silyl ethers of enols (see Refs. 10 and 11), reductive debromination of α-bromoketones, [12] *etc.*

Experimental

IR spectra were obtained on a UR-20 spectrophotometer in a thin layer. NMR spectra were recorded on a Bruker AM-300 spectrometer (^{1}H, 300 and ^{13}C, 75.47 MHz) in $CDCl_3$ using $SiMe_4$ as the internal standard. Commercial Me_3SiI (Aldrich) was used.

5-Allyl-5-chloro-4,4-dimethoxy-3-morpholinocyclopent-2-enone (2). A solution of compound **1** (0.1 g, 0.3 mmol) and Me_3SiI (0.25 mL, 1.2 mmol) in MeCN (5 mL) was stirred at 20 °C for 1 h in an argon atmosphere. Then the reaction mixture was treated with a saturated solution of $NaHCO_3$ (5 mL) and extracted with CH_2Cl_2 (4×10 mL). The combined extracts were washed with a saturated solution of $Na_2S_2O_3$ (5 mL), dried with $MgSO_4$, and concentrated *in vacuo*, and the residue was chromatographed on SiO_2 (ethyl acetate—hexane (2 : 1) as the eluent). Compound **2** was obtained as an oil in 83% yield (75 mg). IR, ν/cm^{-1}: 1600, 1700. ^{1}H NMR, δ: 2.70 (m, 2 H, CH_2); 3.25 and 3.55 (both s, 6 H, OMe); 3.75 (m, 8 H, NCH_2CH_2O); 5.05 (m, 2 H, $=CH_2$); 5.15 (s, 1 H, HC(2)); 5.80—5.90 (m, 1 H, CH=). ^{13}C NMR, δ: 44.12 (CH_2); 47.81 (CH_2N); 51.52 and 53.44 (OMe); 66.66 (CH_2O); 76.46 (C(5)); 100.38 (C(2)); 105.23 (C(4)); 118.40 (CH_2=); 132.79 (CH=); 165.02 (C(3)); 192.05 (C=O). Found (%): C, 55.98; H, 6.60; N, 4.40. $C_{14}H_{20}ClNO_4$. Calculated (%): C, 55.81; H, 6.64; N, 4.65. MS, *m/z*: 303 [M+2]$^+$ (2.6), 301 [M]$^+$ (7.5), 288 (18), 286 [M−Me]$^+$ (52), 276 (9.3), 274 [M−HCN]$^+$ (28), 272 (6), 270 [M−OMe]$^+$ (18), 268 (35), 266 [M−Cl]$^+$ (100).

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Reactions of arensulfenamides with olefins in the presence of picric acid

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N-(2- and 4-Nitrophenylthio)morpholines in the presence of equimolar amounts of picric acid enter into the reaction of electrophilic sulfenylation of the C=C norbornene bond to give bi- and tricyclic sulfides. With cyclohexene, *trans*-2-arylthiocyclohexanol are formed.

Key words: arensulfenamides, picric acid, sulfenylation.

Several examples of activation of electrophilic reactions of sulfenamides by protic acids are known. For example, *N*-(4-nitrophenylthio)acetimide in the presence of CF_3COOH reacts with alkenes to give trifluoroacetates of the corresponding β-arylthioalkanols.[1] The activation of arenesulfenamides by trifluoromethane-

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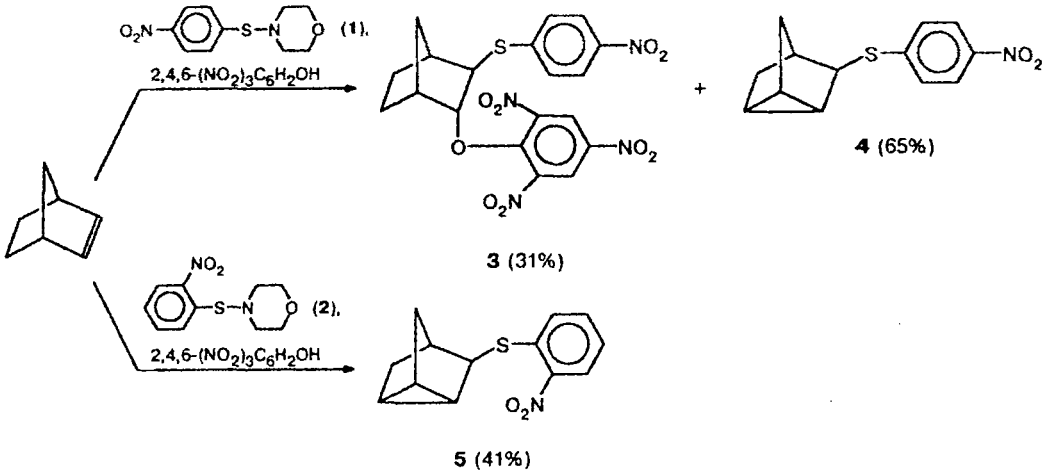
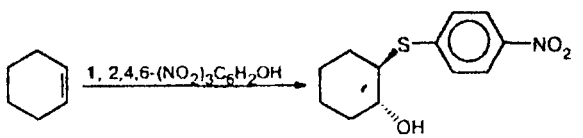
Scheme 1



sulfonic acid results in the formation of the corresponding *trans*-1,2-aminosulfides, and in the presence of nitriles, trimolecular condensation with the formation of amidines occurs.[2] Using sulfamic acid $NH_3 \cdot SO_3$, one can obtain β-sulfamoyl sulfides[3] or β-aminosulfides,[4] depending on the structure of the substrate.

We studied the reactions of 4- and 2-nitrophenylsulfenamides **1** and **2** with alkenes in the presence of picric acid (Scheme 1). The addition—elimination products, *viz.*, sulfides **4** and **5** with the nortricyclane structure, are the main products of the sulfenylation of norbornene. In the case of sulfenamide **1**, the product of 1,2-addition (**3**) was also isolated. In this case, the anion of picric acid is the nucleophile that enters into the reaction in the second stage of electrophilic addition.

In the case of a somewhat less reactive olefin, cyclohexene, used as the substrate, the yield of the reaction product is lower; alcohol **6** was isolated after chromatography, evidently being the product of hydrolysis of the picrate that formed initially. It is known[5] that in similar systems, hydrolysis is substantially facilitated due to the nucleophilic assistance of the arylthio group. Alcohol **6** was not isolated in the analytically pure state; however, its structure was established on the basis of the ^1H and IR spectra and confirmed by the mass spectrometry data (the presence of a molecular ion peak with *m/z* 253).



6 (30%)

In all cases, some quantity of the corresponding diaryl disulfides is formed as the by-product. Morpholinium picrate was also isolated from the reaction mixture and identified from the data of NMR spectroscopy and elemental analysis.

The reactions studied were carried out in $CHCl_3$ at ~20 °C for 12—24 h. Attempts to decrease the reaction time by increasing the temperature (boiling) result in a decrease in the yield of sulfenylation products.

Thus, it is established that picric acid promote electrophilic sulfenylation of alkenes under the action of arenesulfenamides.

Experimental

^1H NMR spectra were recorded on a Varian-VXR-400 instrument (400 MHz). IR spectra were recorded on a UR-20 instrument in Nujol. Mass spectra were obtained on a Varian-MAT-212 instrument (direct inlet, EI). Arenesulfenamides were synthesized by the previously described procedure.[6]

General procedure of sulfenylation. Picric acid (0.25 g, 1.1 mmol) was added to a solution of a sulfenamide (0.24 g, 1 mmol) in anhydrous $CHCl_3$ (20 mL) at 20 °C, and then a solution of olefin (1.2 mmol) in the same solvent was added. The yellow precipitate of morpholinium picrate begins to form after 30 min. The mixture was stirred until arensulfenamide disappeared (TLC control), after which the precipitate was filtered off, the solvent was evaporated *in vacuo*, and the residue was chromatographed on silica gel (Silufol plates; ethyl acetate—light petroleum (1 : 3) as the eluent).

***exo*-2-(4-Nitrophenylthio)-*endo*-3-picryloxynorbornane (3).** R_f 0.40. ^1H NMR ($CDCl_3$), δ: 8.58 (s, 2 H, H arom.); 8.04 (d, 2 H, H arom., J = 8.8 Hz); 7.29 (d, 2 H, H arom., J = 8.8 Hz); 4.38 (t, 1 H, HCO, J = 3.2 Hz); 3.34 (t, 1 H, HCS, J = 3.2 Hz); 2.78 (m, 1 H, HC(1)); 2.36 (m, 1 H, HC(4), J_1 = 3.2 Hz); 2.0—1.4 (m, 6 H). Found (%): C, 47.35; H, 3.47; N, 10.96. $C_{19}H_{16}N_4O_9S$. Calculated (%): C, 47.90; H, 3.39; N, 11.76.

3-(4-Nitrophenylthio)tricyclo[2.2.1.0^{2,6}]heptane (4). R_f 0.88. ^1H NMR ($CDCl_3$), δ: 8.06 (d, 2 H, H arom., J = 8.8 Hz); 7.31 (d, 2 H, H arom., J = 8.8 Hz); 3.29 (br.s, 1 H, HCS); 2.11 (br.s, 1 H, HC(4)); 1.83 (d, 2 H, HC(7), J = 10.8 Hz); 1.48 (m, 2 H); 1.30 (m, 3 H). Found (%):

C, 63.39; H, 5.19; N, 5.19. $C_{13}H_{13}NO_2S$. Calculated (%): C, 63.14; H, 5.30; N, 5.66.

3-(2-Nitrophenylthio)tricyclo[2.2.1.0^{2,6}]heptane (5). R_f 0.82. ^{1}H NMR (CCl_4), δ: 8.00 (d, 1 H, H arom., J = 8.8 Hz); 7.50—7.00 (m, 3 H, H arom.); 3.01 (br.s, 1 H, HCS); 2.10—1.10 (m, 8 H). Found (%): C, 63.13; H, 5.29; N, 5.50. $C_{13}H_{13}NO_2S$. Calculated (%): C, 63.14; H, 5.30; N, 5.66.

***trans*-2-(4-Nitrophenylthio)cyclohexanol (6).** R_f 0.60. ^{1}H NMR ($CDCl_3$), δ: 8.10 (d, 2 H, H arom., J = 8.8 Hz); 7.32 (d, 2 H, H arom., J = 8.8 Hz); 3.48 (q, 1 H, HCO, J = 10.8 Hz); 3.48 (q, 1 H, HCS, J = 10.8 Hz); 2.12 (m, 2 H); 1.75—1.15 (m, 6 H). IR, ν/cm^{-1}: 3120 (OH). MS, m/z: 253 $[M]^+$.

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Synthesis of diaminohydroxyethers *via* 3-(ω-haloalkoxy)-2-hydroxypropyl sulfamates

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Reactions of 3-(ω-haloalkoxy)-2-hydroxypropyl sulfamates with amines or ammonia followed by acid hydrolysis give the corresponding diaminohydroxyethers.

Key words: sulfamates, 1-amino-3-(ω-aminoalkoxy)propan-2-ols.

Functional amino derivatives and in particular amino alcohols are widely used in organic synthesis, in chemistry of polymers, and as biologically active substances.[1—5] In this connection, synthesis of new representatives of amino derivatives and perfection of methods for their preparation remain urgent problems. The use of sulfamic acid and oxiranes as the starting reagents makes it possible to obtain (with rather high selectivity) several previously unknown or hardly accessible functionalized amino alcohols.

Previously,[6] we reported on the synthesis of some diaminoethers by the reactions of sulfamates with diglycidyl ether. However, this method gives only symmetrical diaminodihydroxyethers. In the present work, for the purpose of extending the series of diamines, we propose another method for the synthesis of diaminohydroxyethers, *viz.*, by the reaction of *N*-(3-(ω-haloalkoxy)-2-hydroxypropyl) sulfamates with amines or ammonia in an aqueous medium followed by acid hydrolysis (Scheme 1).

We have previously[7] described the preparation of the starting sulfamate **1**; synthesis of compound **1n** was performed similarly. The reactions of halides **1** with R^1R^2NH were performed at 90—95 °C for 1 h in an aqueous medium with a 5—10-fold excess of an amine. The substitution of halogen by nitrogen was almost quantitative. Then the aminosulfamates **2** were converted by acid hydrolysis (according to the previously used procedure[6]) without purification into diaminohydroxyethers (**3**), which were additionally purified by fractional distillation. The overall yields of **3** (purity 90—95%) are within 70—90%, the yields after distillation and other parameters of the products obtained are presented in Table 1.

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