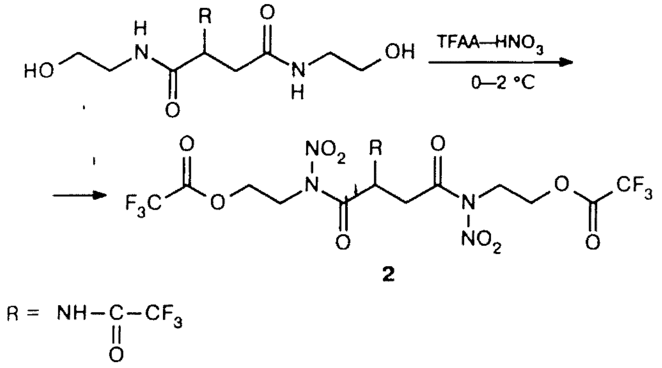
Scheme 2



ν/cm^{-1}: 1178, 1199 (C—F); 1235 (C—O); 1292, 1601 (N—NO$_2$); 1709 (C=O, amide); 1793 (C=O in CF$_3$C(O)O); 3308 (NH).

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New one-pot synthesis of α-hydroxyaldehyde ethyl sulfates from terminal olefins

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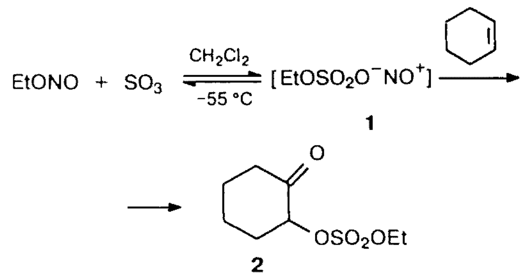
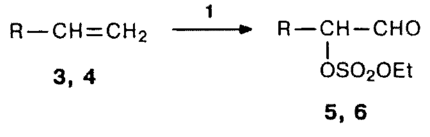
The search for new electrophilic reagents or ways to activate known substrates to increase their electrophilicity are of great importance for synthetic organic chemistry. The method based on the insertion of sulfur trioxide into weak electrophiles or compounds exhibiting no electrophilic properties is an example of such activation.[1,2] Previously, we have described the reaction of SO$_3$ with ethyl nitrite (EtONO) affording nitrosonium ethyl sulfate (**1**). This compound is stable in methylene chloride solution up to −30 °C and reacts easily with various cyclic olefins[3] to give ketosulfates **2**.



We studied the reaction of nitrosonium ethyl sulfate with terminal olefins. Under these conditions, hex-1-ene (**3**) and oct-1-ene (**4**) give the corresponding α-hydroxyaldehyde ethyl sulfates **5** and **6** in 70 % yields.



$$\underset{\mathbf{3,\,4}}{R{-}CH{=}CH_2} \xrightarrow{\mathbf{1}} \underset{\mathbf{5,\,6}}{R{-}\underset{OSO_2OEt}{CH}{-}CHO}$$

R = Bu (**3**, **5**); C$_6$H$_{13}$ (**4**, **6**)

It should be noted that these yields are given for individual compounds isolated by column chromatography. Thus, nitrosonium ethyl sulfate is a convenient synthetic reagent for the transformation of terminal olefins to the derivatives of hydroxyaldehydes. Certainly, its synthetic abilities are not restricted to the reactions described above, and their studies are now in progress.

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Reaction of nitrosonium ethyl sulfate with olefins (general procedure). A solution of freshly distilled EtONO in CH_2Cl_2 was added dropwise to a solution of SO_3 in CH_2Cl_2 cooled to −50 °C with vigorous stirring under argon atmosphere. After addition was completed, the reaction mixture was stirred for 30 min, keeping the temperature ≤ -45 °C, then a solution of an olefin in CH_2Cl_2 was added dropwise for 20 min and the stirring was continued for 15 min at the same temperature. The cold reaction mixture was poured into ice, the organic layer was separated, and the aqueous layer was extracted three times with small portions of chloroform. The combined organic fractions were dried over Na_2SO_4 and the solvent was removed *in vacuo*. The resulting crude product was chromatographed on a silica gel column (μ 40/100 or Silpearl).

2-Hydroxyhexanal ethyl sulfate (5). Starting from solutions of SO_3 (0.95 g, 11.9 mmol) in 20 mL of CH_2Cl_2, EtONO (1.78 g, 23.7 mmol) in 16 mL of CH_2Cl_2, and hex-1-ene (0.4 g, 4.8 mmol) in 20 mL of CH_2Cl_2, the crude product (0.98 g) was obtained, its chromatographic purification (hexane—ethyl acetate—chloroform, 1 : 3 : 3) gave compound **5** (0.75 g, 70 %) as a light oil, R_f 0.16. IR, ν/cm^{-1}: 1760 (C=O); 1400, 1200 (OSO_2O). ^1H NMR ($CDCl_3$), δ: 0.91 (narrow t, 3 H, $C(6)H_3$); 1.20—1.55 (m, 4 H, $C(4)H_2$ and $C(5)H_2$); 1.43 (t, 3 H, CH_3, J = 7.1 Hz); 1.87 (m, 2 H, $C(3)H_2$); 4.45 (m, 2 H, OCH_2); 4.83 (dd, 1 H, HCO, ^1J = 7.0 Hz, ^2J = 5.5 Hz); 9.64 (s, 1 H, CHO). Found (%): C, 42.75; H, 7.19. $C_8H_{16}O_5S$. Calculated (%): C, 42.84; H, 7.19.

2-Hydroxyoctanal ethyl sulfate (6). Starting from solutions of SO_3 (1.67 g, 21 mmol) in 30 mL of CH_2Cl_2, EtONO (2.13 g, 28 mmol) in 25 mL of CH_2Cl_2, and oct-1-ene (1.06 g, 9 mmol), the crude product (2.22 g) was obtained, its chromatographic purification (heptane—ethyl acetate, 3 : 1) gave compound **6** (1.67 g, 70 %) as a light oil, R_f 0.24. IR, ν/cm^{-1}: 1740 (C=O); 1400, 1200 (OSO_2O). ^1H NMR ($CDCl_3$), δ: 0.9 (narrow t, 3 H, $C(8)H_3$); 1.1—2.1 (mm, 13 H, CH_2 aliph. + CH_3); 4.3 (m, 2 H, OCH_2); 4.7 (m, 1 H, HCO); 9.5 (s, 1 H, CHO). Found (%): C, 47.48; H, 7.89. $C_{10}H_{20}O_5S$. Calculated (%): C, 47.60; H, 7.99.

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