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Unusual Oxidations and Reductions in the Conversion of Tellurapyranones to Tellurapyrylium Salts. One-Electron Reductions with Diisobutylaluminum Hydride

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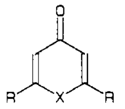
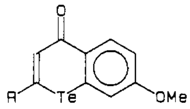
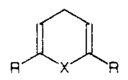
The reduction of chalcogenapyranones with 2 equiv of diisobutylaluminum hydride (DIBAL-H) gives 4*H*-chalcogenapyrans as the major products although dimeric products from coupling of tellurapyranyl radicals are also isolated in one case. Oxidation of the chalcogenapyrans with strong acid gives chalcogenapyrylium salts and hydrogen gas. The DIBAL-H reduction of 2,6-di-*tert*-butyltellurapyranone (**1a**) gave a 62% isolated yield of tellurapyrans **3a** and **8** in a 93:7 ratio and a 29% isolated yield of dimer **7**. The dimer presumably was formed by coupling of two 2,6-di-*tert*-butyltellurapyranyl radicals. The electrochemical reduction of 2,6-di-*tert*-butyltellurapyrylium hexafluorophosphate (**5a**) required 1.04 F/mol generating the 2,6-di-*tert*-butyltellurapyranyl radical (**9**) which dimerized to give tellurapyran dimer **7**. Electrochemical oxidation of **7** required 2.6 F/mol and generated 2 equiv of **5a**. The DIBAL-H reduction of **5a** gave 2,6-di-*tert*-butyltellurapyran (**3a**) and its double bond isomer **8** in a 93:7 ratio and less than 1% of dimer **7**. The addition of 0.5 equiv of water to 1 equiv of DIBAL-H followed by the addition of 1 equiv of **5a** and a second equivalent of DIBAL-H gave an 80:20 mixture of **3a**/**8** to **7**.



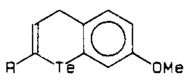
1a; X=Te, R=tert-Bu
1b; X=Te, R=Ph
13a; X=Se, R=tert-Bu
13b; X=S, R=tert-Bu
13c; X=O, R=tert-Bu



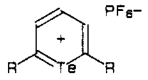
2a, R=tert-Bu
2b, R=Ph
2c, R=H



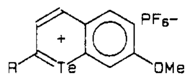
3a; X=Te, R=tert-Bu
3b; X=Te, R=Ph
14a; X=Se, R=tert-Bu
14b; X=S, R=tert-Bu
14c; X=O, R=tert-Bu



4a, R=tert-Bu
4b, R=Ph
4c, R=H



5a; X=Te, R=tert-Bu
5b; X=Te, R=Ph
15a; X=Se, R=tert-Bu
15b; X=S, R=tert-Bu
15c; X=O, R=tert-Bu

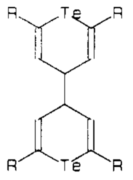


6a, R=tert-Bu
6b, R=Ph

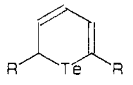
We have observed that the major products from the diisobutylaluminum hydride (DIBAL-H) reduction of tellurapyranones **1** and **2** are, surprisingly, tellurapyrans **3** and **4** and not allylic alcohols, as previously suggested.[1] The conversion of carbonyl groups to methylene groups through tosylhydrazone intermediates using DIBAL-H as a reducing agent has been described[2] although, to the best of our knowledge, the direct conversion of carbonyl groups to methylene groups has not been previously described. While DIBAL-H reduction of carbonyl compounds is thought to involve hydride transfer, a dimeric product is formed during the reduction of **1a** which presumably arises by the coupling of tellurapyranyl radicals produced by a one-electron process. Single-electron-transfer reactions of organoaluminum hydrides are known with heteroaromatic compounds but are uncommon with carbonyl-containing substrates.[3]

The desired products from DIBAL-H reduction of the tellurapyranones were the corresponding alcohols which could be dehydrated to tellurapyrylium salts.[4] Much to our surprise, the tellurapyrans were oxidized by strong acid to give the corresponding tellurapyrylium salts **5** and **6** and hydrogen gas. The tellurapyrans **3** and **4** represent novel classes of hydride donors. The literature contains little precedent for this reaction in the chalcogenapyrans although the addition of hydrogen selenide to 1,5-diphenylpenta-1,5-dione under strongly acidic conditions gave a 2,6-diphenylselenapyrylium salt.[5] Presumably, the selenapyrylium salt was produced from the corresponding selenapyran even though this intermediate was not suggested or described.

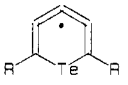
The DIBAL-H reduction of **1a**[6a] gave tellurapyran **3a** in 62% isolated yield and a dimeric product, **7**, in 29% isolated yield. The ^{1}H NMR spectrum of **3a** showed that an isomer of **3a** (compound **8a**) was also produced during the reaction (93:7, **3a**/**8a**). Compounds **3a** and **8a** were not separated. All NMR (^{1}H, ^{13}C, ^{125}Te) spectra of **7** were indicative of C_2 symmetry.



7, R=tert-Bu



8a, R=tert-Bu
8b, R=Ph



9, R=tert-Bu

Table I contains examples of the DIBAL-H reduction of other tellurapyranones **1** and **2**.[6] The tellurapyrans **4** were free of regioisomers (by ^{1}H NMR) while tellurapyran **3b** contained approximately 5% of its regioisomer **8b** (by ^{1}H NMR).

The dihydro compounds **3** and **4** upon heating with HPF_6 in acetic acid gave tellurapyrylium compounds **5** and

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[1] Detty, M. R.; Murray, B. J. *J. Am. Chem. Soc.* **1983**, *105*, 883.

[2] (a) Lightner, D. A.; Gawronski, J. K.; Bouman, T. D. *J. Am. Chem. Soc.* **1980**, *102*, 1983. (b) Lightner, D. A.; Bouman, T. D.; Christ, B. V.; Rodgers, S. L.; Knobeloch, M. A.; Jones, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 6248.

[3] (a) Kaim, W. *J. Am. Chem. Soc.* **1984**, *106*, 1712. (b) Kaim, W. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 783. (c) Kaim, W. *Acc. Chem. Res.* **1985**, *18*, 160.

[4] Detty, M. R.; Murray, B. J. *J. Org. Chem.* **1982**, *47*, 5235.

[5] Es-Seddiki, S.; Le Coustumer, G.; Mollier, Y. *Tetrahedron Lett.* **1981**, 2771.

[6] The chalcogenapyranones **1** were prepared according to reference 6a while the benzo[*b*]tellurapyranones **2** were prepared according to ref 1: (a) Detty, M. R.; Hassett, J. W.; Murray, B. J.; Reynolds, G. A. *Tetrahedron* **1985**, *45*, 4853.

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Table I. DIBAL-H Reduction of Chalcogenapyranoses

compd	major product	% yield[a]	^{1}H NMR ($CDCl_3$), δ [J, Hz]
1a	**3a**	62	6.02 (t), 2.66 (t) [5.4]
1b	**3b**	65	6.15 (t), 2.70 (t) [5.5]
2a	**4a**	82	6.19 (t), 3.25 (d) [5.6]
2b	**4b**	85	6.47 (t), 3.37 (d) [5.8]
2c	**4c**	75	6.31 (d), 5.44 (td), 3.26 (d) [5.5, 10.6]
13a	**14a**	86	5.87 (t), 2.58 (t) [5.0]
13b	**14b**	82	5.62 (t), 2.66 (t) [4.7]
13c	**14c**		4.53 (t), 2.72 (t) [3.3]

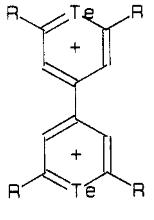
[a] Isolated yield. [b] Chemical shifts of protons attached to chalcogenapyrane ring and coupling between them.

6, respectively (Table II). Gas evolution was observed for every substrate. The reactions of **3a** and **4a** with HPF_6 in acetic acid were conducted in a sealed vessel connected to the inlet of a mass spectrometer (set up for field desorption work). The gas produced during reaction was identified as hydrogen (m^+/e 2, 1) using helium as an internal standard.

Electrochemical Studies. The formation of dimeric products such as **7** has been associated with the dimerization of pyranyl radicals.[7] The fate of tellurapyranyl radicals such as **9** has not been investigated although one might expect one reaction pathway of the radical to lead to dimeric products such as **7**.

The tellurapyrylium salt **5a** allows entry to the tellurapyranyl radical **9**. In dichloromethane with 0.2 M tetra-n-butylammonium fluoroborate (TBAF) as supporting electrolyte, the reduction of **5a**, as determined by cyclic voltammetry (CV), was irreversible with $E_p{}^c = -0.32$ V (vs SCE) at a platinum electrode. The positive scan following reduction showed an irreversible oxidation wave $E_p{}^a = 0.63$ V (vs SCE). Controlled potential electrolysis of a 6.1×10^{-4} M solution of **5a** between 0.0 and −0.5 V (vs SCE) in dichloromethane required 1.04 F/mol and gave dimer **7** as determined by cyclic voltammetry and by UV–visible absorption spectroscopy. The CV of **7** gave $E_p{}^a = 0.63$ V (vs SCE) and a smaller wave in the negative direction, following oxidation, with $E_p{}^c = -0.32$ V. The oxidation of **7** by controlled potential electrolysis between 0.0 and 0.9 V (vs SCE) in dichloromethane required 2.6 F/mol and gave 2 equiv of **5a** as determined by cyclic voltammetry and UV–visible absorption spectroscopy.

Reversible dimerization of pyranyl radicals has been observed upon one-electron reduction of 2,6-diaryl- and 2,6-dialkylpyrylium cations.[7] Electrochemical oxidation of the stable pyran dimers required 2 F/mol and regenerated 2 equiv of the pyrylium cations.[7] Further oxidation of the pyran dimers to the bis(pyrylium) cations was not observed. Oxidation of the tellurapyrylium dimer **7** gave 2 equiv of **5a**—not the bis(tellurapyrylium) dication **10**.



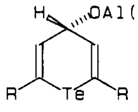
10, R=tert-Bu

The formation of **10** from electrochemical oxidation of **7** can be unequivocally dismissed. The bis(perchlorate) salt of **10** has been prepared.[8] By cyclic voltammetry, **10** displays two reversible redox couples at $E° = +0.14$ V (vs SCE) and at $E°' = +0.31$ V (vs SCE). These couples are absent in the cyclic voltammograms of oxidized **7**.

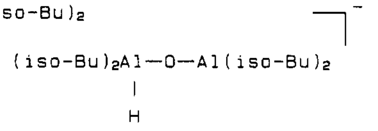
Mechanistic Considerations in the DIBAL-H Reduction. The formation of dimer **7** upon one-electron reduction of **5a** suggests that a radical-producing pathway may be present in the DIBAL-H reduction of **1a**. Other carbon–carbon bond-forming reactions to produce **7** can be postulated based on even-electron intermediates.

The initial addition of DIBAL-H to **1** (or **2**) would presumably proceed via 1,2-addition to the carbonyl to give **11**. Dissociation of **11** could give the tellurapyrylium salt **5** and the dialkylaluminum alkoxide. The second equivalent of DIBAL-H could add a hydride to the tellurapyrylium species to give the pyran compounds or could act as a one-electron reducing agent to give the pyranyl radicals, which could dimerize or abstract hydrogen.[7]

One possible even-electron mechanism for the formation of **7** would involve the use of DIBAL-H as a strong base to abstract a proton from the 4-position of tellurapyran **3a** to generate a new organoaluminum species (formally, a tellurapyranyl anion). The addition of a tellurapyranyl anion to tellurapyrylium cation **5a** could generate a new carbon–carbon bond as has been shown for the addition of Grignard reagents to pyrylium cations.[7b] Tellurapyran **3a** was inert to the conditions of reaction in the presence of 2 equiv of DIBAL-H. The absorption spectrum of the tellurapyran was unchanged upon addition of DIBAL-H. Furthermore, quenching of the reaction mixture with MeOD did not give detectable amounts of deuterium incorporation in recovered **3a**.



11



12

The addition of 1 equiv of DIBAL-H to **1a** in THF gave, following workup, a mixture of products including **5a**, unreacted **1a**, **3a**/**8**, and small amounts of **7**. The presence of **5a** in the reaction mixture suggested that the dissociation of **11** is plausible.

When the DIBAL-H (in hexane) reduction of **1a** was carried out in deuteriated THF, the isolated **3a** contained no detectable deuterium incorporation by ^{1}H NMR or field desorption mass spectroscopy. This result suggested that hydrogen atom abstraction by a pyranyl radical was not important in the production of **3a**. Furthermore, the ^{1}H NMR spectrum of the crude reaction mixture before workup showed the peaks expected from both **3a** and **7** (although integration of the relative amounts was not attempted).

The addition of DIBAL-H to a THF solution of **5a** gave a 93:7 mixture (90%) of **3a** and its isomer **8a** and less than 1% of the dimer **7** by ^{1}H NMR. DIBAL-H alone, does not promote the one-electron reduction of **5a** to its pyranyl radical, **9**. The **3a**:**8a** ratio in this experiment was identical with that produced by the DIBAL-H reduction of **1a** suggesting that tellurapyrylium salt **5a** may have been produced in the reduction of **1a** and may have been an intermediate in the formation of **3a**.

Diisobutylaluminum hydride, alone, does not appear to generate **7** from either **3a** or **5a**. The initial addition of

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(7) (a) Pragst, F.; Ziebig, R.; Seydewitz, U.; Driesel, G. *Electrochim. Acta* **1980**, *25*, 341. (b) Pragst, F.; Janda, M.; Stibor, I. *Electrochim. Acta* **1980**, *25*, 779.

(8) Detty, M. R.; Murray, B. J.; Perlstein, J. H. *Tetrahedron Lett.* **1983**, *24*, 539.

Table II. Reactions of 4*H*-Chalcogenapyrans with HPF_6 To Give Chalcogenapyrylium Salts

compd	product	% yield[a]	mp, °C	^1H NMR (CD_2Cl_2),[b] δ [J, Hz]	E_p^{c},[c] V	E_p^{a},[c] V
3a	**5a**	85	191–194	8.97 (t), 8.50 (d) [9.6]	–0.32	0.63
3b	**5b**	73	205–207	9.03 (t), 8.47 (d) [9.5]		
4a	**6a**	65	213 dec	9.03 (d), 8.57 (d) [9.0]		
4b	**6b**	60	215–217	9.12 (d), 8.47 (d) [9.0]		
14a	**15a**	64	191–192	8.93 (t), 8.55 (d) [8.8]	–0.48	0.64
14b	**15b**	59	188–190	8.94 (t), 8.69 (d) [8.5]	–0.54	0.60
14c	**15c**	22	192–194	9.09 (t), 8.10 (d) [8.2]	–0.58	0.74

[a] Isolated yield. [b] Chemical shifts of chalcogenapyrylium ring protons and coupling between them. [c] Versus SCE. In dichloromethane solution with 0.2 M TBAF as supporting electrolyte at a scan rate of 0.1 V/s at a platinum disk electrode. Substrate concentrations were approximately 5 × 10^{-4} M.

DIBAL-H to **1a** to generate **11** appears to follow a 1,2-hydride addition pathway. However, homolytic cleavage of the carbon–oxygen bond could generate **9** while ionic dissociation of **11** would lead to **5a** and diisobutylaluminum alkoxide which might generate a new reducing agent.

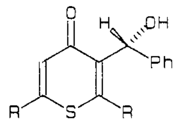
The addition of 0.5 equiv of water to 1 equiv of DIBAL-H presumably generates the dialkylaluminum alkoxide produced by ionic dissociation of **11**. The addition of **5a** to the dialkylaluminum alkoxide generated in this way gives no immediate reaction. However, the addition of a second equivalent of DIBAL-H gives reduction of **5a** to an 80:20 mixture of **3a**/**8a** to **7**. These results suggest that the one-electron reducing agent in these reactions is a complex of DIBAL-H with the dialkylaluminum alkoxide, perhaps **12**.

Reduction of Other Chalcogenapyranones. Other chalcogenapyranones were reduced by DIBAL-H as well as indicated in Table I. Dimeric products were not detected in these reaction mixtures. When compounds **14** were heated with HPF_6 in acetic acid (gas evolution), the corresponding chalcogenapyrylium salts **15** were isolated (Table II). Electrochemical reduction of the chalcogenapyrylium salts **15** (Table II) gave the dimers analogous to **7** presumably through the corresponding pyranyl radicals.[7] The absence of dimeric products in the reaction mixtures giving **14** suggests that the pyranyl radicals are not formed by DIBAL-H in these reactions. As indicated by the reduction potentials listed in Table II, the chalcogenapyrylium salts cover a several hundred millivolt range and differences in reactivity toward a reducing agent would not be unexpected.

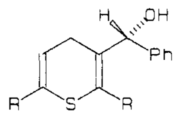
The reduction of 2,6-di-*tert*-butylpyranone (**13c**) with DIBAL-H gave, in addition to pyran **14c**, several minor products. The ^1H NMR spectrum of the reaction mixture revealed the two triplets associated with the olefinic and methylene protons of **14c** and a *tert*-butyl singlet, the integral of which integrated to about 50% of the *tert*-butyl signals present in the crude reaction mixture. The field desorption mass spectrum (FDMS) of the reaction mixture gave an intense signal for the parent ion of **14c**. However, the *tert*-butyl singlets in the ^1H NMR spectrum were numerous and ion clusters at both higher and lower molecular weights relative to **14c** were observed by FDMS. The R_f values of the compounds on both silica gel and alumina with a variety of solvent systems were too similar to permit easy separation.

When the crude reaction mixture from the DIBAL-H reduction of **13c** was oxidized with HPF_6 in acetic acid, pyrylium salt **15c** was isolated in 22% overall yield from **13c**. Gas evolution was observed in this oxidation as well.

The chemistry of the chalcogenapyrans is being explored with particular attention to the reduction of carbonyl-containing substrates via hydride transfer from the pyrans. Compounds of this type bear structural similarity to the NADH mimics recently reported by Meyers and Oppenlaender[9a] and Meyers and Brown.[9b] Like the NADH mimics, thiapyran **17**, produced by DIBAL-H reduction of **16**,[10] has a 1,5-disposition of potential ligands for various metals and has an asymmetric center. The ^1H NMR spectrum of **17** shows the AB pattern expected with doublet of doublets at δ 2.51 and 2.32 with coupling constants, J, of 6.2 and 13.9 Hz. Pyrans such as **17** offer the potential for chiral hydride transfer where the chiral center would not be destroyed by hydride transfer. Furthermore, the differences in redox potentials among the chalcogenapyrans and the chalcogenapyrylium salts may allow more selective reduction of one functional group in the presence of another via hydride transfer.



16, R=tert-Bu



17, R=tert-Bu

Experimental Section

Melting points were determined on a Thomas-Hoover melting-point apparatus and are corrected. ^1H NMR and ^{13}C NMR spectra were recorded on a General Electric QE-300 instrument. Infrared spectra were recorded on a Beckman IR 4250 instrument. UV–visible absorption spectra were recorded on a Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer. ^{125}Te NMR spectra were recorded on a Varian Automated XL 300 spectrometer at 94.704 MHz with a 5-mm broad-band probe. Samples were referenced to $^{125}TePh_2$ (at δ 688 relative to $^{125}TeMe_2$ at δ 0.0) as an external standard run as a neat liquid. The spectra were collected over 1000–5000 transients using a 100 000 Hz sweep width, a pulse time of 10 μs, and a delay time of 1.0 s. The spectra were proton decoupled with Waltz decoupling using 1.5 W of power centered at 5 ppm in the proton window. Tetrahydrofuran (THF) was distilled from benzophenone ketyl prior to use. Glacial acetic acid was used as received from Kodak Laboratory Chemicals. Microanalyses were performed on a Perkin-Elmer C, H, and N analyzer. Tellurium analyses were done by atomic absorption spectroscopy and are accurate to ±1%.

Electrochemical Procedures. A Princeton Applied Research Model 173 potentiostat/galvanostat and a Model 175 Universalt Programmer were used for the electrochemical measurements. The working electrode for cyclic voltammetry was a platinum disk electrode (diameter, 2 mm) obtained from Princeton Applied Research. The working electrode for bulk coulometry was a platinum gauze basket. The auxiliary electrode was a platinum wire. The reference electrode for both the cyclic voltammetry and the coulometry experiments was a AgCl-saturated calomel electrode.

All samples were run in J. T. Baker HPLC-grade dichloromethane or acetonitrile that had been stored over Kodak-type 3A molecular sieves. Electrometric-grade tetra-*n*-butylammonium

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(9) (a) Meyers, A. I.; Oppenlaender, T. *J. Am. Chem. Soc.* **1986**, *108*, 1989. (b) Meyers, A. I.; Brown, J. D. *Ibid.* **1987**, *109*, 3155.

(10) Detty, M. R.; McGarry, L. W. *J. Org. Chem.*, in press.

fluoroborate (Southwestern Analytical Chemicals, Inc.) was recrystallized from ethyl acetate–ether and then dried overnight at 80 °C before it was used as supporting electrolyte at 0.2 M concentration. Argon was used for sample deaeration.

General Procedure for Reduction of Chalcogenapyranones and Benzo[*b*]chalcogenapyranones with Diisobutylaluminum Hydride. Reduction of 2,6-Di-*tert*-butyltellurapyranone (1a). In a flame-dried 50-mL two-necked flask equipped with rubber septum cap and dry argon inlet, tellurapyranone **1a** (1.60 g, 5.00 mmol) was dissolved in 15 mL of dry THF. The resulting solution was cooled to 0 °C. Diisobutylaluminum hydride (7.0 mL of a 1.5 M solution in toluene) was added dropwise via syringe. The addition of each drop for the first 3.5 mL gave a deep blue color that quickly faded. After the addition of 3.5 mL, none of the blue color was detected with further addition. After addition was complete, the reaction was quenched by the addition of 10 mL of moist ether. The resulting solution was poured into 100 mL of ether, and the organic phase was washed with cold 5% HCl (3 × 25 mL) and brine (2 × 50 mL), dried over sodium sulfate, and concentrated. Upon standing, the residual yellow oil partially crystallized. Cold pentane (5 mL) was added, and the resulting mixture was chilled at −20 °C. The pentane solution was decanted from the yellow crystals. The crystals were collected by filtration and were recrystallized from hexanes to give 0.45 g (29%) of the dimer **7** as bright yellow crystals: mp 173–179 °C; ^{1}H NMR ($CDCl_3$) δ 5.95 (dd, 4 H, J = 1.1, 1.9 Hz), 2.48 (m, 2 H), 1.20 (s, 36 H); ^{13}C NMR (CD_2Cl_2) δ 146.9 (s), 128.8 (d), 55.6 (d), 38.8 (s), 31.2 (q); ^{125}Te NMR (CD_2Cl_2) δ 296; FDMS, m^+/e 614 ($C_{26}H_{42}{}^{130}Te_2$); λ_{max} (CH_2Cl_2) 440 nm (ϵ 3130). Anal. Calcd for $C_{26}H_{42}Te_2$: C, 51.2; H, 6.9. Found: C, 51.3; H, 6.5.

The pentane solution that had been decanted from the crystals of **7** was purified by chromatography on silica gel eluted with CH_2Cl_2 to give 0.95 g (62%) of **3a** as a yellow oil. The ^{1}H NMR spectrum of **3a** showed the presence of its double bond isomer **8**. The ratio of **3a**/**8** was 93:7. For **3a**: ^{1}H NMR ($CDCl_3$) δ 6.02 (t, 2 H, J = 5.4 Hz), 2.66 (t, 2 H, J = 5.4 Hz), 1.20 (s, 18 H); FDMS, m^+/e 308; ^{13}C NMR ($CDCl_3$) δ 146.2 (s), 123.6 (d), 39.8 (t), 38.6 (s), 31.4 (q); ^{125}Te NMR ($CDCl_3$) δ 257; λ_{max} (CH_2Cl_2) 345 (ϵ 3900), 420 nm (sh, ϵ 150); FDMS, m^+/e 308 ($C_{13}H_{22}{}^{130}Te$). Anal. Calcd for $C_{13}H_{22}Te$: C, 51.0; H, 7.2. Found: C, 51.3; H, 6.9.

For **8**: ^{1}H NMR ($CDCl_3$) δ 6.07 (m, 1 H), 5.95 (m, 1 H), 5.08 (dd, 1 H, J = 6.5, 8 Hz), 3.52 (d, 1 H, J = 6.5 Hz), 1.20 (s, 9 H), 1.00 (s, 9 H).

The other chalcogenapyranones were reduced by DIBAL-H under similar conditions. The chalcogenapyrans were purified by chromatography on silica gel eluted with dichloromethane to give analytically pure oils.

For **4a**: ^{1}H NMR ($CDCl_3$) δ 7.33 (d, 1 H, J = 2.4 Hz), 7.21 (d, 1 H, J = 8.3 Hz), 6.79 (dd, 1 H, J = 2.4, 8.3 Hz), 6.19 (t, 1 H, J = 5.6 Hz), 3.80 (s, 3 H), 3.25 (d, 2 H, J = 5.6 Hz), 1.22 (s, 9 H); ^{125}Te NMR ($CDCl_3$) δ 391; FDMS, m^+/e 332 ($C_{14}H_{18}O^{130}Te$). Anal. Calcd for $C_{14}H_{18}OTe$: C, 51.0; H, 5.5. Found: C, 50.6; H, 5.4.

For **4b**: ^{1}H NMR ($CDCl_3$) δ 7.40 (m, 2 H), 7.23 (m, 3 H), 7.10 (d, 1 H, J = 3 Hz), 6.73 (dd, 1 H, J = 3, 9 Hz), 6.47 (t, 1 H, J = 5.8 Hz), 3.71 (s, 3 H), 3.37 (d, 2 H, J = 5.8 Hz); ^{125}Te NMR ($CDCl_3$) δ 380; FDMS, m^+/e 352 ($C_{16}H_{14}O^{130}Te$). Anal. Calcd for $C_{16}H_{14}OTe$: C, 54.9; H, 4.0. Found: C, 54.8; H, 4.0.

For **4c**: ^{1}H NMR ($CDCl_3$) δ 7.51 (d, 1 H, J = 8.3 Hz), 7.28 (d, 1 H, J = 2.5 Hz), 6.82 (dd, 1 H, J = 2.5, 8.3 Hz), 6.31 (d, 1 H, J = 10.6 Hz), 5.44 (dt, 1 H, J = 5.5, 10.6 Hz), 3.80 (s, 3 H), 3.26 (d, 2 H, J = 5.5 Hz); FDMS, m^+/e 276 ($C_{10}H_{10}O^{130}Te$). Anal. Calcd for $C_{10}H_{10}OTe$: C, 43.9; H, 3.7. Found: C, 44.3; H, 3.9.

For **14a**: ^{1}H NMR ($CDCl_3$) δ 5.87 (t, 2 H, J = 5.0 Hz), 2.58 (t, 2 H, J = 5.0 Hz), 1.20 (s, 18 H); FDMS, m^+/e 258 ($C_{13}H_{22}Se$).

For **14b**: ^{1}H NMR ($CDCl_3$) δ 5.62 (t, 2 H, J = 4.7 Hz), 2.66 (t, 2 H, J = 4.7 Hz), 1.17 (s, 18 H); FDMS, m^+/e 210 ($C_{13}H_{22}S$).

For **14c**: ^{1}H NMR ($CDCl_3$) δ 4.53 (t, 2 H, J = 3.3 Hz), 2.72 (t, 2 H, J = 3.3 Hz), 1.20 (s, 18 H); FDMS, m^+/e 194 ($C_{13}H_{22}O$).

General Procedure for Conversion of Chalcogenapyrans to Chalcogenapyrylium Salts. Preparation of 2,6-Di-*tert*-butyltellurapyrylium Hexafluorophosphate (5a). Tellurapyran **3a** (0.31 g, 0.10 mmol) was dissolved in 1.5 mL of glacial acetic acid. Hexafluorophosphoric acid (0.30 g of a 60% aqueous solution) was then added. The resulting solution was degassed with vacuum followed by an argon flush for a total of three cycles. The reaction mixture was heated under argon on a steam bath. A vigorous evolution of gas occurred. After 5 min of heating, 20 mL of ether was added to the reaction mixture. The resulting mixture was chilled. The tellurapyrylium salt **5a** was collected by filtration as a white crystalline solid. Recrystallization from 3:1 ether–acetonitrile gave 0.33 g (84%) of **5a**: mp 190.5–193.5 °C; ^{1}H NMR ($CDCl_3$) δ 8.97 (t, 1 H, J = 9.6 Hz), 8.50 (d, 2 H, J = 9.6 Hz), 1.68 (s, 18 H); ^{125}Te NMR (CD_2Cl_2) δ 1304; λ_{max} (CH_2Cl_2) 345 nm (ϵ 8400). Anal. Calcd for $C_{13}H_{21}Te{\cdot}PF_6$: C, 34.7; H, 4.7; F, 25.3; P, 6.9; Te, 28.4. Found: C, 34.9; H, 4.5; F, 25.3; P, 6.0; Te, 26.8.

When the acid oxidation was repeated in the inlet of a mass spectrometer set up for field desorption work, the final degassing cycle included spiking the argon atmosphere with helium to use as a low-mass standard for detecting hydrogen.

The other tellurapyrans **3** and **4** required approximately 15 min of heating for gas evolution to be complete while the other chalcogenapyrans required 30 min.

For **6a**: ^{1}H NMR (CD_2Cl_2) δ 9.03 (d, 1 H, J = 9 Hz), 8.95 (d, 1 H, J = 3 Hz), 8.57 (d, 1 H, J = 9 Hz), 7.51 (dd, 1 H, J = 3, 9 Hz), 4.24 (s, 3 H); ^{125}Te NMR (CD_2Cl_2) δ 11.24. Anal. Calcd for $C_{14}H_{17}OTe{\cdot}PF_6$: C, 35.6; H, 3.6; F, 24.1. Found: C, 35.5; H, 3.6; F, 24.1.

For **6b**: ^{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), 8.4 (d, 1 H, J = 3 Hz), 7.9–7.3 (m, 6 H), 4.00 (s, 3 H); ^{125}Te NMR (CD_2Cl_2) δ 1086. Anal. Calcd for $C_{16}H_{13}OTe{\cdot}PF_6$: C, 37.7; H, 2.6; F, 22.4. Found: C, 37.9; H, 2.5; F, 22.3.

For **15a**: ^{1}H NMR (CD_2Cl_2) δ 8.93 (t, 1 H, J = 8.8 Hz), 8.55 (d, 2 H, J = 8.8 Hz), 1.69 (s, 18 H). Anal. Calcd for $C_{13}H_{21}Se{\cdot}PF_6$: C, 38.9; H, 5.3; P, 7.7; F, 28.4; Se, 19.7. Found: C, 38.9; H, 5.2; P, 7.2; F, 28.3; Se, 20.2.

For **15b**: ^{1}H NMR (CD_2Cl_2) δ 8.94 (t, 1 H, J = 8.5 Hz), 8.69 (d, 2 H, J = 8.5 Hz), 1.65 (s, 18 H). Anal. Calcd for $C_{13}H_{21}S{\cdot}PF_6$: C, 44.1; H, 6.0; S, 9.0. Found: C, 43.8; H, 6.4; S, 9.5.

For **15c**: ^{1}H NMR (CD_2Cl_2) δ 9.09 (t, 1 H, J = 8.2 Hz), 8.10 (d, 2 H, J = 8.2 Hz), 1.58 (s, 18 H). Anal. Calcd for $C_{13}H_{21}O{\cdot}PF_6$: C, 48.4; H, 6.6. Found: C, 48.3; H, 6.6.

DIBAL-H Reduction of 5a. In a 25-mL two-necked flask equipped with dry argon inlet and rubber septum cap, tellurapyrylium salt **5a** (0.045 g, 0.10 mmol) was slurried in 5 mL of dry THF. The resulting mixture was cooled to 0 °C under argon, and the DIBAL-H (0.10 mL of a 1.5 M in toluene solution, 0.15 mmol) was added dropwise via syringe. After addition was complete, the reaction was quenched by the addition of 20 mL of moist ether. The organic solution was washed with cold, 10% HCl (4 × 15 mL), dried over sodium sulfate, and concentrated. The ^{1}H NMR spectrum of the crude reaction mixture showed a 93:7 mixture of **3a** to **8** and trace amounts (<1%) of **7**. It should be noted that use of undried glassware or exposure of solvents to air gives increased amounts of the dimer **7**.

Reduction of Tellurapyranone 1a in Deuteriated THF. Tellurapyranone **1a** (0.44 g, 1.38 mmol) in 2 g of 99.5% THF-d_8 was cooled to 0 °C in an ice bath under an argon atmosphere. DIBAL-H (cooled to 0 °C, 2.93 mmol, 1.95 mL of a 1.5 M solution in hexanes) was added dropwise via syringe. A blue color developed that quickly faded with each drop for the first 0.95 mL. The addition of the next 0.95 mL of DIBAL-H gave a change in color for the reaction mixture from orange to yellow. The reaction mixture was quenched by the addition of 0.2 mL of 1 N NaOH. The reaction mixture was diluted with 50 mL of hexanes. The organic phase was washed with cold, 5% HCl (2 × 25 mL) and brine (2 × 25 mL), dried over sodium sulfate, and concentrated. The dimer **7** crystallized. The pyran **3a** was removed from the dimer by washing the crystals with cold pentane (2 × 5 mL). The dimer **7** was isolated in 0.12 g (29%) yield while the tellurapyran **3a** was isolated in 0.26 g (62%) yield. Both ^{1}H NMR and FDMS analyses of the products showed no detectable deuterium incorporation in the products.

DIBAL-H Reduction of 5a in the Presence of Water. In a 50-mL two-necked flask equipped with rubber septum cap and dry argon inlet, water (27 μL, 1.5 mmol) was added via syringe to a solution of DIBAL-H (3.0 mmol, 2.0 mL of a 1.5 M solution in toluene) in 20 mL of dry THF cooled to 0 °C. After the resulting solution had stirred for 5 min at 0 °C, **5a** (1.35 g, 3.00 mmol) was added as a powder. No apparent reaction occurred.

DIBAL-H (3.8 mmol, 2.5 mL of a 1.5 M solution in toluene) was added dropwise at 0 °C. The first half of the addition produced a transient blue color. After addition was complete, the reaction mixture was a pale yellow solution. Workup as before gave a crude product mixture that showed an 80:20 ratio of **3a**/**8** to **7** by ^1H NMR. The crystalline **7** was isolated in 0.16 g (17%) yield. The **3a**/**8** mixture was isolated in 0.71 g (77%) yield.

DIBAL-H Addition to 3a/8. DIBAL-H (1.5 mmol, 1.0 mL of a 1.5 M solution in toluene) was added dropwise to a solution of **3a** (0.31 g, 1.0 mmol) in 10 mL of dry THF cooled to 0 °C under an argon atmosphere. After addition was complete, the reaction mixture was stirred 1.0 h at 0 °C and the reaction was quenched by the dropwise addition of 0.5 mL of 99% MeOD. The tellurapyran was recovered by the standard workup. Both ^1H NMR and FDMS analyses of the recovered **3a** showed no incorporation of deuterium.

Electrochemical Reduction of Tellurapyrylium Salt 5a. Tellurapyrylium salt **5a** (6.9 mg, 0.015 mmol) was dissolved in 25 mL of a 0.2 M solution of tetra-*n*-butylammonium fluoroborate in dichloromethane to give a 6.1×10^{-4} M solution in **5a**. After the passage of 1.54 C between 0.0 and −0.5 V (vs SCE), the electrolysis was complete with 1.04 F/mol being passed. The CV of the electrolyzed solution showed complete consumption of starting material in a negative scan between 0.0 and −1.5 V (vs SCE). The positive scan showed $E_p^a = 0.63$ V (vs SCE) for **7** while the negative scan following oxidation showed **5a** with $E_p^c = -0.34$ V (vs SCE). The absorption spectrum of the electrolyzed solution was indicative of a 2.8×10^{-4} M solution of **7** assuming an extinction coefficient of 3130 at 440 nm.

Electrochemical Oxidation of the Dimer 7. The dimer **7** (12.8 mg, 0.0210 mmol) was dissolved in 25 mL of a 0.2 M solution of tetra-*n*-butylammonium fluoroborate to give an 8.4×10^{-4} M solution in the dimer. Electrolysis between 0.0 and +0.90 V (vs SCE) resulted in the passage of 5.281 C of current (2.6 F/mol). The oxidized solution was examined by absorption spectroscopy and showed a 1.5×10^{-3} M solution of **5a** assuming an extinction coefficient of 8400 at 345 nm. The CV of the oxidized solution showed complete consumption of starting material in a positive scan between 0.0 and +1.5 V (vs SCE) while the negative scan showed $E_p^c = -0.34$ V (vs SCE) for **5a**.

The oxidized solution was reduced between 0.0 and −0.40 V (vs SCE) resulting in the passage of 4.747 C (90% reversibility) which corresponds to 1.2 F/mol for the reduction of **5a** if one assumes complete consumption of the dimer in the initial oxidation. Both the absorption spectrum and CV of the reduced solution were consistent with dimer **7** at 7.5×10^{-4} M concentration.

DIBAL-H Reduction of Thiapyranone 16. Thiapyranone **16** (0.66 g, 2.0 mmol) in 10 mL of dry THF under an argon atmosphere was cooled to 0 °C. DIBAL-H (6.0 mmol, 4.0 mL of a 1.5 M solution in toluene) was added dropwise via syringe. After addition was complete, the reaction mixture was stirred 0.5 h at 0 °C and was then poured into 100 mL of moist ether. The organic solution was washed with cold, 10% HCl (4 × 25 mL), was dried over sodium sulfate, and was concentrated. Chromatography on silica gel eluted with dichloromethane gave 0.49 g (78%) of the carbinol as an oil: ^1H NMR ($CDCl_3$) δ 7.30 (m, 5 H, aromatics), 6.22 (s, 1 H), 5.49 (t, 1 H, J = 5.4 Hz), 5.33 (s, 1 H), 2.51 (dd, 1 H, J = 6.2, 13.9 Hz), 2.32 (dd, 1 H, J = 6.2, 13.9 Hz), 1.43 (s, 9 H), 1.22 (s, 9 H); IR (film, NaCl) 3420 (s, br), 2960, 1363, 1015, 731, 700 cm^{-1}; FDMS, m^+/e 316 ($C_{20}H_{28}OS$).

Registry No. **1a**, 86029-92-7; **1b**, 80697-46-7; **2a**, 108035-30-9; **2b**, 80697-47-8; **2c**, 84144-56-9; **3a**, 113403-35-3; **3b**, 113403-36-4; **4a**, 113403-37-5; **4b**, 113403-38-6; **4c**, 113403-39-7; **5a**, 90461-54-4; **5b**, 90461-45-3; **6a**, 113403-42-2; **6b**, 84790-99-8; **7**, 113430-65-2; **8a**, 113403-45-5; **13a**, 104698-68-2; **13b**, 76874-66-3; **13c**, 55107-13-6; **14a**, 113403-40-0; **14b**, 71951-50-3; **14c**, 112561-34-9; **15a**, 90461-47-5; **15b**, 113403-43-3; **15c**, 113403-44-4; **16**, 113403-46-6; **17**, 113403-47-7; hexafluorophosphoric acid, 16940-81-1.

Organometallic Complexes of Osmium with Sulfur-Containing Ligands: Synthesis of *cis*-$[Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]^-$ and *cis*-$[Os(N)(CH_2SiMe_3)_2(SCN)_2]^-$ and the Synthesis and X-ray Crystal Structure of *cis*-$[Os(N)(CH_2SiMe_3)_2(2\text{-}S\text{-}NC_5H_4)]_2$

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New mononuclear complexes of osmium with sulfur-containing ligands have been prepared. The reaction of $[N\text{-}n\text{-}Bu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ with 1,2-ethanedithiol and triethylamine produces the osmium dithiolate complex $[N\text{-}n\text{-}Bu_4][Os(N)(CH_2SiMe_3)_2(SCH_2CH_2S)]$. Substitution of the halide on $[N\text{-}n\text{-}Bu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ by potassium thiocyanate gives an equilibrium mixture of two isomers of *cis*-$[N\text{-}n\text{-}Bu_4][Os(N)(CH_2SiMe_3)_2(SCN)_2]$. In the major isomer, both of the thiocyanato groups are bonded to osmium through nitrogen, while in the minor isomer osmium has one thiocyanato and one isothiocyanato ligand. 2-Pyridinethiol displaces both halides in $[N\text{-}n\text{-}Bu_4][Os(N)(CH_2SiMe_3)_2Cl_2]$ in the presence of triethylamine to form two isomers of a neutral dimer in which the 2-pyridinethiolato ligands chelate and bridge the two metal centers. The crystal structure of one isomer of $[Os(N)(CH_2SiMe_3)_2(SC_5H_4N)]_2$ was determined by single-crystal X-ray diffraction: a = 14.388 (4) Å, b = 16.209 (4) Å, c = 10.760 (4) Å, β = 91.64 (3)°, γ = 66.38 (2)°, V = 2170 (2) Å^3, Z = 2, α = 108.25 (2)°, ρ_{calcd} = 1.496 g/cm^3, triclinic space group $P\bar{1}$.

Introduction

Our interest in the influence of other ligands at the metal center on the reactivity of the nitride has led us to prepare a variety of organometallic nitrido complexes of osmium and ruthenium. The substitution of strongly σ-donating alkyl ligands for the more electron-withdrawing chlorides in the complexes $[M(N)Cl_4]^-$ dramatically alters the reactivity of the nitride. Griffith found that $[Os(N)Cl_4]^-$ reacts with tertiary phosphines at nitrogen, with reduction of the metal, to form the phosphine imidato complexes $Os(NPR_3)Cl_3(PR_3)_2$.[1] The alkyl complexes, on the other hand, react with Lewis acids at nitrogen to form adducts

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(1) Pawson, D.; Griffith, W. P. *J. Chem. Soc., Dalton Trans.* 1975, 417.