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The reaction of sulfamic acid derivatives with epoxides.
4. Hydrolysis of 3-chloro-2-hydroxypropylsulfamates

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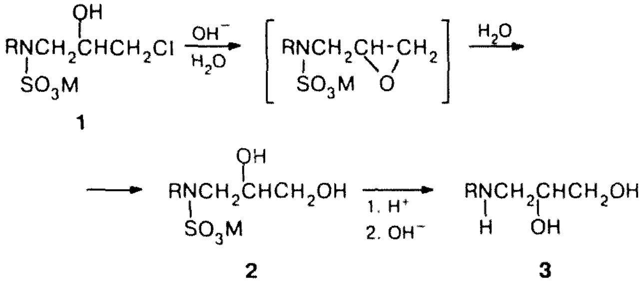
Under basic hydrolysis conditions 3-chloro-2-hydroxypropylsulfamates transform into 2,3-dihydroxypropylsulfamates. Acidic hydrolysis of the latter leads to 3-alkylaminopropane-1,2-diols.

Key words: 3-chloro-2-hydroxypropylsulfamates, 3-alkylaminopropane-1,2-diols, 2,3-dihydroxypropylsulfamates.

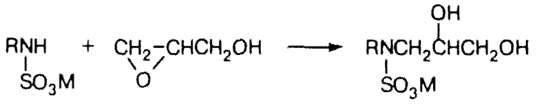
It has been shown previously[1] that the interaction of 3-chloro-2-hydroxypropylsulfamates with amines leads to 3-alkylamino-2-hydroxypropylsulfamates. A similar approach was used in the synthesis of 3-alkylaminopropane-1,2-dioles.



$$\underset{\mathbf{1}}{\mathrm{RN(SO_3M)CH_2CH(OH)CH_2Cl}} \xrightarrow[H_2O]{OH^-} \left[\mathrm{RN(SO_3M)CH_2\overset{O}{CH\text{-}CH_2}}\right] \xrightarrow{H_2O} \underset{\mathbf{2}}{\mathrm{RN(SO_3M)CH_2CH(OH)CH_2OH}} \xrightarrow[2.\ OH^-]{1.\ H^+} \underset{\mathbf{3}}{\mathrm{RN(H)CH_2CH(OH)CH_2OH}}$$

M = K, Na; R = H (**a**), Me (**b**), Et (**c**), Bu (**d**)

2,3-Dihydroxypropylsulfamates (**2**) were obtained as a result of basic hydrolysis of 3-chloro-2-hydroxypropylsulfamates (**1**) (2—5 h at 100 °C), evidently, through intermediate epoxides. To exclude the condensation of the resulting compounds **2** with epoxides, a 50—60-fold molar excess of water was used. The yields of products **2** were 90—95 %. Earlier[2] compounds **2** were prepared by the condensation of sulfaminic acid derivatives with glycidols.



$$\mathrm{RN(SO_3M)H} + \mathrm{\overset{O}{CH_2\text{-}CH}CH_2OH} \longrightarrow \mathrm{RN(SO_3M)CH_2CH(OH)CH_2OH}$$

M = K, Na; R = H, Alk

Subsequent acidic hydrolysis of sulfamates **2** (20—30% H_2SO_4 at 100—110 °C) gave 3-alkylaminopropane-1,2-diols (**3**) in 92—95 % yields. The hydrolysis could also be carried out by the action of 30—37 % HCl or HNO_3.

Under acidic hydrolysis conditions without preliminary isolation of compounds **2**, overall yields of products **3** were 90—95 %.

The structures of compounds **2** and **3** were confirmed by their NMR spectra, as well as by the correla-

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* For Communication 3 see Ref. 1.

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tion of their melting points and refraction indices with those published earlier.[2—4]

Experimental

^1H NMR spectra were registered on a «Bruker AM-300» instrument for solutions in D_2O and acetone-d_6 with TMS as the internal standard.

Potassium 2,3-dihydroxypropylsulfamate (2). KOH (0.7 g, 10.8 mmol, 85 %) was added to solution of **1a** (2.28 g, 10 mmol) in H_2O (10.8 mL, 0.6 mol) and the mixture was stirred for 3—4 h at 100 °C. The solution was evaporated and the residue was recrystallized from MeOH to give potassium 2,3-dihydroxypropylsulfamate (1.92 g, ~91%), m.p. 116—118 °C (*cf.* Ref. 2). Compounds **2c—d** were prepared in a similar manner.

3-Methylaminopropane-1,2-diol (3b). Compound **2a** (4.46 g, 20 mmol) was added to a 30% solution of H_2SO_4 (10 mL) and the mixture was stirred for 8 h at 100 °C and neutralized by a solution of KOH to pH ~12.0. The reaction mixture was evaporated and the product was extacted with $EtOH—Et_2O$. This led to product **3b** (1.99 g, ~95%) with b.p. 98—102 °C (3—4 Torr) (Ref. 3: b.p. 239—241 °C (748 Torr)).

In a similar manner compounds **3a,c,d** were prepared: **3a**, b.p. 127—130 °C (2—3 Topp) (Ref. 4: b.p. 125—128 °C (2 Torr)); **3c**, b.p. 246—248 °C (758 Torr) (Ref. 3: b.p. 244—246 °C (750 Torr)). Compound **3d**, b.p. 106—109 °C (2—3 Torr). ^1H NMR (acetone-d_6, δ, ppm): 0.8—1.5 (m, 7 H, Pr), 2.40—2.65 (m, 4 H, CH_2NCH_2), 3.68 (m, 2 H, CH_2OH), 3.98 (m, 1 H, CHOH). Found (%): N, 10.02. $C_7H_{17}NO_2$. Calculated (%): N, 9.51.

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Interaction of diphenyl sulfide with sulfuryl chloride

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The reaction of diphenyl sulfide with sulfuryl chloride was studied. Depending on the reaction conditions, it occurs either as chlorination of the aromatic ring or as oxidation to give sulfoxide.

Key words: diphenyl sulfide, sulfuryl chloride, oxidation, chlorination.

Reactions of aromatic thioethers with sulfuryl chloride have not been studied much,[1] although reactions involving other electrophilic reagents, including halogens, have been covered adequately.[2] We studied the effect of the reaction conditions on the nature of the products of the interaction between diphenyl sulfide **1** and SO_2Cl_2.

When this reaction is carried out in inert organic solvents (dichloromethane, tetrachloromethane), it appears that a hydrolytically unstable intermediate of the sulfurane type is formed initially; the latter readily decomposes to give diphenyl sulfoxide (**2**). Thus, this process can serve as a convenient method for sulfoxidation of aromatic sulfides that does not involve undesirable further oxidation to sulfones, typical of methods based on the use of traditional oxidizing reagents.

When aluminum chloride is added to the reaction system, both the sulfur atom and the aromatic ring of sulfide **1** are chlorinated to give 4,4′-chlorodiphenyl sulfoxide (**3**), whose mass spectrum has an intense $[M-SO]^+$ peak and no molecular ion peak.

The reaction carried out without a solvent at a **1** : SO_2Cl_2 molar ratio of 1 : 2 gave 4,4′-dichlorodiphenyl sulfide (**4**) in a yield of 92%. Increasing the

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