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Preparation of Long-Chain Alkoxyethoxysulfates and Synthetic Applications

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INTRODUCTION

It is generally known, that surfactants from family of sulfonic acids and sulfuric acid, e. g. salts of long-chain alkylsulfonic acid, alkylbenzenesulfonic acid and long-chain monoalkylsulfates have very broad possibilities for an application in the actual life. The reason of this reality is possibility of their unsophisticated production, price and environmental tact. These are also very important for chemists as micellar catalysts for syntheses realized in water or in two phase liquid-liquid systems[1-4]. In article[2-4] the authors demonstrate very effective action of n-dodecylbenzenesulfonic acid as a Broensted acid-surfactant-combinated catalyst for some condensation reactions in water under colloidal dispersion conditions, i.e. according to green sustainable chemistry principles.

The latest observation in the surfactant chemistry show a very effective action of sulfates derivated from long chain mono-alkylated (poly)ethylene glycols.

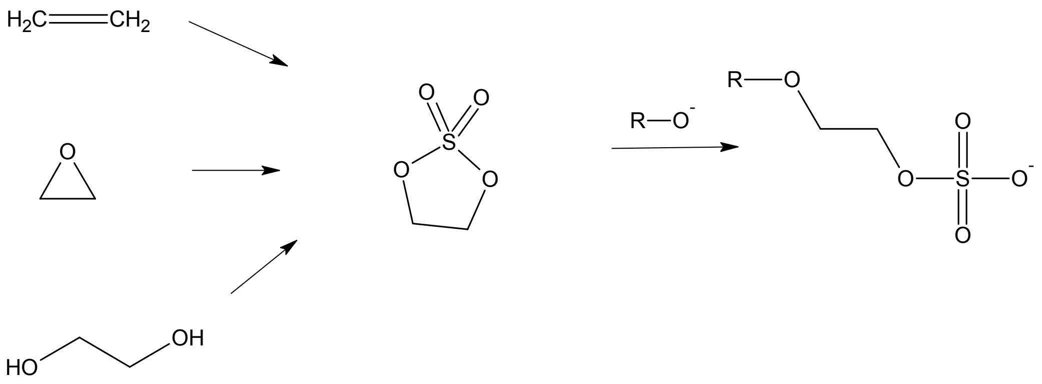
In our contribution it is demonstrate new methods for the preparation of long-chain alkoxyethoxysulfates with $C_{12} – C_{18}$ linear alkyl chains and some their synthetic applications.

RESULTS AND DISCUSSION

We searched new methods for preparation of title long-chain alkoxyethoxysulfates corresponding to the green sustainable chemistry principles – minimum of synthetic steps, acceptable solvents, high atom economy, ambient temperature, waste minimalisation, etc.

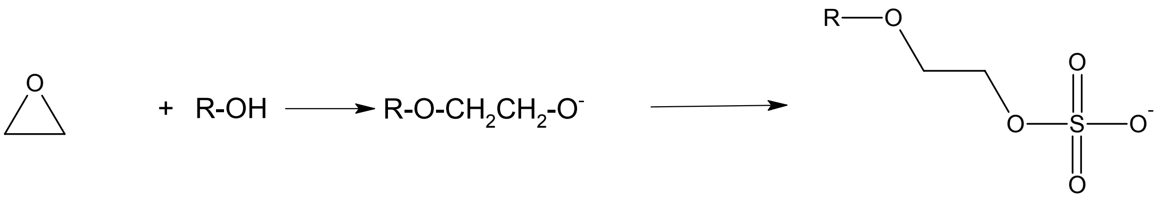
We found the two different ways for preparation of the long chain alkoxy ethoxy sulfates in two-steps processes but both can be realize as one-pot syntheses.

The first is proceeding via 1,3,2-dioxathiolane-2,2-dioxide which is consequently opened by an action of long chain alcoholate giving target product (Scheme 1).



SCHEME 1. Preparation of alkoxyethoxysulfates via 1,3,2-dioxathiolane-2,2-dioxide, R … n-C_{12-18} alkyl chain.

The second way was realized by reaction of the long chain 2-alkyloxyethanolate with chlorosulfonic acid (Scheme 2).



SCHEME 2. Preparation of alkoxyethoxysulfates via 2-alkyloxyethanolates, R … n-C_{12-18} alkyl chains.

1,3,2-Dioxathiolane-2,2-dioxide may be produce by more different ways. The first may be started from ethylene which give 2,2-dioxide by reaction with $Ph\text{-}I^{+}\text{-}SO_3^{-}$ (this betaine can be prepared by sulfonation of phenyliodane oxide by SO_3 and recycled for repeated use). This reaction is described for ethylene in literature[5] in dichloromethane as solvent with 85% yield, reaction time ca 20 min at 15 °C, for general olefin with yields about 80% in article[6].

The second way for 2,2-dioxide preparation from ethylene glycol and sulfuryl dichloride in the presence of triethyl amine as base is described in literature[7]. We are realized this reaction in toluene as a solvent in the presence of K_2CO_3 or $CaCO_3$ as base under solid-liquid PTC conditions used Cetrimide as the catalyst at reactions temperature about 50 °C.

The third one starting from ethylene oxide (reaction have higher atom economy from all mentioned) was not found in literature. We have provided this reaction of ethylene oxide with mixture of conc. sulfuric acid and oleum in toluene as solvent at temperature ca 5 °C or in the same solvents with chlorosulfonic acid in the presence of K_2CO_3 or $CaCO_3$ as bases under above-mentioned PTC conditions at temperature ca 5 °C.

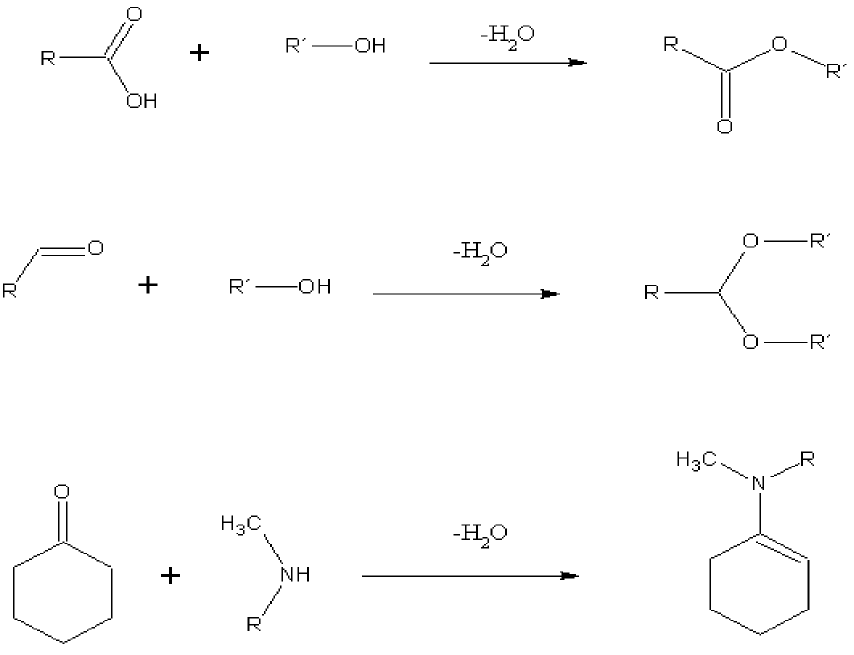
Ring opening of 1,3,2-dioxathiolane-2,2-dioxide skeleton by an action of alcoholate giving alkoxy ethoxy sulfates is described for more cases in literature. Frequently is applied in carbohydrate chemistry and reactions are realized in different aprotic solvents. For long chain alcoholate (C_{12-20}) and 1,3,2-dioxathiolane-2,2-dioxide it is described in[7].

We carried out this process with 1,3,2-dioxathiolane-2,2-dioxide toluene solution (which is prepared in situ by any above mentioned method). This solution is added into mixture of corresponding long chain alcoholate or alcohol-NaOH mixture both in the presence of the phase transfer catalyst (TEBA, Cetrimide) at room temperature and target products were obtained with very good yields (75-85%).

The way starting from long chain 2-alkyloxyethanolates and chlorosulfonic acid is described in literature[8] for C_{12}-chain. Process is realized in chloroform at temperature under 10 °C.

2-Alkyloxyethanolates were formed in situ by an action of ethylene oxide on corresponding long chain alcohol in the presence of NaOH under PTC condition as it is above presented. The chlorosulfonic acid is added in the next step into 2-alkyloxyethanolates suspension at room temperature. Yield of products was 80-90%.

The prepared long-chain alkoxyethoxysulfuric acids were tested in the followed condensation reactions giving water and realized in water – direct esterification reaction of fat acids (stearic, palmitic, oleic acid) by the long chain alcohols (octanol, decanol, dodecanol, octadecanol), direct acetalization of octanal by above mentioned alcohols, enamine formation from cyclohexanone by reactions with N-methyl-N-R-alkylamines (R is octyl, decyl, dodecyl and octadecyl linear chain) – Scheme 3.



SCHEME 3. Model reactions supported by long-chain alkoxyethoxysulfuric acid, R, R′are C_{8-16} alkyl chains.

All reactions were carried out in water emulsion at temperature of highest melt component (ca 40-80 °C), concentration of long-chain alkoxyethoxysulfuric acid was 2-5 mol%, reactions time ca 25-30 hrs. Free acids were obtained in situ by the reaction of water solution their corresponding salts with an equivalent amount of sulfuric acid.

CONCLUSION

The explanation of our observation can be based on a fact that reactions are realized under micellar catalysis conditions into the omega-phase[9]. Here is presented a minimal concentration of water and dehydration step is speeded up by an expression of interacting hydrocarbon lipophilic long chain. Presence of 1,2-ethandioxy units relieves a withdrawal of water molecules. On the same principle the reversible action is blocked and reaction proceeded with high yields.

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