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New method for the synthesis of ethyl β-nitrosoalkyl sulfates from olefins

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Earlier, we have shown that the reaction of ethyl nitrite with SO_3 affords a nitrosating reagent, namely, nitrosonium ethyl sulfate.[1,2] However, a tenfold excess of an alkene is required for the formation of nitroso sulfates; otherwise, the major reaction products are oxo sulfates.[2] It should be noted that nitrosation is of considerable interest because nitroso compounds are intermediate products in the synthesis of amines, oximes, and nitro and oxo compounds.[3]

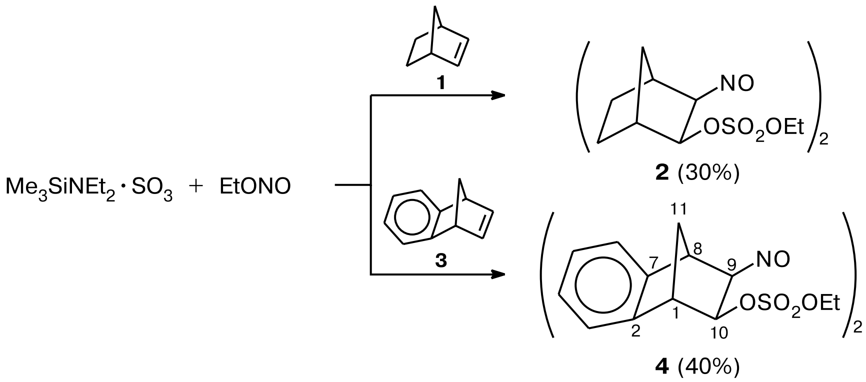
Now we found that ethyl nitrite reacts with norbornene (**1**) in the presence of the *in situ* formed complex $Me_3SiNEt_2 \cdot SO_3$ (complex : alkene = 1 : 1) to give ethyl *cis*-*exo*-(2-nitrosobicyclo[2.2.1]hept-3-yl) sulfate (**2**) as dimeric crystals. An analogous product was obtained from benzonorbornadiene (**3**). In both cases, the process is *syn*-*exo*-nitrosation typical of bicyclo[2.2.1]heptenes.[4,5] It is worth noting that under the above conditions, oxo sulfates are detected only in trace amounts.

Thus, we proposed a new way of nitrosating olefins, which allows simultaneous introduction of both nitroso and sulfate groups into an organic molecule.

Reactions of ethyl nitrite with olefins in the presence of $Me_3SiNEt_2 \cdot SO_3$ (general procedure). A solution of Me_3SiNEt_2 in anhydrous CH_2Cl_2 was slowly added dropwise to a stirred solution of SO_3 in anhydrous CH_2Cl_2 at −25 to −20 °C under dry argon. The reaction mixture was stirred at this temperature for 30 min and cooled to −35 °C. A solution of freshly distilled EtONO in CH_2Cl_2 was added. After the ethyl nitrite was added completely, the reaction mixture was stirred at this temperature for 30 min, and a solution of an olefin in anhydrous CH_2Cl_2 was added. To complete the reaction, the stirred reaction mixture was cooled for an additional 1 h and then allowed to slowly warm to ~20 °C. After the solvent was removed, the crude product was recrystallized from 95% EtOH.

Ethyl *cis-exo*-(2-nitrosobicyclo[2.2.1]hept-3-yl) sulfate (2). The reaction of SO_3 (0.552 g, 6.9 mmol) in 15 mL of CH_2Cl_2, Me_3SiNEt_2 (1.0 g, 6.9 mmol) in 15 mL of CH_2Cl_2, EtONO (1.79 g, 23.9 mmol) in 20 mL of CH_2Cl_2, and norbornene **1** (0.65 g, 6.9 mmol) in 20 mL of CH_2Cl_2 yielded crude product **2** (1.32 g). Recrystallization from 95% EtOH gave dimeric compound **2** (0.515 g, 30%) as colorless crystals, m.p. 140—143 °C (decomp.), R_f 0.17 (hexane—AcOEt, 3 : 1). Found (%): C, 43.36; H, 5.93; N, 5.49. $C_{18}H_{30}N_2O_{10}S_2$. Calculated (%): C, 43.37; H, 6.07; N, 5.62. ^1H and ^{13}C NMR and IR spectroscopic data correlate with the literature data.[2]

Ethyl *cis-exo*-(9-nitrosotricyclo[6.2.1.0^{2,7}]undeca-2(7),3,5-trien-10-yl) sulfate (4). The reaction of SO_3 (0.36 g, 4.5 mmol) in 15 mL of CH_2Cl_2, Me_3SiNEt_2 (0.66 g, 4.5 mmol) in 15 mL of CH_2Cl_2, EtONO (2.18 g, 29.1 mmol) in 20 mL of CH_2Cl_2, and benzonorbornadiene **3** (0.60 g, 4.2 mmol) in 20 mL of CH_2Cl_2 yielded crude product **4** (1.13 g). Recrystallization from 95% EtOH gave dimeric compound **4** (0.50 g, 40%) as colorless crystals, m.p. 110 °C (decomp.), R_f 0.19 (hexane—AcOEt, 3 : 1). Found (%): C, 52.10; H, 4.98; N, 4.62. $C_{26}H_{30}N_2O_{10}S_2$. Calculated (%): C, 52.5; H, 5.05; N, 4.71. ^1H NMR (Varian VXR-400, 400 MHz, $CDCl_3$), δ: 1.46 (t, 3 H, Me, J = 7.0 Hz); 2.14 (dt,



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1 H, *anti*-H(11), *J* = 9.5 Hz, *J* = 1.5 Hz); 2.51 (dt, 1 H, *syn*-H(11), *J* = 9.5 Hz, *J* = 1.4 Hz); 3.73 (br.s, 1 H, H(1)); 3.76 (br.s, 1 H, H(8)); 4.40 (m, 2 H, OCH_2); 4.95 (dd, 1 H, HCO, *J* = 6.1 Hz, *J* = 1.5 Hz); 5.09 (dd, 1 H, HCN, *J* = 6.1 Hz, *J* = 1.0 Hz); 7.10—7.40 (m, 4 H, H arom.). ^{13}C NMR (100 MHz, $CDCl_3$), δ: 14.7 (Me); 45.3, 46.1, 48.3 (C(1), C(8), C(11)); 70.4, 70.5 (C—N, OCH_2); 81.8 (C—O); 122.3, 123.3, 127.6, 128.0, 142.2, 144.6 (C arom.).

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