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Electron-Accepting Molecules Containing Telluropyranyl Groups. The Effect of Tellurium Oxidation State on Reduction Potentials

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Telluropyran-4-ones and benzo[*b*]telluropyran-4-ones could not be oxidized to the corresponding tellurones or telluroxides with hydrogen peroxide, *m*-chloroperbenzoic acid, sodium metaperiodate, *N*-chlorosuccinimide, *tert*-butyl hypochlorite, or 40% peracetic acid. Oxidative addition products were obtained from peracetic acid to give the telluropyranone 10-Te-4 tellurane diacetates. Chlorine, bromine, and iodine gave oxidative addition products as well. The electrochemical reduction of the 10-Te-4 telluranes as followed by cyclic voltammetry and coulometry was an initial two-electron reduction to give the telluropyranone and 2 equiv of the halide or acetate. The reductions were irreversible, perhaps because of the good leaving-group character of the halide or acetate ligands attached to Te. 2,6-Disubstituted telluropyrylium salts in pyridine with triphenylphosphine under aerobic conditions gave oxidative dimerizations to produce 1,1-dioxo(telluropyranylidene)telluropyrans, which, in the case of the 2,2′,6,6′-tetraphenyl derivative, displayed reversible reductions by cyclic voltammetry. Under an argon atmosphere in degassed solvents, the telluropyrylium salts did not give oxidative dimerization. The reaction of the 2,6-disubstituted telluropyrylium salts and triphenylphosphine oxide in pyridine under argon gave the dioxo(telluropyranylidene)telluropyrans and triphenylphosphine. 2-Phenyl-7-methoxybenzo[*b*]telluropyrylium perchlorate reacted with triphenylphosphine, pyridine, and air or with triphenylphosphine oxide (as a melt) to give the 1,1′-dioxo(benzo[*b*]telluropyranylidene)benzo[*b*]telluropyran. The ditelluroxide gave a reversible reduction by cyclic voltammetry, with $E°$ being 0.2 V more negative than that for the tetraphenyl(telluropyranylidene)telluropyran tellurone. The condensation of malononitrile with telluropyranone diacetates gave dicyanomethylidene adducts that displayed reversible reduction waves by cyclic voltammetry. As was observed with the telluropyranone 10-Te-4 telluranes, the oxidative addition of peracetic acid or halogens gave 10-Te-4 telluranes whose first reduction waves are much less negative but irreversible. The condensation of Meldrum's acid with 4-ethoxytelluropyrylium and 4-ethoxybenzo[*b*]telluropyrylium salts gave adducts with reversible or partially reversible reduction waves.

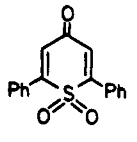
Introduction

Mixed-stack organic metal complexes have been an area of active research for both physicists and chemists. The more common donor halves of such complexes contain two or more group 6a heteroatoms as in tetrathiafulvalenes,[1] (thiopyranylidene)thiopyrans,[2] 1,8-dithianaphthalenes,[3] and tetrathiatetracenes,[4] to name a few. In these systems, the heteroatoms have been systematically varied to give both selenium[3-6] and tellurium[3,4,7,8] analogues of the sulfur-containing compounds. Other systematic variations in the donor halves include substitution with alkyl, aryl, and chalcogen substituents.[2,9]

The acceptor half of mixed-stack complexes has not received the attention or systematic variation of the donor half. Tetracyanoquinodimethane (TCNQ) has been the acceptor of choice,[2] although complexes of tetracyanoethylene, hexacyanobenzene, and various benzoquinone derivatives have been described.[2] Higher benzologues of TCNQ have been prepared but are quite insoluble.[10]

We have been interested in preparing new electron-accepting molecules containing tellurium.[11] One approach would be to incorporate tellurium in a higher oxidation state in a ring system suitably substituted to stabilize a negative charge.

This approach has been successful with various sulfur-containing ring systems. 1,1-Dioxothiopyranone **1**[12,13] 1,1-dioxobenzo[*b*]thiopyranone **2**,[12,14] and 10,10-dioxothioxanthone (**3**)[15,16] have been described as sulfur con-



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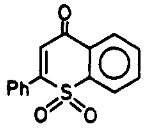

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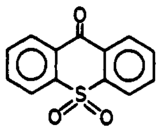

3

taining analogues of quinone, naphthoquinone, and anthroquinone, respectively, since structurally one carbonyl group has been replaced by a sulfone group. Compounds

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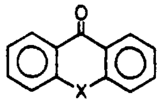
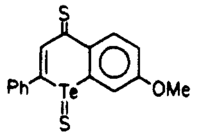
1–3 show reversible reduction to the radical-anion state with $E^\circ = -0.43$ to -0.74 V vs. SCE. The radical anion of **3** has been examined extensively by ESR[16,17] and electronic absorption spectroscopy.[16]

Few analogues of the heavier group 6a elements have been described. Selenoxanthone selenoxide (**4**),[18,19] dichloride (**5**),[19] and telluroxanthone dichloride (**6**)[20] have been prepared, although their reduction potentials and radical-anion stability have not been described. A related structure (**7**), a 1-thioxo-1-telluro 4-thioflavone has been prepared; **7** shows an irreversible reduction by cyclic voltammetry ($Ep_c = -0.90$ V vs. SCE).[21]

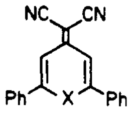


4, X = SeO
5, X = SeCl$_2$
6, X = TeCl$_2$

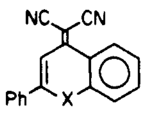


7

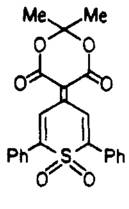
Sulfide and sulfone analogues of TCNQ and tetracyanonaphthoquinodimethane have also been described.[12] The sulfones **9** and **11** display two reversible one-electron reduction waves by cyclic voltammetry ($E^\circ = -0.13$ V vs. SCE for **9** and $E^\circ = -0.23$ V for **11** for the first wave; $E^\circ = -0.75$ V for **9** and $E^\circ = -0.77$ V for **11** for the second wave). The sulfur and oxygen analogues **8**, **10**, and **12** have been prepared, but their reduction potentials have not been described.[12] Other variations such as **13** ($E^\circ = -0.10$ V vs. SCE) in which the cyano groups have been replaced with ester groups have been prepared.[12]



8, X = S
9, X = SO$_2$
12, X = O

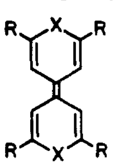


10, X = S
11, X = SO$_2$

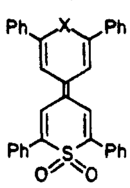


13

A second strategy that has yielded electron-accepting molecules involves increasing the oxidation state of the heteroatom in a donor molecule. The (chalcogenopyranylidene)chalcogenopyrans **14** are good organic donors, presumably because they form an aromatic sextet upon oxidation that stabilizes the open-shell state.[22] Conversely, reduction of these systems is difficult ($Ep_c < -2.0$ V vs. SCE), since the addition of an electron would require an antiaromatic octet in one ring. In the (thiopyranylidene)thiopyrans, the introduction of the sulfone moiety for one or both sulfur atoms greatly lowers the LUMO of the system, making reduction less negative for **15** ($E^\circ = -0.34$ V vs. SCE)[12] and **16**[12] ($Ep_c = -1.04$ V vs. SCE)[23] relative to the corresponding (thiopyranylidene)thiopyran **14**.



14
X = O, S, Se, Te
R = Me, *tert*-Bu, Ph

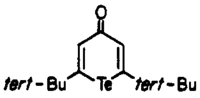


15, X = SO$_2$
16, X = S

Herein we report the first tellurium containing analogues of benzoquinone, naphthoquinone, and TCNQ as well as dioxo(telluropyranylidene)telluropyrans in which the Te is in higher oxidation states. The electrochemical reductions of the telluropyranyl derivatives by cyclic voltammetry are also described. The preparation of the TCNQ analogues and the dioxo(telluropyranylidene)telluropyrans involve chemistry without S and Se precedent. Relative stabilizations of radical anions by tellurone, telluroxide, and telluride groups can also be inferred.

Results and Discussion

Oxidation of Telluropyranones and Benzo[*b*]telluropyranones. The tellurone analogues of telluropyranones **17**[22b] and **18**[22b] and benzo[*b*]telluropyranone **19**[24] were the initial target molecules, since these compounds should also function as building blocks for the other telluropyran derivatives. Attempted oxidation of **17–19** with a variety of reagents including hydrogen peroxide, *m*-chloroperbenzoic acid, sodium metaperiodate, *N*-chlorosuccinimide, *tert*-butyl hypochlorite, and 40% peracetic acid in acetic acid did not give the desired tellurone oxidation products. These oxidants either gave fluffy, insoluble, white precipitates that could not be construed as the tellurones by either spectroscopic or elemental analyses (and were not characterized further) or, in the case of peracetic acid, gave the corresponding 10-Te-4 tellurane[25] products. At 0 °C, peracetic acid oxidation of **17–19** gave the corresponding crystalline telluropyranone diacetates **20–22** in 76%, 72%, and 78% yields, respectively.



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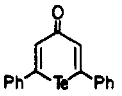

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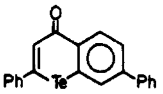

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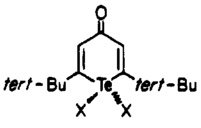
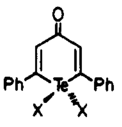
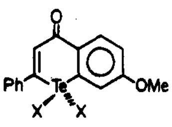


20, X = OAc
23, X = Cl
24, X = Br
25, X = I



21, X = OAc
26, X = Br



22, X = OAc
27, X = Br

Although the tellurones were the desired products, the telluropyranone 10-Te-4 telluranes represent interesting structures that have not been examined as electron acceptors. In these compounds, the Te atom is in a higher oxidation state relative to the telluropyranones. A variety of 10-Te-4 telluranes are easily prepared from the telluropyranones by oxidative addition across Te. Thus, the addition of chlorine, bromine, or iodine to dichloromethane

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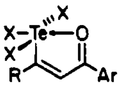
solutions of **16**–**19** gave the crystalline telluropyranone dihalides **23**–**27** in 46–91% yields.

The electrochemical reductions of 1,1-dioxothiopyranones are characterized by reversible one-electron waves, as determined by cyclic voltammetry.[12,14] The radical anions of these compounds have the unpaired spin delocalized through both the sulfone group and the carbon π framework.[16,17] Such might not be the case for telluropyranone 10-Te-4 telluranes, where orbital overlap of Te and C should be less efficient and where good leaving groups are bound to the Te.

Electrochemical Studies of Telluropyranone 10-Te-4 Telluranes. The 10-Te-4 telluranes are reduced at less negative potentials than the corresponding telluropyranones by cyclic voltrammetry. 2,6-Di-*tert*-butyltelluropyranone (**17**) is reduced irreversibly with Ep_c = −1.60 V (vs. SCE). The 10-Te-4 telluranes based on **17** are reduced irreversibly as well with Ep_c = −1.14 V for diacetate **20**, Ep_c = −0.68 V for dichloride **23**, Ep_c = −0.46 V for dibromide **24**, and Ep_c = +0.04 V for diiodide **25**. A second reduction wave at Ep_c = −1.60 V (vs. SCE) is observed for **20**, **23**, **24**, and **25** as well.

The initial reduction appears to be a two-electron reduction of the 10-Te-4 tellurane to the telluropyranone and 2 equiv of the halide or pseudohalide since coulometric reduction of **24** at −0.6 V (vs. SCE) required 2.1 Faradays/mol. Following reversal of the cathodic scans at −2.0 V (vs. SCE), the anodic scans of the appropriate telluropyranone dihalide after reduction show the oxidation of chloride to chlorine (Ep_a = +1.14 V), bromide to bromine (Ep_a = +0.80 V), and iodide to iodine ($E°$ = +0.67 V). The cyclic voltammograms of the telluropyranone 10-Te-4 telluranes are similar to those of the 12-Te-5 pertelluranes **28** and **29** in which the corresponding 10-Te-3 tellurane and 2 equiv of the halide are produced upon reduction.[26]



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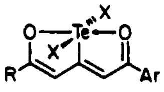

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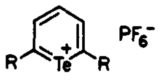
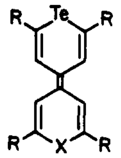
The loss of halide or pseudohalide from the 10-Te-4 telluranes upon reduction is a function of the Te ligands in these systems. Acetate, chloride, bromide, and iodide are good leaving groups. Reduction of the 10-Te-4 telluranes to the radical-anion state followed by leaving group loss would generate a neutral open-shell species. This species might be expected to reduce at a less negative potential than the 10-Te-4 telluranes to generate the telluropyranone and a second equivalent of halide or pseudohalide.

Dioxo(telluropyranylidene)telluropyrans. Although dioxotelluropyranones could not be prepared by direct oxidation of telluropyranones, tellurone and telluroxide analogues of (telluropyranylidene)telluropyrans **15** and **16** were prepared in a somewhat surprising fashion. Attempts to oxidize the Te atoms of (telluropyranylidene)telluropyrans failed because of the facile oxidation to the radical-cation and dication states.[9f] However, attempts to dimerize telluropyrylium salts **30** with pyridine and triphenylphosphine in CH_3CN under an oxygen atmosphere gave 20–25% yields of 1,1-dioxo(telluropyranylidene)telluropyrans **31**. In degassed solvents under an inert atmosphere, the formation of tellurones **31** was not observed from the reaction of **30** with pyridine and triphenylphosphine.



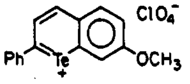
30a, R = Ph
b, R = *tert*-Bu



31, X = TeO_2
32, X = Te

The structures of tellurones **31** were readily identified by analytical and spectroscopic techniques. Both compounds gave parent ion clusters by field-desorption mass spectrometry and elemental analyses consistent with the (telluropyranylidene)telluropyran ring system plus two O atoms. The ring protons are a singlet in the ^{1}H NMR spectra of the (telluropyranylidene)telluropyrans **32**. In the tellurones **31**, the ring protons appear as two doublets with a coupling of 4.5 Hz in each case. In **31a**, two different sets of phenyl-group protons are apparent, and in **31b**, two different *tert*-butyl groups are apparent, separated by 0.03 ppm. The ^{13}C NMR spectra are consistent with tellurone structures **31** as well, displaying 13 distinct carbon signals for **31a** (14 expected) and 9 distinct carbon signals for **31b** (10 expected). In the proton-coupled ^{13}C NMR spectrum of **31b**, two different kinds of proton-bearing olefinic carbons are present, and the four nonproton-bearing olefinic carbons appear in three signals. Two different sets of *tert*-butyl alkyl carbons are present as well. The infrared spectra of **31a** and **31b** are characterized by two strong absorption bands at 1605 and 1260 cm^{-1}, perhaps corresponding to TeO_2 asymmetric and symmetric stretching, respectively. These bands are not present in the infrared spectra of the (telluropyranylidene)telluropyrans.

The oxidative dimerization of telluroflavylium salt **33** with pyridine/triphenylphosphine in air did not give the 1,1-dioxo(telluropyranylidene)telluropyran. Instead, the ditelluroxide **34** was isolated in 25% yield. In carefully degassed solvents under an inert atmosphere, none of the ditelluroxide was formed from **33**.



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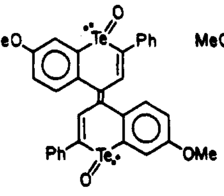

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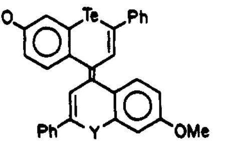

35, Y = Te
36, Y = TeO_2

The structure **34** was assigned to the ditelluroxide from elemental analysis and spectroscopic techniques. Elemental analysis and field-desorption mass spectrometry were both consistent with the (benzo[*b*]telluropyranylidene)benzo[*b*]telluropyran ring system **35**[21] plus two O atoms. The ^{13}C NMR spectrum gave the 14 signals expected from ditelluroxide **34**, not the 28 signals expected from tellurone **36**. The ^{1}H NMR spectrum was consistent with structure **34**, with eight different resonances. The infrared spectra of **34** and **35** were similar, with no obvious bands from the telluroxide functionality in **34**.

The oxidative dimerization of telluropyrylium salts **30** and **33** with pyridine/triphenylphosphine under aerobic conditions was surprising in that (telluropyranylidene)telluropyrans **32** were not oxidized to their radical cations under the same conditions. Attempts to oxidize **31** and **34** further to the ditellurones with hydrogen peroxide, *m*-chloroperbenzoic acid, or sodium metaperiodate gave

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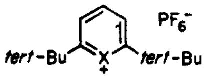
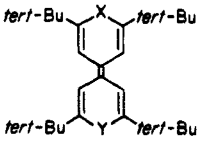
(26) Detty, M. R.; Luss, H. R.; McKelvey, J. M.; Geer, S. M. *J. Org. Chem.* **1986**, *51*, 1692.

mixtures of products that were difficult to isolate or nondescript, fluffy, insoluble precipitates under more forcing conditions. None of these products were characterized further.

The oxidative dimerization could not be extended in a preparatively useful way to selenopyrylium salt **37** and thiopyrylium salt **38**. (Selenopyranylidene)selenopyran **39** was isolated in 71% yield when **37** was treated with pyridine/triphenylphosphine under aerobic conditions in CH_3CN. Careful chromatography of the product mixture from this reaction gave trace amounts (<1%) of selenone **40**. The structure of **40** was assigned on the basis of its ^1H NMR spectrum, in which the ring protons appear as two doublets with a coupling of 4.5 Hz, and its field-desorption mass spectrum, which gives a parent ion cluster consistent with the (selenopyranylidene)selenopyran ring system **39** plus two O atoms. The reaction of thiopyrylium salt **38** with pyridine/triphenylphosphine in CH_3CN under aerobic conditions gave only (thiopyranylidene)thiopyran **41** in 65% yield.



37, X = Se
38, X = S



39, X = Y = Se
40, X = Se, Y = SeO_2
41, X = Y = S

By cyclic voltammetry, the pyrylium salts **30**, **33**, **37**, and **38** were not oxidized between potentials of −1.5 to +1.5 V (vs. SCE) at a Pt electrode in degassed CH_3CN. The addition of pyridine to the CH_3CN solutions of **30**, **33**, **37**, and **38** gave different results for the different systems. The CV scans of solutions of **37** and **38** containing pyridine show the characteristic reversible first and second oxidations of (selenopyranylidene)selenopyran **39** and (thiopyranylidene)thiopyran **41**, respectively.[1b] The telluropyrylium salts **30** and **33**, however, do not give the characteristic waves for the (telluropyranylidene)telluropyrans in CV scans of pyridine-containing CH_3CN solutions but show only the irreversible reductions of **30a** at $Ep_c = -0.15$ V (vs. SCE), **30b** at $Ep_c = -0.37$ V, and **33** at $Ep_c = -0.10$ V.

The introduction of oxygen atoms to form the tellurones was thought to involve direct attack of O_2 at Te. This might not be the case, in that the reaction of **30b** with pyridine and excess triphenylphosphine oxide in degassed CH_3CN under an argon atmosphere gave tellurone **31b** in 17% yield and triphenylphosphine in 18% yield (based on **30b**). Under these conditions, it appears that the source of O is triphenylphosphine oxide.

The benzo[*b*]telluropyrylium salt **33** was heated with an excess of triphenylphosphine oxide as a melt at 220 °C under argon. From this reaction, ditelluroxide **34** was isolated in 25% yield and triphenylphosphine in 30% yield. Again, the triphenylphosphine oxide appears to be the source of O.

The mechanism of these unusual reactions to form tellurone and telluroxide products from telluropyrylium salts and either triphenylphosphine/pyridine/air or triphenylphosphine oxide/pyridine is unclear. We are attempting to improve the yield and increase the scope of these reactions and to elucidate possible mechanistic pathways. Under the reaction conditions described here, the yields are poor. Some unreacted telluropyrylium salts are present in the crude reaction mixtures as well as insoluble tars, which were not characterized.

Table I. Reduction Potentials for Sulfone 16, Tellurones 31, Ditelluroxide 34, and Selenone 40 as Determined by Cyclic Voltammetry[a]

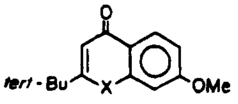
compd	E_1, V	
	Ep_c	Ep_a
16	−1.04[b]	
31a	−1.36	−1.28
31b	−1.10[b]	
34	−1.58	−1.50
40	−1.05[b]	

[a] Measured in volts vs. SCE at a Pt disk electrode at a scan rate of 0.1 V/s in degassed CH_3CN containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte. [b] Irreversible wave with value being the peak potential.

Electrochemical Studies of (Telluropyranylidene)telluropyran Tellurones and Telluroxides. The tellurones **31**, ditelluroxide **34**, and selenone **40** were all reduced at less negative potentials than their (telluropyranylidene)telluropyran or (selenopyranylidene)selenopyran counterparts (Table I). Tellurone **31a** and ditelluroxide **34** gave reversible reduction waves ($i_c/i_a = 1$). The sulfone **16**, tellurone **31b**, and selenone **40** gave irreversible reduction ($i_c/i_a > 1.5$), and only peak potentials are listed. The addition of an electron to these compounds presumably generates a radical anion in which the tellurone, telluroxide, or selenone group inductively stabilizes the negative charge.

In the thioxanthone, 10-oxothioxanthone, and 10,10-dioxothioxanthone (**3**) series the reduction potential of 10-oxothioxanthone lies between that of thioxanthone and **3**.[16] However, $E°$ for the sulfoxide is only 0.1 V more cathodic than that for the sulfone. The reduction potential of the ditelluroxide **34** lies between the reduction potentials of the tellurones **31** and the (telluropyranylidene)telluropyrans **32** and **35**. The 0.2-V difference between $E°$ for **31a** and **34** is similar to the 0.1-V difference between $E°$ for 10-oxothioxanthone and **3**. This suggests that the relative inductive stabilization of an anion by telluroxide and tellurone functionality when compared to the telluride is similar to the relative stabilization of an anion by sulfoxide and sulfone functionality when compared to the sulfide.

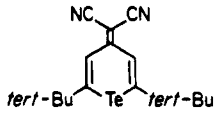
Tellurium Analogues of TCNQ and Sulfone 13. The condensation of 2,6-diphenylthiopyran-4-one or 2-phenylbenzo[*b*]thiopyran-4-one with malononitrile in acetic anhydride gave the dicyanomethylidene adducts **8** and **10** in nearly quantitative yields.[12] However, this procedure failed with telluropyranones **17** and **18** and benzo[*b*]telluropyranones **19** and **42**, giving only unreacted starting materials even in the presence of added amine bases.



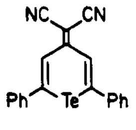
42, X = Te
45, X = $Te(OAc)_2$

In contrast, the diacetates **20** and **21** of the telluropyranones reacted with malononitrile and diisopropylethylamine in CH_3CN to give telluropyranylmalononitrile adducts **43** and **44** in 29% and 24% yields, respectively, as high-melting crystalline solids. The structures of **43** and **44** were easily assigned from their elemental and spectroscopic analyses.

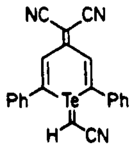
Treatment of the diacetates **22** and **45** with malonitrile and diisopropylethylamine in CH_3CN gave only **19** and **42** as crystalline solids in 55% and 56% yields, respectively.



43



44

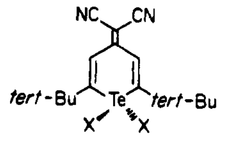


46

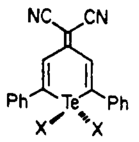
The other products of the reactions were dark, tarry residues, which gave more than 10 bands by thin-layer chromatography. The 10-Te-4 tellurane analogues **23–26** also failed to condense with malononitrile in the presence of amine bases.

A secondary product was obtained from the condensation of malononitrile with **18**. The telluropyranyl ylide **46** was isolated in 11% yield as a yellow, crystalline solid. The structure of **46** was assigned from elemental analysis ($C_{22}H_{13}N_3Te$), from the field-desorption mass spectrum, which gave a parent ion of *m/e* 449 ($C_{22}H_{13}N_3{}^{130}Te$) and a fragment ion of *m/e* 410 (M – C_2HN), and from the ^1H NMR spectrum, which was indicative of an unsymmetrical molecule (two different sets of aromatic resonances, two one-proton singlets at δ 8.27 and 7.21 for the ring protons) with a single proton resonance at δ 5.15 for the proton attached to the ylide C.

We attempted to oxidize **43** and **44** to the corresponding tellurones with a variety of reagents including *m*-chloroperbenzoic acid, sodium metaperiodate, and peracetic acid in acetic acid. Sodium metaperiodate destroyed the ring system under conditions where reaction occurred. Peracetic acid and *m*-chloroperbenzoic acid gave 10-Te-4 telluranes from oxidative addition. The *m*-chloroperbenzoic acid addition products were not purified and characterized. The peracetic acid addition products were characterized as the crystalline diacetates **47** and **48** in 48% and 65% yields, respectively. Chlorine, bromine, and iodine also gave oxidative addition products with **43** and **44** to give the 10-Te-4 telluranes **49–52** in 70–82% yields as crystalline solids.

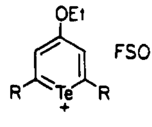


47, X = OAc
49, X = Cl
50, X = Br
51, X = I

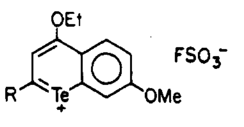


48, X = OAc
52, X = Br

The Meldrum's acid adducts of the telluropyranones **17** and **18** and the benzo[*b*]telluropyranones **19** and **42** were prepared by the condensation of Meldrum's acid with the 4-ethoxytelluropyrylium salts **53–56** in pyridine. The 4-ethoxytelluropyrylium salts were prepared by the alkylation of telluropyranones **17–19** and **42** with ethyl fluorosulfate. The Meldrum's acid adducts **57–60** were isolated as red crystalline solids in 80–92% yields.

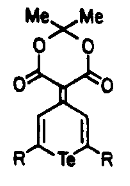


53, R = tert-Bu
54, R = Ph

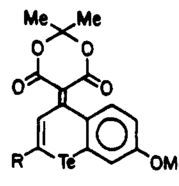


55, R = tert-Bu
56, R = Ph

Electrochemical Studies of Dicyanomethylidene and Meldrum's Acid Adducts of Telluropyrans. The telluropyranones are reduced at more negative potentials than typical acceptor molecules. Telluropyranones **17**, **18**, and **42** have Ep_c = –1.60, –1.58, and –1.60 V (vs. SCE), respectively. Benzo[*b*]telluropyranone **19** reduces with $E°$ = –1.56 V (vs. SCE) for a partially reversible (i_c/i_a = 1.2) first wave (Table I).



57, R = tert-Bu
58, R = Ph



59, R = tert-Bu
60, R = Ph

The condensation products of malononitrile and Meldrum's acid with the telluropyranones **17–19** and **42** (compounds **43**, **44**, and **57–60**) are reduced at much less negative potentials (Table I) than **17–19** and **42**. The first waves are reversible for **43** and **44** with i_c/i_a = 1. The first reduction waves of **57–60** are only partially reversible, with i_c/i_a = 1.1–1.6. The second reduction waves are irreversible, as shown in Figure 1 for **58**.

The oxidative addition products of **43** and **44** with peracetic acid or bromine (**47**, **48**, **50**, **52**) reduced at the least negative potentials of all (Table II). The first cathodic waves in all four compounds were irreversible and appeared to be two-electron reductions. Coulometric reduction of **50** and **52** at –0.2 V vs. SCE required 2.0 Faradays/mol. The products of two-electron reduction would be the malononitrile condensation product and 2 equiv of acetate or bromide, similar to the reduction of the telluropyranone dihalides. The second reduction waves in **47**, **48**, **50**, and **52** were the reversible waves of **43** and **44**.

The ylide **46** displayed more complicated electrochemical behavior. Two irreversible waves were observed in the cathodic direction, with Ep_c = –0.67 V and Ep_c = –0.86 V (vs. SCE) and a reversible wave with $E°$ = –0.96 V (vs. SCE, Table II). The reversible wave described is similar to the wave observed for the reduction of **44**, perhaps indicative of the loss of CHCN from the ylide **46** to give **44**.

ESR Studies. The radical anions of tellurone **31a**, ditelluroxide **34**, and dicyanomethylidene adduct **44** were generated in a coulometric flow reactor, which was a modification of a design by Miner and Kissinger.[27] The working electrode was reticulated vitreous carbon, and the radical anions were generated in dichloromethane or acetonitrile with 0.2 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte. The ESR spectra were recorded as the reduced sample flowed through a flat (0.5 mm) quartz ESR cell. We were unable to detect an ESR signal from these samples.

Although radical cations of (telluropyranylidene)telluropyrans **32** gave detectable ESR signals, albeit broad with no fine structure,[22b] other radical cations in ring systems containing two Te atoms (1,3-ditelluroles[28] or 1,8-Te-bridged naphthalenes[3]) do not give solution ESR signals. Broadening due to spin/orbit coupling was invoked in these systems to account for the lack of signal. Similar arguments could be made for the lack of an ESR signal for the radical anions of **31a**, **34**, and **44**.

The ESR spectra of frozen solutions of the radical anions of **31a**, **34**, and **44** are under investigation. Similarly, the ESR spectra of irradiated, frozen Freon beads containing **31a**, **34**, and **44** are being investigated as well.

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[27] Miner, D. J.; Kissinger, P. T. *Biochem. Pharmacol.* **1979**, *28*, 3285.

[28] Detty, M. R.; Haley, N. F.; Eachus, R. S.; Hassett, J. W.; Luss, H. R.; Mason, M. G.; McKelvey, J. M.; Wernberg, A. A. *J. Am. Chem. Soc.* **1985**, *107*, 6298.

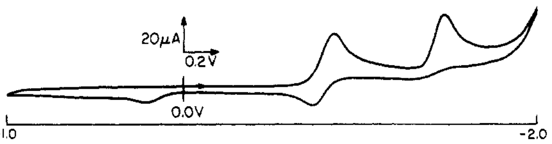

Figure 1. Cyclic voltammogram of **58** in CH_2Cl_2 with 0.1 M TBAF as supporting electrolyte at a platinum disk electrode at a scan rate of 0.1 V/s.

Table II. Redox Potentials for Dicyanomethylidene and Meldrum's Acid Adducts of Telluropyrans as Determined by Cyclic Voltammetry[a]

	E_1, V		E_2, V	
compd	Ep$_c$	Ep$_a$	Ep$_c$	Ep$_a$
9	−0.17	−0.09	−0.79	−0.71
11	−0.32	−0.24	−0.81	−0.73
13	−0.14	−0.06	−0.60	−0.52
19	−1.61	−1.52	−1.96[b]	
43	−1.30	−1.21		
44	−1.03	−0.93		
46[c]	+0.45	+0.52	−0.99	−0.93
47	−0.58[b]		−1.32	−1.20
48	−0.30[b]		−1.03	−0.91
50	+0.10[b]		−1.31	−1.21
52	+0.10[b]		−1.01	−0.92
57	−1.16[d]	−1.02	−1.95[b]	
58	−0.85[d]	−0.73	−1.48[b]	
59	−0.85[d]	−0.75	−1.78[b]	
60	−0.70[d]	−0.55	−1.38[b]	

[a] Potentials vs. SCE in CH_2Cl_2 with 0.2 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte at a Pt disk electrode and a sweep rate of 0.1 V/s. [b] Irreversible wave with value being the peak potential. [c] Additional irreversible cathodic waves at Ep$_c$ = −0.67 V and Ep$_c$ = −0.86 V. [d] Partially reversible wave at 0.1 V/s.

Summary and Conclusions

The oxidation of tellurides to telluroxides and tellurones is not as facile a transformation as the oxidation of sulfides to sulfoxides and sulfones or selenides to selenoxides and selenones. The oxidations of tellurides typically give 10-Te-4 telluranes in which the oxidant has added across the Te atom.[26,29] Diaryl telluroxides can be prepared by dehydrating the corresponding 10-Te-4 tellurane telluroxide hydrates.[30] Successful oxidations of tellurides or telluroxides to tellurones have been rare, with only arylalkyl- and diaryltellurones having been prepared by sodium metaperiodate oxidation of these substrates.[31]

The telluropyranones and dicyanomethylidene telluropyrans give addition products with various oxidants. The oxidants chlorine, bromine, iodine, and peracetic acid give only 10-Te-4 tellurane products from oxidative addition. Stronger oxidants and more forcing conditions give no tellurone products, just destruction of starting materials.

One would expect the LUMO of the telluropyranone and dicyanomethylidene telluropyran 10-Te-4 telluranes to be weighted heavily on Te.[26] The ligands attached to Te in these systems are electronegative groups that are also good leaving groups. In the 10-Te-4 telluranes, the TeX_2 units (X = Cl, Br, I, OAc) can be considered as consisting of three-center four-electron bonds.[26,32] The peak potentials for reduction of the telluropyranone and dicyanomethylidene telluropyran 10-Te-4 telluranes become more negative from diiodides **25** and **51** to dibromides **24**, **50**, and **52** to dichlorides **23** and **49** to diacetates **20**, **47**, and **48**. This is also the order of increasing electronegativity[33] for the ligands X in the TeX_2 unit and presumably the order of increasing Te–X bond strength as well. The irreversible reductions in these systems presumably arise from facile halide or pseudohalide loss in the radical anion.

In the tellurones **31** and ditelluroxide **34**, the LUMO would be expected to be weighted heavily on Te as well. Since good leaving groups are not attached to the Te atoms, reversible reductions are observed for **31a** and for **34**. These reductions are more negative than the reductions of the telluropyranone 10-Te-4 telluranes, which suggests that reductive cleavage of the Te–X bonds in the 10-Te-4 telluranes is a facile process.

The reduction waves for compounds **31**, **34**, **43**, **44**, and **57–60** are at potentials too negative to be useful as acceptors in mixed-stack organic metal complexes.[2] The successful oxidation of such molecules to the tellurone or ditellurone oxidation state should generate compounds with $E° > -0.8$ V (vs. SCE), which would be more compatible with "traditional" donor molecules.

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 instrument. Infrared spectra were recorded on a Beckman IR 4250 instrument. Solvents were used as received from Kodak Laboratory Chemicals. Microanalyses were performed on a Perkin-Elmer C, H, and N analyzer. Tellurium analyses were done by atomic absorption spectroscopy and are accurate to ±1%. All reactions were conducted under normal laboratory lighting.

Telluropyranones **17** and **18**,[22b] benzo[*b*]telluropyranone **19**,[24] and telluropyrylium salts **30** and **33**[24] were prepared as described. For the preparation of **30a** and **30b**, 60% aqueous HPF_6 was substituted for $HClO_4$.

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. The columetric flow reactor, used for generation of electrolysis products, was a modification of a design by Miner and Kissinger.[16] The working electrode was reticulated vitreous carbon (RVC) porosity 100, grade 4, obtained from Normar Industries, Anaheim, CA. An Ag/AgO quasi-reference electrode was used in the flow cell.

All samples were run in J. T. Baker HPLC-grade dichloromethane or acetonitrile that had been stored over Kodak type 3A molecular sieves. Electrometric-grade tetra-*n*-butylammonium tetrafluoroborate ($TBABF_4$) (Southwestern Analytical Chemicals, Inc.) was dried at 80 °C overnight and used as supporting electrolyte at 0.2 M concentration. Argon was used for sample deaeration.

The exit of the electrochemical flow cell was connected to a flat (0.5 mm) ESR cell (Wilmad Glass Company) with Omnifit $^1/_{16}$ in. Teflon tubing and Tefzel connectors. The ESR spectra of the reduction products were obtained on a Bruker ER 200D-SRC 100-kHz spectrometer at ~25 °C.

The reduction products were generated by holding the RVC working electrode at a potential beyond the first reduction wave of the samples but before the onset of the second wave, while the deaerated sample solutions flowed through the cell. With gravity flow, the flow rate through the ESR cell was 2–3 mL/min.

Preparation of Diacetates 20–22. The telluropyranone (3.13 mmol) in 5 mL of dichloromethane and 5 mL of acetic acid was cooled to 0 °C. Peracetic acid (40% in acetic acid, 1.3 g, 6.9 mmol) was added slowly. The mixture was stirred for 5 min at 0 °C and then diluted with water (100 mL). The product was extracted with dichloromethane (3 × 25 mL), and the combined extracts

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(29) (a) Detty, M. R. *J. Org. Chem.* **1980**, *45*, 274. (b) Uemura, S.; Fujuzawa, S. *Tetrahedron Lett.* **1983**, *24*, 4347. (c) Irgolic, K. J. *The Organic Chemistry of Tellurium*; Gordon and Breach: New York, 1978.

(30) Ley, S. V.; Veerholz, C. A.; Barton, D. H. R. *Tetrahedron* **1981**, *37*, Suppl. No. 1, 213.

(31) Lee, H.; Cava, M. P. *J. Chem. Soc., Chem. Commun.* **1981**, 277.

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

(33) Mullay, J. *J. Am. Chem. Soc.* **1984**, *106*, 5842.

were washed with water (3 × 25 mL) and brine (25 mL), dried over sodium sulfate, and concentrated. The residue was recrystallized to give the corresponding diacetate.

For **20**: 77% yield; mp 161–165 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 6.3 (s, 2 H), 1.92 (s, 6 H), 1.47 (s, 18 H); IR (KBr) 2900, 1600, 1000, 909 cm^{-1}; field-desorption mass spectrum (FDMS), *m/e* 381 (M – OAc). Anal. Calcd for $C_{17}H_{26}O_5Te$: C, 46.6; H, 6.0. Found: C, 47.0; H, 6.1.

For **21**: 80% yield; mp 137–141 °C (EtOH); ^{1}H NMR ($CDCl_3$) δ 7.41 (m, 10 H), 6.25 (s, 2 H), 1.97 (s, 6 H); FDMS, *m/e* 421 (M – OAc). Anal. Calcd for $C_{21}H_{18}O_5Te$: C, 52.8; H, 3.8. Found: C, 52.5; H, 3.9.

For **22**: 79% yield; mp 189–191 °C (CH_3CN); ^{1}H NMR ($CDCl_3$) δ 8.47 (d, 1 H, J = 9 Hz), 7.70 (m, 3 H), 7.50 (m, 3 H), 7.17 (m, 1 H), 6.96 (s, 1 H), 3.90 (s, 3 H), 1.80 (s, 6 H); IR (KBr) 1630, 1585, 1280, 665 cm^{-1}. Anal. Calcd for $C_{20}H_{18}O_6Te$: C, 49.8; H, 3.9. Found: C, 49.6; H, 3.5.

Preparation of Dichloride 23. Chlorine gas was bubbled into a carbon tetrachloride solution (50 mL) of telluropyranone **17** (1.6 g, 5.0 mmol) until the solution became colorless. The reaction mixture was concentrated, and the residue was recrystallized from CH_3CN to give 1.55 g (79%) of **23**: mp 163.5–166 °C (CH_3CN); ^{1}H NMR ($CDCl_3$) δ 6.10 (s, 2 H), 1.50 (s, 18 H); IR (KBr) 2990, 1635, 1480, 1376, 1310, 1260, 910 cm^{-1}. Anal. Calcd for $C_{13}H_{20}Cl_2OTe$: C, 40.0; H, 5.2; Te, 32.7; Cl, 18.1. Found: C, 39.9; H, 5.2; Te, 32.9; Cl, 17.7.

Preparation of Dibromides 24, 26, and 27. The bromine (2.0 g, 6.2 mmol) in 5 mL of dichloromethane was added dropwise to a solution of telluropyranone (5.0 mmol) in 20 mL of dichloromethane. After addition was complete, the reaction mixture was concentrated. Recrystallization of the residue gave the dibromides.

For **24**: 71% yield; mp 225–227.5 °C (CH_3CN); ^{1}H NMR ($CDCl_3$) δ 6.12 (s, 2 H), 1.60 (s, 18 H); IR (KBr) 2960, 2920, 2850, 1615, 1470, 900 cm^{-1}. Anal. Calcd for $C_{13}H_{20}Br_2OTe$: C, 33.0; H, 4.2; Te, 26.6; Br, 33.3. Found: C, 33.0; H, 4.2; Te, 26.2; Br, 31.9.

For **26**: 79% yield; mp 208–210 °C (CH_3CN); ^{1}H NMR ($CDCl_3$) δ 7.75 (m, 4 H), 7.55 (m, 6 H), 6.45 (s, 2 H); IR (KBr) 3020, 1615, 1585, 1445, 1205, 765 cm^{-1}. Anal. Calcd for $C_{17}H_{12}Br_2OTe$: C, 39.3; H, 2.3; Te, 24.6. Found: C, 39.8; H, 2.5; Te, 24.4.

For **27**: 84% yield; mp 220–222 °C (CH_3CN); ^{1}H NMR ($CDCl_3$) δ 8.63 (d, 1 H, J = 9 Hz), 8.80 (m, 2 H), 7.57 (m, 3 H), 7.31 (m, 2 H), 6.70 (s, 1 H), 3.95 (s, 3 H); IR (KBr) 1635, 1590, 1255, 1025, 765 cm^{-1}. Anal. Calcd for $C_{16}H_{12}O_2Br_2Te$: C, 36.7; H, 2.3; Te, 24.4; Br, 30.5. Found: C, 36.9; H, 2.4; Te, 24.7; Br, 29.3.

Preparation of Diiodide 25. Iodine (0.254 g, 1.0 mmol) was added to a stirred solution of the telluropyranone **17** (0.32 g, 1.0 mmol) in 10 mL of dichloromethane. The mixture was stirred for 15 min at ambient temperature and concentrated. The residue was recrystallized from CH_3CN to give 0.26 g (46%) of **25**: mp 114–130 °C dec; ^{1}H NMR ($CDCl_3$) δ 6.95 (s, 2 H), 1.35 (s, 18 H); IR (KBr) 1970, 1625, 1585, 1280, 1190, 1155 cm^{-1}. Anal. Calcd for $C_{13}H_{20}I_2OTe$: C, 27.2; H, 3.5; Te, 22.2. Found: C, 27.0; H, 3.5; Te, 22.5.

Preparation of $\Delta^{4,4'}$-1,1-Dioxo-2,2′,6,6′-tetraphenylbi-4*H*-telluropyran (31a). A solution of 2,6-diphenyltelluropyrylium hexafluorophosphate (**30a**, 0.49 g, 1.0 mmol) in 2 mL of pyridine and 2 mL of CH_3CN in a 50-mL flask was heated on a steam bath for 1.5 h. The reaction mixture was concentrated. Chromatography of the residue on silica gel gave 0.085 g (25%) of **31a** as a yellow solid: mp 134.5–136.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.27 (d, 2 H, J = 4.5 Hz), 8.00 (d, 2 H, J = 4.5 Hz), 7.90 (m, 2 H), 7.80 (m, 2 H), 7.53 (m, 3 H), 7.40 (m, 3 H); ^{13}C NMR ($CDCl_3$) δ 192.1, 160.8, 149.6, 145.7, 139.7, 137.1, 134.3, 131.9, 129.2, 129.0, 128.4, 127.1, 126.5; IR (KBr) 3050, 1605, 1446, 1260, 1055, 831, 815, 750 cm^{-1}; FDMS, *m/e* 724 ($C_{34}H_{24}O_2{}^{130}Te_2$). Anal. Calcd for $C_{34}H_{24}O_2Te_2$: C, 56.7; H, 3.4; Te, 35.5. Found: C, 56.8; H, 3.4; Te, 35.9.

Preparation of $\Delta^{4,4'}$-1,1-Dioxo-2,2′,6,6′-tetra-*tert*-butylbi-4*H*-telluropyran (31b). (a) A solution of 2,6-di-*tert*-butyltelluropyrylium hexafluorophosphate (**30b**, 0.45 g, 1.0 mmol) and triphenylphosphine (100 mg) in 2 mL of pyridine and 2 mL of CH_3CN in a 50-mL flask was heated on a steam bath for 1.5 h. The reaction mixture was concentrated in vacuo. Careful chromatography on silica gel eluted with dichloromethane gave 0.13 g (20%) of **31b** as a yellow waxy solid: mp 130–136 °C. (b) A solution of **30b** (0.45 g, 1.0 mmol) and triphenylphosphine oxide (0.55 g, 2.0 mmol) in 2 mL of degassed pyridine and 2 mL of degassed acetonitrile was heated at reflux under argon for 3.5 h. The reaction mixture was concentrated in vacuo. Chromatography of the residue on silica gel eluted with 1:1 (v/v) hexane/dichloromethane gave 0.055 g (18%) of triphenylphosphine and 0.044 g (17%) of **31b**: ^{1}H NMR ($CDCl_3$) δ 8.25 (d, 2 H, J = 4.5 Hz), 7.53 (d, 2 H, J = 4.5 Hz), 1.36 (s, 18 H), 1.33 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 202.3 (s), 177.5 (s), 148.4 (s), 140.8 (d), 133.5 (d), 43.0 (s), 39.6 (s), 33.6 (q), 28.7 (q); IR (KBr) 1605, 1260 cm^{-1}; FDMS, *m/e* 644 ($C_{26}H_{40}O_2{}^{130}Te_2$). Anal. Calcd for $C_{26}H_{40}O_2Te_2$: C, 48.8; H, 6.3; Te, 39.9. Found: C, 49.1; H, 6.2; Te, 39.5.

Preparation of $\Delta^{4,4'}$-1,1′-Dioxo-2,2′-diphenyl-7,7′-dimethoxybi-4*H*-benzo[*b*]telluropyran (34). (a) A solution of 2-phenyl-7-methoxybenzo[*b*]telluropyrylium perchlorate (**33**, 0.35 g, 0.79 mmol) and triphenylphosphine (50 mg) in 2 mL of pyridine in a 25-mL flask was heated on a steam bath for 1.5 h. The reaction mixture was concentrated in vacuo. Chromatography on silica gel eluted with dichloromethane gave 0.070 g (25%) of **34** as a yellow solid: mp 118–119 °C; ^{1}H NMR ($CDCl_3$) δ 8.27 (s, 2 H), 7.81 (m, 4 H), 7.71 (d, 2 H, J = 9 Hz), 7.52 (m, 6 H), 7.41 (m, 4 H), 6.93 (dd, 2 H, J = 2.5, 9 Hz), 3.87 (s, 6 H); ^{13}C NMR ($CDCl_3$) δ 193.2 (s), 159.1 (s), 144.4 (s), 142.0 (s), 141.1 (s), 137.9 (s), 137.1 (d), 131.9 (d), 131.4 (d), 129.1 (d), 128.4 (d), 115.3 (d), 115.2 (d), 55.6 (q); IR (KBr) 1614, 1595, 1508, 1329, 1270, 1231, 1175, 1096, 1023, 871, 852, 722, 699, 655 cm^{-1}; UV λ_{max} (CH_2Cl_2) (log ϵ) 348 nm (4.35); FDMS, *m/e* 732 ($C_{32}H_{24}O_4{}^{130}Te_2$). Anal. Calcd for $C_{32}H_{24}O_4Te_2$: C, 52.9; H, 3.3; Te, 35.1. Found: C, 53.2; H, 3.3; Te, 35.4. (b) Flavylium **33** (0.50 g, 1.0 mmol) and triphenylphosphine oxide (5.0 g, 0.018 mol) were mixed and heated to melting (~220 °C) under argon. The resulting melt was stirred for 15 min. The reaction mixture was cooled to ambient temperature and purified by chromatography on silica gel eluted with dichloromethane to give triphenylphosphine and the desired product. The ditelluroxide was recrystallized from hexane to give 0.18 g (25%) of **34** as yellow crystals: mp 118–119 °C.

Preparation of $\Delta^{4,4'}$-1,1-Dioxo-2,2′,6,6′-tetra-*tert*-butylbi-4*H*-selenopyran (40). A solution of 2,6-di-*tert*-butylselenopyrylium hexafluorophosphate (**37**, 4.01 g, 10.0 mmol) in 20 mL of pyridine and 20 mL of CH_3CN in a 250-mL flask was heated on a steam bath for 3.5 h. The reaction mixture was cooled to ambient temperature. (Selenopyranyl)selenopyran **39** precipitated and was collected by filtration to give 3.62 g (71%) of **40**.[22b] The filtrate was concentrated in vacuo. Chromatography on silica gel eluted with 1:1 (v/v) hexane/dichloromethane gave 0.021 g (0.8%) of selenone **40** as a pale yellow glass: ^{1}H NMR ($CDCl_3$) δ 7.80 (d, 2 H, J = 4.5 Hz), 7.02 (d, 2 H, J = 4.5 Hz), 1.37 (s, 36 H); FDMS, *m/e* 544 ($C_{26}H_{40}O_2{}^{80}Se_2$).

Preparation of 43. Diisopropylethylamine (2.6 g, 20 mmol) was added to a mixture of malononitrile (1.8 g, 27 mmol) and diacetate **20** (8.76 g, 20.0 mmol) in 50 mL of acetonitrile. The mixture was heated for 15 min on a steam bath. Upon cooling, shiny platelets precipitated, which were collected by filtration to give 2.10 g (29%) of **20**: mp 185–187 °C; ^{1}H NMR ($CDCl_3$) δ 7.48 (s, 2 H), 1.36 (s, 18 H); IR (KBr) 2900, 2180, 1570, 1440, 1300 cm^{-1}; field-desorption mass spectrum (FDMS), *m/e* 370 ($C_{16}H_{20}N_2{}^{130}Te$). Anal. Calcd for $C_{16}H_{20}N_2Te$: C, 52.2; H, 5.4; N, 7.6. Found: C, 52.2; H, 5.5; N, 7.6.

Preparation of 44 and 46. Diisopropylethylamine (0.39 g, 3.0 mmol) was added to a mixture of malononitrile (0.20 g, 3.0 mmol) and diacetate **21** (1.0 g, 2.3 mmol) in 10 mL of acetonitrile. The mixture was heated for 15 min on a steam bath and cooled to ambient temperature. The red precipitate was collected by filtration and recrystallized from acetonitrile, giving 0.23 g (24%) of **44**: mp 240–242.5 °C. The mother liquors from the crude reaction mixture were cooled to 0 °C. A yellow solid was collected by filtration and recrystallized from acetonitrile, giving 0.12 g (11%) of **46**: mp 259.5–262.5 °C.

For **44**: ^{1}H NMR ($CDCl_3$) δ 7.73 (s, 2 H), 7.49 (m, 10 H); IR (KBr) 2180, 1570, 1430, 1310 cm^{-1}; UV λ_{max} (CH_2Cl_2) 485 nm (ϵ 27 000), 340 (14 000); FDMS, *m/e* 410 ($C_{20}H_{12}N_2{}^{130}Te$). Anal. Calcd for $C_{20}H_{12}N_2Te$: C, 58.8; H, 3.0; N, 6.9. Found: C, 58.6; H, 3.0; N, 6.8.

For **46**: ^{1}H NMR ($CDCl_3$) δ 8.27 (s, 1 H), 8.50 (m, 10 H), 7.21 (s, 1 H), 5.15 (s, 1 H); IR (KBr) 3300, 2190, 1610, 1510 cm^{-1}; UV λ_{max} (CH_2Cl_2) 425 nm (ϵ 5000), 359 (14 000); FDMS, *m/e* 449

($C_{22}H_{13}N_3{}^{130}Te$), 410 (M – CHCN). Anal. Calcd for $C_{22}H_{13}N_3Te$: C, 59.1; H, 2.9; N, 9.4. Found: C, 58.9; H. 3.0; N, 9.1.

Preparation of Diacetate 47. Compound **18** (1.15 g, 3.13 mmol) in 5 mL of dichloromethane and 5 mL of acetic acid was cooled to 0 °C. Peracetic acid (40% in acetic acid, 1.3 g, 6.9 mmol) was added slowly. The mixture was stirred for 5 min at 0 °C and then diluted with water (100 mL). The product was extracted with dichloromethane (3 × 25 mL). The combined organic extracts were washed with water (3 × 25 mL) and brine (25 mL), dried over sodium sulfate, and concentrated. The residue was recrystallized from 20% EtOAc/pentane to give 0.73 g (48%) of **47**: mp 131.5–132.5 °C; ^1H NMR ($CDCl_3$) δ 6.90 (s, 2 H), 1.83 (s, 18 H); IR (KBr) 2900, 2240, 1660, 1190, 660 cm^{-1}; FDMS, *m/e* 488 ($C_{20}H_{26}N_2O_4{}^{130}Te$). Anal. Calcd for $C_{20}H_{26}N_2O_4Te$: C, 49.4; H, 5.4; N, 5.8. Found: C, 49.4; H, 5.3; N, 5.6.

Preparation of Dichloride 49. Chlorine gas was bubbled into a CCl_4 solution (50 mL) of **43** (1.84 g, 5.0 mmol) until the solution became colorless. The reaction mixture was concentrated, and the residue was recrystallized from CH_3CN to give 1.80 g (82%) of **49**: mp 218.5–221.5 °C; ^1H NMR ($CDCl_3$) δ 6.75 (s, 2 H), 1.58 (s, 18 H); IR (KBr) 2980, 2315, 1630, 1590, 1505, 1480, 1370, 1315, 1230, 880 cm^{-1}. Anal. Calcd for $C_{16}H_{20}Cl_2N_2Te$: C, 43.8; H, 4.6; N, 6.4. Found: C, 43.8; H, 4.6; N, 6.6.

Preparation of Dibromides 50 and 52. Bromine (2.0 g, 6.2 mmol) in 5 mL of dichloromethane was added dropwise to a solution of **43** or **44** (5.0 mmol) in 20 mL of dichloromethane. After addition was complete, the reaction mixture was concentrated. Recrystallization of the residue from acetonitrile gave the dibromides **50** and **52**.

For **50**: 70% yield; mp 207–208 °C; ^1H NMR ($CDCl_3$) δ 6.85 (s, 2 H), 1.63 (s, 18 H); IR (KBr) 2980, 2220, 1620, 1580, 1470, 1360, 1315, 875 cm^{-1}. Anal. Calcd for $C_{16}H_{20}Br_2N_2Te$: C, 36.4; H, 3.8; N, 5.3. Found: C, 36.6; H, 4.0; N, 5.1.

For **52**: 79% yield; mp 243–244 °C; ^1H NMR ($CDCl_3$) δ 7.80 (m, 4 H), 7.60 (m, 6 H), 7.05 (s, 2 H); IR (KBr) 2220, 1620, 1565, 1450, 760 cm^{-1}. Anal. Calcd for $C_{20}H_{12}Br_2N_2Te$: C, 42.3; H, 2.1; N, 4.9. Found: C, 42.3; H, 2.2; N, 5.4.

Preparation of Diiodide 51. Iodine (0.254 g, 1.0 mmol) was added to a stirred solution of **43** (0.37 g, 1.0 mmol) in 10 mL of dichloromethane. The reaction mixture was stirred for 15 min at ambient temperature and concentrated. The residue was recrystallized from CH_0CN to give 0.31 g (50%) of **51**: mp 110–140 °C dec; ^1H NMR ($CDCl_3$) δ 7.48 (s, 2 H), 1.38 (s, 18 H); IR (KBr) 2980, 2310, 1600, 1460, 1325, 880 cm^{-1}. Anal. Calcd for $C_{16}H_{22}I_2N_2Te$: C, 30.9; H, 3.2; N, 4.5. Found: C, 30.8; H, 3.2; N, 4.5.

Preparation of Meldrum's Acid Adduct 57. Telluropyranone 17 (23.0 g, 0.0719 mol) was added to 92 mL of ethyl fluorosulfate under an argon atmosphere. The mixture was warmed on a steam bath for 5 min and cooled to ambient temperature. Anhydrous ether (1 L) was added, precipitating the fluorosulfate salt **53**. The chalky gray salt was washed with ether (2 × 500 mL) and collected by filtration. The material was used without further purification: FDMS, *m/e* 351 ($C_{15}H_{25}OTe$).

Meldrum's acid (23.0 g, 0.0720 mol) was dissolved in 230 mL of pyridine, and the fluorosulfate was added as a powder. The mixture was stirred for 5 min at ambient temperature and concentrated. The residue was dissolved in 250 mL of methylene chloride. The solution was washed with 5% HCl, dried over $MgSO_4$, and concentrated to give 24.5 g (78%) of the Meldrum's acid adduct **57** as an orange crystalline solid: mp 155–158 °C; ^1H ($CDCl_3$) δ 9.25 (s, 2 H), 1.53 (s, 6 H), 0.48 (s, 18 H); IR (KBr) 2970, 1672, 1580, 1295, 1190 cm^{-1}; FDMS, *m/e* 448 ($C_{19}H_{26}O_4Te$). Anal. Calcd for $C_{19}H_{26}O_4Te$: C, 51.2; H, 5.9; Te, 28.6. Found: C, 52.4; H, 6.2; Te, 27.8.

Preparation of Meldrum's Acid Adduct 58. 2,6-Diphenyltelluropyranone (**18**; 0.98 g, 2.7 mmol) was added to 4 mL of freshly distilled ethyl fluorosulfate. The mixture was heated under nitrogen on a steam bath until solution occurred, and then the reaction vessel was placed in a 60 °C water bath for 5 min. Upon cooling, the product crystallized. Trituration with 90 mL of anhydrous ethyl ether and filtration gave 1.27 g (96%) of **54** as a yellowish solid. Recrystallization from acetonitrile gave an air- and moisture-sensitive yellow solid: mp 208–210 °C; UV λ_{max} (CH_2Cl_2) 295 nm (ϵ 17 900), 385 (15 700). Anal. Calcd for $C_{19}H_{17}FO_4STe$: C, 46.76; H, 3.51; F, 3.89; S, 6.57; Te, 26.15. Found: C, 46.21; H, 3.11; F, 4.50; S, 6.65; Te, 28.21.

Meldrum's acid (1.44 g, 0.01 mol) was dissolved in 25 mL of pyridine. The 4-ethoxy-2,6-diphenyltelluropyrylium fluorosulfate (**54**, 5.0 g, 0.01 mol) was added as a powder, giving a dark red solution. Immediately after addition, the solution was concentrated under vacuum. The residue was purified by chromatography on Florisil (100/200 mesh) eluted with dichloromethane to give 4.0 g (80%) of the adduct **58** as a red solid: mp 199–201 °C; ^1H NMR ($CDCl_3$) δ 9.35 (s, 2 H), 7.67–7.33 (m, 10 H), 1.68 (s, 6 H); IR (KBr) 1666, 1566, 1425, 1300, 1185, 925, 698 cm^{-1}; FDMS, *m/e* 488 (M$^+$, $C_{23}H_{18}O_4Te$). Anal. Calcd for $C_{23}H_{18}O_4Te$: C, 56.8; H, 3.7; Te, 26.3. Found: C, 56.5; H, 3.8; Te, 25.2.

Preparation of Meldrum's Acid Adduct 59. Benzotelluropyranone **42** (22.0 g, 0.064 mol) was dissolved in 66 mL of CH_3CN. Ethyl fluorosulfate (8.2 g, 0.064 mol) was added. The reaction mixture was heated on a stream bath under argon for 2 min. The reaction mixture was cooled to ambient temperature and poured into a solution of Meldrum's acid (9.2 g, 0.064 mol) in 36 mL of pyridine. The solution was stirred for 15 min at ambient temperature and concentrated. The residue was dissolved in 300 mL of dichloromethane. The solution was washed with 3% HCl (3 × 200 mL) and then with water (200 mL), dried over $MgSO_4$, and concentrated. Recrystallization from toluene gave 28.0 g (86%) of **59**: mp 225–227 °C; ^1H NMR ($CDCl_3$) δ 8.85 (s, 1 H), 7.55 (d, 1 H, *J* = 9 Hz), 7.37 (d, 1 H, *J* = 3 Hz), 6.87 (dd, 1 H, *J* = 3.9 Hz), 3.83 (s, 3 H), 1.87 (s, 6 H), 1.40 (s, 9 H); IR (KBr) 1680 cm^{-1}; FDMS, *m/e* 472 ($C_{20}/H_{22}O_5{}^{130}Te$). Anal. Calcd for $C_{20}H_{22}O_5Te$: C, 51.1; H, 4.7; Te, 27.1. Found: C, 51.1; H, 4.6; Te, 28.0.

Preparation of Meldrum's Acid Adduct 60. Benzotelluropyranone **19** (5.0 g, 0.014 mol) was added to 20 mL of freshly distilled ethyl fluorosulfate. The mixture was stirred under nitrogen at 60 °C for 10 min. Ether (200 mL) was added, precipitating a red solid. The solid was collected by filtration and recrystallized from acetonitrile to give 6.0 g (87%) of **56**: mp 215–216 °C; ^1H NMR (CD_3CN) δ 9.20 (d, 1 H, *J* = 9 Hz), 8.35 (s, 1 H), 8.03 (d, 1 H, *J* = 2.5 Hz), 7.70 (m, 5 H), 7.50 (dd, 1 H, *J* = 2.5, 9 Hz), 4.80 (quartet, 2 H, *J* = 7 Hz), 4.13 (s, 3 H), 1.83 (t, 3 H, *J* = 7 Hz); IR (KBr) 1600, 1550, 1290 (br), 1230 cm^{-1}. Anal. Calcd for $C_{18}H_{17}FO_5STe$: C, 43.9; H, 3.5; S, 6.5; Te, 25.9. Found: C, 41.8; H, 3.2; S, 7.1; Te, 26.7.

Meldrum's acid (0.29 g, 2.0 mmol) was dissolved in 10 mL of pyridine. The sulfate **56** (1.0 g, 2.0 mmol) was added as a powder, immediately giving a dark red solution. The solution was concentrated in vacuo. The residue was purified by chromatography on silica gel eluted with dichloromethane to give 0.90 g (92%) of **60** as a red solid. Recrystallization from toluene gave material with mp 207–209 °C: ^1H NMR ($CDCl_3$) δ 9.13 (s, 1 H), 7.80–6.80 (m, 3 H), 3.80 (s, 3 H), 1.88 (s, 6 H); IR (KBr) 1680, 1595, 1555, 1433, 1200, 1085 cm^{-1}; FDMS, *m/e* 492 ($C_{22}H_{18}TeO_5$). Anal. Calcd for $C_{22}H_{18}TeO_5$: C, 53.9; H, 3.7; Te, 26.0. Found: C, 53.7; H, 3.7; Te, 25.9.