Cyclization of 3-(Arylchalcogeno)propenoyl Chlorides. 2. Chalcogen and Substituent Control in the Regiochemistry of Intramolecular Acylation. Preparation of Benzo[b]telluropyrones

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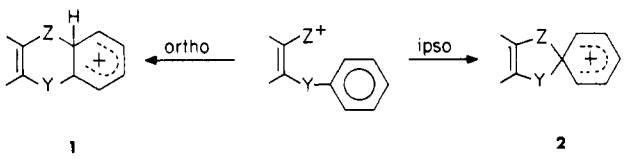
Abstract: The regiochemistry of cyclization of β-(arylchalcogeno)propenoyl chlorides is sensitive to the nature of the chalcogen and substituents in the arylchalcogen ring. Arylthio groups give only ortho acylation and benzo[b]thiapyrone products. The phenylseleno group gives ortho acylation and benzo[b]selenopyrone products. However, a more active ring system (naphthyl) or an activating substituent in the para position gives ipso attack and 1,2-oxaselenol-1-ium chloride products. Phenyltelluro, naphthyltelluro, and all para-substituted aryltelluro groups give exclusive ipso attack and 1,2-oxatellurol-1-ium products. If one or more ortho–para-activating, meta-deactivating groups by σ^+ substituent constants (F, CH_3O) are placed meta to the carbon bearing tellurium, ortho acylation is observed to give benzo[b]telluropyrone products. The additions of Grignard reagents and diisobutylaluminum hydride to the carbonyl carbon of the benzo[b]telluropyrones were examined as well as the electrophilic alkylation of the carbonyl oxygen with ethyl fluorosulfonate.

Intramolecular electrophilic attack on arylthio, arylseleno, and aryltelluro groups has been reported frequently in the literature. For cationic groups on a vicinal carbon relative to arylthio and arylseleno groups, two types of electrophilic attack have been observed (Scheme I). Ortho substitution has been observed for cyclizations of 3-(arylthio)-[1,2] and 3-(arylseleno) propenoic acids[2-5] and -propenoyl chlorides, presumably through an intermediate such as **1**. 4*H*-Benzo[b]thiopyran-4-ones and selenopyran-4-ones are the isolated products from such attack. In certain systems, however, ipso attack[6] has been observed to give spirocyclic intermediates[7] such as **2**. Diaryl thioethers bearing an ortho azido group give such intermediates upon pyrolysis.[8] *o*-(Phenylseleno)benzoyl chloride upon treatment with zinc chloride gives *o*-(chloroselenenyl)benzophenone, presumably via ipso acylation.[9] In aryltelluro-substituted molecules, only ipso acylation has been observed.[9,10]

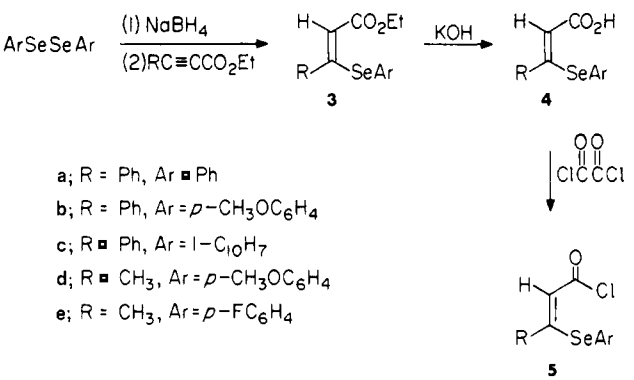
The cyclization of 3-arylchalcogeno-substituted propenoic acids and acid chlorides has been of interest to us as a convenient route to 4*H*-benzo[b]chalcogenopyran-4-ones.[2] The failure of (*Z*)-3-(phenyltelluro)propenoyl chlorides[10,11] to undergo ortho acylation to give benzotelluropyrones was disappointing. This failure was somewhat surprising in view of the fact that phenylthio- and phenylseleno-substituted cinnamic acids give the corresponding benzothiopyrones and benzoselenopyrones in excellent yields upon treatment with methanesulfonic acid/phosphorus pentoxide.[2,12] We sought to achieve ortho acylation in the aryltelluro systems.

Herein we report substituent control in selecting ipso vs. ortho acylation in (*Z*)-3-(arylchalcogeno)propenoyl chlorides upon treatment with aluminum chloride. This study provides synthetic entry to two new classes of heterocycles—telluroflavones (4*H*-2-arylbenzo[b]telluropyran-4-ones) and 1,2-oxaselenol-1-ium chlorides—as well as a simple, high-yield route to substituted tellurochromones (2-alkyl- and 2-H-4*H*-benzo[b]telluropyran-4-ones). Several transformations of telluroflavones and tellurochromones are also described.

Scheme I



Scheme II



Results and Discussion

Chalcogen Effect. The rearrangement via ipso acylation of *o*-(phenyltelluro)benzoyl chlorides has been attributed to the polarizability of tellurium and its electronegativity.[9] In view of the fact that *o*-(phenylseleno)benzoyl chloride undergoes an identical rearrangement (selenium is more electronegative and less polarizable than tellurium), we felt that the limits of reaction should be better defined.

We prepared a series of arylseleno-substituted propenoyl chlorides as shown in Scheme II. Diaryl diselenides were either commercially available or prepared by treating the aryl Grignard reagent with selenium metal.[13] The diaryl diselenides were reduced to sodium arylselenides with sodium borohydride. Addition of ethyl phenylpropiolate or ethyltetrolate gave *Z* esters **3**, which were saponified with ethanolic potassium hydroxide to

(1) Bossert, F. *Liebigs Ann. Chem.* **1964**, *680*, 40.
(2) Wadsworth, D. H.; Detty, M. R. *J. Org. Chem.* **1980**, *45*, 4611.
(3) Bossert, F. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 879.
(4) Tolmachev, A. I.; Shulezhko, L. M.; Kisilenko, A. A. *Zh. Obshch. Khim.* **1967**, *37*, 367.
(5) Rawet, A.; Renson, M. *Bull. Soc. Chim. Belg.* **1966**, *75*, 260.
(6) Perrin, C.; Skinner, G. *J. Am. Chem. Soc.* **1971**, *93*, 3389.
(7) Newman, M. S. *Acc. Chem. Res.* **1972**, *5*, 354.
(8) Messer, M.; Farge, D. *Bull. Soc. Chim. Fr.* **1968**, 2832. Cadogan, J. I. G.; Kulik, S. *J. Chem. Soc. D* **1970**, 436.
(9) Piette, J.-L.; Thibaur, P.; Renson, M. *Tetrahedron* **1978**, *34*, 655.
(10) Detty, M. R.; Murray, B. J.; Smith, D. L.; Zumbulyadis, N. *J. Am. Chem. Soc.* **1983**, *105* (preceding paper in this issue).
(11) Dereu, N.; Renson, M. *J. Organomet. Chem.* **1981**, *208*, 11.
(12) Eaton, P. E.; Carlson, G. R.; Lee, J. T. *J. Org. Chem.* **1973**, *38*, 4071.
(13) Piette, J.-L.; Renson, M. *Bull. Soc. Chim. Belg.* **1970**, *79*, 353.

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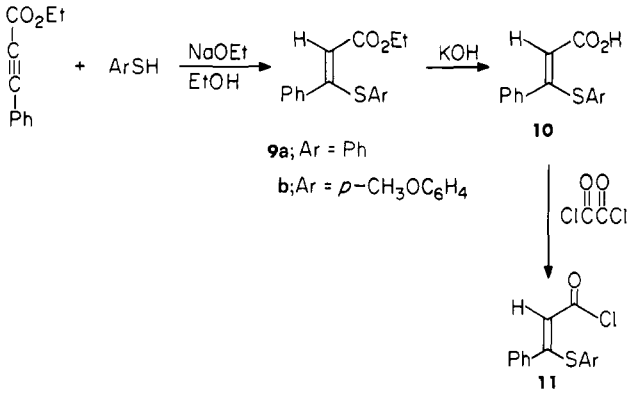
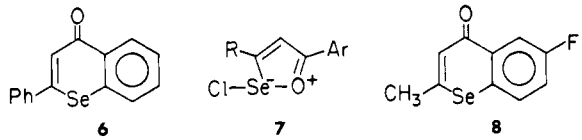
Scheme III



give the corresponding acids **4**. The acid chlorides **5** were obtained by treating the carboxylic acids with oxalyl chloride at room temperature.

The acid chloride **5a** gave complete conversion to selenoflavone **6** upon treatment with aluminum chloride. No other product containing selenium was detected.

Acid chlorides **5b** and **5d** upon either heating or reacting with aluminum chloride gave rearrangement products identified as 3-phenyl- and 3-methyl-5-(*p*-methoxyphenyl)-1,2-oxaselenol-1-ium chlorides (**7a** and **7c**, respectively). The spectral properties of **7a**



6 **7** **8**

a ; R = Ph, Ar = *p*-$CH_3OC_6H_4$

b ; R = Ph, Ar = 1-$C_{10}H_7$

c ; R = CH_3, Ar = *p*-$CH_3OC_6H_4$

d ; R = CH_3, Ar = *p*-FC_6H_4

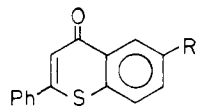
and **7c** were similar to those reported for oxatellurolium chlorides.[10] The IR carbonyl stretching frequency of **7a** was a strong band at 1543 cm^{-1}. The olefinic proton appeared in the ^1H NMR as a low-field singlet at δ 7.52. The molecule exhibited a strong absorption band at 378 nm (log ϵ 4.40), ~40 nm shorter than the corresponding band in the tellurium analogues.[10]

The 1-naphthyl derivative **5c** upon treatment with aluminum chloride gave oxaselenolium chloride **7b**. No benzoselenopyrone products were detected.

Acid chloride **5e** gave two products upon treatment with aluminum chloride. The major product, isolated in 36% yield by chromatography on silica gel, was identified as oxaselenolium chloride **7d**. The minor product, isolated in 24% yield, was identified as selenochromone **8**.

Two (arylthio)cinnamoyl chlorides were also examined. The materials were prepared as shown in Scheme III. The addition of ethyl phenylpropiolate to a solution of an arylthiol in sodium ethoxide and ethanol gave predominantly the (*Z*)-cinnamate esters **9**.[2] Small amounts of the *E* isomers were detected but not isolated. Saponification with ethanolic potassium hydroxide gave carboxylic acids **10**. The acids were converted to the acid chlorides **11** with oxalyl chloride.

Upon treatment with aluminum chloride, both **11a** and **11b** gave only thiaflavones **12a** and **12b**, respectively. No other products were detected.



12a, R = H

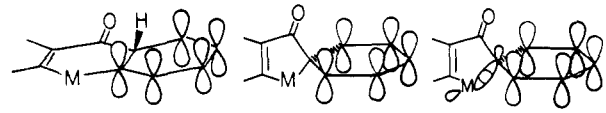
b, R = OCH_3

Presumably, the benzoselenopyrone and benzothiapyrone products arise from ortho acylation, as represented by **1**. The oxaselenolium products arise by ipso acylation, as represented by **2**. In arylseleno-substituted propenoyl chlorides, ipso and ortho acylation compete. Substituent effects can influence the preference for site of attack in these systems.

Arylthio- and aryltelluro-substituted propenoyl chlorides appear to represent two extremes. Arylthio groups prefer ortho attack to give benzothiapyrone products, exclusively. Aryltelluro groups, on the other hand, prefer ipso attack to give only oxatellurolium products.

The crossover in reactivity that is observed by changing either the nature of the chalcogen or the substituents on the arylseleno groups can be rationalized, although not unequivocally. As one proceeds down the group 6A elements, the size of the atom increases (covalent radii of 1.03, 1.17, and 1.37 Å for S, Se, and Te, respectively)[14] and, presumably, so does the polarizability.[9] Tellurium is also much more electropositive (2.01) than either sulfur (2.44) or selenium (2.48).[15]

The intermediate σ complexes for ipso and ortho acylation as well as the transition states leading to them can be stabilized by the group 6A element. In **13**, the intermediate for ortho acylation,



M = S, Se, Te

13 **14** **15**

the heteroatom can stabilize the positive charge by back-donation of electrons from a filled p orbital to the π framework. Similarly, the back-donation of electrons from the heteroatom can stabilize the spirocyclic intermediate by a spiroconjugative interaction as in **14**.[16] As the size of the group 6A element increases, the overlap of orbitals in **13** should decrease as a 2p orbital on carbon interacts with a 4p (Se) or 5p (Te) orbital. On the other hand, the larger orbitals should interact more favorably than the smaller orbitals with the carbon π framework in **14**. The contributions of filled 3d and 4d orbitals for Se and Te cannot be dismissed from either intermediate.

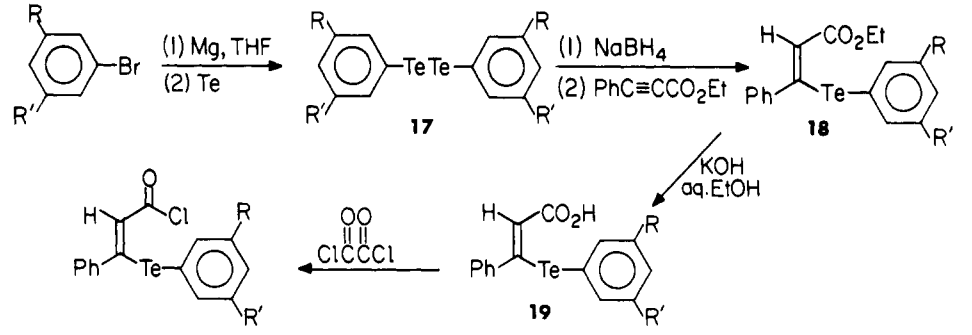
Electronegativity differences can also be used to rationalize the preference of the aryltelluro groups for ipso acylation. The tellurium–carbon bond should be polarized, with the carbon atom claiming the greater electron density because of the more electropositive nature of tellurium. If the intermediate for ipso attack is redrawn as in **15**, the tellurium–carbon σ bond should be capable of interaction with the π framework, with the greater electron density being closer to carbon. This should be a stabilizing factor. Since sulfur and selenium are more similar to carbon in electronegativity, such stabilization should be less pronounced. Furthermore, as the acylating species attacks the aryltelluro ring, the greater electron density at the carbon bearing tellurium should stabilize the transition leading to the ipso σ complex as opposed to the transition leading to the ortho σ complex.

Of the three elements, selenium appears to be the only one that is not predisposed to undergo either ipso or ortho attack, since the course of reaction changes as hydrogen is replaced with activating substituents in the para position. If the substituent can donate electrons (either through hyperconjugation or back-donation), the transition leading to the ipso σ complex will be stabilized because of increased electron density at the carbon bearing selenium.

Although the discussion thus far has been directed primarily to transition-state phenomena, ground-state phenomena may also be invoked. If the two σ complexes are in equilibrium and the rate-determining steps of proton loss or nucleophilic attack of

(14) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry"; Wiley: New York, 1966; p 106.
(15) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 264.
(16) Semmelhack, M. F.; Weller, H. N.; Foos, J. S. *J. Am. Chem. Soc.* **1977**, *99*, 292.

Scheme IV



20a; R = H, R′ = CH_3
b; R = H, R′ = F
c; R = H, R′ = OCH_3
d; R = R′ = OCH_3

Table I. Substituent Constants and Intramolecular Acylation Data for Acid Chlorides **20**

compd	R	R′	σ_p^{+a}	σ_m^{+a}	ortho/ipso
20a	H	CH_3	−0.256	−0.065	0
20b	H	F	−0.247	0.352	0.06
20c	H	OCH_3	−0.648	0.047	25
20d	OCH_3	OCH_3	−0.648	0.047	>100

[a] Reference 18c.

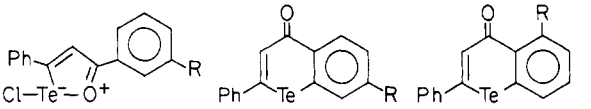
chloride are similar, then the equilibrium ratio of the two σ complexes will determine product ratios. Stabilizing influences as represented by **13–15** should influence this ratio.

Preparation of 4*H*-Benzo[*b*]telluropyran-4-one. In view of the above discussion and the observation that the rate of ipso acylation is extremely substituent sensitive,[10] it should be possible to use substituents to bias the reactivity of various (aryltelluro)propenoyl chlorides to give preferential ortho attack. The approach should involve either strongly activating the ortho positions to electrophilic attack, strongly deactivating the position for ipso attack, or a combination of both. Substituents on the meta position of the aryltelluro group seemed particularly well suited.

Various meta-substituted (aryltelluro)cinnamoyl chlorides were prepared as shown in Scheme IV. Diaryl ditellurides (**17**) were prepared by treating the Grignard reagent formed from the corresponding *m*-bromo aromatic compound with tellurium metal. 1-Bromo-3,5-dimethoxybenzene was prepared by treating 3,5-dimethoxyaniline with sodium nitrite and hydrobromic acid followed by treatment with cuprous bromide.[17] Reduction of the ditellurides with sodium borohydride in ethanolic tetrahydrofuran (THF) followed by the addition of ethyl phenylpropiolate gave (*Z*)-cinnamate esters **18**. Saponification with ethanolic potassium hydroxide gave the acids **19**, which were treated with oxalyl chloride to give the acid chlorides **20**. No thermal rearrangements of the acid chlorides were observed.

The σ^+ substituent constants for the compounds **20** in the meta and para positions are given in Table I.[18] These substituents were chosen for the following reasons. The methyl group activates the ortho and para positions to a reasonable extent, but it is also weakly activating in the meta position. The fluoro group is similar to the methyl group in activating the ortho and para positions, but it deactivates the meta position. The methoxyl group is strongly ortho–para activating and weakly meta deactivating.

Upon treatment with aluminum chloride at −78 °C in methylene chloride, the acid chlorides **20** gave products from both ortho and ipso acylation. These results are compiled in Table I. The methyl-substituted derivative **20a** gave only the product of ipso attack, **21a**. None of the flavone products, **22a** and **23a**, could be detected.

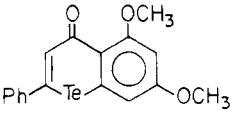


21 **22a**, R = CH_3; **b**, R = F; **c**, R = OCH_3 **23**

The fluoro-substituted derivative **20b** gave a 16:1 mixture of two products. The major product was the product of ipso attack, oxatellurolium chloride **21b**. The minor product was telluroflavone **22b**. None of the isomeric telluroflavone **23b** was isolated.

The methoxy-substituted acid chloride **20c** gave a product mixture in which the product of ipso attack, oxatellurolium chloride **21c**, was present in ~4% yield (by ^{1}H NMR spectroscopy). The telluroflavone **22c** was present in 92% yield, and its isomer, **23c**, was present in 4% yield.

The dimethoxy-substituted acid chloride **20d** gave only ortho attack to give **24**. Telluroflavone **24** was isolated in 90% yield. No other products were detected.



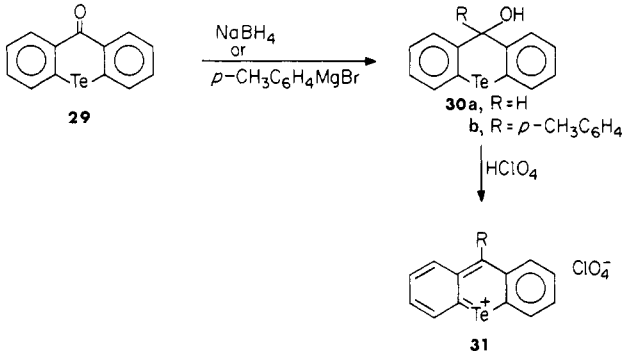
24

The cinnamic acids **19c** and **19d** behaved similarly upon treatment with methanesulfonic acid/phosphorus pentoxide.[12] Compound **22c** was isolated in 90% yield from **19c**, and **24** was isolated in 85% yield from **19d**.

The four telluroflavones thus prepared show similar spectral properties. Their UV spectra have an absorption maximum at 381–388 nm in methylene chloride with a moderate molar extinction coefficient of 5300–7700. These values are ~30 nm more bathochromic than the same band for selenoflavone (**6**), which is at 357 nm. The IR spectra of the telluroflavones display two strong bands, one at 1600–1610 cm^{-1} and the other at 1585–1590 cm^{-1}. These bands are also present in the thia- and selenoflavones. The ^{1}H NMR spectra of the telluroflavones show a sharp singlet for the α proton of the enone at δ 7.31–7.41. The protons of the phenyl groups attached to the β position of the enone are approximately a singlet at δ 7.37–7.47. The peri proton closest to the carbonyl on the benzo-fused ring in **22b** appears as a doublet (J = 9 Hz) at δ 8.65, and in **22c**, as a doublet of doublets (J = 6, 9 Hz) at δ 8.68. This signal is absent, of course, in **23c** and **24**.

(17) Buck, J. S.; Ide, W. S. "Organic Syntheses"; Wiley: New York, 1943; Collect. Vol. II, p 132.
(18) (a) Hammett, L. P. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1970. (b) Wells, P. R. *Chem. Rev.* **1963**, *63*, 171. (c) Swain, C. G.; Lupton, E. C., Jr. *J. Am. Chem. Soc.* **1968**, *90*, 4328.

Scheme V

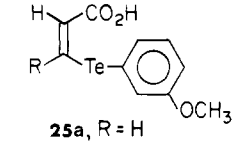


29 30a, R=H b, R=p-CH3C6H4 31

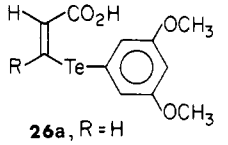
These results show that the regiochemistry of intramolecular acylations on arylchalcogen groups is sensitive to the influence of substituents. With the exception of arylthio groups, which seem predisposed to ortho acylation, arylseleno and aryltelluro groups undergo both ipso and ortho acylation, depending on the nature and position of substituents. With arylseleno groups, ortho–para-activating substituents para to the carbon bearing selenium promote ipso acylation, but the phenylseleno group itself undergoes ortho acylation. With aryltelluro groups, ortho acylation occurs with one or more σ_p^+-activating, σ_m^+-deactivating substituents meta to the carbon bearing tellurium. All other meta substituents or any ortho or para substituents thus far examined[10] give only ipso substitution with aryltelluro groups.

Of the two effects, ortho–para activation appears to be more important than meta deactivation if one compares the fluoro and methoxyl substituents (Table I). The methoxyl group is a much stronger σ_p^+-activating group, and fluoro is a much stronger σ_m^+-deactivating group. With para-substituted (arylseleno)-propenoyl chlorides **5b** and **5e**, the methoxyl-substituted materials give ipso (para) attack only, and the fluoro-substituted material gives both ortho and ipso attack.

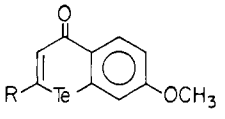
This strategy is easily extended to the preparation of tellurochromones. The acids **25** and **26** were prepared by direct sapo-



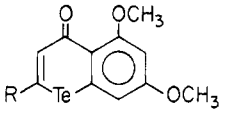
25a, R = H
b, R = CH_3



26a, R = H
b, R = CH_3



27a, R = H
b, R = CH_3

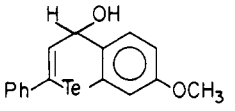


28a, R = H
b, R = CH_3

nification of the esters produced by the addition of ethyl propiolate or ethyl tetrolate to the corresponding sodium aryltelluride. The acids were cyclized either by conversion to the acid chlorides followed by aluminum chloride treatment or by treatment with methanesulfonic acid/phosphorus pentoxide[12] to give, in excellent yields, the tellurochromones **27** and **28**, whose spectral properties were similar to those of related chromones described by Dereu and Renson.[11]

Chemistry of Benzo[*b*]telluropyrones. The chemistry of benzo[*b*]telluropyrones has not been described in the literature. However, certain transformations of telluroxanthone (**29**) have been reported (Scheme V).[19] The carbonyl group of **29** undergoes attack by sodium borohydride or Grignard reagents to give the telluroxanthols **30**. Treatment of **30** with perchloric acid gave the telluroxanthylium perchlorates **31**. We have conducted similar transformations with the benzo[*b*]telluropyrones.

Although sodium borohydride does not attack the benzo[*b*]-telluropyrones, diisobutylaluminum hydride preferentially attacks the carbonyl carbon. Thus telluroflavone **22c** is reduced by diisobutylaluminum hydride to a mixture of products in which the major product appears to be alcohol **32** (^{1}H NMR). Attempts



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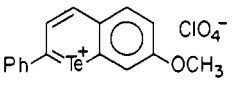

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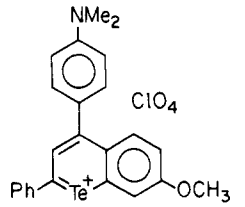
to separate the product mixture by chromatography on silica gel, Florisil, or alumina gave decomposition. The crude alcohol mixture was treated with perchloric acid to give the flavylium perchlorate **33**.[20] The ^{1}H NMR spectrum of **33** was characterized by two coupled, one-proton doublets at δ 9.13 and 8.50 (J = 9.5 Hz).

The carbonyl carbon of both telluroflavones and tellurochromones was easily attacked by Grignard reagents. Thus, the reaction of **22c** with the Grignard reagent prepared from magnesium and *p*-bromo-*N*,*N*-dimethylaniline followed by treatment with perchloric acid gave the flavylium dye **34** [λ_{max} (CH_2Cl_2)



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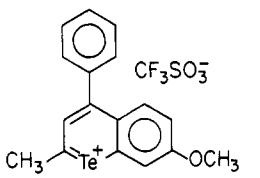
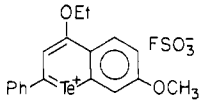


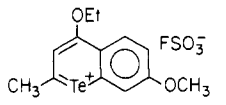
35

678 nm (ϵ 30 000)]. Similarly, the reaction of tellurochromone **27b** with phenylmagnesium bromide followed by treatment with trifluoromethanesulfonic acid gave flavylium species **35**.

The carbonyl oxygen of the benzo[*b*]telluropyrones is sensitive to electrophilic attack. Treatment of **22c** and **27b** with ethyl fluorosulfonate gave the 4-ethoxybenzo[*b*]telluropyrylium species **36** and **37**, respectively. These compounds were easily hydrolyzed in aqueous base to the starting carbonyl compounds.

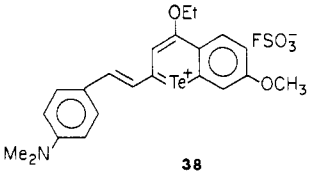


36

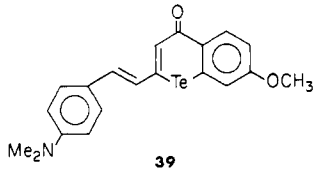


37

Compound **37** is an interesting compound in that it was easily elaborated into more complicated benzo[*b*]telluropyrones. The condensation of **37** with *p*-(dimethylamino)benzaldehyde in hot acetic anhydride gave the benzo[*b*]telluropyrylium dye **38** [λ_{max}



38



39

(CH_2Cl_2) 695 nm (ϵ 95 000)]. This was easily hydrolyzed by potassium carbonate in aqueous acetonitrile to give benzo[*b*]-telluropyrone **39**, quantitatively.

Other reactions of the benzo[*b*]telluropyrones are being examined. Of particular interest are transformations at the 4-position.

Summary and Conclusions

The Friedel–Crafts cyclization of β-(arylchalocogeno)propenoyl chlorides and propenoic acids gives products derived from both

(19) Sadekov, E. I.; Ladatko, A. A.; Sadekova, E. I.; Minkin, V. I. *Khim. Geterotsikl. Soedin.* **1980**, 274.

(20) The hexafluorophosphate and tetrafluoroborate salts were also prepared.

ipso and ortho attack. The regiochemistry of acylation is sensitive to the nature of the chalcogen and to the nature and position of substituents in the arylchalcogeno groups. Arylthio groups undergo only ortho acylation to give benzo[*b*]thiapyrone products even in systems that should favor ipso attack by having a strongly activating group in the para position. Arylseleno groups activated by methoxyl substituents in the para position give only ipso acylation and oxaselenolium products. The phenylseleno group, on the other hand, gives only ortho attack and benzo[*b*]selenopyrone products. A *p*-fluoro substituent gives both ortho and ipso attack. All para-substituted aryltelluro groups appear predisposed to ipso attack.[10] However, if ortho–para-activating, meta-deactivating (by σ^+ constants) substituents are placed in the meta position of the aryltelluro group, ortho acylation can be observed. We believe that these are the first documented examples of substituents diverting ipso attack in an electrophilic aromatic substitution reaction.

The use of (3-methoxyphenyl)telluro and (3,5-dimethoxyphenyl)telluro groups allows simple syntheses of telluroflavones and tellurochromones in good yield from propenoic acids. The telluroflavones have not been prepared by other methods.

The carbonyl carbon of the benzo[*b*]telluropyrones is susceptible to nucleophilic attack, but the carbonyl oxygen is susceptible to electrophilic attack. Thus, diisobutylaluminum hydride reduces the carbonyl functions to alcohols, which are converted to benzo[*b*]telluropyrylium species upon acid treatment. Similarly, Grignard reagents add to the carbonyl carbon to give alcohols, which yield benzo[*b*]telluropyrylium compounds upon acid treatment. Ethyl fluorosulfonate alkylates the carbonyl oxygen to give 4-ethoxybenzo[*b*]telluropyrylium fluorosulfonates.

The 2-methyl compound **37** condensed with various aldehydes to give dyes. These dyes were hydrolyzed in aqueous base to give more complex benzo[*b*]telluropyrones.

The chemistry of the oxaselenolium chlorides has not been examined. The chemistry of these systems and other transformations of the benzo[*b*]telluropyrones are being investigated.

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. ^{13}C NMR spectra were recorded on a Varian CFT-20 instrument. Infrared spectra were recorded on a Beckman IR 4250 instrument. UV–visible spectra were recorded on a Cary 17 spectrophotometer. Solvents were obtained from Kodak Laboratory Chemicals and were used as received. Dry tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Ethyl propiolate and ethyl phenylpropiolate were purchased from Aldrich Chemicals. Ethyl 2-butynoate was prepared by the literature procedure[21] by Synthetic Chemicals Division, Eastman Kodak Co. Tellurium and selenium shot were purchased from Ventron Corp. (Alfa Inorganics). Microanalyses were performed on a Perkin-Elmer C, H, and N analyzer. Tellurium analyses were done by atomic absorption spectroscopy.

General Procedure for Ditelluride and Diselenide Preparation. Di-*m*-anisyl Ditelluride. *m*-Bromoanisole (5.82 g, 0.0311 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 reaction. After the mixture was stirred for several minutes, the iodine color faded. The rest of the *m*-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, tellurium shot (3.81 g, 0.0300 mol) was added, and the mixture was stirred at reflux for 3 h. The mixture was cooled to 0 °C, and 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, dried over sodium sulfate, and concentrated. The ditelluride (6.03 g, 87%) was isolated as a dark red oil after chromatography on silica gel (1/1 (v/v) ether/hexane, R_f 0.8 on thin-layer chromatography) and was used immediately. Upon standing, the compound gave tellurium metal and diaryltelluride.

Bis(*m*-fluorophenyl) Ditelluride. 3-Bromofluorobenzene (13.8 g, 0.0789 mol) was treated with magnesium (2.4 g, 0.10 mol) and tellurium shot (10.0 g, 0.0789 mol) as described to give 15.8 g (89%) of di-*m*-fluoro ditelluride as a dark red oil after chromatography on silica gel (1/1 (v/v) ether/hexane, R_f 0.8 by TLC).

Di-*m*-tolyl Ditelluride. *m*-Bromotoluene (25.0 g, 0.146 mol) was treated with magnesium (3.9 g, 0.16 mol) and tellurium shot (18.5 g, 0.146 mol) as described to give 15.5 g (49%) of di-*m*-tolyl ditelluride as a dark red oil after chromatography on silica gel (1/1 (v/v) ether/hexane, R_f 0.8 by TLC).

Bis(3,5-dimethoxyphenyl) Ditelluride. 3,5-Dimethoxybromobenzene (4.34 g, 0.0200 mol) was treated with magnesium (0.60 g, 0.025 mol) and tellurium shot (2.55 g, 0.0200 mol) as described to give 2.32 g (44%) of bis(3,5-dimethoxyphenyl) ditelluride as a red crystalline solid (recrystallized from methanol), mp 118.5–121 °C. Anal. Calcd for $C_{16}H_{18}O_4Te_2$: C, 36.3; H, 3.4; Te, 48.2. Found: C, 36.6; H, 3.5; Te, 47.1.

Di-*p*-anisyl Diselenide. *p*-Bromoanisole (11.2 g, 0.0600 mol) was treated with magnesium (2.0 g, 0.083 mol) and selenium shot (4.80 g, 0.0600 mol) as described to give 4.2 g (38%) of di-*p*-anisyl diselenide (recrystallized from methanol) as a yellow powder, mp 55–57 °C.

Di-1-naphthyl Diselenide. 1-Bromonaphthalene (42.0 g, 0.203 mol) was treated with magnesium (5.6 g, 0.23 mol) and selenium shot (15.8 g, 0.200 mol) as described to give 20.5 g (40%) of di-1-naphthyl diselenide (recrystallized from methanol) as yellow needles, mp 88.0–89.5 °C. Anal. Calcd for $C_{20}H_{14}Se_2$: C, 58.3; H, 3.4; Se, 38.3. Found: C, 58.3; H, 3.6; Se, 37.7.

3,5-Dimethoxybromobenzene. Sodium nitrite (22 g, 0.31 mol) was dissolved in 50 mL of water, and the solution was added slowly to 100 mL of 48% hydrobromic acid cooled to −10 °C. 3,5-Dimethoxyaniline (45.9 g, 0.300 mol) was added as a powder. The mixture was vigorously stirred for 5 min and then poured into 28.6 g (0.200 mol) of cuprous bromide in 100 mL of 48% hydrobromic acid heated to boiling in a 3-L flask. After addition, the product was removed by steam distillation. The steam distillate (~500 mL) was filtered through a sintered-glass frit. The crude product was recrystallized from 2/1 (v/v) acetone/water to give 14.0 g (21.5%) of 3,5-dimethoxybromobenzene as tan needles: mp 64–66 °C; ^{1}H NMR ($CDCl_3$) δ 6.64 (d, 2 H, J = 2 Hz), 6.35 (t, 1 H, J = 2 Hz), 3.76 (s, 6 H); IR (KBr) 3050, 2920, 1600, 1590, 1430, 1300, 1200, 1155, 1080, 940, 853, 820, 793 cm^{-1}; mass spectrum, *m/e* 184.

General Procedure for the Addition of Sodium Aryltellurides and Arylselenides to Acetylenic Esters. The diaryl ditelluride or diaryl diselenide 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 or the yellow color of the diselenide faded. The appropriate acetylenic ester (ethyl phenylpropiolate, ethyl tetrolate, ethyl propiolate) in ethanol (2 mmol/mL) was added in one portion, and the 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 esters were recrystallized from methanol. Table II gives physical data for the esters.

For **3a**: mass spectrum, *m/e* 332 ($C_{17}H_{16}O_2Se$). Anal. Calcd for $C_{17}H_{16}O_2Se$: C, 61.6; H, 4.9; Se, 23.8. Found: C, 61.7; H, 4.8; Se, 23.5.

For **3b**: mass spectrum, *m/e* 382 ($C_{21}H_{18}O_2Se$). Anal. Calcd for $C_{21}H_{18}O_2Se$: C, 66.1; H, 4.8; Se, 20.7. Found: C, 66.1; H, 4.7; Se, 20.3.

For **3c** (methyl ester): mass spectrum, *m/e* 348 ($C_{17}H_{16}O_3Se$). Anal. Calcd for $C_{17}H_{16}O_3Se$: C, 58.8; H, 4.6; Se, 22.7. Found: C, 58.5; H, 4.6; Se, 22.6.

For **3d**: mass spectrum, *m/e* 300 ($C_{13}H_{16}O_3Se$).

For **3e**: mass spectrum, *m/e* 288 ($C_{12}H_{13}FO_2Se$).

For **18a**: mass spectrum, *m/e* 396 ($C_{18}H_{18}O_2Te$). Anal. Calcd for $C_{18}H_{18}O_2Te$: C, 54.9; H, 4.6; Te, 32.4. Found: C, 54.6; H, 4.6; Te, 32.1.

For **18b**: mass spectrum, *m/e* 400 ($C_{17}H_{15}FO_2Te$). Anal. Calcd for $C_{17}H_{15}FO_2Te$: C, 51.3; H, 3.8; Te, 32.1. Found: C, 51.5; H, 3.5; Te, 31.6.

For **18c**: mass spectrum, *m/e* 412 ($C_{18}H_{18}O_3Te$). Anal. Calcd for $C_{18}H_{18}O_3Te$: C, 52.7; H, 4.4; Te, 31.1. Found: C, 52.7; H, 4.4; Te, 30.8.

For **18d**: mass spectrum, *m/e* 442 ($C_{19}H_{20}O_4Te$). Anal. Calcd for $C_{19}H_{20}O_4Te$: C, 51.9; H, 4.6; Te, 29.0. Found: C, 51.7; H, 4.6; Te, 29.0.

Preparation of Ethyl (*Z*)-3-((4-Methoxyphenyl)thio)cinnamate (9b). Sodium metal (0.50 g, 0.022 mol) was dissolved in 20 mL of ethanol. *p*-Methoxythiophenol (2.00 g, 0.0143 mol) was added (exothermic) in 5 mL of ethanol, followed by ethyl phenylpropiolate (2.49 g, 0.0143 mol). The solution was stirred for 20 min at room temperature, and then 25 mL of water was added, precipitating the ester. Recrystallization of the crude product from methanol gave 2.60 g (58%) of pure *Z* isomer: mp 77–79 °C; ^{1}H NMR ($CDCl_3$) δ 7.10 (s, 5 H), 7.08 (d, 2 H, J = 8 Hz), 6.52 (d, 2 H, J = 8 Hz), 5.97 (s, 1 H), 4.23 (q, 2 H, J = 7 Hz), 3.65

(21) Smith, W. N.; Kuehn, E. D. *J. Org. Chem.* **1973**, *38*, 3588.

Table II. Preparation of R(ArY)C=CHCO$_2$Et

compd	R	ArY	yield,[a] %	mp, °C	^{1}H NMR[b] ($CDCl_3$), δ	IR,[c] cm^{-1}
3a	Ph	PhSe	85	107–109	6.31	1690
3b	Ph	4-$CH_3OC_6H_4Se$	69	86.5–89.5	6.37	1690
3c	Ph	1-$C_{10}H_7Se$	83	150–151.5[d]	6.32	1688
3d	CH_3	4-$CH_3OC_6H_4Se$	98	oil	6.18	1685
3e	CH_3	4-FC_6H_4Se	92	oil	6.20	1685
18a	Ph	3-$CH_3C_6H_4Te$	68	79–81	6.67	1665
18b	Ph	3-FC_6H_4Te	60	81–84	6.67	1670
18c	Ph	3-$CH_3OC_6H_4Te$	98	57–58	6.69	1670
18d	Ph	3,5-$(CH_3O)_2C_6H_3Te$	86	81–82	6.70	1670

[a] Isolated yield. [b] Chemical shift of α proton in enone. [c] C=O stretching frequency. [d] Methyl ester.

Table III. Preparation of R(ArY)C=CHCO$_2$H

compd	R	ArY	yield,[a] %	mp, °C	^{1}H NMR[b] ($CDCl_3$), δ	IR,[c] cm^{-1}
4a	Ph	PhSe	81	171–175	6.30	1650
4b	Ph	4-$CH_3OC_6H_4Se$	91	184.5–187.5	6.42	1670
4c	Ph	1-$C_{10}H_7Se$	92	164.5–165	6.33	1663
4d	CH_3	4-$CH_3OC_6H_4Se$	40	152–159[d]	6.20	1675
4e	CH_3	4-FC_6H_4Se	38	162–168[d]	6.25	1660
10a	Ph	PhS	86	138–144	6.20	1660
10b	Ph	4-$CH_3OC_6H_4S$	96	140–143	5.93	1660
19a	Ph	3-$CH_3C_6H_4Te$	93	148–149.5	6.75	1650
19b	Ph	3-FC_6H_4Te	90	158 (dec)	6.71	1650
19c	Ph	3-$CH_3OC_6H_4Te$	94	145–147	6.70	1660
19d	Ph	3,5-$(CH_3O)_2C_6H_3Te$	96	174.5–177.5	6.67	1655
25a	H	3-$CH_3OC_6H_4Te$	82	95–99	7.00	1650
25b	CH_3	3-$CH_3OC_6H_4Te$	89	141–143.5	6.60	1650
26a	H	3,5-$(CH_3O)_2C_6H_3Te$	91	129–131	7.00	1650
26b	CH_3	3,5-$(CH_3O)_2C_6H_3Te$	63	155–160	6.65	1650

[a] Isolated yield. [b] Chemical shift of α proton in enone. [c] C=O stretching frequency. [d] Some *E* isomer present.

(s, 3 H), 1.30 (t, 3 H, J = 7 Hz); IR (KBr) 1695, 1600, 1590, 1495 cm^{-1}; mass spectrum, m/e 314 ($C_{18}H_{18}O_3S$). Anal. Calcd for $C_{18}H_{18}O_3S$: C, 68.8; H, 5.8; S, 10.2. Found: C, 68.7; H, 6.1; S, 10.6.

General Procedure for the Saponification of β-(Arylchalcogeno)-propenoates. The ester was dissolved in hot (50 °C) ethanol (1 g of ester/20 mL of ethanol). To this solution was added aqueous 30% potassium hydroxide (2 mL/g of ester). The solution was stirred at 50 °C for 2 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% hydrochloric acid. The acidified solution was extracted with several portions of methylene chloride. The combined methylene chloride extracts were dried over sodium sulfate and concentrated to give the crude acid. Recrystallization from acetonitrile gave pure acid. Physical and spectral properties are contained in Table III.

For **4a**: mass spectrum, m/e 304 ($C_{15}H_{12}O_2Se$). Anal. Calcd for $C_{15}H_{12}O_2Se$: C, 59.4; H, 4.0; Se, 26.0. Found: C, 59.1; H, 3.8; Se, 25.6.

For **4b**: mass spectrum, m/e 334 ($C_{16}H_{14}O_3Se$). Anal. Calcd for $C_{16}H_{14}O_3Se$: C, 57.7; H, 4.2; Se, 23.7. Found: C, 57.5; H, 4.3; Se, 23.7.

For **4c**: mass spectrum, m/e 354 ($C_{19}H_{14}O_2Se$). Anal. Calcd for $C_{19}H_{14}O_2Se$: C, 64.6; H, 4.0; Se, 22.4. Found: C, 64.2; H, 4.3; Se, 22.0.

For **4d**: mass spectrum, m/e 272 ($C_{11}H_{12}O_3Se$). Anal. Calcd for $C_{11}H_{12}O_3Se$: C, 48.7; H, 4.5; Se, 29.1. Found: C, 48.7; H, 4.5; Se, 29.2.

For **4e**: mass spectrum, m/e 260 ($C_{10}H_9FO_2Se$). Anal. Calcd for $C_{10}H_9FO_2Se$: C, 46.3; H, 3.5; F, 7.3; Se, 30.5. Found: C, 46.3; H, 3.6; F, 6.9; Se, 29.9.

For **9a**: mass spectrum, m/e 256 ($C_{15}H_{12}O_2S$).[2]

For **9b**: mass spectrum, m/e 286 ($C_{16}H_{14}O_2S$). Anal. Calcd for $C_{16}H_{14}O_2S$: C, 67.1; H, 4.9; S, 11.2. Found: C, 67.4; H, 5.0; S, 11.0.

For **19a**: mass spectrum, m/e 368 ($C_{16}H_{14}O_2Te$). Anal. Calcd for $C_{16}H_{14}O_2Te$: C, 52.5; H, 3.9; Te, 34.9. Found: C, 52.2; H, 3.9; Te, 34.5.

For **19b**: mass spectrum, m/e 372 ($C_{15}H_{11}FO_2Te$).

For **19c**: mass spectrum, m/e 384 ($C_{16}H_{14}O_3Te$). Anal. Calcd for $C_{16}H_{14}O_3Te$: C, 50.3; H, 3.7; Te, 33.4. Found: C, 50.0; H, 3.6; Te, 33.5.

For **19d**: mass spectrum, m/e 414 ($C_{17}H_{16}O_4Te$). Anal. Calcd for $C_{17}H_{16}O_4Te$: C, 49.6; H, 3.9; Te, 31.0. Found: C, 49.5; H, 3.9; Te, 29.6.

For **25a**: mass spectrum, m/e 308 ($C_{10}H_{10}O_3Te$). Anal. Calcd for $C_{10}H_{10}O_3Te$: C, 39.3; H, 3.3; Te, 41.7. Found: C, 39.2; H, 3.3; Te, 41.7.

For **25b**: mass spectrum, m/e 322 ($C_{11}H_{12}O_3Te$). Anal. Calcd for $C_{11}H_{12}O_3Te$: C, 41.3; H, 3.8; Te, 39.9. Found: C, 40.9; H, 3.9; Te, 39.5.

For **26a**: mass spectrum, m/e 338 ($C_{11}H_{12}O_4Te$). Anal. Calcd for $C_{11}H_{12}O_4Te$: C, 39.3; H, 3.6; Te, 38.0. Found: C, 39.5; H, 3.8; Te, 37.9.

For **26b**: mass spectrum, m/e 352 ($C_{12}H_{14}O_4Te$).

General Procedure for the Conversion of β-(Arylchalcogeno)propenoic Acids to Acid Chlorides. Under a nitrogen atmosphere, the acrylic acids were added to oxalyl chloride (1 g of acid/5 mL of oxalyl chloride). The 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, which were used without further purification.

Acid chlorides **5b** and **5d** gave oxaselenolium chlorides **7a** and **7c** upon heating at 40 °C for 1 h.

For 3-phenyl-5-(4-methoxyphenyl)-1,2-oxaselenol-1-ium chloride (**7a**): mp 174–175.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.90 (d, 2 H, J = 9 Hz), 7.52 (s, 1 H), 7.32 (s, 5 H), 6.88 (d, 2 H, J = 9 Hz), 3.78 (s, 3 H); IR (KBr) 1603, 1543, 1489, 1180, 825, 760, 690 cm^{-1}; λ_{max} (CH_2Cl_2) 378 nm (log ε 4.40); mass spectrum, m/e 352 ($C_{16}H_{13}ClO_2Se$). Anal. Calcd for $C_{16}H_{13}ClO_2Se$: C, 54.6; H, 3.7; Cl, 10.1; Se, 22.5. Found: C, 54.6; H, 3.8; Cl, 10.4; Se, 22.7.

For 3-methyl-5-(4-methoxyphenyl)-1,2-oxaselenol-1-ium chloride (**7c**): mp 166–168 °C; ^{1}H NMR ($CDCl_3$) δ 7.95 (d, 2 H, J = 9 Hz), 7.60 (q, 1 H, J = 1.2 Hz), 6.95 (d, 2 H, J = 9 Hz), 3.90 (s, 3 H), 2.88 (d, 3 H, J = 1.2 Hz); IR (KBr) 1605, 1540, 1515, 1244, 1178, 1020, 818 cm^{-1}; mass spectrum, m/e 290 ($C_{11}H_{11}ClO_2Se$). Anal. Calcd for $C_{11}H_{11}ClO_2Se$: C, 45.6; H, 3.8; Cl, 12.2; Se, 27.3. Found: C, 45.7; H, 4.1; Cl, 12.7; Se, 26.7.

General Procedure for the Reaction of β-(Arylchalcogeno)propenoyl Chlorides with Aluminum Chloride. The propenoyl chloride derivatives were dissolved in methylene chloride (1 g/10 mL) under a nitrogen atmosphere. The 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. After stirring for 1 h at room temperature, the reaction mixture was poured into ice water, and the products were extracted with several portions of methylene chloride. The combined methylene chloride extracts were dried over sodium sulfate and concentrated. The residues were recrystallized from methanol if ^{1}H NMR spectroscopy showed a single product.

***4H*-2-Phenylbenzo[*b*]selenopyran (6).** Acid chloride **5a** (3.22 g, 0.0100 mol) was treated with aluminum chloride (1.47 g, 0.0110 mol) as described to give 2.43 g (85%) of **6** as a yellow crystalline solid: mp 127–130 °C; ^{1}H NMR ($CDCl_3$) δ 8.61 (m, 1 H), 7.48 (m, 8 H), 7.35 (s, 1 H); IR (KBr) 1605, 1590, 1330, 778, 760 cm^{-1}; λ_{max} (CH_2Cl_2) 357

nm (log ϵ 3.75); mass spectrum, *m/e* 286 ($C_{15}H_{10}OSe$).

3-Phenyl-5-(1-naphthyl)-1,2-oxaselenol-1-ium Chloride (7b). Acid chloride **5c** (3.72 g, 0.0100 mol) was treated with aluminum chloride (1.47 g, 0.0110 mol) as described to give 2.94 g (79%) of **7b** as a gold crystalline solid: mp 133–135 °C; ^{1}H NMR ($CDCl_3$) δ 8.70 (m, 1 H), 7.95 (m, 3 H), 7.65 (s, 1 H), 7.55 (m, 3 H), 7.54 (s, 5 H); IR (KBr) 1570, 1540, 1320, 1231, 775, 695 cm^{-1}; λ_{max} (CH_2Cl_2) 378 nm (log ϵ 4.19); mass spectrum, *m/e* 372 ($C_{19}H_{13}ClOSe$). Anal. Calcd for $C_{19}H_{13}ClOSe$: C, 61.4; H, 3.5; Cl, 9.5; Se, 21.2. Found: C, 61.1; H, 3.2; Cl, 9.8; Se, 21.3.

Cyclization of Acid Chloride 5e. Acid chloride **5e** (6.38 g, 0.0230 mol) was treated with aluminum chloride (3.5 g, 0.026 mol) as described. The ^{1}H NMR spectrum of the crude reaction mixture showed two products. Chromatography of the mixture on silica gel eluting with methylene chloride gave 1.27 g (24%) of 4*H*-2-methyl-6-fluorobenzo[*b*]selenopyrone (**8**), mp 132–135 °C, and 2.19 g (36%) of 3-methyl-5-(4-fluorophenyl)-1,2-oxaselenol-1-ium chloride (**7d**), mp 158–159 °C.

For **8**: ^{1}H NMR ($CDCl_3$) δ 8.20 (d × d, 1 H, *J* = 3, 10 Hz), 7.51 (d × d, 1 H, *J* = 5, 10 Hz), 7.23 (m, 1 H), 6.92 (q, 1 H, *J* = 1.2 Hz), 2.53 (d, 3 H, *J* = 1.2 Hz); IR (KBr) 1605, 1590, 910, 850, 820, 715 cm^{-1}; mass spectrum, *m/e* 242 ($C_{10}H_7FOSe$). Anal. Calcd for $C_{10}H_7FOSe$: C, 49.8; H, 2.9; Se, 32.7. Found: C, 49.9; H, 3.0; Se, 33.0.

For **7d**: ^{1}H NMR ($CDCl_3$) δ 7.85 (d × d, 2 H, *J* = 6, 9 Hz), 7.35 (q, 1 H, *J* = 1 Hz), 7.05 (d × d, 2 H, *J* = 9, 9 Hz), 2.65 (d, 3 H, *J* = 1 Hz); IR (KBr) 1600, 1565, 1229, 800 cm^{-1}; mass spectrum, *m/e* 278 ($C_{10}H_8ClFOSe$).

4*H*-2-Phenylbenzo[*b*]thiapyrone (12a). Acid chloride **11a** (2.74 g, 0.0100 mol) was treated with aluminum chloride (1.47 g, 0.0110 mol) as described to give 2.02 g (85%) of **12a** as a yellow solid: mp 122–123 °C; ^{1}H NMR ($CDCl_3$) δ 8.55 (m, 1 H), 7.45 (m, 8 H), 7.35 (s, 1 H); IR (KBr) 1605, 1590, 1330, 775 cm^{-1}; mass spectrum, *m/e* 238 ($C_{15}H_{10}OS$).[2]

4*H*-2-Phenyl-6-methoxybenzo[*b*]thiapyrone (12b). Acid chloride **11b** (3.04 g, 0.0100 mol) was treated with aluminum chloride (1.47 g, 0.0110 mol) as described to give 1.90 g (71%) of **12b** as a yellow solid: mp 152–154 °C; ^{1}H NMR ($CDCl_3$) δ 7.82 (d, 1 H, *J* = 2 Hz), 7.50 (m, 2 H), 7.35 (m, 4 H), 7.07 (s, 1 H), 7.07 (m, 1 H), 3.80 (s, 3 H); IR (KBr) 1605, 1595 cm^{-1}; mass spectrum, *m/e* 268 ($C_{16}H_{12}O_2S$). Anal. Calcd for $C_{16}H_{12}O_2S$: C, 71.6; H, 4.5; S, 11.9. Found: C, 71.6; H, 4.7; S, 11.8.

3-Phenyl-5-(3-methylphenyl)-1,2-oxatellurol-1-ium Chloride (21a). Acid chloride **20a** (3.86 g, 0.0100 mol) was treated with aluminum chloride (1.47 g, 0.0110 mol) as described to give 3.55 g (92%) of **21a** as a red oil: ^{1}H NMR ($CDCl_3$) δ 8.26 (s, 1 H), 7.75 (m, 2 H), 7.30 (s, 5 H), 7.25 (m, 2 H), 2.35 (s, 3 H); IR (KBr) 3055, 1590, 1530, 755, 690 cm^{-1}; λ_{max} (CH_2Cl_2) 422 nm (log ϵ 4.36); mass spectrum, *m/e* 386 ($C_{16}H_{13}ClOTe$).

Cyclization of Acid Chloride 20b. Acid chloride **20b** (6.82 g, 0.0176 mol) was treated with aluminum chloride (2.7 g, 0.020 mol) as described. The residue was recrystallized from methanol to give 5.30 g (78%) of 3-phenyl-5-(3-fluorphenyl)-1,2-oxatellurol-1-ium chloride (**21b**) as a red solid, mp 111.5–114 °C. The mother liquors were concentrated and purified by chromatography on silica gel eluting with 5% acetone in methylene chloride to give 0.30 g (4.9%) of 4*H*-2-phenyl-7-fluorobenzo[*b*]telluropyran (**22b**) as a gold solid, mp 138.5–139.5 °C.

For **21b**: ^{1}H NMR ($CDCl_3$) δ 8.35 (s, 1 H), 7.75 (m, 2 H), 7.92 (s, 5 H), 7.40 (m, 2 H); IR (KBr) 1595, 1530, 1480, 891, 842, 790 cm^{-1}; λ_{max} (CH_2Cl_2) 436 nm (log ϵ 4.40); mass spectrum, *m/e* 390 ($C_{15}H_{10}ClFOTe$).

For **22b**: ^{1}H NMR ($CDCl_3$) δ 8.68 (d × d, 1 H, *J* = 6, 9 Hz), 7.40 (s, 5 H), 7.45 (m, 1 H), 7.17 (m, 1 H); IR (KBr) 1605, 1590 cm^{-1}; λ_{max} (CH_2Cl_2) 385 nm (log ϵ 3.89); mass spectrum, *m/e* 354 ($C_{15}H_9OFTe$). Anal. Calcd for $C_{15}H_9OFTe$: C, 51.1; H, 2.6; Te, 36.3. Found: C, 51.2; H, 2.6; Te, 36.4.

Cyclization of Acid Chloride 20c. Acid chloride **20c** (8.04 g, 0.0200 mol) was treated with aluminum chloride (2.94 g, 0.022 mol) as described. The ^{1}H NMR spectrum displayed three methoxy signals in a ratio of 1:25:1 at δ 3.92, 3.88, and 3.80, respectively. A singlet corresponding to $\sim^1/_3$ of the height of the singlet at δ 3.80 was present at δ 8.40. These signals were assigned to oxatellurolium chloride **21c**. Chromatography of the reaction mixture on silica gel gave 5.26 g (73%) of 4*H*-2-phenyl-7-methoxybenzo[*b*]telluropyrone (**22c**), mp 117–118 °C, and 0.29 g (4%) of 4*H*-2-phenyl-5-methoxybenzo[*b*]telluropyrone (**23c**), mp 157–159 °C. The oxatellurolium chloride **21c** was not isolated.

For **22c**: ^{1}H NMR ($CDCl_3$) δ 8.64 (d, 1 H, *J* = 9 Hz), 7.45 (s, 1 H), 7.42 (s, 5 H), 7.18 (d, 1 H, *J* = 3 Hz), 7.00 (d × d, 1 H, *J* = 3, 9 Hz); 3.88 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 185.5, 161.5, 144.1, 141.1, 133.3, 131.1, 130.2, 129.3, 127.2, 126.8, 116.5, 116.1, 55.6; IR (KBr) 1595, 1580 cm^{-1}; λ_{max} (CH_2Cl_2) 388 nm (log ϵ 3.72); mass spectrum, *m/e* 360 ($C_{16}H_{12}O_2Te$). Anal. Calcd for $C_{16}H_{12}O_2Te$: C, 52.8; H, 3.3; Te, 35.1. Found: C, 52.5; H, 3.0; Te, 34.9.

For **23c**: ^{1}H ($CDCl_3$) δ 7.38 (m, 5 H), 7.35 (s, 1 H), 7.22 (m, 2 H), 6.88 (m, 1 H), 3.92 (s, 3 H); IR (KBr) 1612 cm^{-1}; mass spectrum, *m/e* 366 ($C_{16}H_{12}O_2Te$). Anal. Calcd for $C_{16}H_{12}O_2Te$: C, 52.8; H, 3.3; Te, 35.1. Found: C, 52.8; H, 3.2; Te, 35.0.

4*H*-2-Phenyl-5,7-dimethoxybenzo[*b*]telluropyrone (24). Acid chloride **20d** (2.71 g, 0.00633 mol) was treated with aluminum chloride as described to give 2.23 g (90%) of **24** as a yellow solid: mp 98–100 °C; ^{1}H NMR ($CDCl_3$) δ 7.35 (m, 5 H), 7.30 (s, 1 H), 6.77 (d, 1 H, *J* = 2 Hz), 6.45 (d, 1 H, *J* = 2 Hz), 3.89 (s, 3 H), 3.78 (s, 3 H); IR (KBr) 1610, 1590 cm^{-1}; λ_{max} (CH_2Cl_2) 381 nm (log ϵ 3.81); mass spectrum, *m/e* 396 ($C_{17}H_{14}O_3Te$). Anal. Calcd for $C_{17}H_{14}O_3Te$: C, 51.8; H, 3.6. Found: C, 51.7; H, 3.5.

4*H*-7-Methoxybenzo[*b*]telluropyrone (27a). Acid **25a** (1.20 g, 3.92 mmol) was added to a solution of 1 g of phosphorus pentoxide in 10 mL of distilled methanesulfonic acid. The mixture was stirred for 4 h at room temperature and then added dropwise to 250 mL of saturated sodium bicarbonate solution. This mixture was extracted with methylene chloride (3 × 50 mL). The combined methylene chloride extracts were dried over sodium sulfate and concentrated. The residue was recrystallized from methanol to give 0.76 g (67%) of **27a**: mp 102–103 °C; ^{1}H NMR ($CDCl_3$) δ 8.53 (d, 1 H, *J* = 11.4 Hz), 8.62 (d, 1 H, *J* = 8.4 Hz), 7.15 (m, 2 H), 3.83 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 184.4, 161.1, 134.0, 133.4, 129.0, 125.5, 124.5, 117.0, 116.1, 55.6; IR (KBr) 1595 cm^{-1}; λ_{max} (CH_2Cl_2) 370 nm (log ϵ 3.82); mass spectrum, *m/e* 290 ($C_{10}H_8O_2Te$). Anal. Calcd for $C_{10}H_8O_2Te$: C, 41.7; H, 2.8. Found: C, 41.7; H, 3.0.

4*H*-2-Methyl-7-methoxybenzo[*b*]telluropyrone (27b). Acid **25b** (16.0 g, 0.0500 mol) was added to a solution of 10 g of phosphorus pentoxide in 100 mL of distilled methanesulfonic acid. Workup as before gave 10.1 g (67%) of **27b** as a red solid: mp 97–99 °C; ^{1}H NMR ($CDCl_3$) δ 8.58 (d, 1 H, *J* = 9 Hz), 7.0 (m, 3 H), 3.82 (s, 3 H), 2.53 (d, 3 H, *J* = 1.2 Hz); IR (KBr) 1595, 1520, 1370, 1030, 820 cm^{-1}; mass spectrum, *m/e* 304 ($C_{11}H_{10}O_2Te$). Anal. Calcd for $C_{11}H_{10}O_2Te$: C, 43.8; H, 3.3; Te, 42.3. Found: C, 43.5; H, 3.2; Te, 41.4.

4*H*-5,7-Dimethoxybenzo[*b*]telluropyrone (28a). Acid **26a** (1.10 g, 0.00328 mol) was treated with phosphorus pentoxide/methanesulfonic acid as described to give 0.77 g (74%) of **28a** as a tan powder: mp 152–155 °C; ^{1}H NMR ($CDCl_3$) δ 8.21 (d, 1 H, *J* = 11.4 Hz), 7.27 (d, 1 H, *J* = 11.4 Hz), 6.75 (d, 1 H, *J* = 2 Hz), 6.48 (d, 1 H, *J* = 2 Hz), 3.90 (s, 3 H), 3.83 (s, 3 H); IR (KBr) 1580, 1255, 1030, 820 cm^{-1}; mass spectrum, *m/e* 320 ($C_{11}H_{10}O_3Te$). Anal. Calcd for $C_{11}H_{10}O_3Te$: C, 41.6; H, 3.2. Found: C, 41.7; H, 3.1.

4*H*-2-Methyl-5,7-dimethoxybenzo[*b*]telluropyrone (28b). Acid **26b** (2.25 g, 6.45 mmol) was treated with phosphorus pentoxide/methanesulfonic acid as described to give 1.31 g (62%) of **28b** as a tan powder: mp 127.5–129 °C; ^{1}H NMR ($CDCl_3$) δ 6.91 (q, 1 H, *J* = 1.2 Hz), 6.67 (d, 1 H, *J* = 2 Hz), 6.40 (d, 1 H, *J* = 2 Hz), 3.87 (s, 3 H), 380 (s, 3 H), 2.40 (d, 3 H, *J* = 1.2 Hz); IR (KBr) 1605, 1595, 1270, 1060, 1030 cm^{-1}; mass spectrum, *m/e* 334 ($C_{12}H_{12}O_3Te$). Anal. Calcd for $C_{12}H_{12}O_3Te$: C, 43.4; H, 3.6. Found: C, 43.4; H, 3.7.

Reduction of 22c with Diisobutylaluminum Hydride. Preparation of 2-Phenyl-7-methoxybenzo[*b*]telluropyrylium Perchlorate (33). Flavone **22c** (1.81 g, 5.00 mmol) was dissolved in 20 mL of dry THF. The resulting solution was cooled to −78 °C, and 5.5 mL of a 20% solution of diisobutylaluminum hydride in hexane was added dropwise via syringe. After addition was complete, the cooling bath was removed and the reaction mixture was warmed slowly to ambient temperature. Sodium hydroxide solution (20 mL, 1 N) was added. The mixture was stirred for 1 h at room temperature and then poured into 100 mL of ether. The organic phase was washed with brine, dried over sodium sulfate, and concentrated. The residue was dissolved in 25 mL of acetic acid, and 2 mL of 70% perchloric acid was added. When the solution had cooled, a red solid precipitated. The crystalline product was collected by filtration, washed with several portions of ether, and air-dried to give 1.13 g (50%) of **33** as a brick-red solid: mp 150 °C dec; ^{1}H NMR (CD_3CN) δ 9.12 (d, 1 H, *J* = 9 Hz) 8.70 (d, 1 H, *J* = 9 Hz), 8.47 (d, 1 H, *J* = 9 Hz), 8.40 (br s, 1 H), 7.9–7.3 (m, 6 H), 4.00 (s, 3 H); IR (KBr) 1600, 1485, 1350, 1210, 1090 cm^{-1}; λ_{max} (CH_2Cl_2) 285 nm (log ϵ 4.47), 386 (3.94); mass spectrum, *m/e* 351 ($C_{16}H_{13}OTe$). Anal. Calcd for $C_{16}H_{13}ClO_5Te$: C, 42.9; H, 2.9; Te, 28.5. Found: C, 43.3; H, 2.9; Te, 28.0.

Preparation of 2-Phenyl-4-(*p*-(dimethylamino)phenyl)-7-methoxybenzo[*b*]telluropyrylium Perchlorate (34). *p*-Bromo-*N*,*N*-dimethylaniline (0.38 g, 2.0 mmol) was added to a slurry of magnesium turnings (0.24 g, 10 mmol) in 3 mL of dry THF. The mixture was warmed at reflux for 3.0 h. Telluroflavone **22c** (0.50 g, 1.4 mmol) was dissolved in 2 mL of THF and added dropwise to the Grignard reagent. The mixture was stirred at reflux for 2 h and then cooled to 0 °C; 25 mL of saturated ammonium chloride was added dropwise (vigorous evolution of gas). The products were extracted with methylene chloride (3 × 25 mL), and the combined extracts were dried over sodium sulfate and concentrated. The

residue was taken up in 20 mL of acetic acid, and 1 mL of 70% perchloric acid was added, giving an intense blue-green color. The solution was warmed for 10 min on a steam bath and then cooled to room temperature. Ether (20 mL) was added. When the solution was allowed to stand, **34** precipitated as a green-black solid. The solid was collected by filtration to give 0.34 g (44%) of material: mp 164–170 °C dec; λ_{max} (CH_2Cl_2) 678 nm (log ϵ 4.46); mass spectrum *m/e* 470 ($C_{24}H_{22}ONTe$). Anal. Calcd for $C_{24}H_{22}ClO_5NTe$: C, 50.8; H, 3.9; N, 2.5. Found: C, 50.8; H, 4.2; N, 2.7.

Preparation of 2-Methyl-4-phenyl-7-methoxybenzo[*b*]telluropyrylium Trifluoromethanesulfonate (35). Bromobenzene (1.57 g, 10.0 mmol) in 5 mL of dry THF was added dropwise to a slurry of magnesium turnings (0.41 g, 17 mmol) in 3 mL of dry THF. After 1 mL was added, a 20-mg crystal of iodine was added. When the iodine color faded, the rest of the bromobenzene solution was added dropwise. The mixture was warmed at reflux for 1 h. Tellurochromone **27b** (1.00 g, 3.31 mmol) in 5 mL of dry THF was added. The mixture was warmed at reflux for 1 h more and then cooled to 0 °C. Saturated ammonium chloride solution (10 mL) was added dropwise (gas evolution), and the mixture was diluted with 100 mL of water. The products were extracted with methylene chloride (3 × 25 mL). The combined extracts were dried over sodium sulfate and concentrated. The residue was taken up in 20 mL of trifluoromethanesulfonic acid, and the mixture was warmed on a steam bath for 0.5 h. Ice (20 g) was added, precipitating the product. The material was collected by filtration and washed sequentially with 20-mL portions of 1/1 (v/v) methanol/water, methanol, 1/1 (v/v) methanol/ether, and ether. The material was dried to give 1.22 g (72%) of **35** as a lavender solid: mp 153–163 °C dec; IR (KBr) 1600, 1450, 1275, 1225, 1030, 760, 695 cm^{-1}; mass spectrum, *m/e* 365 ($C_{17}H_{15}OTe$). Anal. Calcd for $C_{18}H_{15}F_3O_4STe$: C, 42.2; H, 3.0. Found: C, 42.1; H, 3.4.

Preparation of 2-Phenyl-4-ethoxy-7-methoxybenzo[*b*]telluropyrylium Fluorosulfonate (36). Telluroflavone **22c** (5.0 g, 0.014 mol) was added to 20 mL of freshly distilled ethyl fluorosulfonate. The mixture was stirred under nitrogen at 60 °C for 10 min. The reaction mixture was cooled to ambient temperature and 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 **36**: 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 (d × d, 1 H, J = 2.5, 9 Hz), 4.80 (q, 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, 43.8; H, 3.2; S, 7.1; Te, 26.7.

Preparation of 2-Methyl-4-ethoxy-7-methoxybenzo[*b*]telluropyrylium Fluorosulfonate (37). Tellurochromone **27b** (1.00 g, 3.31 mmol) was added in one portion to 10 mL of freshly distilled ethyl flurosulfonate under argon at 75 °C. After stirring for 0.5 h, the reaction mixture was cooled to 0 °C, precipitating the product. The product was collected by filtration and washed with dry ether and dry acetonitrile to give 1.31 g (92%) of a yellow solid. The compound was unstable (dec 100 °C) and hygroscopic and was used immediately after preparation.

Preparation of Dye 38. *p*-(Dimethylamino)benzaldehyde (0.30 g, 2.0 mmol) and **37** (0.43 g, 1.0 mmol) were mixed in 3 mL of acetic anhydride. The mixture was warmed on a steam bath for 2 min and then chilled to 0 °C, precipitating 0.40 g (71%) of **38** as a green solid. Recrystallization from acetonitrile gave 0.33 g (59%) of **38** as a metallic green solid: mp 163–167 °C; λ_{max} (CH_2Cl_2) 485 nm (log ϵ 3.86), 695 (4.98). Anal. Calcd for $C_{22}H_{24}FNO_5STe$: C, 47.0; H, 4.3; N, 2.5. Found: C, 47.0; H, 4.1; N, 2.5.

Preparation of Benzo[*b*]telluropyrone 39. The dye **38** (0.12 g, 0.21 mmol) was dissolved in 10 mL of acetonitrile, and 10 mL of 10% aqueous potassium carbonate was added. The mixture was warmed on a steam bath for 15 min and cooled. The product crystallized as fine yellow needles to give 0.09 g (100%) of **39**: mp 123–127 °C; ^1H NMR ($CDCl_3$) δ 8.55 (d, 1 H, J = 9 Hz), 7.35 (d, 2 H, J = 9 Hz), 7.2–6.8 (m's, 4 H), 6.8–6.5 (m's, 3 H), 3.85 (s, 3 H), 3.00 (s, 6 H); IR (KBr) 1595, 1575, 1540, 1315, 1275, 1153, 1030, 950 cm^{-1}; mass spectrum, *m/e* 435 ($C_{20}H_{19}NO_2Te$). Anal. Calcd for $C_{20}H_{19}NO_2Te$: C, 55.5; H, 4.4; N, 3.2. Found: C, 55.1; H, 4.5; N, 3.3.

Registry No. 3a, 70678-10-3; **3b**, 84144-09-2; **3c**, 84144-10-5; **3d**, 84144-11-6; **3e**, 84144-12-7; **4a**, 84144-17-2; **4b**, 84144-18-3; **4c**, 84144-19-4; **4d**, 84144-20-7; **4e**, 84144-21-8; **5a**, 84144-42-3; **5b**, 84144-38-7; **5c**, 84144-43-4; **5d**, 84144-39-8; **5e**, 84144-45-6; **6**, 4512-97-4; **7a**, 84144-40-1; **7b**, 84144-44-5; **7c**, 84144-41-2; **7d**, 84144-47-8; **8**, 84144-46-7; **9a**, 34875-02-0; **9b**, 84144-37-6; **10a**, 34874-91-4; **10b**, 84144-22-9; **11a**, 84144-48-9; **11b**, 84144-49-0; **12a**, 784-62-3; **12b**, 789-98-0; **17a**, 56821-75-1; **17b**, 36062-88-1; **17c**, 56821-76-2; **17d**, 84144-31-0; **18a**, 84144-13-8; **18b**, 84144-14-9; **18c**, 84144-15-0; **18d**, 84144-16-1; **19a**, 84144-23-0; **19b**, 84144-24-1; **19c**, 84144-25-2; **19d**, 84144-26-3; **20a**, 84144-05-8; **20b**, 84144-06-9; **20c**, 84144-07-0; **20d**, 84144-08-1; **21a**, 84144-50-3; **21b**, 84144-51-4; **21c**, 84144-53-6; **22b**, 84144-52-5; **22c**, 80697-47-8; **23c**, 84144-54-7; **24**, 84144-55-8; **25a**, 84144-27-4; **25b**, 84144-28-5; **26a**, 84144-29-6; **26b**, 84144-30-9; **27a**, 84144-56-9; **27b**, 84144-57-0; **28a**, 84144-58-1; **28b**, 84144-59-2; **33**, 84144-62-7; **34**, 84144-64-9; **35**, 84144-67-2; **36**, 84144-69-4; **37**, 84144-71-8; **38**, 84144-73-0; **39**, 84144-74-1; $(p\text{-}CH_3OC_6H_4Se)_2$, 38762-70-8; $(1\text{-}C_{10}H_7Se)_2$, 1787-80-0; $m\text{-}BrC_6H_4OCH_3$, 2398-37-0; $m\text{-}BrC_6H_4F$, 1073-06-9; $m\text{-}BrC_6H_4CH_3$, 591-17-3; $p\text{-}BrC_6H_4OCH_3$, 104-92-7; $1\text{-}C_{10}H_7Br$, 90-11-9; $3,5\text{-}(CH_3)_2C_6H_3Br$, 20469-65-2; Te, 13494-80-9; $3,5\text{-}(CH_3)_2C_6H_3NH_2$, 10272-07-8; $m\text{-}CH_3OC_6H_4TeNa$, 84144-32-1; $m\text{-}FC_6H_4TeNa$, 84144-33-2; $m\text{-}CH_3C_6H_4TeNa$, 84144-34-3; $3,5\text{-}(CH_3)_2C_6H_3TeNa$, 84144-35-4; $p\text{-}CH_3OC_6H_4SeNa$, 41422-62-2; $1\text{-}C_{10}H_7SeNa$, 84144-36-5; $PhC{\equiv}CCO_2Et$, 2216-94-6; $CH_3C{\equiv}CCO_2Et$, 4341-76-8; $HC{\equiv}CCO_2Et$, 623-47-2; $p\text{-}CH_3OC_6H_4SH$, 696-63-9; ClCOCOCl, 79-37-8; $p\text{-}BrC_6H_4NMe_2$, 586-77-6; BrC_6H_5, 108-86-1; $p\text{-}Me_2NC_6H_4CHO$, 100-10-7; Se, 7782-49-2; 2-phenyl-7-methoxybenzo[*b*]telluropyran-4-ol, 84144-60-5; 2-methyl-7-methoxybenzo[*b*]telluropyran-4-ol, 84144-65-0.