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CHEMISTRY

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Abstract

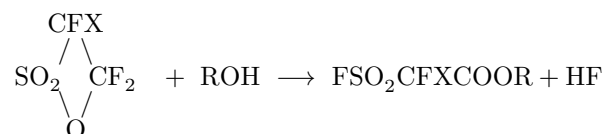
Full Text

CHEMISTRY

Academician I. L. KNUNYANTS, G. A. SOKOLSKII, M. A. BELAVENTSEV

STRUCTURE AND REACTIVITY OF FLUORINE-CONTAINING β -SULTONES

It was shown earlier (¹⁻³) that the reaction of fluorinated olefins with sulfur trioxide gives four-membered cyclic compounds, β -sultones. The reactivity of fluorine-containing β -sultones was evaluated (⁴⁻⁶) only with respect to their reaction with nucleophilic compounds—amines, alcohols, water, mercaptans, hydrogen sulfide, and carboxylic acids. In all cases the formation of the corresponding derivatives of α -sulfofluoridecarboxylic acids was observed, for example:

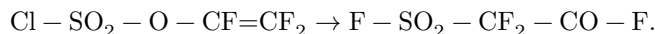


However, there were insufficient grounds for interpreting the mechanism of these reactions. Subsequently we discovered new facts that made it possible not only to explain the direction of these reactions, but also to reveal the multifaceted reactivity of fluorine-containing β -sultones.

Some of the most interesting observations are connected with the preparation and study of the properties of the trifluorovinyl ester of chlorosulfonic acid. This compound was obtained by the interaction of tetrafluoroethylene with chlorosulfonic acid and was identified by alkylation of the latter with bis(trifluorovinyl)mercury.

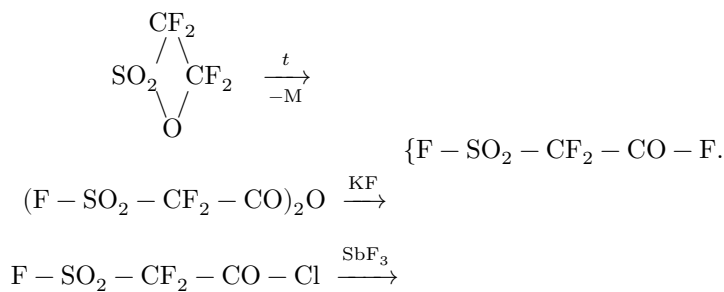


In studying the chemical properties of trifluorovinyl chlorosulfate, attempts were made to exchange the chlorine atom for fluorine. Halogen exchange occurs on heating trifluorovinyl chlorosulfate with zinc fluoride to 80-100°. However, instead of the expected trifluorovinyl fluorosulfate, its isomer, sulfofluoridedifluoroacetyl fluoride, was isolated:

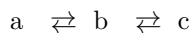


Such a course of the process can be explained only by assuming the intermediate formation of trifluorovinyl fluorosulfate (a), its subsequent isomerization to tetrafluoroethane- β -sultone (b), and, finally, isomerization of the latter to sulfofluoridedifluoroacetyl fluoride (c). This direction of the process is probably determined by the temperature conditions of the reaction.

Indeed, upon heating tetrafluoroethane- β -sultone above 80° , its isomerization occurs and sulfofluoridedifluoroacetyl fluoride is formed; this was identified by the reactions of sulfofluoridedifluoroacetic anhydride with potassium fluoride and of the acid chloride of the same acid with antimony fluoride.

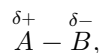


The observations presented make it possible to postulate the following chain of transformations, determined by the character of electronic effects in the molecule of tetrafluoroethane- β -sultone (b) and its isomers (a, c)

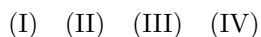


The possibility of anionotropic changes in the molecule of tetrafluoroethane- β -sultone undoubtedly also determines the nature of its reactivity toward various reagents.

Thus, when tetrafluoroethane- β -sultone is acted upon by some polar reagent



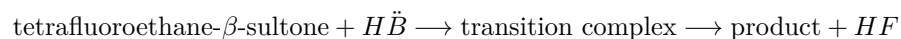
formation of one of four transition reaction complexes is possible, with the following types of conjugation of the addends:



The assignment of the transition reaction complex to one or another structural type is evidently determined by the electron-donor or electron-acceptor character of the reagent $A - B$ used. If this reagent is nucleophilic, transition

complexes of type I or II may be formed, type I being more justified in view of the possibility of electrostatic orientation of the electrophilic fragment of the reagent ($\overset{\delta+}{A}$) toward the oxygen atom of the sultone. If the reagent $A - B$ is electrophilic, formation of transition complexes of type III or IV is possible, type IV likewise being more justified for the reason already considered. In the realization of structures I or III, derivatives of sulfocarboxylic acids should be formed, whereas in the case of structures II or IV, derivatives of alkylsulfuric acids should be formed.

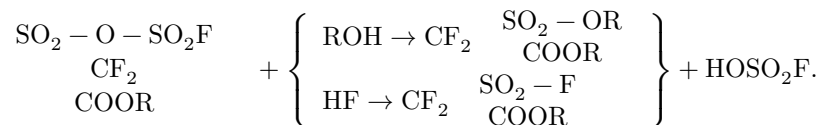
From these positions, the direction of the reaction of fluorine-containing β -sultones with amines, alcohols, water, mercaptans, hydrogen sulfide, and carboxylic acids becomes clear; it proceeds through an intermediate reaction complex of type I with subsequent formation of derivatives of sulfofluoridecarboxylic acids.



According to an analogous scheme, the reaction of tetrafluoroethane- β -pyrosultone with alcohols is carried out. In the first stage, formation of a transition complex takes place, which is converted into an acyclic pyrosulfonyl compound



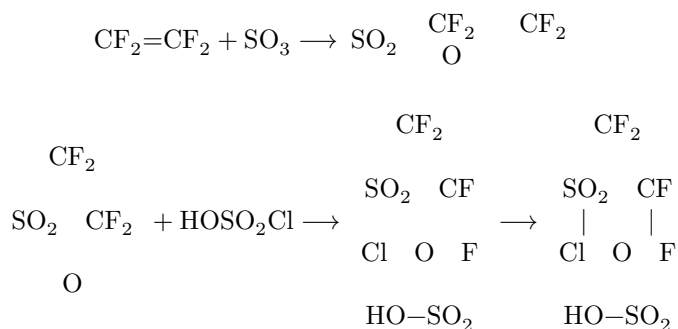
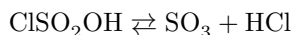
The pyrosulfonyl compound formed is extremely reactive and undergoes further changes. If the reaction is carried out using an excess of alcohol, acylation of the latter occurs with formation of a diester of sulfocarboxylic acid. If, however, one mole of alcohol is used for the reaction, the hydrogen fluoride evolved in the first stages undergoes acylation, and an ester of sulfofluorodifluoroacetic acid is formed



The results of the experiments ⁽⁷⁾ are in strict agreement with the explanation given.

From the same standpoint, the formation of trifluorovinyl chlorosulfate in the reaction of tetrafluoroethylene with chlorosulfonic acid may be considered. It is known that chlorosulfonic acid, owing to equilibrium dissociation, always

contains a certain amount of sulfuric anhydride. In this connection, in the first stage of the reaction, interaction of tetrafluoroethylene specifically with sulfuric anhydride probably takes place, and the tetrafluoroethane- β -sultone formed is then acted upon by chlorosulfonic acid. The latter is an electrophilic compound and therefore can form with the β -sultone a transition reaction complex of type IV, which then generates the final reaction products.



Indeed, on treatment of tetrafluoroethane- β -sultone with chlorosulfonic acid, a reaction takes place accompanied by formation of trifluorovinyl chlorosulfate and fluorosulfonic acid.

Thus, the experimental data presented previously and considered in the present communication are in complete agreement with the propositions advanced concerning the formation and structure of transition reaction complexes, which in turn confirms the nature of the electronic effects in the molecule of fluorine-containing β -sultones.

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Note: Figure translations are in progress. See original paper for figures.

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