

REED'S SULFOCHLORINATION REACTION

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The sulfochlorination reaction which was discovered by the American, Reed, consists of the simultaneous reaction of SO_2 and chlorine with saturated aliphatic hydrocarbons in the presence of light. The reaction proceeds very smoothly and yields sulfonylchlorides which can be converted by hydrolysis into aliphatic sulfonic acids and their salts which are important as detergents. The by-products formed consist of sulfonylchlorides which are more or less chlorinated in the organic part of the molecule. Very little is known about the location of the sulfo group and on the directing effect of halogen atoms in the molecule. In order to clarify the reaction mechanism, experiments were carried out using low-molecular weight aliphatic and cycloaliphatic hydrocarbons and halogenated hydrocarbons of known structure.

The first reactions were carried out with cyclohexane and cyclopentane. With cyclohexane a solid crystalline compound was obtained besides cyclohexanesulfonylchloride, and this compound could be identified as trans-1,4-cyclohexane-disulfonylchloride. The compound is converted into trans-1,4-dichlorocyclohexane when it is heated above its melting point and this latter compound was found to be identical with the material made synthetically from trans-chinone and HCl.

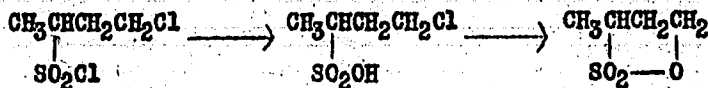
The splitting off of SO_2 which takes place in this case is also observed when cyclohexanesulfonylchloride is distilled under vacuum and it is not easy to prepare this compound in the pure form. The same phenomenon is an obstacle to the purification of other aliphatic sulfonylchlorides.

The sulfonylchloride of cyclopentane can also be easily prepared and nothing new is to be reported on this compound which is described in the literature. Our findings do not deviate from those described in the patent by Du Pont on the same reaction.

The reaction of sulfur dioxide and chlorine with simple chloroparaffins should give an indication about the relative position which the sulfonylchloride group will assume with respect to the halogen already present in the molecule. 1-Chlorobutane was investigated which reacts in the usual way easily with SO_2 and chlorine. The reaction mixture obtained consists of non-reacted 1-chlorobutane, chlorobutanesulfonylchloride and dichlorobutane which can be separated easily by distillation under vacuum. The boiling point analysis indicated the presence of 1,2-dichlorobutane as main product, whereas the amount of 1,3-dichlorobutane formed was smaller and only very little 1,4-dichlorobutane was obtained. The sulfonylchlorides were not entirely uniform and could not be separated into uniform fractions by distillation under vacuum, although their tendency for splitting off SO_2 was not quite as strong as that of cyclohexanesulfonylchloride. With respect to the attempts to obtain crystalline derivatives, only the reaction with liquid ammonia was successful which yielded the uniform, well-crystallized amide of a chlorobutane sulfonic acid, probably 1-chlorobutane-3-sulfonic acid.

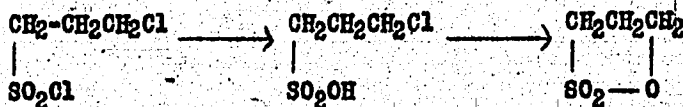
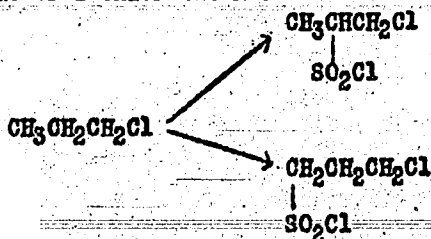
Proof for the structure of the chlorobutanesulfonylchlorides is based on the following thoughts: In principle, the sulfonylchloride group can enter the chlorobutane molecule at three different points; the introduction into the CH_2Cl

group can be considered as impossible since it was found that no sulfonylchlorides are formed with compounds in which each carbon atom is linked to chlorine as e. g. - ethylenschloride. This leaves the possibility of introducing the sulfo group in the 2-, 3- and 4- positions. On hydrolysis with water a mixture of the corresponding chlorobutanesulfonic acid results and the question arises if it would be possible to split off hydrochloric acid by heating the sulfonic acid. This possibility is based on the fact that β -halogen carboxylic acids are converted easily into unsaturated carboxylic acids, whereas γ - and δ -halogen carboxylic acids are converted to lactones. In the case of a γ -halogen sulfonic acid, it was therefore, to be expected that an inner anhydride, a sulfolactone or sultone, would be formed. Actually, on heating under vacuum to 160 - 200°C., strong development of HCl took place and, at the same time, a water-insoluble oil distilled over. This was found on subsequent distillation to have a practically constant boiling point of 150°C. at 12 mm. Hg and the distillate was a colorless neutral liquid. Analysis indicates that it is the inner anhydride of a hydroxybutanesulfonic acid. For the time being, this compound which is not described in the literature has been named butanesultone; it is easily obtainable by the procedure described with a yield of about 60% of the theory.



This makes it rather certain that in the sulfochlorination of 1-chlorobutane the sulfo group enters to at least 80% in the 3-position. It is true that the 1-chlorobutane-4-sulfonic acid could form a sultone by splitting off HCl (δ -sultone); the presence of a 1-chlorobutane-4-sulfonic acid in large quantities seems, however, to be extremely unlikely since investigation of 1-chloropropane indicated that it is very difficult to sulfochlorinate a methyl group in the end position.

The sulfochlorination of 1-chloropropane proceeds generally in the same way as that of 1-chlorobutane.

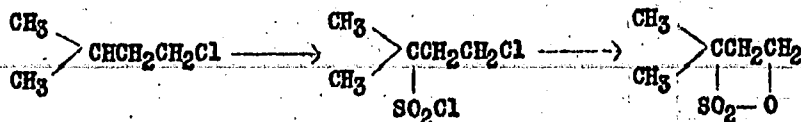


The chloropropanesulfonic acids which are obtained from the reaction mixture by hydrolysis behave considerably different from the chlorobutanesulfonic acid; only a very small yield of neutral distillate was obtained which gave a very small amount of the simplest and also, up to now, unknown sultone. The compound is a solid and has a melting point of 31°C.; it has a great tendency to crystallise.

The compound which, for the time being, should be called propanesultone is the simplest, not-yet-described representative of the class of sultones. The compound could also be prepared by another method which will be described below.

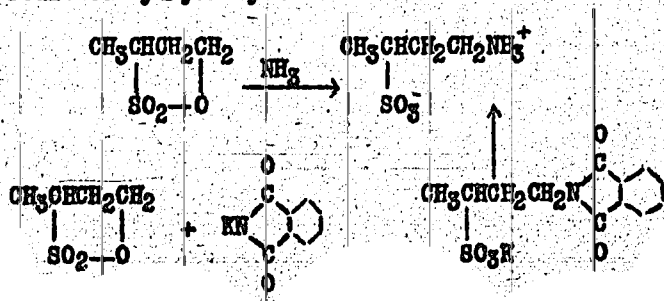
From the behavior of the sulfonic acids obtained from 1-chloropropane, it can be seen that the introduction of the sulfo group takes place, mainly, in the β -position to the halogen and the methyl group is only substituted to a small extent, because it can hardly be expected that 1-chloropropane-2-sulfonic acid would form a β -sultone in the unlikely case that it splits-off HCl. On the other hand, the results show that in the case of 1-chlorobutane the hydrogens of the methyl group have not been substituted or only to a very slight extent so that it is rather certain that the structure of the butanesultone corresponds to a 1,3-sultone.

It looks as if the sulfonylchloride group would enter the molecule as far away as possible from the carbon which is substituted by halogens but that it avoids the methyl group. Under these conditions it appeared interesting to study the behavior of 1-chloroisopentane which can be easily obtained from amylalcohol. In this case we have a tertiary carbon atom in the 3-position to the chlorine-substituted carbon and it would be expected that this tertiary carbon atom would facilitate the introduction of substituents. On distillation under vacuum of the chloroisopentane sulfonic acid which was obtained by sulfochlorination and hydrolysis, 80% of the theoretical yield of an inner anhydride was obtained which has been named isopentanesultone.

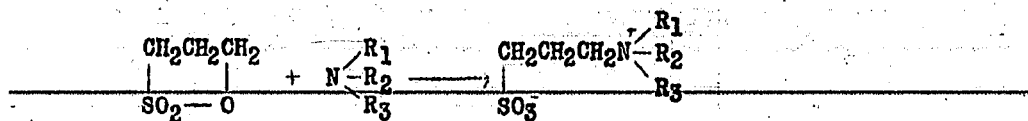


It seems, therefore, entirely possible to direct the introduction of the sulfonylchloride group by suitable substituents and this possibility is at present under investigation. The experimental work is directed mainly towards the synthesis of halogen alkyl sulfonic acids which have the sulfo group and the halogen in the 1,3-position and are, therefore, able to form sultone. Based on data in the older literature (Markwald and Frahm, (1898)) which pertain to the preparation of hydroxypropanesulfonic acid from allyl alcohol and potassium bisulfite, experiments were carried out with hydroxypropanesulfonic acid made from allyl alcohol. On distillation under vacuum of this acid the same propanesultone was obtained which was also isolated from the sulfochlorination mixture of 1-chloropropane. The yield of this interesting compound was not too satisfactory by this method, either, and experiments are under way to develop a good method of preparation.

The sultones react energetically with ammonia and form aminalkylsulfonic acids. This is indicated by the solubility behavior of the compound obtained from butanesultone which is practically insoluble in alcohol but easily soluble in water. The fact that the same compound is obtained from butanesultone and phthalimide potassium followed by hydrolysis can be considered as additional evidence.



Primary and secondary aliphatic and aromatic amines like ethylamine, diethylamine or aniline behave like ammonia. Aromatic amines with negative substituents can be easily reacted and the behavior of 1-aminocanthraquinone is remarkable. This compound reacts easily with propane- or butanesultones and forms a deep red dye which is easily soluble in water and dyes wool a reddish blue from an acid solution. Tertiary amines also react easily with these sultones under formation of quarternary ammonium compounds.



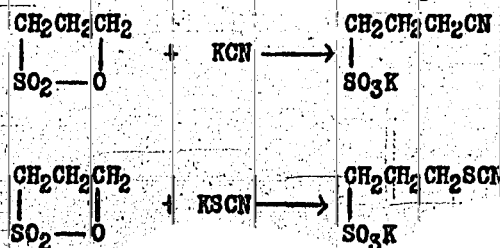
The compounds of propane- and butanesultone with dimethylaniline, pyridine, quinoline and isoquinoline are very well crystallized and are well suited for the identification of the sultones because they are only slightly soluble in organic solvents; they are easily soluble in water. Experiments are under way to react primary bases containing long aliphatic chains in order to obtain capillary-active compounds. The reaction of tertiary amines with at least 1 long-chain aliphatic substituent is planned also. The compounds obtained in this way are expected to be useful as disinfectants.

The sultones derived from aliphatic hydroxyalkylsulfonic acids generally add to compounds containing basic groups. The addition compounds formed in this way are inner salts. In this respect the sultones behave analogous to the alkylesters of organic sulfonic acids or sulfuric acid, e. g., dimethylsulfate. It was, consequently, to be expected that all those compounds which are alkylated by dimethylsulfate would also react with sultones and this expectation has been fulfilled by all compounds which have been tried.

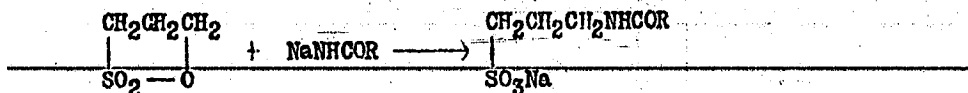
It has long been known that dimethylsulfate reacts easily with potassium iodide under the formation of potassium methylsulfate and methyl iodide. The sultones also reacted very easily with potassium iodide, forming the potassium salt of iodoalkylsulfonic acid; 1-iodopropane-3-sulfonic acid and 1-iodobutane-3-sulfonic acid in the form of their well-crystallized salts have thus become easily available. Potassium bromide and potassium fluoride behave analogous to potassium iodide; however, their reaction requires higher temperatures.



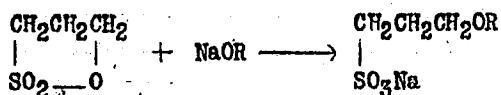
With potassium cyanide the salts of the cyanoalkylsulfonic acids are formed, whereas potassium thiocyanate which reacts already at room temperature leads to the well-crystallized salts of the thiocyanatesulfonic acids which are slightly soluble in organic solvents.



Analogous to the reaction of dimethylsulfate with alkali salts of organic acids, the esters of hydroxyalkylsulfonic salts are formed by reaction with sultone. The products obtained in the case of salts of higher fatty acids, lauric acid, stearic acid or oleic acid are capillary-active and are good detergents which is not astonishing since their structure resembles that of Igepon A. In similar fashion, the sodium salts of the amides of carboxylic acids can be reacted with sultone. In this case, detergents and textile agents are obtained when the amides of higher fatty acids are used.



Alcoholates and phenolates also react easily with sultones and form ether-like products.



When higher alcohols are used, products which are easily soluble in water are obtained which have good detergent properties, whereas the products obtained from naphthol have good wetting characteristics. Sodium cellulose reacts at ordinary temperature with propane- and butanesultone giving ether-like cellulose derivatives which are soluble in water and the solutions have a comparatively low viscosity. They can be used as thickeners, sizing and for similar purposes.

Mercaptides, e. g., sodium thiophenate can also react with sultone forming thioethersulfonic acids.



The reaction of metal compounds of hydrocarbons with sultones also proceeds easily. The reaction with fluorene sodium leads to a compound whose aqueous solution has detergent and strongly wetting properties. Carbacene can also be reacted in the form of its sodium compound. The examples which could be further extended indicate that the reactions carried out with sultones are typical alkylation reactions. They are, in principle, analogous to alkylation obtained with organic sulfonic acid alkyl esters. However, since the sultones are inner esters of hydroxyalkylsulfonic acids, simultaneously with the alkyl group a sulfo group is always introduced into the reacting molecule. The products obtained in this way are always salts of substituted alkyl sulfonic acids which usually are easily soluble in water. The importance of the new sulfoalkylation reaction for the chemical industry is obvious. It can be compared to the reaction of alkyleneoxydes which have attained great technical importance.