The last quantity, S_0, is available from

$$S_0 = M_0(a_0 - b)/W'_0$$

W'_0 = mg of pure reactant combusted
a_0 = rate of drift (mV/min) from CO_2 from W'_0 mg.

The value of S_0 used in the computation of percentages was the average of four separate determinations. The results of these calculations are set forth in Table III.

Registry No.—**5,** 23042-41-3; **6,** 7006-52-2; **7,** 619-26-1; **8,** 60498-57-9; **9,** 60498-58-0; **10,** 60498-59-1; **11,** 35966-84-8.

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(2) To whom correspondence should be addressed.
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Synthesis and Chemistry of Some 2-Aminoethenesulfonyl Fluorides. An Unusual Manganese Dioxide Oxidation

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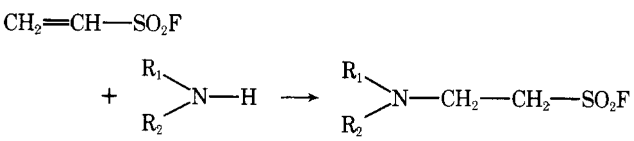
Some recent work in this laboratory demonstrated the facile fluorosulfonylethylation of various amines with vinylsulfonyl fluoride.[1] We wish to report that β-fluorosulfonylethylamines 1 are dehydrogenated by active manganese dioxide to afford novel 2-aminoethenesulfonyl fluorides.

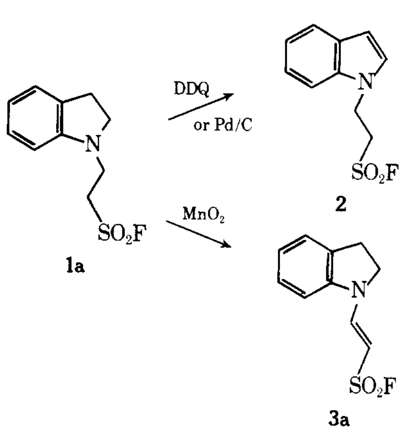


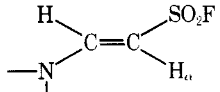
$$CH_2{=}CH{-}SO_2F + R_1R_2N{-}H \longrightarrow R_1R_2N{-}CH_2{-}CH_2{-}SO_2F$$

1

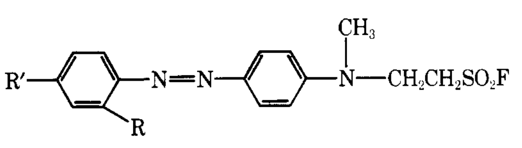
R = H, alkyl, or aryl

Jansen and co-workers have described the dehydrogenation of indolines with active manganese dioxide.[2] We found that, although indole **2** could be prepared from indoline **1a** by using dichlorodicyanobenzoquinone or palladium on carbon, reaction of **1a** with active MnO_2 afforded a new substance, **3a,** which was isomeric with **2.** Compound **3a** was assigned the enaminosulfonyl fluoride structure shown on the basis of its empirical formula and spectral properties (see Experimental Section). In particular, the ^1H NMR spectrum of **3a** points to the presence of a highly polarized olefinic system, wherein H_α is coupled with the fluorine atom.

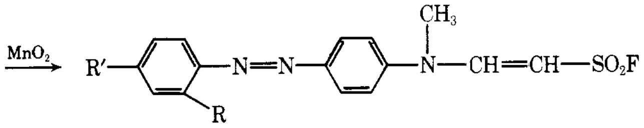




In view of the unusual course of this oxidation, the reaction of a series of substituted 2-aminoethanesulfonyl fluorides with MnO_2 was carried out; Table I gives the structures and yields. Two additional examples were provided by the preparation of dyes **3g** and **3h.** Further experiments delineated the scope of the oxidation. Sulfonyl fluorides **4** and **5** did not react with MnO_2, and β-cyanoethylamine **6** was converted to enamine **7** very slowly and in poor yield.



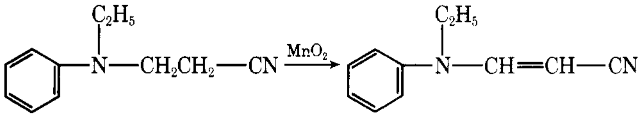
1g, R = SO_2CH_3; R′ = NO_2
1h, R = H; R′ = SO_2F



3g, R = SO_2CH_3; R′ = NO_2(56%)
3h, R = H; R′ = SO_2F(59%)

$$\underset{\mathbf{4}}{CH_3(CH_2)_2CH_2SO_2F} \xrightarrow{MnO_2} \text{no reaction}$$

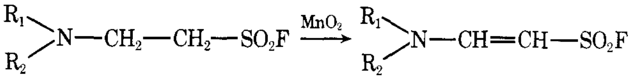
$$\underset{\mathbf{5}}{ClCH_2CH_2SO_2F} \xrightarrow{MnO_2} \text{no reaction}$$



6 **7**(22%)

Henbest and co-workers[3,4] have reported the isolation of low yields of enamines as intermediates in the MnO_2 dealkylation of tertiary amines; the enamines were generally unstable in the presence of MnO_2. In the case at hand, the stability of enaminosulfonyl fluorides (vide infra) could account for the good yields obtained. One possible mechanism for the oxidation involves the following electron-transfer process. That electron transfer from β-fluorosulfonylethylamines does indeed lead to the observed products was demonstrated by uv irradiation of **1b** in the presence of benzophenone; **3b** was

Table I.[a] MnO_2 Oxidation of Substituted 2-Aminoethanesulfonyl Fluorides



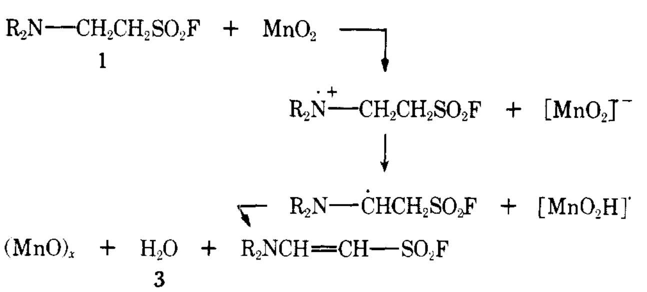
$$R_1R_2N-CH_2-CH_2-SO_2F \xrightarrow{MnO_2} R_1R_2N-CH=CH-SO_2F$$

1a–f **3a–f**

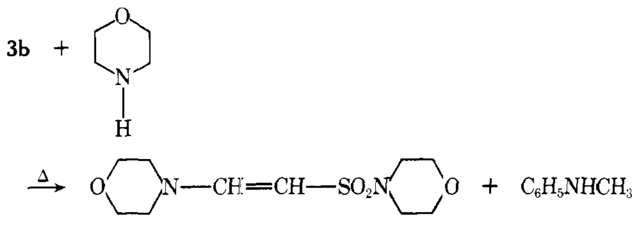
	Starting material		Product			
	R_1	R_2	R_1	R_2	Yield, %	Mp, °C
1a	(1-indolinyl)		**3a** (1-indolinyl)		95	142.5–143.5
1b	C_6H_5	CH_3	**3b** C_6H_5	CH_3	84	52.5–53.5
1c	C_6H_5	C_2H_5	**3c** C_6H_5	C_2H_5	96[b]	Oil
1d	CH_3	CH_3	**3d** CH_3	CH_3	33[b]	Oil
1e	C_6H_5	H	**3e** C_6H_5	H	42	115–117
1f	C_6H_5	$CH_2CH_2SO_2F$	**3f** C_6H_5	$CH_2CH_2SO_2F$	86	96–97.5

[a] Yields are based on isolated products; all compounds gave satisfactory elemental and spectral analyses unless otherwise noted. [b] Satisfactory combustion analysis not obtained; ir, NMR, mass, and uv spectra in agreement with assigned structure.

produced cleanly. Previous work[5–7] has established the electron-transfer mechanism in amine–benzophenone photochemical redox systems.



Aminoethenesulfonyl fluorides **3a–h** were found to be very stable, and selective reactions of the enamine or sulfonyl fluoride functions were not observed. Compound **3b**, for example, reacted with morpholine only at reflux to give **8** and *N*-methylaniline as the sole products. Compound **3b** did not react with cyclopentadiene and was not reduced to **1b** even under forcing conditions.[8]



8

In summary, it has been found that β-fluorosulfonylethylamines undergo facile dehydrogenation by active MnO_2 to afford novel enaminosulfonyl fluorides, probably via an electron-transfer mechanism.[11] The product enamines are resonance stabilized and react with nucleophiles only under forcing conditions.

Experimental Section

Melting points are uncorrected. Infrared spectra were recorded using a Perkin-Elmer Model 137 instrument; NMR spectra were obtained with Varian EM-360 and JEOLCO MH-100 spectrometers. Mass spectra were taken with a Consolidated Electrodynamics Corp. Model 21-110B spectrometer system.

Starting Materials. The substituted 2-aminoethanesulfonyl fluorides **1a–h** were prepared from vinylsulfonyl fluoride and the appropriate amine in ether solution according to the general procedure described previously.[1] Active manganese dioxide was prepared by the procedure of Attenburrow et al.,[9] or by air oxidation of ammoniacal manganese salts.[10]

General Procedure for MnO_2 Oxidation. The preparation of **3a** serves as a typical example. A solution of 10.6 g (0.046 mol) of 2-(2,3-dihydro-1*H*-indol-1-yl)ethanesulfonyl fluoride (**1a**) in 300 ml of chloroform was treated with 100 g of active MnO_2 and stirred vigorously for 2 h at 27 °C. The mixture was then filtered (Celite, $CHCl_3$ wash), and the filtrate stripped in vacuo to afford 10.1 g (95%) of 2-(2,3-dihydro-1*H*-indol-1-yl)ethenesulfonyl fluoride (**3a**) as an odorless, tan solid. The analytical sample was thrice recrystallized from ethanol and had mp 142.5–143.5 °C; ir (mull) 6.16, 6.28, 7.27, 8.42, and 11.03 μ; NMR (acetone-d_6) δ 8.30 (d, J = 13 Hz, 1 H), 7.38 (m, 4 H), 5.58 (d of d, J = 3.5, 13 Hz, 1 H), 4.0 (m, 2 H), and 3.37 (m, 2 H); uv (EtOH) λ_{max} (ϵ) 313 nm (24 078), 279 (21 655); mass spectrum *m/e* 227 (P).

Anal. Calcd for $C_{10}H_{10}FNO_2S$: C, 52.83; H, 4.44; N, 6.17. Found: C, 52.92; H, 4.60; N, 6.10.

Photochemical Preparation of 3b from 1b. A solution of 0.10 g of **1b** and 0.20 g of benzophenone in 30 ml of acetonitrile was irradiated with a bank of 16 Rayonet 3200-Å lamps for 16 h. Careful thin layer chromatography (TLC) analysis (two solvent systems) of the light brown reaction mixture disclosed the presence of **1b** and **3b** in ca. 1/1 ratio, in addition to benzophenone and benzpinacol.

4-{[2-(4-Morpholinyl)ethenyl]sulfonyl}morpholine (8). A mixture of 1.0 g of **3b** and 10 g of morpholine was refluxed for 4.0 h, at which time TLC analysis showed loss of **3b** and formation of *N*-methylaniline and a new, more polar, product. The reaction mixture was stripped in vacuo and the brown semisolid residue chromatographed on silica gel 1.5-mm plates (3% CH_3OH in $CHCl_3$ elution). Isolation of the (polar) product band gave 0.67 g (55%) of **8** as an oil which crystallized when scratched. An analytical sample was recrystallized from ethanol: mp 120.5–121.5 °C; ir (mull) 6.20, 6.80, 7.58, 8.78, 8.98 (br), 9.39, 10.70, 11.26, 11.48, 11.77, 12.56, and 13.8 μ (br); NMR ($CDCl_3$) δ 7.08 (d, J = 13 Hz, 1 H), 4.84 (d, J = 13 Hz, 1 H), 3.80 (m, 8 H), 3.29 (m, 4 H), 3.06 (m, 4 H); mass spectrum *m/e* 262 (P).

Anal. Calcd for $C_{10}H_{18}N_2O_4S$: C, 45.78; H, 6.92; N, 10.68. Found: C, 45.93; H, 6.78; N, 10.82.

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Registry No.—**1a**, 60538-03-6; **1b**, 60353-82-4; **1c**, 60353-81-3; **1d**, 660-13-9; **1e**, 60353-00-6; **1f**, 60353-09-5; **3a**, 60538-04-7; **3b**, 60538-05-8; **3c**, 60538-06-9; **3d**, 60538-07-0; **3e**, 60538-08-1; **3f**, 60538-09-2; **8**, 60538-10-5; vinylsulfonyl fluoride, 677-25-8; R_1R_2NH (R_1R_2 = 1-indolinyl), 120-72-9; R_1R_2NH (R_1 = Ph; R_2 = Me), 100-61-8; R_1R_2NH (R_1 = Ph; R_2 = Et), 103-69-5; R_1R_2NH (R_1 = Me; R_2 = Me), 124-40-3; R_1R_2NH (R_1 = Ph; R_2 = H), 62-53-3; MnO_2, 1313-13-9; morpholine, 110-91-8.

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