Oxidation of Telluropyrylium Dyes with Ozone, Chlorine, and Bromine. Differing Regiochemical and Kinetic Behavior with Respect to Oxidations of Oxygen-, Sulfur-, and Selenium-Containing Dyes

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Oxidations of telluropyrylium dyes **1**–**3** with ozone in water, chlorine in carbon tetrachloride, or bromine in carbon tetrachloride gave second-order rate constants of $\geq 10^9$ L mol^{-1} s^{-1} using stopped-flow techniques to measure rates of oxidation. Aqueous ozone gave initial oxidation of the tellurium atoms of **1**–**3** to produce hydroxytelluranes **4**–**6**, respectively. Oxidative addition of chlorine or bromine across a tellurium atom of **1**–**3** gave the corresponding tellurium(IV) dihalides. With excess ozone, a second oxidation was observed with a second-order rate constant of $(1.3 \pm 0.1) \times 10^6$ L mol^{-1} s^{-1}. Chalcogenopyrylium dyes **7**–**10** which contain only oxygen, sulfur, and/or selenium heteroatoms reacted with smaller rate constants for oxidation. Chlorine and bromine gave second-order rate constants within 1 order of magnitude of those of telluropyrylium dyes for reactions with **7**–**10**. Ozone was more than 100 000 times less reactive toward chalcogenopyrylium dyes **7**–**9** relative to telluropyrylium dyes **1**–**3** with second-order rate constants $(1.1 \pm 0.1) \times 10^4$ L mol^{-1} s^{-1} for **7**, $(8.5 \pm 0.9) \times 10^3$ L mol^{-1} s^{-1} for **8**, and $(5.4 \pm 0.6) \times 10^3$ L mol^{-1} s^{-1} for **9**. With dyes **7**–**10**, ozone destroyed the π-framework of the dye while chlorine and bromine gave mono- and dihalogenation of the trimethine bridge of the dye.

One property of telluropyrylium dyes distinctly different from those of the lighter chalcogen analogues is the formation of isolable, oxidative-addition products upon reaction of the tellurium atom with oxidants such as singlet oxygen,[1] hydrogen peroxide,[1,2] chlorine,[3,4] or bromine.[3,4] The resulting tellurium(IV) species have exhibited useful chemical properties. These materials function as oxidants for various substrates and regenerate the tellurium(II) state of the dyes. Similarly, thermal reductive elimination of chlorine, bromine, or hydrogen peroxide from the tellurium(IV) species also regenerates the tellurium(II) state. The tellurium(II)–tellurium(IV)–tellurium(II) shuttle has been utilized to convert oxygen, light, and water into stored chemical energy in the form of the hydrogen peroxide.[5]

The catalytic potential of the tellurium(II)–tellurium(IV) shuttle in these main-group organometallic compounds depends not only upon the relative rates of redox reactions at the tellurium atom(s) in these molecules but also upon the rates of reaction of the organic π-framework with oxidizing species. If reactions at tellurium are much faster than reactions of the carbon π-framework, then the tellurium(II)–tellurium(IV) shuttle might show large turnover numbers in catalytic reaction schemes.

The second-order rate constants for oxidation of tellurium(II) to tellurium(IV) that have been measured to date cover a wide range. Hydrogen peroxide reacts with a second-order rate constant of 10^0–10^1 L mol^{-1} s^{-1}.[1,5] The second-order rate constant for oxidative addition of chlorine to telluropyrylium dyes was estimated to be greater than 10^4 L mol^{-1} s^{-1} by conventional spectroscopic techniques.[4] Singlet oxygen reacts with telluropyrylium dyes with a second-order rate constant of greater than 10^8 L mol^{-1} s^{-1} in aqueous solution.[1,5] The rate constants for oxidation of tellurium(II) to tellurium(IV) suggest that organotellurium compounds might be useful not only in catalytic redox schemes but also as scavengers of highly reactive oxidants which are biologically hazardous or destructive toward manufactured materials.

One such oxidant is ozone. Ozone, which has a relatively long lifetime, poses environmental concerns in confined areas and is reactive toward a variety of substrates.[6–10] Ozone can lower the lifetime of many manufactured materials such as butadiene rubber and other polymers and can undergo oxidation reactions with molecules in the polymers. Ozone attacks carbon–carbon double bonds to produce ozonides and, in systems containing multiple carbon–carbon double bonds, all sites are often attacked.[8] Sulfides[6,9] and thiones[6,10] are attacked by ozone to give sulfoxides and sulfines, respectively. Ether, carbonyl, and allylic and benzylic carbons can also be attacked by ozone to produce more highly oxidized groups.[6] In devices such as electrophotographic copies that incorporate a corona discharge, ozone production is a legitimate concern.

In other chemical systems utilizing inorganic bromide and iodide salts, oxidation (either from air or ionizing

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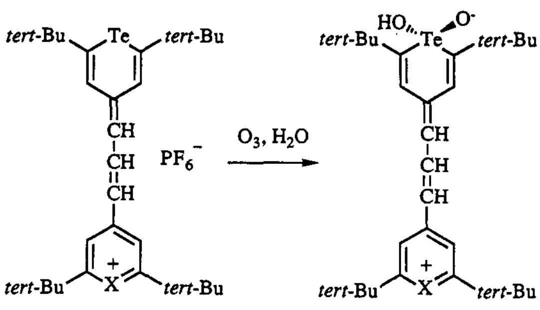
Scheme 1



1, X = Te
2, X = Se
3, X = S

4, X = Te
5, X = Se
6, X = S

radiation, as examples) can occur to give free halogens. The free halogens are also reactive with a variety of substrates. In addition, bromine and iodine absorb blue light, which can interfere with some imaging applications.

In this manuscript, we examine the reactions of chalcogenopyrylium dyes with a series of oxidants (ozone, chlorine, and bromine) that can both add across carbon–carbon double bonds and oxidize heteroatoms such as sulfur, selenium, and tellurium. In pyrylium, thiopyrylium, and selenopyrylium dyes, these oxidants appear to attack the carbon π-framework in that the dye chromophores are lost. These oxidants oxidize tellurium at faster rates than oxidation of the π-framework in telluropyrylium dyes. The use of stopped-flow spectroscopy allows the measurement of the second-order rate constants for these oxidations with ozone, chlorine, and bromine.

Results and Discussion

A. Oxidation of Chalcogenopyrylium Dyes with Ozone. Products of Ozonolysis of Telluropyrylium Dyes in Water. The products of oxidation of telluropyrylium dyes **1**–**3** with ozone in water were determined to be telluranes **4**–**6**. A 5.0 × 10^{-6} M aqueous solution of dye **1** was exposed to a stream of oxygen containing 3.2% ozone by weight. The absorption spectrum of dye **1** [λ_{max} 810 nm, ϵ 150 000 ± 10 000 L mol^{-1} cm^{-1}] was lost and was replaced by a new band [λ_{max} 510 nm, ϵ 55 000 ± 2000 L mol^{-1} cm^{-1}] with an isosbestic point at 580 nm for the transformation. Identical spectroscopic behavior is observed for the oxidation of **1** with either singlet oxygen or hydrogen peroxide.[1,2,5] The final optical density at 510 nm is consistent with a 5.0 × 10^{-6} M solution of **4** being produced as shown in Scheme 1 and suggests that oxidation at tellurium is faster than oxidation of the carbon π-framework.

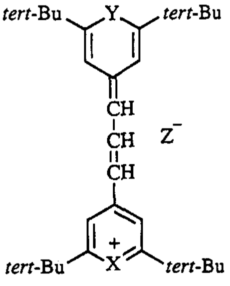
Similar results were obtained with both **2** and **3** in water where oxidation with ozone gave **5** and **6**, respectively. Starting with a 5.0 × 10^{-6} M aqueous solution of **2**, **5**, was obtained with λ_{max} 502 nm (ϵ 55 000 ± 2000 L mol^{-1} cm^{-1}). Similarly, starting with a 5.0 × 10^{-6} M aqueous solution of **3**, **6** was obtained with λ_{max} 480 nm (ϵ 50 000 ± 2000 L mol^{-1} cm^{-1}). Again, the absorption of the oxidized dyes suggested that oxidation of the tellurium atoms of **2** and **3** was much more rapid than oxidation of the carbon π-framework. Isosbestic points were observed at 565 nm for the oxidation of **2** and at 550 nm for the oxidation of **3**.

Non-tellurium-containing dyes **7**–**10** do not give similar products with aqueous ozone. Upon exposure to the oxygen stream containing 3.2% ozone, aqueous solutions of dyes **7**–**10** lose the long-wavelength chromophores of the chalcogenopyrylium dye but no new chromophore develops in the visible region. The products of ozonolysis of these compounds were not identified.

Table 1. Absorption Properties and Rates of Reaction with Ozone of Dyes 1–3 and 7–9 in Water

dye	λ_{max} (H_2O), nm	ϵ, L mol^{-1} cm^{-1}	$k_1(O_3)$,[a] L mol^{-1} s^{-1}	λ_{k_1},[b] nm	$k_2(O_3)$,[c] L mol^{-1} s^{-1}
1	810	150000 ± 80000	≥10^9	510	(1.3 ± 0.1) × 10^6
	348	1500 ± 100			
2	770	130000 ± 8000	≥10^9	500	
	345	1500 ± 100			
3	750	110000 ± 8000	≥10^9	485	
	330	1600 ± 100			
7	730	280000 ± 10000	(1.1 ± 0.1) × 10^4	630	
	345	1500 ± 100			
8	708	250000 ± 10000	(8.5 ± 0.9) × 10^3	350	
	345	1200 ± 100			
9	685	260000 ± 10000	(5.4 ± 0.6) × 10^3	630	
	340	1500 ± 100			

[a] At 293 K. Second-order rate constant for first reaction with ozone. Value based on the average of at least five runs with error limits of 2σ given. [b] Wavelength of kinetic trace. [c] At 293 K. Second-order rate constant for second reaction with ozone.



7, X=Y=Se, Z=CF_3SO_3
8, X=S, Y=Se, Z=PF_6
9, X=Y=S, Z=PF_6
10, X=Y=O, Z=PF_6
11, X=O, Y=S, Z=PF_6

Kinetic Studies of the Addition of Ozone to Chalcopyrylium Dyes in Water. Rate constants for the reaction of ozone with dyes **1**–**3** and **7**–**9** were measured using stopped-flow techniques. For telluropyrylium dyes **1**–**3**, rate constants were determined from the rate of appearance of the oxidized products **4**–**6**, respectively. For dyes **7**–**9**, rate constants were measured by the disappearance of the long-wavelength-absorbing dye chromophore or by the disappearance of weaker absorption maxima in the near ultraviolet (around 350 nm). Spectral properties of aqueous solutions of dyes **1**–**3** and **7**–**9** are compiled in Table 1.

A standard solution of ozone was prepared by saturating water at 275 K with a stream of oxygen containing 3.2% by weight of ozone. From the solubility of ozone in water (0.96 g L^{-1})[11] and the partitioning of ozone between water and the oxygen stream (0.45),[12] a 2 × 10^{-4} M aqueous solution of ozone was obtained. This solution was mixed with an equal volume of 1 × 10^{-5} M solutions of the dyes **7**–**9** in the stopped-flow spectrophotometer at 293.0 K to give pseudo-first-order kinetics for the disappearance of the dye. This is illustrated in Figure 1 for dye **8** where Figure 1a shows the spectral changes from 300 to 650 nm associated with ozonolysis and Figure 1b shows the kinetic

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(12) Reference 6, p 10.

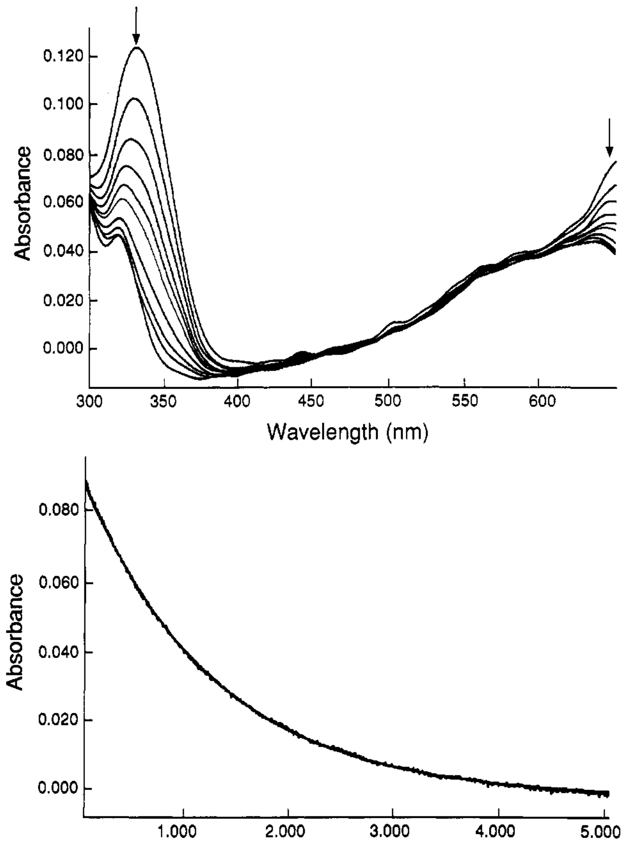

Figure 1. (a, top) Spectral changes from 300 to 650 nm associated with ozonolysis of 5 × 10^{-6} M dye **8** with 1 × 10^{-4} M ozone. (b, bottom) Typical kinetic trace at 350 nm with a first-order curve fit for the disappearance of **8**. Five runs were averaged to give values of $k_1(O_3)$ [$k_1(O_3)$ = (8.5 ± 0.9) × 10^3 L mol^{-1} s^{-1} for **8**].

trace at 350 nm for the disappearance of **8** [$k_1(O_3)$ = (8.5 ± 0.9) × 10^3 L mol^{-1} s^{-1}]. Kinetic traces were measured at different wavelengths, and rate constants were determined from curve fitting to first- or second-order rise or decay. Transient spectra were calculated by slicing the appropriate time points across a series of kinetic traces at different wavelengths and splining the points of a specific time group. The second-order rate constants for ozonolysis of **7–9** are compiled in Table 1 and are on the order of 10^3–10^4 L mol^{-1} s^{-1}.

A second feature of Figure 1a is the appearance of two weak bands at 590 and 640 nm. These bands correspond to λ_{max} in water for chalcogenopyrylium dyes **10** and **11**, respectively.[1] These dyes could be formed via chalcogen–oxygen exchange reactions initiated perhaps by ozone addition either to the heteroatom or to the π-framework adjacent to the heteroatom. The 590-nm band was also present in reactions of **7** and **9** with ozone. On the basis of relative extinction coefficients,[1] the chalcogen–oxygen exchange products are formed in not more than 5% yield at 293.0 K.

Aqueous solutions of the tellurpyrylium dyes **1–3** are much more reactive toward ozone than dyes **7–9**. At 1 × 10^{-4} M ozone (the ozone concentration after mixing in the spectrophotometer), the reaction with dyes **1** was essentially complete after the 1.2-ms dead time of the stopped-flow spectrophotometer.[13] A second reaction was observed with dye as the limiting reagent; the chromophore of **4**, with a λ_{max} of 510 nm (the oxidation product of **1**), is lost with a second-order rate constant of (1.3 ± 0.1) × 10^6 L mol^{-1} s^{-1} at 293.0 ± 0.1 K (based on the average of five runs). One isosbestic point is observed at 430 nm, which is lost upon further reaction of the new product. The oxidation of **4** may be either ozonolysis of the π-framework or oxidation of the second tellurium atom in the molecule, the magnitude of the rate constant is similar to values of the second-order rate constant for the oxidation of either olefins or sulfides with ozone.[6]

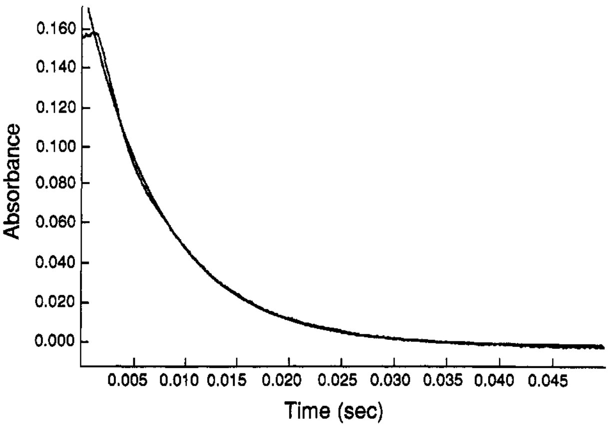

Figure 2. Kinetic trace at 510 nm and a second-order curve fit for the oxidation of 5 × 10^{-6} M dye **1** with 2 × 10^{-6} M ozone.

The 2 × 10^{-4} M solution of ozone was diluted 50-fold to give a 4 × 10^{-6} M solution of ozone. When mixed with the 1 × 10^{-5} M solution of **1** in the stopped-flow spectrophotometer, ozone is the limiting reagent. As shown in Figure 2, for the kinetic trace of oxidation of **1** at 510 nm and 293.0 ± 0.1 K, the formation of the final 10% of **4** was observed which corresponds to a half-life of ≤0.3 ms for the reaction and a second-order rate constant of ≥10^9 L mol^{-1} s^{-1} [(2 ± 1) × 10^9 L mol^{-1} s^{-1} from curve fitting in Figure 2].

Similar results were obtained for oxidation of 1 × 10^{-5} M solutions of dyes **2** and **3** with 4 × 10^{-6} M solutions of ozone in the stopped-flow spectrophotometer. The rate constants for the appearance of **5** and **6**, respectively, were both ≥10^9 L mol^{-1} s^{-1}.

Kinetic Studies of the Oxidation of Telluropyrylium Dyes 1–3 with Chlorine and Bromine. The oxidative addition products of chlorine and bromine with telluropyrylium dyes have been described.[3,4] The addition of a slight excess of chlorine to dyes **1** and **2** gives **12**[3] and **13**,[4] respectively. Similarly, oxidative addition of bromine to **1** and **2** gives **14**[3] and **15**[3], respectively.

A 1 × 10^{-5} M solution of chlorine in carbon tetrachloride was mixed with a 1 × 10^{-5} M solution of **1–3** in 99% carbon tetrachloride (dichloromethane equivalent to 1% by volume was used to dissolve the dye, and the resulting solution was then diluted with carbon tetrachloride) in the stopped-flow spectrophotometer at 293.0 ± 0.1 K. The dead time of our stopped-flow spectrometer is 1.2 ms.[13] These reactions were essentially complete upon mixing within the error of the spectrophotometer for all three days. Assuming that at least 6 half-lives had passed in the 1.2-ms dead time in these reactions, a half-life of ≤0.2 ms with 5 × 10^{-6} M limiting reagent gives second-order rate constants of ≥10^9 L mol^{-1} s^{-1}, which approach that of diffusion control. Identical results were obtained with a 1 × 10^{-5} M solution of bromine in carbon tetrachloride

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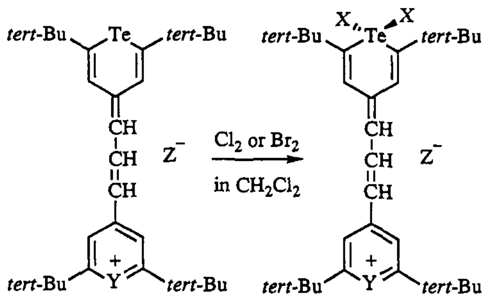
Scheme 2



1, Y=Te, Z=PF$_6$
2, Y=Se, Z=CF$_3$SO$_3$

12, X=Cl, Y=Te, Z=PF$_6$
13, X=Cl, Y=Se, Z=CF$_3$SO$_3$
14, X=Br, Y=Te, Z=PF$_6$
15, X=Br, Y=Se, Z=CF$_3$SO$_3$

Table 2. Second-Order Rate Constants for the First (k_1) and Second (k_2) Reactions of Dyes 1–3 and 7–10 with Chlorine and Bromine

dye	X	k_{rel}[a]	$k_1(X_2)$,[b,c] L mol^{-1} s^{-1}	λ_{k_1,k_2}, nm	$k_2(X_2)$,[b] L mol^{-1} s^{-1}
1	Cl	1	$\geq 10^9$ [2×10^9]	530	
2	Cl		$\geq 10^9$	520	
3	Cl		$\geq 10^9$	510	
7	Cl	0.33	$(6 \pm 1) \times 10^8$	365	$(2.8 \pm 0.5) \times 10^7$
8	Cl	0.25	$(5 \pm 1) \times 10^8$	640	
9	Cl	0.5	–[d] [1×10^9]	640	$(9.5 \pm 1.8) \times 10^7$
10	Cl	0.33	$(6 \pm 2) \times 10^8$	640	$(3.9 \pm 0.8) \times 10^7$
1	Br	1	$\geq 10^9$ [2×10^9]	520	
2	Br		$\geq 10^9$	520	
3	Br		$\geq 10^9$	510	
7	Br	0.2	$(5 \pm 1) \times 10^8$	640	$(1.9 \pm 0.2) \times 10^7$
8	Br	0.33	[6×10^8]		
9	Br	0.2	$(5 \pm 1) \times 10^8$	640, 500	$(5.8 \pm 0.4) \times 10^6$
10	Br	0.14	$(1.9 \pm 0.1) \times 10^8$	614	$(4.4 \pm 0.4) \times 10^5$

[a] Relative rates at 293.0 K determined by the addition of limiting amounts of chlorine or bromine (5 mol %) to equimolar solutions of dye **1** and dye **7**, **9**, or **10**. Values are averages of at least five runs where $k_{rel} = [1 - (\text{Abs } A_{final}/\text{Abs } A_{initial})]/[1 - (\text{Abs } \mathbf{1}_{final}/\text{Abs } \mathbf{1}_{initial})]$. Absorbance loss under these conditions is assumed to be pseudo first order. [b] At 293.0 ± 0.1 K. Values are averages of at least five runs with error limits of 2σ given. [c] Values in square brackets based on relative rate data. [d] Only one rate constant was observed. Value is assumed to be $k_2(X_2)$ on the basis of relative rate data.

and 1×10^{-5} M 99% carbon tetrachloride solutions of **1–3** with second-order rate constants of $\geq 10^9$ L mol^{-1} s^{-1}.

Kinetic Studies of the Reactions of Chalcogenopyrylium Dyes 7–10 with Chlorine and Bromine. Under second-order conditions (a slight excess of halogen) two reactions were observed for the additions of chlorine and bromine to dyes **7–10** at 293.0 ± 0.1 K. With both halogens, the first reaction was faster than the second (Table 2). With chlorine, the first reaction is no more than 1 order of magnitude faster than the second reaction. With bromine, the first reaction is 2–3 orders of magnitude faster than the second. The relative rates of the two reactions are illustrated in Figure 3 for the mixing of a 2.5×10^{-5} M solution of bromine and a 1×10^{-5} M solution of **10**. The kinetic traces of Figure 3 were recorded at 614 nm and show increasing absorbance at this wavelength for the first reaction (Figure 3a) and decreasing absorbance for the second reaction (Figure 3b). Rate constants for the addition of chlorine and bromine to **1–3** and **7–10** are compiled in Table 2. A third reaction was observed under pseudo-first-order conditions (1×10^{-3} M halogen) with dye as the limiting reagent where the chromophore of the dye produced during the second reaction is lost with a much smaller rate constant than that observed for the first two reactions (approximately 10^4 L mol^{-1} s^{-1}).

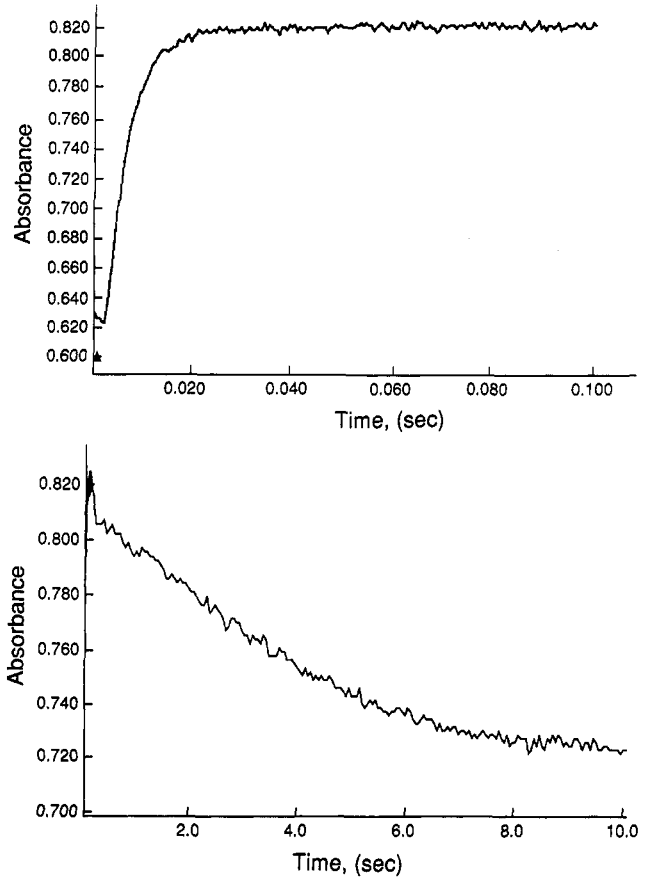


Figure 3. Typical kinetic traces at 614 nm for the reaction of 5×10^{-6} M dye **10** with 1.3×10^{-5} M bromine in carbon tetrachloride: (a, top) a rapid initial reaction showing an increase in absorption at 614 nm followed by (b, bottom) a slower reaction showing a decrease in absorption at 614 nm.

The two different reactions observed during the halogenations correspond to initial formation of the monohalide dyes **16–21** from the corresponding monohalide dye for the second reaction. Transient spectra illustrating both the product of the fast reaction and the slow reaction from Figure 3 for the bromination of **10** are shown in Figure 4. Two different isosbestic points are shown: one at 610 nm for the fast reaction and one at 634 nm for the slow reaction.

Preparative Studies of the Addition of Chlorine and Bromine to Chalcogenopyrylium Dyes 7, 9, and 10. The additions of chlorine or bromine to dyes **7**, **9**, and **10** gave products which were quite different than those of the tellurium-containing dyes. Oxidation of the heteroatoms was not observed; instead, halogenation of the trimethine bridge was observed as shown in Scheme 3. The absorption maxima (and extinction coefficients) of the dyes **7–10**, monobromides **19–21**, and their dihalogenated products **22–27** are compiled in Table 3.

The addition of 2.5 equiv of chlorine to **7** has been described, and **22** was isolated in 41% isolated yield via this procedure.[4] In this reaction, small amounts of the monochloro product **16** cocrystallized with **22**. However, **16** could not be separated from **22**. The addition of 1 equiv of chlorine to **7** gave a mixture of unreacted starting dye **7**, dye **22**, and small amounts of **16**, as observed by ^{1}H NMR spectroscopy. The ^{13}C NMR spectrum of **22** consists of seven lines, which is consistent with the symmetrical structure. The parent ions of both **16** and **22** were observed in the field desorption mass spectrum of the mixture.

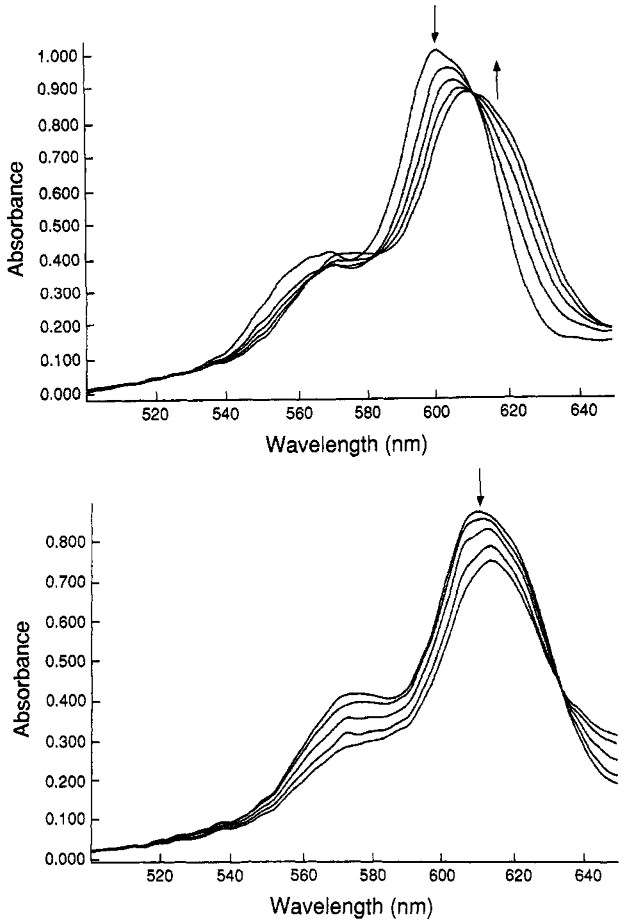


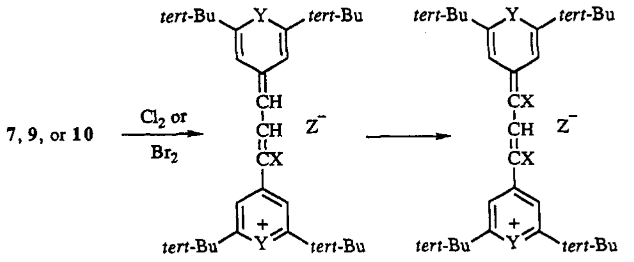
Figure 4. Transient spectra illustrating both the product of (a, top) the fast reaction and (b, bottom) the slow reaction from Figure 4 for the bromination of 5 × 10^{-6} M dye **10** with 1.3 × 10^{-5} M bromine in carbon tetrachloride.

The chlorination of **7** with 2.5 equiv of chlorine produced at least two other products which did not have symmetry about a 2-fold axis (three and four different *tert*-butyl groups, respectively, by ^{1}H NMR spectroscopy). The downfield protons in the ^{1}H NMR spectra of both products were singlets. The appearance and ratio of these materials were dependent on chlorine stoichiometry as well as the concentration of reactants. Addition of chlorine to **22** also generated these materials. Presumably, these products arise from the slower reaction described in the stopped-flow kinetics following the two halogenation reactions of the trimethine bridge. Field desorption mass spectrometry indicated products with parent ion clusters between *m/z* 1100 and 1250, which is consistent with oxidative dimerization.

Chlorinations of **9** and **10** gave similar results. The addition of 2.5 equiv of chlorine to **9** under the conditions employed for the chlorination of **7** gave a mixture of unreacted **9**, **23**, and other more highly chlorinated products. The crystalline **23** (24% isolated yield) was most readily prepared by the slow addition of 2 equiv of chlorine in carbon tetrachloride (0.001 M) to a 1 × 10^{-4} M solution of **9** in dichloromethane. The ^{1}H NMR spectrum of dye **23** was consistent with the proposed structure with three singlets at δ 8.86 (1 H), 7.75 (broad, 4 H), and 1.71 (36 H) while field desorption mass spectroscopy gave a parent ion of *m/z* 523 for $C_{29}H_{41}{}^{35}Cl_2S_2$, which is also consistent with dichlorination of the trimethine bridge.

The addition of 2.5 equiv of chlorine (0.001 M in CCl_4) to **10** (1 × 10^{-4} M in CH_2Cl_2) gave **24** in 63% isolated yield. The crystalline **24** was characterized by its ^{1}H NMR spectrum, which consisted of three singlets at δ 8.68 (1 H), 7.71 (broad, 4 H), and 1.65 (36 H), and by its field desorption mass spectrum, which gave a parent ion cluster at *m/z* 491 for $C_{29}H_{41}{}^{35}Cl_2O_2$, which is consistent with dichlorination of the trimethine bridge.

Scheme 3



16, X=Cl, Y=Se, Z=CF_3SO_3	**22**, X=Cl, Y=Se, Z=CF_3SO_3
17, X=Cl, Y=S, Z=PF_6	**23**, X=Cl, Y=S, Z=PF_6
18, X=Cl, Y=O, Z=PF_6	**24**, X=Cl, Y=O, Z=PF_6
19, X=Br, Y=Se, Z=CF_3SO_3	**25**, X=Br, Y=Se, Z=CF_3SO_3
20, X=Br, Y=S, Z=PF_6	**26**, X=Br, Y=S, Z=PF_6
21, X=Br, Y=O, Z=PF_6	**27**, X=Br, Y=O, Z=PF_6

Table 3. Absorption Properties of Dyes 7–10, Monobromo Derivatives 19–21, and Dihalo Derivatives 22–27 in Dichloromethane

dye	$\lambda_{max}(CH_2Cl_2)$, nm	ε, L mol^{-1} cm^{-1}
7	750	300 000 ± 10 000
	342	2200 ± 100
8	733	285 000 ± 10 000
	345	2000 ± 100
9	714	265 000 ± 10 000
	342	2000 ± 100
10	605	205 000 ± 10 000
19	753	215 000 ± 20 000[a]
20	722	170 000 ± 20 000[a]
21	620	150 000 ± 20 000[a]
22	802	120 000 ± 5 000
23	754	100 000 ± 5 000
24	648	115 000 ± 5 000
25	793	145 000 ± 5 000
26	749	120 000 ± 5 000
27	650	110 000 ± 5 000

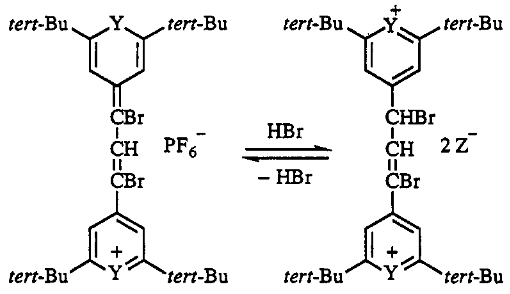
[a] The uncertainty in values of ε is large and is based on starting concentration of unsubstituted dye and the estimation of the end point for monobromination.

Bromination of **7** followed a pathway similar to that for chlorination. The addition of 2.5 equiv of bromine (0.001 M in CCl_4) to **7** (1 × 10^{-4} M in CH_2Cl_2) gave **25** in 83% isolated yield. The ^{1}H NMR spectrum of **25** consisted of a one-proton singlet at δ 8.34, a four-proton singlet at δ 7.97, and a thirty-six proton singlet at δ 1.45 while the field desorption mass spectrum of **25** gave a parent ion cluster of *m/z* 707 for $C_{29}H_{41}{}^{79}Br_2{}^{80}Se_2$, which is consistent with dibromination of the trimethine bridge. The ^{13}C NMR spectrum of **25** consists of seven lines, which is again consistent with the proposed symmetry of the molecule.

The addition of 2.5 equiv of bromine (0.001 M in CCl_4) to **9** (1 × 10^{-4} M in CH_2Cl_2) gave **26** in 73% isolated yield. The ^{1}H NMR spectrum of **26** consisted of a one-proton singlet at δ 8.60, a four-proton singlet at δ 7.78, and thirty-six-proton singlet at δ 1.43. The field desorption mass spectrum of **26** gave a parent ion cluster at *m/z* 611 for $C_{29}H_{41}{}^{79}Br_2S_2$, which is consistent with dibromination of the trimethine bridge.

Under more concentrated conditions, the addition of bromine to **9** gave a product from HBr addition to **26**. In a 5-mm NMR tube in $CDCl_3$ at 0.05 M, the addition of 2.5 equiv of bromine to **9** gave a yellow solution with a set of

Scheme 4



26, X=Y=S
27, X=Y=O

28, X=Y=S
29, X=Y=O

^{1}H NMR signals consisting of a one-proton singlet at δ 8.955, a one-proton singlet at δ 8.79, a one-proton doublet at δ 8.19 (J = 9 Hz), a one-proton doublet at δ 6.41 (J = 9 Hz), an eighteen-proton singlet at δ 1.70, and an eighteen-proton singlet at δ 1.67. The absorption spectrum of this product in dichloromethane gave a λ_{max} of 442 nm. Dilution of the sample reduced the intensity of the 442-nm band with the appearance of the infrared-absorbing chromophore for **26** with a λ_{max} of 749 nm.

These results are consistent with the protonation of **26** with HBr to give the bis(thiopyrylium) salt **28**, as shown in Scheme 4. Protonation would short circuit the π-framework of **26** leading to a shorter-wavelength absorption maximum. The ^{1}H NMR spectrum of **28** shoud display two signals for the two different 2,6-di-*tert*-butylthiopyrylium rings in addition to the two coupled protons on the three-carbon bridge joining the rings.

The addition of bromine to **10** gave results similar to those for the addition of bromine to **9**. Under dilute conditions, the dibromo pyrylium dye **27** was formed whose ^{1}H NMR spectrum consisted of a one-proton singlet at δ 8.14, a broad, four-proton singlet at δ 7.78, and a thirty-six-proton singlet at δ 1.58. Under more concentrated conditions, the protonated dye **29** was the major product. The ^{1}H NMR spectrum of **29** consisted of a two-proton singlet at δ 8.32, a two-proton singlet at δ 8.23, a one-proton doublet at δ 8.25 (J = 9 Hz), a one-proton doublet at δ 6.38 (J = 9 Hz), an eighteen-proton singlet at δ 1.60, and an eighteen-proton singlet at δ 1.59. The absorption spectrum of **29** gave a maximum at 402 nm. A sample of **29** was diluted to 5×10^{-6} M to give the absorption spectrum of **27** in dichloromethane (λ_{max} of 650 nm).

The addition of 1.0 equiv of bromine to a 0.050 M solution of **9** in CD_2Cl_2 in a 5-mm NMR tube gave a series of exchange-broadened lines in the ^{1}H NMR spectrum at δ 8.51 (1 H), 8.24 (2 H), 7.78 (2 H), and 6.53 (1 H). The *tert*-butyl signal was somewhat sharper at δ 1.595. Dilution of this sample with dichloromethane to 5.0×10^{-6} M gave λ_{max} 722 nm. The addition of a second equivalent of bromine to this sample generated the ^{1}H NMR spectrum of **28**. These data are consistent with formation of monobromide **20** which undergoes reversible protonation and deprotonation with the HBr generated in the substitution reaction to give the observed broadening in the ^{1}H NMR spectrum. These data also suggest that the dibromides **25–27** are formed via the intermediacy of monobromides **19–21**.

The preparative studies were consistent with the products observed under the conditions of the stopped-flow kinetics and suggested that both chlorine and bromine added to the π-framework of the chalcogenopyrylium dyes **7**, **9**, and **10**. In the telluropyrylium dyes **1–3**, oxidative addition of the halogen appeared to be much faster than addition to the π-framework. Pyrylium, thiopyrylium, and selenopyrylium dyes **7–10** reacted with halogenation of the trimethine bridge. The resulting dihalide dyes can react with acids generated during halogenation or with excess halogen to give other products.

Relative Rate Studies for the Oxidative Addition of Chlorine across the Tellurium Atom of Telluropyrylium Dyes. Although the rates of oxidative addition of chlorine or bromine across the tellurium atom of telluropyrylium dyes **1–3** were too fast for accurate measurement by stopped-flow kinetics, relative rates of reaction for dye **1** and the dyes **7–10** were determined by competition experiments for limited amounts of chlorine and bromine. With the dyes present in equimolar concentrations and both in excess of halogen, the change in absorbance should follow pseudo-first-order kinetics at low conversions. Values of relative rates, k_{rel}, are compiled in Table 2.

Since the rate constants for addition of chlorine and bromine to **4–7** can be determined by stopped-flow kinetics, the values of k_{rel} can be used in combination with k_1 (the second-order rate constant for the first halogenation) to give second-order rate constants for the oxidative addition of chlorine and bromine across the tellurium atom of dye **1**. These values are indicative of a second-order rate constant of 2×10^9 L mol^{-1} s^{-1} for oxidative addition of either chlorine or bromine to **1**.

The relative rate data suggested that the rate constant determined by stopped-flow spectroscopy in the chlorination of **9** was not k_1, but was most likely k_2 (the second-order rate constant for the second halogenation). The relative rate data suggested that the value of k_1 for **9** should be close to 1×10^9 L mol^{-1} s^{-1} (roughly half as reactive as **1**), not the observed value of 9.5×10^7 L mol^{-1} s^{-1}. The latter value is consistent with the other values of k_2 for chlorination.

Conclusions

The series of chalcogenopyrylium dyes represented by **1–3** and **7–10** has been oxidized by a variety of oxidants which include hydrogen peroxide[15] and singlet oxygen[2] in addition to the oxidants described here. Comparative rates and relative rates of oxidation for this series suggest that pyrylium dye **10** is the least reactive member of the series toward these oxidants with second-order rate constants increasing from 1×10^{-4} L mol^{-1} s^{-1} for oxidation with hydrogen peroxide[1,5] to 6×10^8 M^{-1} s^{-1} for oxidation with chlorine.

Intuitively, one would expect the relative rate differences between tellurium-containing dyes **1–3** and non-tellurium-containing dyes **7–10** to become smaller as the kinetic reactivity of the oxidant toward tellurium increases. This trend is observed with hydrogen peroxide, singlet oxygen, chlorine, and bromine. However, the relative rates of reaction with ozone do not follow the trend described above.

The telluropyrylium dyes **1–3** are $\geq 10^5$ times more reactive than corresponding pyrylium, thiopyrylium, and selenopyrylium dyes **7–10** even though ozone reacts with tellurium with second-order rate constants of $\geq 10^9$ L mol^{-1} s^{-1}. This is in marked contrast to the very small differences

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(14) Marquardt algorithm[15] is based on the routine Curfit in: Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

(15) Marquardt, D. W. *J. Soc. Ind. Appl. Math.* **1963**, *11*, 431.

in relative rates for reactions of chlorine and bromine (with reactivities comparable to that of ozone toward telluropyrylium dyes **1–3**) with the chalcogenopyrylium dye series **1–3** and **7–10**.

This unexpected reactivity of tellurium in telluropyrylium dyes with ozone coupled with the generation of a new visible-absorbing dye chromophore upon oxidations offers some interesting technological possibilities. It should be possible to design systems based on organotellurium compounds to act as visual or spectroscopic indicators of ozone. The large second-order rate constants for reaction at tellurium also suggest possibilities for environmental scavengers of ozone. Thermal reductive elimination of hydrogen peroxide from the oxidized products such as **4–6** would regenerate the scavenging system.

Experimental Section

Melting points were determined on a Thomas-Hoover melting point apparatus and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded on a General Electric QE-300 spectrometer or on a Varian Gemini-200 spectrometer. UV–visible–near infrared spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Infrared spectra were recorded on a Beckman IR 4250 instrument. Microanalyses were performed on a Perkin-Elmer 240 C, H, and N Analyzer. Telluropyrylium dyes **1–3** and chalcogenopyrylium dyes **7–10** were prepared according to ref 1. Dichloromethane and carbon tetrachloride were obtained as anhydrous from Aldrich Chemical Co. and were used as received. Distilled water was purified with a Milli-Q Water System made by Millipore Corp. to a resistance of 16–17 MΩ-cm^{-1} before use.

Preparation of Stock Solutions of Chalcogenpyrylium Dyes. A. In Water. A 1.0×10^{-5} M solution of **1–3** or **7–9** in water was prepared by 10-fold dilution of a 1.00×10^{-4} M aqueous solution of the appropriate dye. A 5.00×10^{-5} mol sample of the dye was dissolved in approximately 5 mL of ethanol. The resulting solution was then diluted to 500.0 mL with purified distilled water. Solutions of telluropyrylium dyes **1–3** were protected from light.

B. In Carbon Tetrachloride. A 1.0×10^{-5} M solution of **1–3** or **7–9** in CCl_4 was prepared by 10-fold dilution of a 1.00×10^{-4} M solution of the appropriate dye in CCl_4. A 2.50×10^{-5} mol sample of the dye was dissolved in approximately 2.5 mL of CH_2Cl_2. The resulting solution was then diluted to 250.0 mL with CCl_4. Solutions of telluropyrylium dyes **1–3** were protected from light.

Preparation of Stock Solutions of Chlorine and Bromine in Carbon Tetrachloride. A stock solution of 0.010 M chlorine in CCl_4 was prepared by diluting 0.35 g (5.0 mmol) of chlorine to 500 mL with CCl_4. Serial dilution gave the 1.0×10^{-3}, 1.0×10^{-5}, and 2.5×10^{-5} M solutions employed in this study. Similarly, 0.80 g (5.0 mmol) of bromine was diluted to 500 mL with CCl_4 to give the 0.010 M stock solution of bromine. Again, serial dilution gave the 1.0×10^{-3}, 1.0×10^{-5}, and 2.5×10^{-5} M solutions employed in this study.

Preparation of Stock Solutions of Ozone in Water. Ozone was produced with a Model G1-L Ozone Generator (PCI Ozone Corp., West Caldwell, NJ) equipped with a Model HC-1 sampler (PCI Ozone Corp., West Caldwell, NJ). The generator voltage was set to produce a 3.2% by weight stream of ozone in oxygen. The output tube was attached to a gas-dispersion tube. The dispersion tube was immersed in cold, distilled water (275 K) and the water was saturated with the ozone–oxygen mixture over a 10-min period. Assuming that Henry's law is observed and on the basis of the solubility of ozone/oxygen in water (0.96 g L^{-1})[11] and the partitioning of the gas between water and the atmosphere (0.45),[12] a 2×10^{-4} M solution of ozone in water is obtained. This solution was diluted by a factor of 10 by addition of a 10.0-mL aliquot to a 90.0-mL aliquot of a 5.0×10^{-5} M aqueous solution of **1**. The optical density at 510 nm from the generation of **4** was 1.06 in a 1-cm cell which is consistent with an ozone concentration of $(1.9 \pm 0.1) \times 10^{-4}$ M in the stock solution. Serial dilution gave the 4×10^{-6} M ozone solution employed in this study.

Stopped-Flow Experiments. All stopped-flow experiments were performed on a Sequential DX17 MV stopped-flow spectrometer (Applied Photophysics, Leatherhead, U.K.). All experiments incorporated the instrument in stopped-flow mode only. The sample handling unit was fitted with two drive syringes that are mounted inside a thermostated bath compartment which allowed for variable temperature experimentation. The optical detection cell was set up in the 10-mm path length. First- and second-order curve fitting and rate constants used a Marquardt algorithm.[14,15] Absorption spectra at indicated time points were calculated through software provided by Applied Photophysics. This consisted of slicing the appropriate time points across a series of kinetic traces (at different wavelengths) and then splining the points of a specific time group. The stock solutions of dyes and oxidants at appropriate concentrations described above were utilized in the stopped-flow experiments.

Competition Experiments for Chlorine and Bromine as the Limiting Reagent. Solutions of **1** and one dye **7–10** at 5.0×10^{-6} M in each were prepared in 100.0 mL of dichloromethane. To these solutions were added 0.050-mL aliquots of 0.001 M solutions of either chlorine or bromine in CCl_4. The halogen added corresponds to about 5 mol % of the total dye content. The change in absorbance for the two dyes was noted and was assumed to follow pseudo-first-order kinetics.

Chlorination of 7. Selenopyrylium dye **7** (5.85 g, 0.0100 mol) was dissolved in 200 mL of dichloromethane. To this solution was added 20 mL of a 0.50 M solution of chlorine in carbon tetrachloride (0.0100 mol). The resulting solution was stirred 3 min at ambient temperature and was concentrated. The residue was recrystallized from 10% acetonitrile in ethyl ether to give 1.65 g (25%) of dye **22** as metallic green crystals, mp 170.5–172.5 °C: ^{1}H NMR ($CDCl_3$) δ 8.67 (s, 1 H), 8.13 (s, 4 H), 1.54 (s, 36 H); IR (KBr) 2960, 1586, 1465 (br, s), 1328, 1253, 1190, 1155, and 675 cm^{-1}; ^{13}C NMR ($CDCl_3$) δ 177.8, 152.0, 136.5, 124.0, 123.8, 42.0, 31.8; λ_{max} (CH_2Cl_2) 802 nm (ϵ 120 000 L mol^{-1} cm^{-1}); FDMS *m/z* 619 ($C_{29}H_{41}{}^{35}Cl_2{}^{80}Se_2$). Anal. Calcd for $C_{29}H_{41}Cl_2Se_2{\cdot}Cl$: C, 53.27; H, 6.32; Cl, 16.26. Found: C, 53.21; H, 6.18; Cl, 16.50.

For 16: ^{1}H NMR ($CDCl_3$) δ 8.83 (d, 1 H, $J = 15$ Hz), 8.015 (s, 4 H), 6.92 (d, 1 H), 1.50 (s, 36 H); FDMS *m/z* 585 ($C_{29}H_{42}{}^{35}Cl^{80}Se_2$).

Chlorination of 9. The addition of 2.5 equiv of chlorine (250 mL of 0.001 M Cl_2 in CCl_4) to **9** (0.061 g, 0.10 mmol) in 1 L of CH_2Cl_2 gave **23** following concentration of the reaction mixture. Crystalline **23** was recrystallized from CH_3CN/ether to give 0.016 g (24%), mp 177–178 °C: ^{1}H NMR ($CDCl_3$) δ 8.86 (1 H), 7.75 (broad, 4 H), 1.71 (36 H): FDMS *m/z* 523 ($C_{29}H_{41}{}^{35}Cl_2S_2$). Anal. Calcd for $C_{29}H_{41}Cl_2S_2{\cdot}PF_6$: C, 52.01; H, 6.17. Found: C, 51.89; H, 6.44.

Chlorination of 10. The addition of 2.5 equiv of chlorine (250 mL of 0.001 M Cl_2 in CCl_4) to **10** (0.057 g, 0.10 mmol) in 1 L of CH_2Cl_2 gave **24** following concentration of the reaction mixture. Crystalline **24** was recrystallized from CH_3CN/ether to give 0.041 g (64%), mp 175–178 °C: ^{1}H NMR ($CDCl_3$) δ 8.68 (1 H), 7.71 (broad, 4 H), 1.65 (36 H); FDMS *m/z* 491 ($C_{29}H_{41}{}^{35}Cl_2O_2$). Anal. Calcd for $C_{29}H_{41}Cl_2O_2{\cdot}PF_6$: C, 54.64; H, 6.48. Found: C, 55.01; H, 6.14.

General Procedure for Preparative Scale Brominations. Bromination of 7. Triflate dye **7** (0.060 g, 0.086 mmol) was dissolved in 860 mL of dichloromethane. To this solution was added 250 mL of a 0.001 M solution of bromine in carbon tetrachloride (0.25 mmol). The resulting solution was stirred at ambient temperature for 5 min. The reaction mixture was concentrated, and the residue was recrystallized from 2.0 mL of acetonitrile diluted with 10.0 mL of ether. Upon chilling, 0.061 g (83%) of bronze crystals of **25** were collected, mp 165–175 °C dec: ^{1}H NMR ($CDCl_3$) δ 8.34 (s, 1 H), 7.95 (s, 4 H), 1.45 (s, 36 H); ^{13}C NMR (CD_2Cl_2) δ 197.5, 159.9, 137.6, 133.3, 131.2, 44.4, 31.6; FDMS *m/z* 707 ($C_{29}H_{41}{}^{79}Br_2{}^{80}Se_2$). Anal. Calcd for $C_{29}H_{41}Br_2Se_2{\cdot}CF_3SO_3$: C, 42.07; H, 4.83. Found: C, 41.56; H, 4.53. We were unable to obtain a satisfactory analysis for this material presumably due to a mixture of tribromide and triflate counterions.

Bromination of 9. The addition of 2.5 equiv of bromine (250 mL of 0.001 M solution of bromine in CCl_4) to **9** (0.060 g, 0.10 mmol) in 1 L of CH_2Cl_2 gave **26**. The crude product was recrystallized from 1 mL of CH_3CN and 10 mL of ether to give 0.055 g (73% isolated yield) of **26**, mp 163–170 dec: ^1H NMR ($CDCl_3$) δ 8.60 (1 H), 7.78 (4 H), 1.43 (s, 36 H); FDMS *m/z* 611 for $C_{29}H_{41}{}^{79}Br_2S_2$. Anal. Calcd for $C_{29}H_{41}Br_2S_2{\cdot}PF_6$: C, 45.92; H, 5.45. Found: C, 45.56; H, 5.23.

Bromination of 10. The addition of 2.5 equiv of bromine (250 mL of 0.001 M solution of bromine in CCl_4) to **10** (0.057 g, 0.10 mmol) in 1 L of CH_2Cl_2 gave **27**. The crude product was recrystallized from 1 mL of CH_3CN and 10 mL of ether to give 0.018 g (25% isolated yield) of **27**, mp 158–170 dec: ^1H NMR ($CDCl_3$) δ 8.14 (1 H), 7.78 (4 H), 1.58 (s, 36 H); FDMS *m/z* 579 for $C_{29}H_{41}{}^{79}Br_2O_2$. Anal. Calcd for $C_{29}H_{41}Br_2O_2{\cdot}PF_6$: C, 47.95; H, 5.69. Found: C, 47.56; H, 5.43.

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