

for  $C_3H_{18}Br_2MoN_2$ : C, 24.14; H, 4.57; N, 7.04. Found: C, 26.35; H, 5.13; N, 7.11.

**Tris(*tert*-butylimido)(trimethylsilo)rhodium (10)** was prepared by stirring a mixture of 2.38 g of trimethylsilyl perhenate, 12 mL of *tert*-butyl(trimethylsilyl)amine, and 24 mL of hexamethyldisiloxane for 48 h. The solvent was removed, and the residue was distilled through an air-cooled condenser under high vacuum. To the resultant yellow oil was added 3 mL of hexamethyldisiloxane. Cooling to  $-40^\circ C$  afforded 2.3 g (64%) of **10** as bright yellow crystals, mp  $36-38^\circ C$ . NMR (benzene- $d_6$ ):  $\delta$  0.23 (s, 9 H, SiMe), 1.36 (s, 27 H, *t*-Bu). Anal. Calcd for  $C_{15}H_{36}N_3OReSi$ : C, 36.87; H, 7.42; N, 8.59. Found: C, 36.46; H, 7.34; N, 8.90.

**( $\mu$ -Oxo)( $\mu$ -trimethylsilo)( $\mu$ -perhenato)bis[bis(*tert*-butylimido)(trimethylsilo)rhodium (11)** was prepared as in the above procedure but with a reduced amount (6 mL) of *tert*-butyl(trimethylsilyl)amine. After 24 h, the solution was filtered, concentrated, and cooled to  $-40^\circ C$  to afford yellow crystals of **11** suitable for X-ray diffraction. Anal. Calcd for  $C_{25}H_{63}N_4O_8Re_3Si_3$ : C, 25.22; H, 5.33; N, 4.71. Found: C, 25.44; H, 5.48; N, 4.56.

**Trimethylsilyl pertechnetate** was prepared as follows. To a solution of 1.1 g of ammonium pertechnetate in 20 mL of  $H_2O$  (New England Nuclear) was added 1.5 g of silver nitrate. The resultant yellow precipitate of silver pertechnetate was collected by filtration and dried in vacuo (1.50 g, 91%). This material was suspended in 10 mL of hexamethylsiloxane, and 0.6 g of chlorotrimethylsilane was added. After 2 h, 0.745 g of white solid (94% of theoretical for  $AgCl$ ) was removed by filtration. The solvent was removed in vacuo to afford 1.23 g of white solid, which melted to a colorless oil at room temperature. The NMR spectrum (toluene- $d_6$ ) consisted of a singlet at

$\delta -0.07$ .

**Acknowledgment.** The author thanks Dr. G. W. Parshall for suggesting this area of research and his colleagues at Du Pont's Central Research Department for many stimulating discussions during the course of these studies. Thanks are also due to Dr. J. C. Kauer for a sample of 1-norbornanecarboxylic acid and to Dr. R. L. Harlow for preliminary x-ray crystallographic studies on compounds **5a** and **6**. I am grateful to W. M. Gray and J. W. Lockhart for skilled technical assistance.

**Registry No.** **1a**, 69039-11-8; **1b**, 69039-12-9; **2**, 84416-72-8; **3a**, 70024-35-0; **3b**, 71852-01-2; **5a**, 71851-94-0; **5b**, 71851-95-1; **5c**, 84416-73-9; **6**, 72207-45-5; **7a**, 72207-46-6; **8a**, 73448-07-4; **8b**, 73448-06-3; **9a**, 84416-75-1; **9b**, 84416-76-2; **10**, 73321-57-0; **11**, 73460-33-0; (dtc) $_3Ta(NBu-t)$ , 84416-70-6;  $(Me_3SiO)_2CrO(NBu-t)$ , 83619-58-3;  $(t-BuNH)_2(t-BuN)(CH_3)W[N(t-Bu)(ZnCH_3)]$ , 84416-74-0;  $Me_3SiOReO_3$ , 16687-12-0;  $TaCl_5$ , 7721-01-9;  $LiNMe_2$ , 3585-33-9;  $LiNHBu-t$ , 37828-54-9;  $Ta(NMe_2)_5$ , 19824-59-0;  $t-BuNH_2$ , 75-64-9;  $NbCl_5$ , 10026-12-7;  $Cs_2$ , 75-15-0;  $VCl_3$ , 7718-98-1;  $Me_3SiN_3$ , 4648-54-8;  $(Me_3SiO)_3OVCl$ , 5590-56-7;  $t-BuNH(SiMe_3)$ , 5577-67-3;  $RNH(SiMe_3)$  ( $R = 1$ -adamantyl), 36960-58-4;  $CrO_3$ , 1333-82-0;  $MoCl_2O_2$ , 13637-68-8;  $RNH(SiMe_3)$  ( $R = 1$ -norbornyl), 84416-77-3;  $Me_2Zn$ , 544-97-8;  $Me_3SiOReO_3$ , 16687-12-0; vanadium oxide trichloride, 7727-18-6; benzaldehyde, 100-52-7; hexamethyldisiloxane, 107-46-0; ammonium pertechnetate, 13598-66-8; chlorotrimethylsilane, 75-77-4.

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## New Routes to Bis(*F*-alkyl) Sulfones

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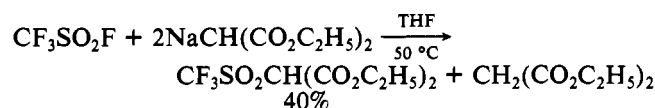
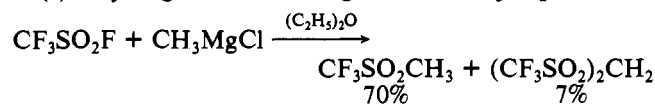
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Bis(*F*-alkyl) sulfones result from the interaction of  $CF_3SO_2F$  with  $C_2F_4$  at  $90-100^\circ C$  and surprisingly from  $SOF_4$  with  $C_2F_4$  at  $25^\circ C$ , both in the presence of  $CsF$  in diglyme. Hydrolysis of bis(*F*-alkyl) sulfoxyl difluorides also gives sulfones.

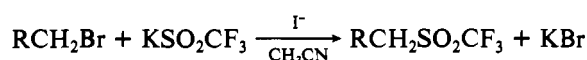
### Introduction

Bis(polyfluoroalkyl) sulfones and other less fluorinated sulfones continue to be the subjects of considerable study, particularly in cases where the  $R_fSO_2^-$  group is utilized either as a nucleophile or as a nucleophilic leaving group.<sup>2-6</sup> Some examples of the known synthetic pathways for sulfone preparation include the following:

(I) alkyl organometallic reagents with  $CF_3SO_2F$ .<sup>7,8</sup>

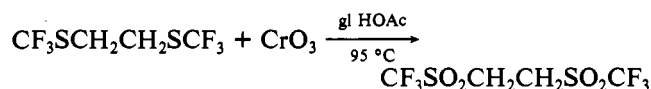
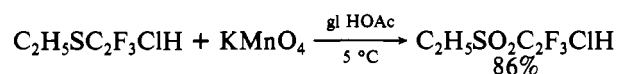


(II) alkyl bromides and potassium *F*-methanesulfonate<sup>9</sup>



$R = C_6H_5$  (95%);  $C_6H_5CO$  (80%);  $n-C_3H_7$  (70%)

(III) oxidation of sulfides and sulfoxides<sup>10-12</sup>



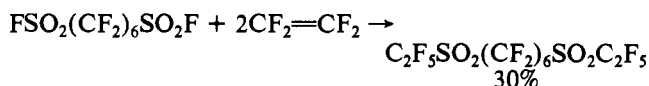
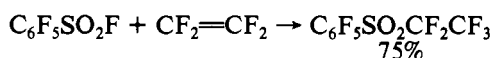
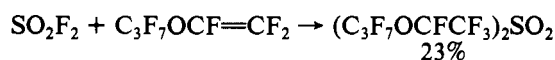
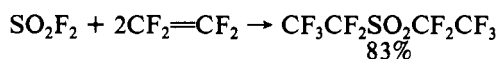
While all of the preceding methods are effective in preparing partially fluorinated sulfones, their utility in producing poly-

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- (2) Hendrickson, J. B.; Sternbach, D. D.; Bair, K. W. *Acc. Chem. Res.* **1977**, *10*, 306.
- (3) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 1.
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- (11) Harris, J. F., Jr. *J. Org. Chem.* **1967**, *32*, 2063.
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fluorinated or totally fluorinated sulfones has not been demonstrated.

The pioneering work of Temple<sup>13</sup> is a benchmark in the synthesis of bis(*F*-alkyl) or *F*-alkyl *F*-aryl sulfones via the reactions of SO<sub>2</sub>F<sub>2</sub> or R<sub>1</sub>SO<sub>2</sub>F with *F*-olefins in the presence of CsF in diglyme at 60–80 °C, e.g.

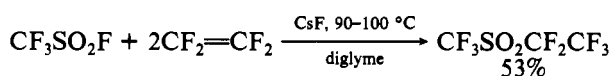


The electrochemical fluorination of dimethyl sulfone has been reported to give bis(*F*-methyl) sulfone.<sup>14</sup>

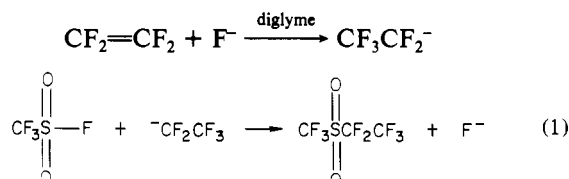
We now wish to report that selected bis(*F*-alkyl) sulfones can be prepared by one or more of three methods that are discussed below.

### Results and Discussion

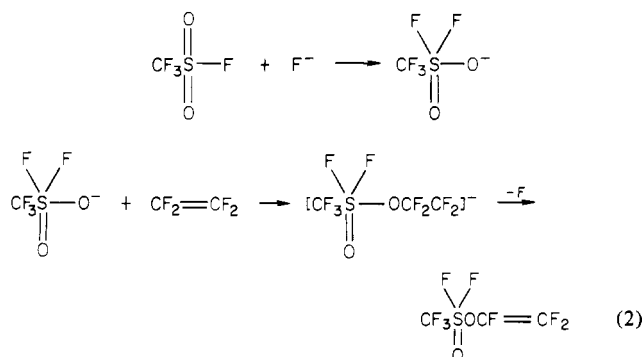
In a reaction that is strictly analogous to Temple's C<sub>6</sub>F<sub>5</sub>S-O<sub>2</sub>F addition to C<sub>2</sub>F<sub>4</sub> shown above, we have demonstrated that CF<sub>3</sub>SO<sub>2</sub>F will add to C<sub>2</sub>F<sub>4</sub>, viz.



in what we believe to be the first example of such an addition by CF<sub>3</sub>SO<sub>2</sub>F. As others before us have observed, attempts to add CF<sub>3</sub>SO<sub>2</sub>Cl to similar systems resulted only in the addition of CF<sub>3</sub> and Cl to the olefin with concomitant release of SO<sub>2</sub>. Two possible mechanisms for the successful addition of CF<sub>3</sub>SO<sub>2</sub>F to the *F*-olefin are



or if the F<sup>-</sup> ion had attacked the CF<sub>3</sub>SO<sub>2</sub>F initially, the scheme (2) could be written. However, no evidence for a vinyl product

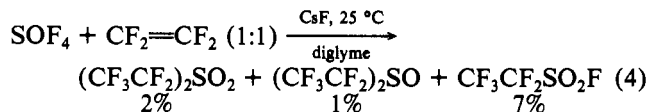
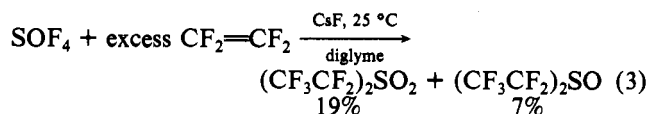


was observed; thus, mechanism (1) must be the one operative in this case.

It was surprising to note that under the conditions used all other olefins that were tried (CF<sub>2</sub>=CFCl, CF<sub>2</sub>=CHCl,

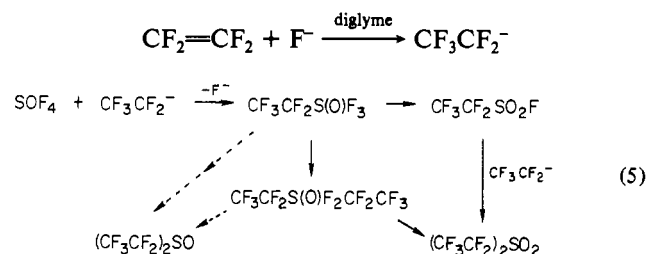
CFCl=CFCl, *c*-C<sub>4</sub>F<sub>6</sub>) gave only trace quantities or none of the sulfone derivatives.

The reaction of thionyl tetrafluoride with tetrafluoroethylene leads somewhat unexpectedly to bis(*F*-ethyl) sulfone, (see eq 3 and 4). In both cases, but in larger amounts for (4), a



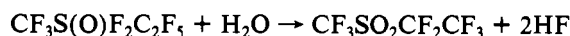
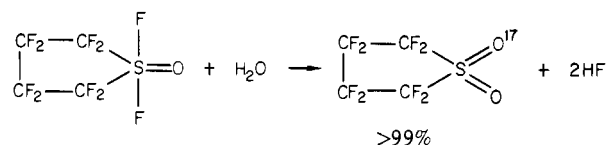
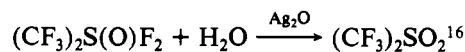
reactive intermediate was produced but was not characterized. The sulfone, (CF<sub>3</sub>CF<sub>2</sub>)<sub>2</sub>SO<sub>2</sub>, had been prepared previously and its synthesis was confirmed by comparing the <sup>19</sup>F NMR spectra.<sup>13</sup> The sulfoxide, (CF<sub>3</sub>CF<sub>2</sub>)<sub>2</sub>SO, was prepared earlier in our laboratory and all spectral data are identical.<sup>15</sup>

The mechanism for this reaction is thought to involve the steps shown in (5). It is not clear at what stage a reduction

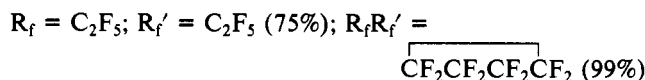
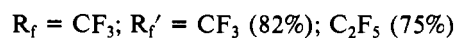
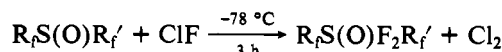


step gives rise to the sulfoxide, nor is it understood what species acts as the reductant. Since many of the compounds produced by this method can be more readily synthesized by using other routes, further studies were not pursued.

In some current studies involving the reactions of (CF<sub>3</sub>)<sub>2</sub>S(O)F<sub>2</sub>, the observation was made that hydroxy-containing species (including water) were effective in forming the sulfone, (CF<sub>3</sub>)<sub>2</sub>SO<sub>2</sub>, e.g.



This method of hydrolysis of sulfoxidylfluorides to form sulfones is the most versatile and comprehensive one. The sulfoxidylfluorides can be readily prepared via the fluorination of bis(*F*-alkyl) sulfoxides with chlorine monofluoride,<sup>17,18</sup> viz.



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and subsequently hydrolyzed to the sulfone in high yield.

### Experimental Section

**Materials.** The compounds used in this work were obtained from commercial sources [CsF (Aldrich),  $\text{CF}_2=\text{CFCl}$ ,  $\text{CF}_2=\text{CHCl}$ ,  $\text{CFCl}=\text{CFCl}$ ,  $\text{c-C}_4\text{F}_6$ ,  $\text{CF}_3\text{SO}_2\text{Cl}$  (PCR)] and used without further purification.

**General Procedure.** Most gases and volatile liquids were handled in a conventional Pyrex glass vacuum manifold equipped with a Heise Bourdon tube gauge and a Televac vacuum gauge, which were connected directly to the manifold. Gaseous materials were measured with the assumption of the ideal gas law. Nonvolatile materials were weighed. Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer using a 10-cm cell equipped with KBr windows for volatile compounds and using a liquid film on KBr plates for nonvolatile liquids.  $^{19}\text{F}$  NMR spectra were obtained on a Varian EM-360L spectrometer and a JEOL FX-90Q spectrometer operating at 54.6 and 84.3 MHz, respectively.  $^1\text{H}$  NMR spectra were recorded on either a Varian EM-360 or EM-360L spectrometer operating at 60.0 MHz or a JEOL FX-90Q spectrometer at 89.56 MHz. All bands are reported relative to  $\text{CCl}_3\text{F}$  or  $\text{Me}_4\text{Si}$ . The usual solvent was  $\text{CDCl}_3$ . Mass spectra were obtained with a Perkin-Elmer Hitachi RMU-6E spectrometer operating at 17 eV. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, West Germany, or at the University of Idaho.

**Reaction of  $\text{C}_2\text{F}_4$  with  $\text{CF}_3\text{SO}_2\text{F}$ .** To a 75-mL stainless-steel vessel equipped with a stainless-steel Hoke valve and ball bearings were added 136 mmol of predried CsF, 209 mmol of diglyme (dried over sodium), and 49 mmol of  $\text{CF}_3\text{SO}_2\text{F}$ . A 9.9-mmol sample of  $\text{C}_2\text{F}_4$  was added, and the reaction mixture was heated to 100 °C (1 h) with shaking (10 min). Additional amounts of  $\text{C}_2\text{F}_4$  were added (with shaking, 1 h): 11.8 mmol (90 °C, 1 h) and 20.5 mmol (80–90 °C, 57 h). The products of the reaction were separated by fractional condensation;  $\text{CF}_3\text{SO}_2\text{CF}_2\text{CF}_3$  was obtained in 53% yield. The infrared spectrum has the following bands ( $\text{cm}^{-1}$ ): 1425 (s), 1329 (m), 1240 (vs, sh at 1213), 1117 (ms), 980 (m), 880 (w), 834 (w), 761 (w), 622 (s, sh at 650), 558 (m), 524 (m). The  $^{19}\text{F}$  NMR spectrum consists of three peaks:  $\text{CF}_3\text{S}$  ( $\phi$  -71.2),  $\text{CF}_2$  ( $\phi$  -112.9), and  $\text{CF}_3\text{C}$  ( $\phi$  -78.8) in the ratio of 3:2:3;  $J_{\text{CF}_3\text{S}-\text{CF}_2} = 8.4$  Hz,  $J_{\text{CF}_3\text{C}-\text{CF}_2} = 1.3$  Hz, and  $J_{\text{CF}_3\text{S}-\text{CF}_3\text{C}} = 2.3$  Hz. A molecular ion was not observed but other appropriate fragment ions were found: 183 ( $\text{M} - \text{CF}_3$ )<sup>+</sup>, 133 ( $\text{M} - \text{CF}_2\text{CF}_3$ )<sup>+</sup>,

119 ( $\text{M} - \text{CF}_3\text{SO}_2$ )<sup>+</sup>, 100 ( $\text{M} - \text{CF}_3\text{SO}_2\text{F}$ )<sup>+</sup>, and 69 ( $\text{CF}_3$ )<sup>+</sup>.

Anal. Calcd: S, 12.72; F, 60.3. Found: S, 12.87; F, 61.1.

**Reaction of  $\text{CF}_3\text{SO}_2\text{F}$  with  $\text{CF}_2=\text{CFCl}$ ,  $\text{CF}_2=\text{CHCl}$ ,  $\text{CFCl}=\text{CFCl}$ , and  $\text{c-C}_4\text{F}_6$ .** With use of essentially the same method reported for  $\text{C}_2\text{F}_4$ , these fluoroolefins reacting with  $\text{CF}_3\text{SO}_2\text{F}$  failed to produce any sulfone derivative except in trace quantities.

**Reaction of Excess  $\text{C}_2\text{F}_4$  with  $\text{SOF}_4$ .** To the 75-mL stainless-steel vessel used with  $\text{CF}_3\text{SO}_2\text{F}$  were added 57 mmol of CsF, 237 mmol of diglyme, and 15.1 mmol of  $\text{SOF}_4$ . Excess  $\text{C}_2\text{F}_4$  was then added (49.8 mmol), and the mixture was warmed to 32 °C (12 h) and at room temperature (67 h) with vigorous shaking. The products of the reaction were separated by fractional condensation. The following products were found in the -78 °C trap:  $(\text{CF}_3\text{CF}_2)_2\text{SO}_2$ , 2.8 mmol;  $(\text{CF}_3\text{CF}_2)_2\text{SO}$ , 1.0 mmol. The trap at -146 °C contained a reactive compound, which when warmed to room temperature in glass decomposed. The -40 °C trap contained diglyme and the dimer of TFE.

**Reaction of  $\text{C}_2\text{F}_4$  with  $\text{SOF}_4$ .** To a 150-mL stainless-steel reaction vessel equipped with a stainless-steel Whitey valve and stainless-steel ball bearings were added 82 mmol of CsF, 248 mmol of diglyme, 16.5 mmol of  $\text{SOF}_4$ , and 18.9 mmol of  $\text{C}_2\text{F}_4$ . The reaction was shaken vigorously (108 h) at room temperature. The products of the reaction were separated by fractional condensation. The following products were found:  $(\text{CF}_3\text{CF}_2)_2\text{SO}$ , 0.4 mmol;  $(\text{CF}_3\text{CF}_2)_2\text{SO}_2$ , 0.1 mmol;  $\text{CF}_3\text{CF}_2\text{SO}_2\text{F}$ , 1.1 mmol. Other products identified were  $\text{SO}_2\text{F}_2$ , and the dimer of  $\text{C}_2\text{F}_4$ . The fraction of -196 °C also contained an unidentified substance that could not be characterized due to its instability.

**Reaction of  $\text{CF}_3\text{S(O)F}_2\text{CF}_2\text{CF}_3$  with Water.** To a 100-mL Pyrex glass vessel equipped with a Kontes Teflon stopcock and Teflon-coated stirring bar were added 44 mmol of CsF, 6 mmol of  $\text{H}_2\text{O}$ , and 0.75 mmol of  $\text{CF}_3\text{S(O)F}_2\text{CF}_2\text{CF}_3$ . After the mixture was stirred at room temperature for 3 days, 0.46 mmol of  $\text{CF}_3\text{SO}_2\text{CF}_2\text{CF}_3$  was recovered; yield 61%. The infrared of the product agreed with that found previously by reacting  $\text{C}_2\text{F}_4$  with  $\text{CF}_3\text{SO}_2\text{F}$ .

**Acknowledgment** is expressed to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation (Grants CHE-8100156 and CPE-8114393) for support of this research. We thank Dr. G. Knerr for NMR and mass spectra.

**Registry No.**  $\text{C}_2\text{F}_4$ , 116-14-3;  $\text{CF}_3\text{SO}_2\text{F}$ , 335-05-7;  $\text{CF}_3\text{SO}_2\text{CF}_2\text{CF}_3$ , 84416-69-3;  $\text{SOF}_4$ , 13709-54-1;  $(\text{CF}_3\text{CF}_2)_2\text{SO}_2$ , 14930-22-4;  $(\text{CF}_3\text{CF}_2)_2\text{SO}$ , 33622-19-4;  $\text{CF}_3\text{CF}_2\text{SO}_2\text{F}$ , 354-87-0;  $\text{CF}_3\text{S(O)F}_2\text{CF}_2\text{CF}_3$ , 33564-24-8.

(18) Sauer, D. T.; Shreeve, J. M. *Z. Anorg. Allg. Chem.* 1971, 385, 113.

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## Electron Transfer. 60. Reduction of Carboxylato-Bound Chromium(V) with Hydroxylamine<sup>1</sup>

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The chelated bis(carboxylato)chromium(V) complex I reacts smoothly with  $\text{NH}_2\text{OH}^+$  at pH 3.6–4.7 in the presence of an excess of the parent carboxylic acid. The spectral, magnetic, and ion-exchange properties of the chromium products support the formulation of these as structures II and III,  $\text{NO}^+$  derivatives of low-spin chromium(I) rather than  $\text{NO}^-$  complexes of chromium(III). The reaction is retarded by increasing acidity or by addition of unbound carboxylato ligand. The empirical rate law (eq 1) is consistent with a mechanism initiated by rapid and reversible loss of one carboxylato group from the Cr(V) oxidant (with  $K_{\text{diss}} = 5.8 \times 10^{-2}$  M), followed by formation of a Cr(V)– $\text{NH}_2\text{OH}$  precursor complex (with attendant deprotonation) ( $k = 0.38 \text{ M}^{-1} \text{ s}^{-1}$ ) and then by an act of internal electron transfer involving a net 4e change. It further appears that the two Cr(I)–NO products, one an uncharged dichelate and the other a 1+ monochelate, result from a competition between the parent carboxylate anion and solvent water for a coordinatively unsaturated Cr(I) intermediate. No evidence for intervention of a chromium(III) intermediate was obtained.

The first air-stable water-soluble carboxylato derivatives of chromium(V) were described in 1979.<sup>2</sup> Shortly afterward,

experiments dealing with the reduction, using hydrazine, of one of these complexes, sodium bis(2-ethyl-2-hydroxybutyrate)oxochromate(V) (I) were reported;<sup>3</sup> this study indicated that the reaction proceeded smoothly through a pair

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