

REACTION OF DICHLOROMETHANESULFINATE WITH ALKALIES: ROLE OF CHLOROSULFENE AS AN INTERMEDIATE

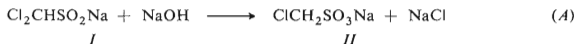
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It was found that dichloromethanesulfinate (*I*) reacts with alkali solutions under formation of salts of chloromethanesulfonic acid (*II*) in high yields. The course of this reaction, involving a selective splitting off of the chlorine atom under simultaneous oxidation of the sulfinic group to a sulfonic one, is rationalized as a nucleophilic attack of a water molecule, or a hydroxyl, on the highly reactive chlorosulfene intermediate. If the alkaline decomposition of *I* is carried out in anhydrous pyridine in the presence of aromatic amines as nucleophiles, chloromethanesulfonanilides *IV* are formed. *S*-Alkyl ester of thiosulfonic acid, which under identical conditions was expected in the reaction with benzylmercaptan as nucleophile, evidently reacts very easily with excess mercaptan under formation of disulfide and chloromethanesulfonic acid (*VI*).

Recently we have described the hydrolytic reaction of trichloromethanesulfonyl chloride in alkaline medium, leading in one reaction step to high yields of corresponding salts of dichloromethanesulfonic acid¹ (*I*). The alkali salt of chloromethanesulfonic acid (*II*) has now been identified as a by-product of this hydrolysis, which under suitable conditions may also become the main product. That is, we have found that under the effect of alkalis on *I* a selective splitting off of one chlorine atom takes place under simultaneous oxidation of the sulfinic group to the sulfonic group. The reaction may be formulated by the equation (*A*):



Chloromethanesulfonate *II* was identified by conversion to the corresponding sulfonyl chloride and chloromethanesulfonanilide and to benzylthiuronium salt, and further by ¹H-NMR spectrometry. The reaction course and the validity of equation (*A*) was controlled by argentometric titration of chlorides and by the determination of sulfinate concentration decrease by titration with chloramine T. The exclusion of air oxygen, representing a possible reagent and one used for the oxidation of sulfinites to sulfonates², did not have any effect on the result of the reaction. Reaction (*A*) represents a suitable method of preparation of *II* (and other salts as well), so far only accessible by the reaction under pressure of alkali sulfite with dichloromethane.

The use of organic bases (pyridine and triethylamine) instead of alkali hydroxide leads to the same result, but the reaction proceeds more slowly. Thus, for example, while after three hours' heating of *I* with an equimolecular amount of sodium hydroxide a 86% conversion to *II* was observed, in the case of pyridine the conversion was 60% after the same reaction time, and in the case of triethylamine only 11%. A longer reaction time, 6 hours, led in the case of pyridine to a 82% conversion and in the case of triethylamine it increased to 52%. In both cases of prolonged reaction times a disagreement was observed between the conversion determination of chlorides by titration and the determination of unreacted sulfinate, in the sense that the determination of unreacted sulfinate gave higher conversion values, *i.e.* 87% in the case of pyridine and 75% in that of triethylamine. This is a striking difference, especially in the latter case. This also means that in consequence of a lower reaction rate of the main reaction the side reaction can also take place, especially simple oxidation to dichloromethanesulfonate, the signal of which could be found in the $^1\text{H-NMR}$ spectrum of the end product when triethylamine was used.

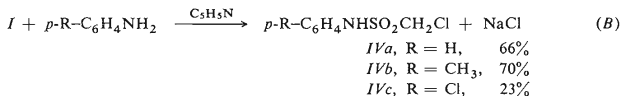
A reaction having a similar result, *i.e.* dehalogenation of the sulfinate under simultaneous oxidation, has been described in the preparation of 1-chloroethanesulfonic acid by reduction of the corresponding sulfonyl chloride with zinc, when ethanesulfonic acid was isolated³ as the product. This isolated report has been revised recently by King and Beatson⁴ who suppose an intermediary formation of the highly reactive methylsulfene in this reaction, which then affords ethanesulfonic acid by addition of one molecule of water.

We suppose that similarly in our case of the decomposition of *I* the sulfene reactive intermediate *III* (Scheme 1) is responsible for the result. The mechanism of its formation can so far only be supposed; in accordance with the work of King and Beatson⁴ we suppose a monomolecular, thermal decomposition of *I*, while the role of the base remains unclear. The formation of the anion of sulfonic acid by a nucleophilic addition of hydroxyl or water to the dipolar ylide structure *III* is in accordance with present knowledge on the reactivity of sulfenes⁵, which has also been supported recently by the publication of the MO-SCF-CNDO calculation of the hypothetical molecule of sulfene, from which a high electrophilicity of the sulfur atom and – on the contrary – a high nucleophilicity of the carbon atom⁶ ensue.



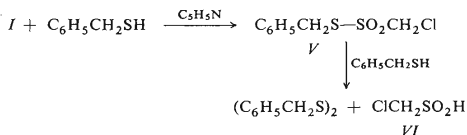
SCHEME 1

The assumption of the formation of *III* as a reactive intermediate in alkaline cleavage of *I* is confirmed by the results of the reactions carried out in the presence of other nucleophiles than water. In these reactions *I* was cleaved with pyridine in anhydrous medium in the presence of aromatic amines or of benzyl mercaptan. In the first case corresponding chloromethanesulfonanilides were formed, as supposed (*IVa-c*, reaction (*B*)), and that in preparatively important amounts.



This reaction simultaneously represents a new route for the synthesis of chloromethanesulfonanilides which were so far only accessible by the general method starting from chloromethanesulfonyl chloride and aromatic amines.

During the experiment aiming at the use of benzyl mercaptan as a nucleophile for the reaction with chlorosulfene, instead of the expected *S*-benzyl ester of chloromethanethiosulfonic acid (*V*), only dibenzyl disulfide was isolated, practically in 100% yield. This result may be explained by supposing that the primarily formed ester *V* reacts further to the disulfide by thioalkylation reaction with excess mercaptan (Scheme 2). This consecutive reaction takes place easily even at room temperature⁷. The water soluble reaction products indicate the presence of sulfonates, and in their ¹H-NMR spectra the signal at δ 4.50 ppm, which can be assigned to chloromethanesulfonic acid (*VI*) formed during the thioalkylation reaction, is present in addition to the signal of unreacted *I*.



SCHEME 2

From these facts it follows that in addition to alkanesulfonyl chlorides (by hydrogen chloride elimination) chloroalkanesulfonates (by elimination of chlorine atom) can also be used as a source of sulfenes. At the same time the reactivity of the generated sulfenes seems to be quite analogous in both cases.

EXPERIMENTAL

Starting Compounds and Methods

Sodium dichloromethanesulfinate was prepared on reaction of trichloromethanesulfonyl chloride with aqueous sodium hydroxide solution¹. Using repeated extraction with ethanol a product was obtained containing according to titration with chloramine T 97–98% of sulfinate. The sulfinate content was determined by titration with chloramine T according to Uhlenbrock⁸. The ¹H-NMR spectra were measured on a Tesla BS 467, 60 MHz, instrument, in D₂O solutions, using sodium 2,2-dimethyl-2-silapentane 5-sulfonate (DSS) as internal reference. The melting points were measured on a Kofler block and they are corrected.

Alkaline Degradation of Dichloromethanesulfinate

A) *In aqueous alkaline medium*: Solid NaOH (4 g; 0.1 mol) was added to a solution of sodium dichloromethanesulfinate (17.1 g, 0.1 mol) in 250 ml of water and the mixture was refluxed for 3 hours. Argentometric determination of chlorides indicated a 88% conversion, while the titration of unreacted sulfinate indicated a 86% conversion to sodium chloromethanesulfonate. The mixture was evaporated and the residue extracted with methanol. On cooling of the methanolic solution the sodium salt of chloromethanesulfonic acid crystallized out (11.1 g; 73%). After recrystallization from methanol the melting point was 259–261°C (ref.⁹ gives m.p. 261 to 262.5°C). In the ¹H-NMR spectrum a single sharp singlet could be observed, with $\delta = 4.78$ ppm.

Benzylthiuronium salt, prepared in a known manner¹⁰ and crystallized from water, had m.p. 97–98°C. For C₉H₁₃ClN₂O₃S₂ (296.8) calculated: 36.42% C, 4.41% H, 11.94% Cl, 9.44% N; found: 36.39% C, 4.48% H, 11.64% Cl, 9.28% N.

Chloromethanesulfonyl chloride was prepared by reacting the sodium salt with PCl₅ and POCl₃, according to Goldwhite and co-workers¹¹ and it was identified by comparison of its elution time with the substance obtained by chlorination of trithiane¹², and also by converting it to chloromethanesulfonanilide, m.p. 79–80°C (lit.¹² gives 81–82°C). The mixture melting point with a product obtained directly from dichloromethanesulfinate by the procedure described below was undepressed.

B) *In pyridine or triethylamine*: Pyridine (0.8 g, 0.01 mol) or triethylamine (1.01 g, 0.01 mol), respectively, were added to a solution of I (1.71 g, 0.01 mol) in 50 ml of water, and the solutions were refluxed. The reaction course was followed by withdrawing samples and determination of chlorides and the unreacted sulfinate in them. The total reaction time was 6 hours, and the final conversion was 87% (or 82% according to chloride determination) in the case of pyridine, and 75% (or 52% when calculated per Cl⁻) in the case of triethylamine. The evaporation of the mixture and the ¹H-NMR analysis indicated the dominant presence of the signal for ClCH₂SO₃⁻ at 4.77 ppm., in addition to low signals of the unreacted Cl₂CHSO₂⁻ (δ 6.30 ppm.) and Cl₂CHSO₃⁻ (δ 6.60 ppm.).

Reaction of Dichloromethanesulfinate with Aromatic Amines

Aromatic amine (0.1 mol) was added to a stirred suspension of 0.1 mol of sodium dichloromethanesulfinate in 50 ml of pyridine and the mixture was refluxed for 7 hours. After pouring into 100 ml of water it was neutralized with dilute sulfuric acid and extracted with chloroform. The extract was evaporated and the residue crystallized from aqueous ethanol. The following yields were thus obtained in individual cases: 13.6 g (66%) IVa, m.p. 79–80°C (lit.¹² gives

81–82°C), 15.4 g (70%) *IVb*, m.p. 96–97°C (lit.¹² gives 96–97°C), and 5.5 g (23%) *IVc*, m.p. 103–105°C (lit.¹³ gives 104–105°C).

Reaction of Dichloromethanesulfinic acid with Benzyl Mercaptan

Benzyl mercaptan (12.42 g, 0.1 mol) was added to a stirred suspension of 17.1 g (0.1 mol) of *I* in 50 ml of pyridine and the mixture was refluxed in an inert atmosphere for 4 hours. After pouring it into 100 ml of water and acidification with dilute sulfuric acid (1 : 4) the mixture was extracted with diethyl ether. The residue of the ethereal extract (12.4 g, m.p. 64–68°C) immediately gave on crystallization from ethanol pure dibenzyl disulfide, m.p. 70–71°C. The aqueous layer was alkalinized with solid NaOH, the main part of pyridine was extracted with ether and the residual solution was evaporated at a slightly elevated temperature (not exceeding 35°C). In the ¹H-NMR spectrum of the residue the signals of the unreacted Cl₂CHSO₂⁻ (singlet at δ 6.30 ppm. and of the ClCH₂SO₃⁻ formed (singlet at δ 4.77 ppm.) were found, but also a singlet at δ 4.50 ppm which can be assigned to chloromethanesulfinic acid or its salt.

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