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THE FACILE ADDITION OF FLUOROSULFURIC ACID TO AN EPOXIDE

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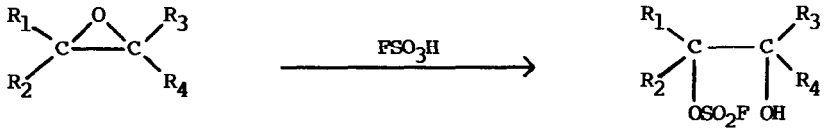
Abstract. Fluorosulfuric acid, a very poor nucleophile, was found to add to several epoxides, yielding 1,3,2-dioxathiolane 2,2-dioxides. These cyclic sulfates could also be obtained by reacting the epoxides with sulfur trioxide. The intermediacy of the fluorosulfate of a 1,2-diol, which readily cyclized in base, has been demonstrated in one case.

Fluorosulfuric acid, one of the strongest protic acids known, has been extensively used in nmr studies, alone or in combination with Lewis acids. In large part, this use of FSO_3H is made possible by the very low nucleophilicity and therefore the low chemical reactivity of the acid toward organic molecules. One exception to this pattern is described.

The direction of the initial bond breaking in acid-catalyzed reactions of epoxides can usually be explained on the basis of the relative stability of incipient carbonium ion intermediates. By this criterion, **1** is expected to be quite resistant to molecular rearrangement since opening of one carbon-oxygen bond would generate a primary carbonium ion, while opening of the other would produce another high energy carbonium ion, one destabilized by two adjacent carbonyl groups.

The epoxyester **1** was treated with FSO_3H under the mild conditions used with other glycidic esters.[1] A CCl_4 or $CHCl_3$ solution containing an excess of FSO_3H was kept at 0 °C for 1 h. It was poured over ice, and the organic extract washed with $NaHCO_3$ and dried. A single product was observed, along with a small amount of starting material. Purification by tlc yielded an oil (42% yield). Its nmr spectrum showed 3 types of hydrogens in the ratio found in **1** (3:2:1), suggesting that no molecular rearrangement with group migration had taken place. While ester groups were clearly intact (triplet at 1.35 and quartet at 4.4 ppm, J = 7 Hz), the remaining hydrogens appeared as a singlet at 5.1 ppm, considerably lower than in the original oxirane (3.2 ppm). The carbon-13 nmr showed the $COOCH_2CH_3$ group (163.1, 64.9, and 13.9), one quaternary carbon (83.7) and one additional carbon (71.7 ppm) to which the low field protons must have been attached. The ir spectrum contained strong bands at 1425 and 1230 cm^{-1} characteristic of organic sulfates. Finally, the highest peak in the mass spectrum was at m/e 269.0326, corresponding to the introduction of the elements of H + SO_3.

Three isomeric dioxathiolane 2,2-dioxide structures (**2**, **3**, **4**) were consistent with the spectral data (assuming the capture of one H by the molecular ion in the mass spectrometer), but an unambiguous assignment was difficult on the basis of these data alone.



1 $R_1 = R_2 = H$, $R_3 = R_4 = COOC_2H_5$

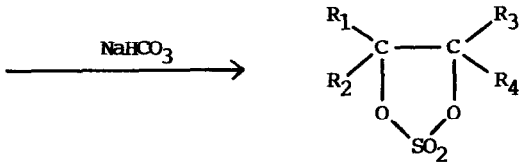
5 R_1, $R_2 = H$, CH_3, $R_3 = CONH_2$, $R_4 = COOC_2H_5$

8 $R_1 = H$, $R_2 = CH_3$, $R_3 = R_4 = COOC_2H_5$

10 $R_1 = R_2 = CH_3$, $R_3 = R_4 = COOC_2H_5$

12 $R_1 = CH_3$, $R_2 = R_3 = H$, $R_4 = COOC_2H_5$

6 R_1, $R_2 = H$, CH_3, $R_3 = CONH_2$, $R_4 = COOC_2H_5$

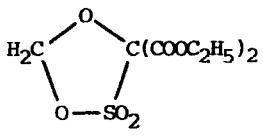


4 $R_1 = R_2 = H$, $R_3 = R_4 = COOC_2H_5$

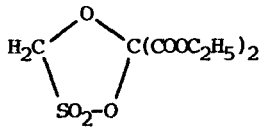
7 R_1, $R_2 = H$, CH_3, $R_3 = CONH_2$, $R_4 = COOC_2H_5$

9 $R_1 = H$, $R_2 = CH_3$, $R_3 = R_4 = COOC_2H_5$

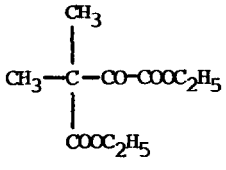
13 $R_1 = CH_3$, $R_2 = R_3 = H$, $R_4 = COOC_2H_5$



2



3



11

Structures **2** and **3**, which would have followed from the opening of the C-C bond in **1**, are 1,4,2-dioxathiolane 2,2-dioxides. Little is known about the chemistry and spectral data of this ring system, except for one report that its photolysis or thermolysis generated an epoxide by

lamp.

A simple synthesis of the 1,3,2-dioxathiolane 2,2-dioxide (cyclic sulfate) system treats an oxirane with SO_3.[4,5] This procedure, applied to **1**, yielded a product identical in all respects to that obtained in the FSO_3H reaction, which must therefore be **4**. The nmr signal at 5.1 ppm, assigned to the protons at C-5 agrees with the data on ring protons in cyclic sulfates, found at 5.0-5.3 ppm.[6]

Several other examples of this new reaction of FSO_3H with epoxides have been uncovered, but the process lacks generality. Further substitution of **1** with one methyl group still resulted in FSO_3H addition (**8** to **9**), but the presence of two methyls, favoring the more facile formation of a tertiary carbonium ion, led to a molecular rearrangement with carboethoxyl group migration (**10** to **11**).

The unambiguous proof for the conservation of the contiguity of the ring carbons in going from an original oxirane to a final product was derived from a study with **12**, with protons on adjacent carbons, allowing for an easier nmr analysis. The ring protons in the reaction product appeared as a multiplet at 5.35 ppm, in support of **13**, whereas a structure related to **2** or **3** would have required one singlet and one quartet (with different chemical shifts) for these protons.

A careful analysis of the reaction of **5** with FSO_3H revealed the formation of an intermediate. For example, when the crude reaction mixture was poured over ice and extracted without neutralization, crystalline **6** was obtained as a single isomer of undetermined stereochemistry in 74% yield. When a solution of **6** was washed with dil. $NaHCO_3$, the cyclic product **7** was formed quantitatively. As with all the cyclic sulfates mentioned in this note, the same product was obtained by reacting the initial oxirane (here **5**) with SO_3.[7]

The detailed mechanism of the addition of FSO_3H to the less substituted epoxides is unknown. The actual formation of a primary (in the case of **1** and **5**) or secondary carbonium ion (in the case of **8**) trapped by reaction with the solvent, or the more likely nucleophilic attack by the solvent onto a protonated epoxide are alternatives which deserve consideration. In either case, the ring closure occurs through base-catalyzed dehydrofluorination during the work-up.

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6. Mueller, K. F.; Cziesla, M. J. J. Org. Chem. **1969**, 34, 917; Tong, Y. C.; Tomalia, D. A.; Sheetz, D. P. U. S. Patent 3,454,597, 1969.

7. **6**: M.p. 93-97 ^{o}C, nmr (CD_3COCD_3) 7.3 (br s, 1 H, disappeared in the presence of D_2O, 5.85 (q, J = 6, 1 H), 4.3 (q, J = 7, 1 H), 4.25 (br s, 2 H), 1.6 (d, J = 6, 3 H), 1.3 (t, J = 7, 3 H); ^{19}F nmr (CD_3COCD_3): s 41.3 ppm downfield from intern. $CFCl_3$; ^{13}C nmr (CD_3COCD_3) 169.5 and 168.4 (CO), 89.4 ($\underline{C}HOSO_2F$), 81.9 ($\underline{C}[CONH_2][COOC_2H_5]$), 63.9 ($CH_2$), 14.6 ($CH_3$), 13.95 ($\underline{C}H_3CH_2O$); mass spec. 274 (M + 1); Anal. Calcd. for $C_7H_{12}FNO_7S$: C 30.77, H 4.33, S 11.73; Found C 30.88, H 4.37, S 11.87.

   7: m.p. 124-127 ^{o}C, nmr (CD_3COCD_3) 7.45 (br s, 2 H), 5.6 (q, J = 6, 1 H), 4.35 (q, J = 7, 2 H), 1.65 (d, J = 6, 3 H), 1.35 (t, J = 7, 3 H); ^{13}C nmr (CD_3COCD_3:CD_3SOCD_3, 50:1) 164.8 and 163.2 (CO), 88.9 ($\underline{C}[CONH_2][CO_2C_2H_5]$), 83.0 ($\underline{C}HCH_3$), 63.99 ($CH_2$), 15.8 ($CH_3$), 13.95 ($\underline{C}H_3CH_2$); ir (nujol) 3320 and 3200 (NH_2), 1740 (CO, ester), 1685 (CO, amide), 1400 and 1245 cm^{-1} ($ROSO_2OR$); Anal. Calcd. for $C_7H_{11}NO_7S$: C 33.20, H 4.38, N 5.53, S 12.66; Found C 32.96, H 4.10, N 5.54, S 12.74.

   9: Nmr ($CDCl_3$) 5.5 (q, J = 6.5, 1 H), 4.4 (q, J = 7, 4 H), 1.6 (d, J = 6.5, 3 H), and 1.35 (t, J = 7, 6 H); ^{13}C nmr ($CDCl_3$) 163.2 and 162.5 (CO), 87.4 ($\underline{C}\{COOC_2H_5\}_2$), 81.2 ($\underline{C}HCH_3$), 64.1 ($CH_2$), 15.5 ($CH_3$), 13.9 and 13.8 ($CH_3$, esters); ir (film) 1750, 1400, 1220 cm^{-1}; mass spec. m/e 283 (M + 1).

   11: Nmr ($CDCl_3$) 4.3 (q, J = 7, 2 H), 4.2 (q, J = 7, 2 H), 1.4 (s, 6 H), 1.35 (t, J = 7, 3 H), and 1.2 (t, J = 7, 3 H); ^{13}C nmr ($CDCl_3$) 191.9, 172.6 and 160.2 (CO), 62.4 and 61.3 (CH_2), 21.7 and 21.6 (CH_3), 13.8 and 13.7 (CH_3, esters); mass spec. m/e 216 (M + 1). 2,4-DNP deriv., m.p. 157.5-158.5 ^{o}C, Anal. Calcd. for $C_{16}H_{20}N_4O_8$: C 48.49, H 5.09, N 14.14; Found C 48.27, H 4.98, N 14.01.

   13: Nmr ($CDCl_3$) 5.35 (m, 2 H), 4.4 (q, J = 7, 2 H), 1.6 (m, 3 H) and 1.35 (t, J = 7, 3 H); ^{13}C nmr ($CDCl_3$) 164.1 (CO), 79.7 and 79.5 (CH), 63.0 (CH_2), 15.05 (CH_3) and 14.0 (CH_3, ester); ir (film) 1750, 1380, 1200; mass spec. 211 (M + 1).

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