

Short Communication

Desulfonation of Alkanesulfonates and Sulfonyl Chlorides

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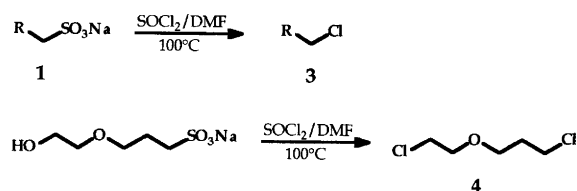
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Sulfonate esters with groups that are difficult to eliminate, can form stabilized α -sulfonyl carbanions which can be alkylated¹ or nitrated.² However, a limiting factor in reactions where the sulfonate ester group is used as an activating and directing group in *C*-alkylation reactions, is the difficulties normally associated with a final removal of the sulfonate ester moiety. A method has been reported³ in which a number of aliphatic sulfur compounds, *e.g.*, sulfonic acids were reacted with triphenylphosphine in the presence of iodine to give the corresponding alkyl iodides in high yields.

As part of an attempt to develop an efficient sulfonate ester mediated alkylation method, we were interested in desulfonation transformations, as by this procedure the *d*¹-type sulfonate molecule was conveniently transformed into an *a*¹-type alkylation substrate. We here report a new convenient procedure for the transformation of a series of primary aliphatic sulfonic acids into the corresponding alkyl chlorides.

Sodium alkanesulfonates, **1**, and alkanesulfonyl chlorides, **2**, readily reacted with thionyl chloride in DMF at 100 °C to form the corresponding alkyl chlorides, **3**, in high isolated yields, Scheme 1. Phenyl and alkyl alkanesulfonate esters as well as alkanesulfonamides were not converted into alkyl halides under these conditions. Analysis of the reaction mixtures by the GLC clearly indicated that at room temperature the corresponding sulfonyl chlorides were formed as intermediates from sodium sulfonates. However, when the reaction was carried out at 100 °C for 1 h desulfonation took place and alkyl halides were formed in a clean reaction with no appreciable amounts of by-products. Substrate molecules containing hydroxy groups, were converted into dichlorides, *e.g.*, **4**. Representative examples are shown in Table 1.

Normally the sulfonic acid and SOCl₂ were used in a 1:1.6 molar ratio. However, it was interesting to note that for desulfonation of sulfonyl chlorides only catalytic amounts of SOCl₂ (*e.g.*, 10 mol %) were required. The



Scheme 1.

reaction rates were only slightly higher upon addition of a 3–5 fold excess of LiCl. Also, reaction of a sulfonyl chloride with LiCl in DMF at 100 °C did not result in formation of detectable amounts of alkyl chlorides.

To rationalize these results we propose that the Vilsmeier salt, *N,N*-dimethylchloroformamidium chloride, **5**, reacts with the alkanesulfonyl chloride forming an adduct, which in an intramolecular reaction forms the alkyl halide, **3**, and subsequently the salt **5**, which can further react with more alkanesulfonyl chloride, Scheme 2. Thus, this mechanism may explain why only catalytic amounts

Table 1.

| Substrate | Product | Yield ^a (%) |
|-----------|---------|------------------------|
| | | 81 |
| | | 53 |
| | | 68 |
| | | 46 |
| | | 58 |

^a Isolated yield.

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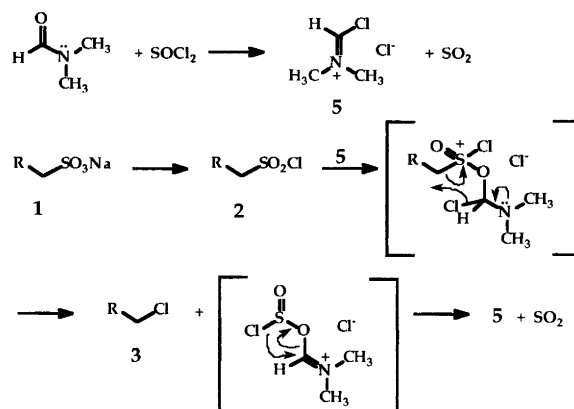
of SOCl_2 were required for the conversion of alkanesulfonyl chlorides. The salt **5** can be prepared by reacting DMF with thionyl chloride⁴ or phosphoryl chloride.⁵ An alternative mechanism involves a nucleophilic displacement of the sulfonate moiety with Cl^- . This type of mechanism has been proposed for the conversion of alcohols into alkyl halides with SOCl_2 in DMF.⁶

The desulfonation reaction represents a convenient, mild and selective method for the conversion of the non-volatile sodium alkanesulfonates into the corresponding more volatile alkyl chlorides. This suggests that the transformation may find use for, e.g., GLC analysis of sulfonates. We are currently exploring this application with commercial sulfonate surfactants.

Experimental

Desulfonation of sodium sulfonates and sulfonyl chlorides with thionyl chloride in DMF. General procedure.

To a slurry or solution of 1.0 mmol of a sodium sulfonate or sulfonyl chloride in 10 ml of DMF was added 0.2 g, 1.6 mmol of thionyl chloride. The resulting reaction mixture was heated at 100°C for 1 h and then cooled to room temperature, and, after addition of water (25 ml), extracted with ether. The organic solution was then dried over anhydrous magnesium sulfate and the solvent evaporated off under reduced pressure, leaving behind the desired alkyl chloride. Volatile products were identified by GLC analysis and authentic samples using internal standards for determination of yields. The results are summarized in Table 1. All the spectroscopic and chromatographic properties of the products were in full agreement with the assigned structures or with those of authentic samples.



Scheme 2.

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