum and a reflux condenser. The flasks were immersed in a constant-temperature bath at 67 °C. At appropriate intervals (6 h for **6**, 15 min for **32**, 24 h for **34**), 0.30-mL aliquots were withdrawn and placed in 5-mm NMR tubes. The ratio of the olefinic singlets for starting acid chloride and oxatellurolium chloride was determined. The rearrangements of **6** and **32** were followed over two half-lives; **34** showed no detectable reaction after 72 h. The half-lives of **6** and **32** were 1 and 30 h, respectively.

Determination of ^{125}Te NMR Spectra. The ^{125}Te spectra were obtained at 63.21 MHz on a wide-bore 200-MHz multinuclear NMR spectrometer developed in our laboratories. The sample (~100 mg) in 8–10 mL of $CDCl_3/CHCl_3$ was contained in 20-mm NMR tubes. The chemical shifts are given with respect to bis(diethyldithiocarbamato)tellurium(II), a compound which we have established as a convenient ^{125}Te NMR reference.[28,32]

Determination of the X-ray Crystal Structure of 3-Phenyl-5-(4-methoxyphenyl)-1,2-oxatellurol-1-ium Chloride (16). Orange crystals of **16** (M_r 400.33) were obtained as thick, tabular chunks upon recrystallization from methanol. The crystals were mounted in random orientation to a glass fiber with Eastman 910 adhesive. The crystal dimensions were 0.30 × 0.28 × 0.19 mm.

Cell Data. The crystals were determined to be triclinic, $P\bar{1}$, with a = 11.323 (3) Å, b = 17.441 (2) Å, c = 7.838 (5) Å, α = 93.73 (2)°, β = 93.59 (3)°, γ = 85.46 (1)°. The unit cell constants were obtained by computer centering of 25 reflections, followed by least-squares refinement of the setting angles. The cell volume is 1537 (1) Å^3 with d_c = 1.730 g/cm^3 for four molecules per cell and d_m = 1.62–1.73 g/cm^3. The radiation had λ = 0.7107 Å (Mo Kα). The crystal had $F(000)$ = 776, μ(Mo Kα) = 22 cm^{-1}, and equivalent positions of $\pm(x, y, z)$.

Data Collection. The data were collected on an Enraf Nonius CAD4 diffractometer with Mo Kα radiation from a graphite incident-beam monochromator at 23 ± 1 °C. The ω–2θ scan technique was used with a scan rate of 1.8–40° 2θ/min and a scan range of 2θ(Mo Kα_1) − 0.6° to 2θ(Mo Kα_2) + 0.6° for $0° < 2\theta(\text{Mo K}\alpha) < 50°$. The intensities of 5393 unique reflections were determined. Three reflections were remeasured periodically and showed no systematic variation during the experiment.

Data Reduction. Intensities were calculated according to the following:

$$I = ASK(C - RB)$$

where A is the attenuator factor, S is the scan rate, K is the scale factor, C is the total integrated peak count, R is the ratio of peak time to background time, and B is the total background count. Standard deviations were calculated according to the following:

$$\sigma^2(I) = \left(\frac{I\,\sigma(A)}{A}\right)^2 + \left(\frac{I\,\sigma(K)}{K}\right)^2 + (ASK)^2(C + R^2B)$$

$$\sigma(F_o) = \left(\frac{I + \sigma(I)}{Lp}\right)^{1/2} - F_o$$

where $(Lp)^{-1}$ is the Lorentz–polarization correction and $F_o = (I/Lp)^{1/2}$ is the observed structure factor. Lorentz and polarization corrections were made. A correction for changes in intensity of the standard reflections was not necessary. Absorption corrections were not made. From the dimensions and orientation of the crystal, we estimate a maximum absorption error of ±10% for the intensities. All reflections were considered to be observed. There were 534 reflections with $I < 0$. These were set equal to zero and used in all calculations.

Structure Solution. The structure was solved in space group $P\bar{1}$ by the heavy-atom method. An $(E^2 - 1)$ Patterson map yielded the positions of the two Te atoms in the asymmetric unit. The remaining 38 non-H atoms were located in an electron density map phased by the Te atoms. After least-squares refinement with anisotropic thermal parameters, the 26 H atoms were located from a difference electron density map.

Refinement. *Refinement was by block-diagonal least squares*[33] *with* 4 × 4 blocks for the hydrogen atoms, which had isotropic thermal parameters, and 9 × 9 blocks for the non-hydrogen atoms, which had anisotropic thermal parameters. The function minimized was $\sum w(|F_o| - |F_c^*|)^2$, where

$$F_c^* = KF_c\left(1 + g\left[\frac{\cos^2 2\alpha + \cos^4 2\theta}{(\cos^2 2\alpha + \cos^2 2\theta)\sin 2\theta}\right]F_c^2\right)^{-1/4}$$

in which K is the scale factor, g is an extinction parameter,[34] 2α is the Bragg angle of the monochromator, and F_c is the usual calculated structure factor. Weights were defined as

$$w^{-1} = \sigma^2(F_o) + (rF_o)^2 + p$$

The coefficients r and p were chosen to make the averages of $\sum w(|F_o| - |F_c^*|)^2$ approximately constant for groups of increasing F_o and $\sin\theta/\lambda$.[35] The agreement indices are $R = \sum(||F_o| - |F_c^*||)/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c^*|)^2/\sum wF_o^2]^{1/2}$. Scattering factors were obtained from a standard compilation,[36] and the anomalous scattering corrections for Te and Cl were applied.

Refinement proceeded smoothly, although after the addition of H a damping factor of 0.4 was necessary to eliminate oscillation of the parameter shifts. The following values pertain to the final least-squares cycle: R = 0.043, R_w = 0.038, esd of an observation on unit weight = 1.34, number of atoms = 66, number of parameters varied = 466, number of reflections used = 5393, weighting coefficients r = 0.02 and p = 0, g = 0.79 (12) × 10^{-6}, K = 0.3604 (4), maximum parameter shift/esd = 0.40, and final difference electron density range: −0.60 to +0.84 e/Å^3.

The residual density on the final difference map was primarily associated with Te and Cl. Excluding the Te and Cl regions, the range of residual density was −0.38 to +0.46 e/Å^3.

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Registry No. **6**, 84280-80-8; **9**, 84280-81-9; **10**, 84280-82-0; **15**, 84280-83-1; **16**, 84280-84-2; **17**, 82296-85-3; **19**, 84280-85-3; **20**, 84280-86-4; **21**, 84280-87-5; **23**, 84280-88-6; **26**, 84280-90-0; **26** ethyl ester, 84280-91-1; **27**, 84280-92-2; **27** ethyl ester, 84280-93-3; **28**, 84280-94-4; **29**, 84280-95-5; **30**, 84280-96-6; **32**, 84280-97-7; **34**, 84280-98-8; **35**, 84280-99-9; **36**, 84281-00-5; **37**, 84281-01-6; **37** acid, 84281-02-7; **37** ethyl ester, 84281-03-8; **38** acid, 84281-04-9; **38** ethyl ester, 84281-05-0; **39**, 84281-06-1; **40**, 84281-07-2; **41**, 84281-08-3; **42**, 84281-09-4; **43**, 84281-11-8; **44**, 84281-12-9; **45**, 84281-13-0; **46**, 84281-14-1; **47**, 84281-16-3; **48**, 84281-18-5; Te, 13494-80-9; ^{125}Te, 14390-73-9; TeO_3^{2-}, 15852-22-9; Ph_2Te, 1202-36-4; $(C_{16}H_{33})_2Te$, 71766-42-2; *p*-bromoanisole, 104-92-7; di-*p*-anisyl ditelluride, 35684-37-8; *p*-bromoacetophenone ethylene ketal, 4360-68-3; 1-bromonaphthalene, 90-11-9; di-1-naphthyl ditelluride, 32294-58-9; *o*-bromotoluene, 95-46-5; di-*o*-tolyl ditelluride, 36692-34-6; *p*-bromoacetophenone, 99-90-1; di-*p*-tolyl ditelluride, 32294-57-8; ethyl phenylpropiolate, 2216-94-6; methyl phenylpropiolate, 4891-38-7; ethyl tetrolate, 4341-76-8; ethyl propiolate, 623-47-2; sodium *p*-anisyltelluride, 41491-34-3; sodium *p*-acetylphenyltelluride, 84281-19-6; sodium *p*-tolyltelluride, 41568-72-3; sodium 1-naphthyltelluride, 84281-20-9; sodium *o*-tolyltelluride, 84281-21-0; oxalyl chloride, 79-37-8; silver trifluoroacetate, 2966-50-9; sodium iodide, 7681-82-5; silver tetrafluoroborate, 14104-20-2; lithium bromide, 7550-35-8.

Supplementary Material Available: Listings of the atomic parameters and the observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

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