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A Mechanism for Heteroatom Scrambling in the Synthesis of Unsymmetrical Chalcogenopyrylium Trimethine Dyes

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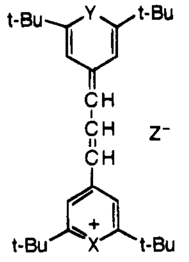
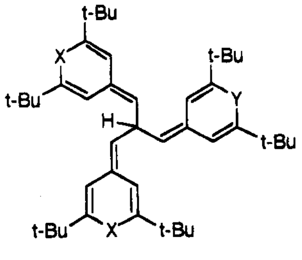
The chalcogenopyrylium trimethine dyes **1** have chromophores with large extinction coefficients, narrow bandwidths, and absorption maxima in water that vary between 590 (X = Y = O) and 810 nm (X = Y = Te).[1] The dyes **1** have found utility in several commercial applications including optical recording,[2] electrophotography,[3] and thermal dye transfer[4] and in medical applications including the photodynamic therapy of cancer[1,5] and as detectors of reducing microorganisms.[6] The tellurium-containing dyes have served as catalysts for the activation of hydrogen peroxide and as catalysts for solar energy storage.[7] The utility of dyes in this series is due in part to the control of wavelengths of absorption and other photophysical properties available through the various possible combinations of heteroatoms.[1]



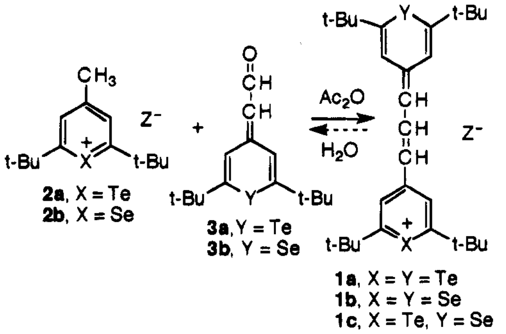
1, X, Y = O, S, Se, Te



4, X, Y = O, S, Se, Te
4a, X = Y = Te

Although the synthesis of symmetrical dyes **1** (X = Y) is straightforward, the synthesis of unsymmetrical analogues (X ≠ Y) has been complicated by the scrambling of heteroatoms during synthesis to give mixtures of dyes. The general synthetic approach to dyes of this type is shown in Scheme 1 and has been utilized in the synthesis of both symmetrical and unsymmetrical dyes with acetic anhydride functioning as both a weak base and solvent.[1] With nonbasic counterions such as tetrafluoroborate, perchlorate, or hexafluorophosphate, the synthesis of unsymmetrical dyes **1** gives high yields of the desired products, but detectable amounts of the symmetrical counterparts are present. With counterions such as chloride or bromide, which have more Lewis basicity, scrambling of the chalcogenopyranyl rings is observed to give a statistical distribution of dyes.[1b] The counterion dependence is illustrated in Scheme 1 for the condensation of selenopyrylium salts **2b** with telluropyranyl aldehyde **1a**. Labeling studies have shown that the heteroatom scrambling involves the entire chalcogenopyranyl ring and not just the heteroatoms.[1b] One plausible mechanistic explanation offered for the observed scrambling is a reverse aldol reaction in unsymmetrical dyes **1** to give scrambling of the chalcogen atoms in intermediates **2** and **3**.[1b]

Scheme 1



$$\mathbf{2b} + \mathbf{3a} \xrightarrow{Ac_2O} \mathbf{1a} + \mathbf{1b} + \mathbf{1c}$$

	1a	1b	1c
Z = PF_6	2	7	91
Z = Cl	25	25	50

The synthesis of unsymmetrical dyes **1** is important to our continuing evaluation of the use of these materials as sensitizers for photodynamic therapy.[5a] In this paper, we report our reinvestigation of the heteroatom scrambling described above and offer a new mechanistic description in which tris(chalcogenopyranylmethylidene)methanes **4** are formed as intermediates in the heteroatom scrambling.

The reverse aldol reaction with dyes **1** would be a simple hydrolysis/acetolysis of the dye via the addition of water or acetic acid. A sample of **1c** as the chloride salt, free of either **1a** or **1b**, was dissolved in acetic anydride and either 1 equiv of water or 2 equiv of acetic acid added. After several hours at reflux, no apparent scrambling was observed spectrophotometrically in either reaction. It should be noted that the reaction of water (0.05 M) with acetic anhydride (solvent) at reflux has a half-life of approximately 3 min as monitored by the appearance of acetic acid via gas chromatography. Typically, the synthesis of the dyes according to Scheme 1 is complete within 15 min as is the the scrambling in the preparation of **1c** (Z = Cl). These data suggest that the reverse aldol process is kinetically incompatible with the scrambling mechanism.

In the absence of the reverse aldol as a likely mechanism for heteroatom scrambling, we reasoned that some other intermediate was formed during the synthesis of dyes **1**. The condensation reactions of **2** and **3** to give **1** presumably involve deprotonation of the 4-methylchalcogenopyrylium salt to give the corresponding 4-methylidenechalcogenopyran **5**. This species is perhaps the

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[1] (a) Detty, M. R.; Merkel, P. B. *J. Am. Chem. Soc.* **1990**, *112*, 3845. (b) Detty, M. R.; Merkel, P. B.; Hilf, R.; Gibson, S. L.; Powers, S. K. *J. Med. Chem.* **1990**, *33*, 1108.

[2] (a) Detty, M. R.; Thomas, H. T. U.S. Pat. 4,584,258, 1986. (b) Fleming, J. C.; Detty, M. R. U.S. Pat. 5,356,685, 1994. (c) Fleming, J. C.; Detty, M. R.; Saeva, F. D. U.S. Pat. 5,362,536, 1994.

[3] Detty, M. R.; Murray, B. J.; Perlstein, J. H. U.S. Pat. 4,365,017, Dec 1982.

[4] Burberry, M. S.; Tutt, L. W.; Detty, M. R. U.S. Pat. 5,256,620, 1993.

[5] (a) Detty, M. R.; Merkel, P. B.; Gibson, S. L.; Hilf, R. *Oncol. Res.* **1992**, *4*, 367. (b) Kessel, D. *Photochem. Photobiol.* **1991**, *53*, 73. (c) Detty, M. R.; Powers, S. K. U.S. Pat. 5,047,419, 1991. (d) Modica-Napolitano, J. S.; Joyal, J. L.; Ara, G.; Oseroff, A. R.; Aprille, J. R. *Cancer Res.* **1990**, *50*, 7876. (e) Powers, S. K.; Walstad, D. L.; Brown, J. T.; Detty, M. R.; Watkins, P. J. *J. Neuro-Oncol.* **1989**, *7*, 179. (f) Detty, M. R.; Merkel, P. B.; Powers, S. K. *J. Am. Chem. Soc.* **1988**, *110*, 5920.

[6] Detty, M. R. U.S. Pat. 5,082,771, 1992.

[7] (a) Detty, M. R. *Phosphorus, Sulfur, Silicon* **1992**, *67*, 383. (b) Detty, M. R.; Gibson, S. L. *Organometallics* **1992**, *11*, 2147. (c) Detty, M. R.; Gibson, S. L. *J. Am. Chem. Soc.* **1990**, *112*, 4086.

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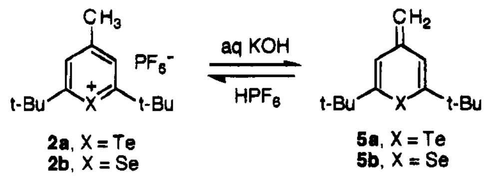
Scheme 2



intermediate that reacts with the carbonyl of aldehydes **3**. The trimethine dyes **1** might be sufficiently electrophilic to react with compounds **5** to give the tris(chalcogenopyranylmethylidene)methanes **4** following deprotonation.

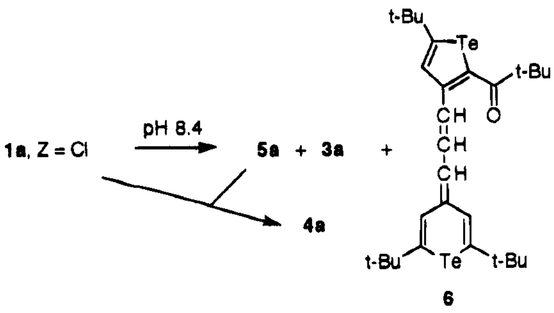
The 4-methylidenechalcogenopyrans **5** were prepared from deprotonation of the corresponding 4-methylchalcogenopyrylium salts as shown in Scheme 2. An ethanolic solution of salt **2** was added to a deoxygenated pH 9.3 buffer (0.25 M dibasic potassium phosphate) solution under argon at ambient temperature. Following extraction into ether, the 4-methylidenechalcogenopyrans were purified via chromatography on basic alumina eluted with toluene as air-sensitive oils in 92 and 88% isolated yields for **5a** and **5b**, respectively.[8]

The 2-fold symmetry of compounds **5** was apparent from their proton and carbon NMR spectra. The proton spectra of both **5a** and **5b** were each characterized by three singlets corresponding to the olefinic protons, the exocyclic methylene, and the *tert*-butyl groups, respectively. The carbon spectra were characterized by four resonances corresponding to the olefinic carbons and two resonances corresponding to the *tert*-butyl carbons.

The structures of compounds **5** were also confirmed by protonation at the exocyclic carbon (Scheme 2). The addition of HPF_6 to **5a** or **5b** gave the original 4-methylchalcogenopyrylium salt **2a** or **2b** in 85 or 80% isolated yields, respectively.

The tris(telluropyranylmethylidene)methane **4a** was first isolated during hydrolysis studies of **1a** (Z = Cl) at various values of pH. Preparative scale synthesis of **4a** was realized with the slow addition of an ethanolic solution of dye **1a** (Z = Cl) to a carefully deoxygenated phosphate buffer solution at pH 8.4. Tris(telluropyranylmethylidene)methane **4a** and telluropyranyl aldehyde **3a** were isolated in 69 and 80% yields, respectively. The same products were observed at lower pH, but rates of reaction slowed with decreasing pH. In the synthesis of **4a**, small amounts of the ring-contracted ketone **6** (<5%) were isolated, which probably reflects the rigor of the deoxygenation.[9] In the absence of rigorous deoxygenation and at higher pH, the ring-contracted ketone **6** was the major product.

Scheme 3



The 3-fold symmetry of **4a** was apparent from both carbon and proton NMR spectra. The ^{13}C spectrum consisted of 11 signals (six olefinic and five aliphatic, Figures 1 and 2 in the supporting information). In the coupled ^{13}C spectrum of **4a**, the olefinic carbons at δ 139.4, 135.9, and 133.4 have no proton substituents while the olefinic carbons at δ 131.6, 126.7, and 119.9 have one proton substituent each. The methine carbon was observed at δ 35.6. The quaternary carbons of the two different *tert*-butyl groups were observed at δ 39.6 and 38.9 while the methyl resonances of the *tert*-butyl groups were observed at δ 31.2 and 31.0. The ^1H NMR spectrum displayed two *tert*-butyl singlets, two three-proton olefinic singlets, and a three-proton olefinic doublet coupled to a one-proton quartet (δ 4.53, J = 9 Hz). The mass spectrum of **4a** was consistent with the desired compound (m/z 970 for $C_{43}H_{64}{}^{130}Te_3$), displaying the appropriate isotope pattern for a molecule with three tellurium atoms.

The isolation of **4a** under these conditions suggested that basic hydrolysis of dye **1a** initially gave a mixture of aldehyde **3a** and methylidene **5a** (Scheme 3). Compound **5a** generated *in situ* in this manner and then reacted with dye **1a** to give **4a**. The addition of preformed **5a** to a deoxygenated dichloromethane solution of **1a** (Z = Cl) with 1 equiv of pyridine also gave **4a** but in only 20% isolated yield.

If the compounds **4** were formed during the condensation reactions of Scheme 1, they would need to be cleaved in the presence of acid to give the heteroatom scrambling. The addition of a 5-fold excess of HPF_6 to an acetic anhydride solution of **4a** gave the absorption spectrum of **1a** (Λ_{max} 830 nm in CH_2Cl_2). A mixture of **1a** and **2a** with Z = PF_6 was isolated from this mixture. The fragmentation of compounds **4a** in the presence of acid suggested that unsymmetrical tris(chalcogenopyranylmethylidene)methanes might be intermediates in the scrambling of heteroatoms in the preparation of unsymmetrical dyes **1**.

Unsymmetrical tris(chalcogenopyranylmethylidene)methanes **4** would be the expected initial products from the reaction of a dye **1** with a 4-methylidenechalcogenopyran **5** where the three chalcogen atoms are nonidentical. Reversible fragmentation of compounds **4** would lead to heteroatom scrambling. To test this hypothesis, 15 mol % of either **5a** or **5b** was added to a de-

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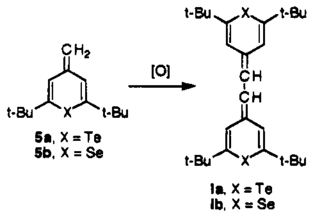
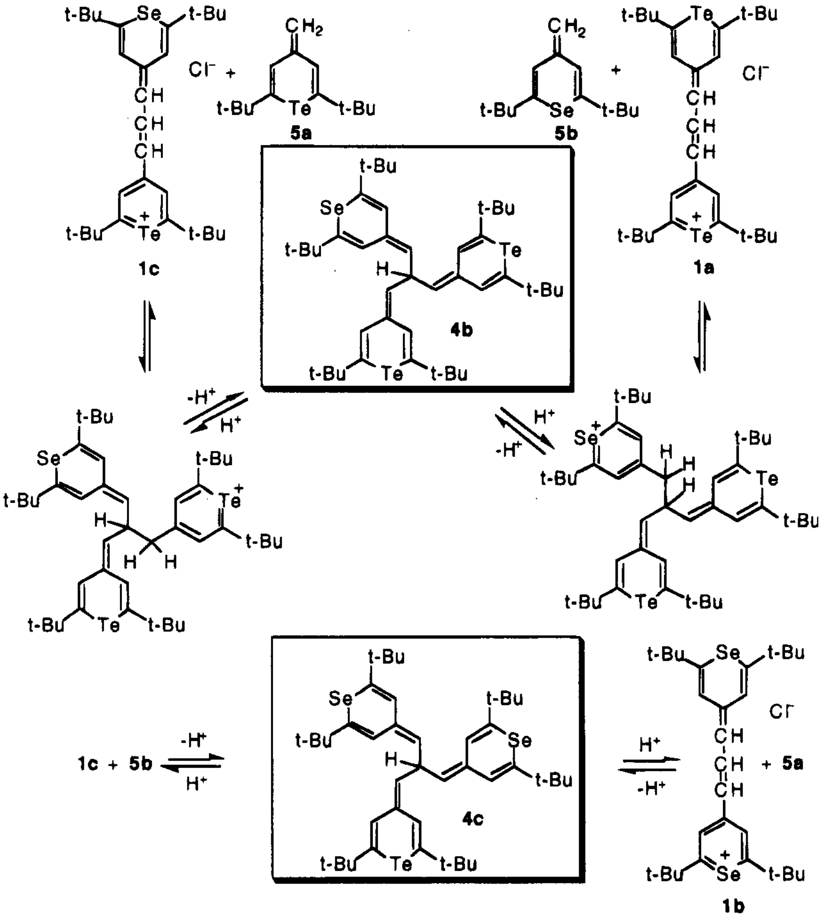
[8] The methylidene compounds were easily oxidized in aerated solutions giving, among other products, the dimeric bipyranylidenes **I**. The bipyranylidenes **I** were partially separated from other oxidation products via chromatography on alumina eluted with dichloromethane in 20% isolated yield (in approximately 90% purity) for **Ia** and 24% isolated yield for **Ib** (in approximately 90% purity). The ^1H NMR spectra of **Ia** and **Ib** were characterized by three 2-proton singlets for the olefinic protons of the bridge and the ring (δ 6.46, 6.24, and 5.79 for **Ia**; δ 6.56, 6.27, and 5.51 for **Ib**) as well as two 18-proton singlets for the *tert*-butyl groups (δ 1.27 and 1.22 for **Ia**; δ 1.26 and 1.21 for **Ib**). The isotope clusters in the mass spectra were consistent with two tellurium atoms in **Ia** (m/z 638 for $C_{28}H_{42}{}^{130}Te_2$) and two selenium atoms in **Ib** (m/z 538 for $C_{28}H_{42}{}^{80}Se_2$).



[9] Compound **6** has been prepared from **1a** and hydrogen peroxide as described in: Detty, M. R. *Organometallics* **1991**, *10*, 702. Presumably, the addition of hydroxide to a carbon bearing the heteroatom in **1a** followed by air-oxidation of the tertiary alcohol would lead to intermediates similar to those of the peroxide addition.

Scheme 4



oxygenated acetic anhydride solution of unsymmetrical dye **1c** (X = Te, Y = Se, Z = Cl) at reflux. Aliquots were diluted into CH_2Cl_2 and monitored spectrophotometrically. Following addition of the methylidene compound, new absorption bands at 750 and 830 nm were observed while the band at 786 nm (corresponding to **1c**) was diminished. The final product mixture was close to a statistical distribution of heteroatoms.[1b] (Figures 3 and 4 of the supporting information.)

The scrambling observed with **1c** and catalytic **5a** suggests that the unsymmetrical tris(chalcogenopyranylmethylidene)methane **4b** is formed as an intermediate. Protonation at the selenopyranylmethylidene carbon leads to symmetrical telluropyrylium dye **1a** and selenopyranylmethylidene **5b**, which could then react further, as outlined in Scheme 4. Similarly, the addition of **5b** to **1c** would generate tris(chalcogenopyranylmethylidene)methane **4c** where protonation of the telluropyranyl methylidene carbon leads to symmetrical selenopyrylium dye **1b** and telluropyranyl methylidene **5a**.

The formation of unsymmetrical tris(chalcogenopyranylmethylidene)methanes **4** during the synthesis of unsymmetrical dyes **1** according to Scheme 1 is a probable route to heteroatom scrambling. A reverse aldol mechanism for heteroatom scrambling appears too slow to be a significant contributor to the chalcogen scrambling mechanism. We are investigating other preparative routes to compounds **4** in order to explore the properties of these compounds.

Experimental Section

Chalcogenopyrylium dyes **1** were prepared as previously described.[1b] Ether extractions were washed with brine and dried over magnesium sulfate prior to concentration.

Preparation of 2,6-Di-*tert*-butyltelluropyrylium Hexafluorophosphate (2a). 2,6-Di-*tert*-butyl-4*H*-telluropyran-4-one (2.25 g, 7.00 mmol)[10] was dissolved in 12 mL of dry THF under an argon atmosphere. Methylmagnesium bromide (1.4 M, 14 mL, 20 mmol) was added dropwise via syringe (exothermic!). After addition was complete, the reaction mixture was stirred for 0.5 h at ambient temperature. The reaction mixture was poured into a mixture of 100 g of ice–water and 17 mL of 60% HPF_6. The tan powder was collected by filtration, washed with water (3 x 50 mL) and ether (3 x 50 mL), and dried to give 2.96 g (93%) of **2a** as an off-white powder. An analytical sample, mp 176–178.5 °C, was prepared by recrystallization from ethanol: ^1H NMR (CD_3CN) δ 8.39 (s, 2 H), 2.46 (s, 3 H), 1.58 (s, 18 H); FDMS m/z 321 ($C_{14}H_{23}{}^{130}Te$). Anal. Calcd for $C_{14}H_{23}TePF_6$: C, 36.24; H, 5.00. Found: C, 36.60; H, 5.00.

Preparation of 2,6-Di-*tert*-butylselenopyrylium Hexafluorophosphate (2b). 2,6-di-*tert*-butyl-4*H*-selenopyran-4-one (4.00 g, 14.8 mmol)[10] in 25 mL of dry THF under an argon atmosphere was treated with methylmagnesium bromide (1.4 M, 20 mL, 28 mmol) as described for the synthesis of **2a**. Product yield was 4.42 g (72%) of **2b** as a white powder. An analytical sample, mp 197.5–199 °C, was prepared by recrystallization from ethanol: ^1H NMR (CD_3CN) δ 8.34 (s, 2 H), 2.66 (s, 3 H), 1.54 (s, 18 H); FDMS, m/z 271 ($C_{14}H_{23}{}^{80}Se$). Anal. Calcd for $C_{14}H_{23}SePF_6$: C, 40.49; H, 5.58. Found: C, 40.46; H, 5.54.

Preparation of -4-Methylidene-2,6-di-*tert*-butyl-4*H*-telluropyran (5a). 2,6-Di-*tert*-butyl-4-methyltelluropyrylium hexafluorophosphate (**2a**, 0.232 g, 0.500 mmol) was dissolved in 2 mL of ethanol and was added to 50 mL of a pH 9.3 buffer (0.25 M dibasic potassium phosphate), which had been deoxygenated by argon bubbling. After addition was complete, the products were extracted into ether. The crude product was purified via flash chromatography on silica gel eluted with toluene to give 0.146 g (92%) of **5a** as a yellow oil: ^1H NMR ($CDCl_3$) δ 6.31 (s, 2 H), 5.04 (s, 2 H), 1.23 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 145.9 (s), 137.9 (s), 125.6 (d), 117.0 (t), 39.3 (s), 32.0

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(10) Detty, M. R.; Hassett, J. W.; Murray, B. J.; Reynolds, G. A. *Tetrahedron* **1985**, *41*, 4853.

(q); FDMS *m/z* 320 ($C_{14}H_{22}{}^{130}Te$). Anal. Calcd for $C_{14}H_{22}Te$: C, 52.89; H, 6.98. Found: C, 53.09; H, 6.65.

Reprotonation of 5a To Give 2a. To a solution of 0.100 g (0.31 mmol) of **5a** in 5 mL of ethanol under an argon atmosphere was added 0.11 g (0.46 mmol) of 60% aqueous HPF_6. The resulting mixture was cooled in an ice bath, and the white crystalline solid was collected by filtration, washed with water (5 × 10 mL) and ether (3 × 10 mL), and dried to give 0.123 g (85%) of 2,6-di-*tert*-butyl-4-methyltelluropyrylium hexafluorophosphate (**2a**).

Preparation of 4-Methylidene-2,6-di-*tert*-butyl-4*H*-selenopyran (5b). 2,6-Di-*tert*-butyl-4-methylselenopyrylium hexafluorophosphate (**2b**, 0.208 g, 0.500 mmol) was dissolved in 2 mL of ethanol and was added to 50 mL of a pH 9.3 buffer (0.25 M dibasic potassium phosphate) as described above for the preparation of **6a**. Product yield was 0.119 g (88%) of a yellow oil: ^1H NMR ($CDCl_3$) δ 6.35 (s, 2 H), 4.79 (s, 2 H), 1.22 (s, 18 H); ^{13}C NMR ($CDCl_3$) δ 140.0 (s), 126.0 (s), 120.0 (d), 110.3 (t), 37.95 (s), 30.3 (q); FDMS, *m/z* 270 ($C_{14}H_{22}{}^{80}Se$). Anal. Calcd for $C_{14}H_{22}Se$: C, 62.42; H, 8.23. Found: C, 62.63; H. 8.05.

Reprotonation of 5b To Give 2b. To a solution of 0.135 g (0.50 mmol) of **5b** in 5 mL of ethanol under an argon atmosphere was added 0.16 g (0.70 mmol) of 60% aqueous HPF_6. The resulting mixture was cooled in an ice bath, and the white crystalline solid was collected by filtration, washed with water (5 × 10 mL) and ether (3 × 10 mL), and dried to give 0.166 g (80%) of 2,6-di-*tert*-butyl-4-methylselenopyrylium hexafluorophosphate (**2b**).

Preparation of Tris(2,6-di-tert-butyltelluropyranyl)methylidene)methane (4a). A. Basic Hydrolysis. Dye **1a** (Z = Cl, 0.136 g, 0.20 mmol) was dissolved in 2 mL of ethanol. The resulting solution was added dropwise to 20 mL of a deoxygenated buffer solution at pH 8.4 (0.25 M dibasic potassium phosphate with pH adjustment with 0.25 M monobasic potassium phosphate). An orange crystalline solid formed. The products were extracted into ether. The product mixture was purified by flash chromatography on silica gel eluted with 10% EtOAc−CH_2Cl_2. Compounds **4a** and **6** coeluted first followed by the telluropyranyl aldehyde **3a**. The addition of 1 mL of hexane to the mixture of **4a/6** gave burnt-orange crystals of **4a**, which were collected by filtration and dried to give 0.066 g (69%) of the product, mp 207−208 °C. The hexane solution contained approximately 8 mg of ketone **6** as determined by spectral comparison to an authentic sample.[9] The telluropyranyl aldehyde **3a**[11] was slower to elute and was isolated in 0.028 g (80%) yield.

For **3a**: ^1H NMR ($CDCl_3$) δ 10.21 (d, 1 H), 8.02 (s, 1 H), 6.66 (s, 1 H), 5.87 (d, 1 H), 1.33 (s, 9 H), 1.29 (s, 9 H); IR (film) 1640 cm^{-1}; FDMS *m/z* 348 ($C_{15}H_{22}{}^{130}Te$).

For **4a**: ^1H NMR ($CDCl_3$) δ 6.52 (s, 3 H), 6.20 (s, 3 H), 5.31 (d, 3 H, J = 9 Hz), 4.53 (q, 1 H, J = 9 Hz), 1.215 (s, 27 H), 1.18 (s, 27 H); ^{13}C NMR ($CDCl_3$) δ 139.4 (s), 135.9 (s), 133.4 (s), 131.6 (d), 126.7 (d), 119.9 (d), 39.6 (s), 38.9 (s), 35.6 (d), 31.2 (q), 31.0 (q); FDMS *m/z* 970 ($C_{43}H_{64}{}^{130}Te_3$). Anal. Calcd for $C_{43}H_{64}Te_3$: C, 53.58; H, 6.69. Found: C, 53.60, H, 6.53.

B. With Preformed 5a. Dye **1a** (Z = Cl, 0.068 g, 0.10 mmol) and pyridine (9 μL, 0.008 g, 0.1 mmol) were dissolved in 1 mL of CH_2Cl_2. Telluropyranyl methylidene **5a** (0.032 g, 0.10 mmol) in 1 mL of CH_2Cl_2 was added, and the resulting mixture was stirred at ambient temperature for 1 h. The reaction mixture was placed directly on a silica flash column and eluted with CH_2Cl_2 to give 0.019 g (20%) of **4a**.

Protonolysis of 4a To Give 1a and 2a. To a solution of **4a** (0.050 g, 0.052 mmol) in 5 mL of acetic anhydride was added 0.062 g (0.26 mmol) of 60% aqueous HPF_6. The pale red solution immediately turned a much deeper yellow green. A 3.0 μL aliquot of the reaction mixture was diluted into 3 mL of CH_2Cl_2 and the absorption spectrum measured to give λ_{max} of 830 nm with an absorbance of 1.75 in a 1-cm cell (theoretical absorbance of 2.06 based on 100% conversion to **1a** and ϵ of 330 000 L mol^{-1} cm^{-1}).[1] The reaction mixture was concentrated to approximately 1 mL, and 10 mL of ether was added. The resulting solution was chilled, and the precipitate was collected. ^1H NMR analysis of the solid was consistent with roughly a 1:1 mixture of **1a**[1b] and **2a**. For **1a** (Z = PF_6): ^1H NMR (CD_3CN) δ 8.70 (t, 1 H, J = 13.5 Hz), 6.61 (br s, 4 H), 6.99 (d, 2 H, J = 13.5 Hz), 1.51 (s, 36 H). For **2a**: ^1H NMR (CD_3CN) δ 8.39 (s, 2 H), 2.46 (s, 3 H), 1.58 (s, 18 H).

Scrambling of Heteroatoms in 1c with Catalytic 5a. A sample of **1c** (0.127 g, 0.20 mmol) was dissolved in 4 mL of hot acetic anhydride. A 16 μL aliquot of the resulting solution was diluted into 100 mL of CH_2Cl_2. To the bulk acetic anhydride solution was added 0.010 g (0.031 mmol) of **5a** in 1 mL of acetic anhydride under an argon atmosphere. The resulting solution was heated at reflux for 10 min. A 20 μL aliquot of the reaction mixture was diluted into 100 mL of CH_2Cl_2. Comparison of the absorption spectra of starting material (Figure 3 of the supporting information) and reaction mixture (Figure 4 of Supplementary Material) showed a decrease in the absorption of **1c** at 786 nm (absorbance change from 1.8 to 1.2) and two new absorbance bands at 830 nm (**1a**,[1] absorbance of 0.5) and 750 nm (**1b**,[1] absorbance of 0.7).

Scrambling of Heteroatoms in 1c with Catalytic 5b. A sample of a mixture of **1c** (0.127 g, 0.20 mmol) and 0.009 g (0.03 mmol) of **5a** was treated as described above. Comparison of the absorption spectra of starting material and reaction mixture showed a decrease in the absorption of **1c** at 786 nm (absorbance change from 1.8 to 1.3) and two new absorbance bands at 830 nm (**1a**,[1] absorbance of 0.45) and 750 nm (**1b**,[1] absorbance of 0.75).

Supporting Information Available: Figures 1 and 2, which show the uncoupled and coupled ^{13}C NMR spectra, respectively, of compound **4a**, and Figures 3 and 4, which show the absorption spectra of pure **1c** and **5a**-induced scrambling of the heteroatoms, respectively (4 pages). This material is contained in libraries on microfiche, immediately follows the article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[11] The aldehyde **3a** has been described and an analytical sample characterized as its dimethyliminium tetrafluoroborate salt. However, spectral data for **3a** have not been reported: Detty, M. R.; Luss, H. R. *Organometallics* **1988**, *7*, 1131.