FLUORINE CONTAINING β-SULTONES

PART 7. USE OF TETRAFLUOROETHANE-β-SULTONE IN ACETYLATION

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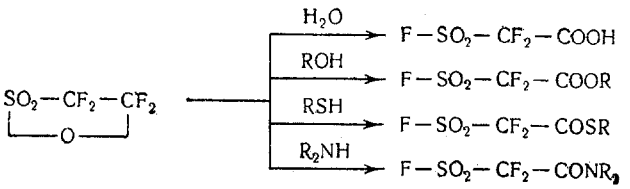
We reported earlier [1] that fluorine containing β-sultones reacted energetically with various compounds which contained active hydrogen atoms. The products of this reaction were shown to be the corresponding derivatives of fluorine substituted β-fluorosulfonyl-carboxylic acids, for example:

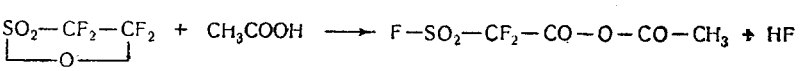


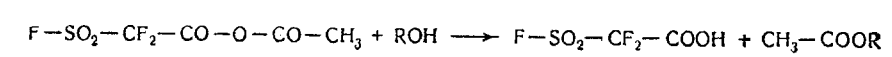
It might be expected that the interaction of fluorine containing β-sultones with carboxylic acids would occur in an analogous way; in this case the reaction products ought to be mixed anhydrides of the corresponding carboxylic and β-fluorosulfonyl-carboxylic acid. The properties of these compounds should undoubtedly be analogous to the properties of known mixed acid anhydrides which possess energetic acylating properties [2].

TABLE

No. of expts.	Alkyl acetate	Acylation temp. °C	Separation technique	Yield, %	No. of expts.	Alkyl acetate	Acylation temp. °C	Separation technique	Yield, %
1	Methyl acetate	0	A	98	10	β-Chloroethyl acetate	10	B	88
2	Ethyl acetate	0	A	98	11	β-Methoxyethyl acet.	10	B	85
3	n-Propyl acetate	0	A	98	12	Allyl acetate	10	B	80
4	i-Propyl acetate	0	A	95	13	Phenyl acetate	20	B	72
5	n-Butyl acetate	10	A	95	14	p-Tolyl acetate	20	B	70
6	n-Amyl acetate	10	B	92	15	Glycol monoacetate	10	B	75
7	n-Hexyl acetate	20	B	90	16	Glycerol monoacetate	10	B	70
8	cyclo-Hexyl acetate	20	B	80	17	Glycol diacetate	20	B	80
9	Benzyl acetate	20	B	85	18	Glycerol triacetate	20	B	77

In fact on mixing tetrafluoroethane-β-sultone with glacial acetic acid (taken in equimolar quantities) an energetic reaction was observed, accompanied by spontaneous heating of the mixture and evolution of hydrogen fluoride. The formation of a mixed anhydride of fluorosulfonyl-difluoroacetic and acetic acids was confirmed by the formation of the corresponding alkyl acetates when the reaction mixture was treated with various alcohols (see the table). Fluorosulfonyl-difluoroacetic acid occurred with the other products of alcoholysis of the mixture of tetrafluoroethane-β-sultone and acetic acid. The process is described by the following equations:





Analogous results were obtained by using substituted and unsaturated alcohols, and also phenols.

The formation of the corresponding half or complete ester occurs in acylation of multiatomic alcohols, depending on the order of mixing the reagents and the quantity of multiatomic alcohols used. Thus, on adding an equimolar mixture of tetrafluoro-β-sultone and acetic acid to an equimolar quantity of glycol, glycol monoacetate is formed, whereas on adding a half molar quantity of glycol to a mixture of the sultone and acid, glycol diacetate is formed. In a similar way glycerol monoacetate and glycerol triacetate are obtained.

The absence of esters of fluorosulfonyldifluoroacetic acid from the reaction products and the exclusive production of alkyl acetates are in line with known ideas on the mechanism of acylation with mixed anhydrides. There is no doubt that the mixed anhydride formed under the conditions given is inclined to dissociate in one way only - into a fluorosulfonyldifluoroacetate anion and an acetyl cation; the latter acylates the alcohol or phenol.

$$F—SO_2—CF_2—CO—O—CO—CH_3 \rightleftarrows F—SO_2—CF_2—COO^- + CH_3—CO^+$$

$$CH_3—CO^+ + ROH \rightarrow CH_3—COOR + H^+$$

$$F—SO_2—COO^- + H^+ \rightleftarrows F—SO_2—CF_2—COOH$$

This direction of dissociation of the mixed anhydride is explained by the considerable difference in strength of acetic and fluorosulfonyldifluoroacetic acids.

Thus, tetrafluoroethane-β-sultone can be successfully used as a reagent which considerably facilitates the esterification of alcohols and phenols with acetic acid. There is no doubt that esterification with other carboxylic acids could be carried out in a similar way. It is evident that other fluorine containing β-sultones could be used for this purpose.

EXPERIMENTAL

Acetylation of alcohols. Glacial acetic acid (0.1 m) was added to stirred and ice cooled tetrafluoroethane-β-sultone (0.1 M) in a teflon reactor. At a temperature of 0-20° (see Table) the absolute alcohol (0.1 M) was added. The reaction mixture was poured into a cooled solution of potassium fluoride (10 g) in water (30 ml). The alkyl acetate was isolated by one of the methods A or B: A. The only layer was separated, dried over magnesium sulfate, and distilled. B. The mixture was extracted with ether; the ether extracts were combined, dried over magnesium sulfate, and fractionated.

Glycol diacetate was obtained in an analogous manner from 0.1 M tetrafluoroethane-β-sultone, 0.1 M acetic acid, and 0.05 M glycol.

Glycerol triacetate was obtained similarly from 0.1 M tetrafluoroethane-β-sultone, 0.1 M acetic acid, and 0.033 M glycerol.

Glycol monoacetate. A mixture of 0.1 M tetrafluoroethane-β-sultone and 0.1 M acetic acid was added dropwise with stirring at room temperature to 0.1 M glycol. The product was worked up by method B.

Glycerol monoacetate was obtained similarly from 0.1 M glycerol and a mixture of 0.1 M tetrafluoroethane-β-sultone and 0.1 M acetic acid.

Isolation of fluorosulfonyldifluoroacetic acid. To an equimolar mixture of tetrafluoroethane-β-sultone and glacial acetic acid an equal quantity by weight of ethanol was added with stirring and cooling. The solution was twice dehydrofluorinated with calcined potassium fluoride. It was then fractionated by heating on the water bath initially at atmospheric pressure and then at reduced pressure. Fluorosulfonyldifluoroacetic acid [3] was isolated by a second distillation at atmospheric pressure. The yield was 95%. In a similar way a 92% yield of fluorosulfonyldifluoroacetic acid was obtained when methanol was used.

SUMMARY

1. The reaction between tetrafluoroethane-β-sultone and glacial acetic acid has been studied.

2. A new method for preparing acetates has been developed. It consists of treating an alcohol or phenol with an equimolar mixture of tetrafluoroethane-β-sultone and acetic acid.

LITERATURE CITED

1. M. A. Dimitriev, G. A. Sokol'skii, and I. L. Knunyants, Dokl. AN SSSR. 124, 581 (1959).
2. J. M. Tedder, Chem. Rev. 55, 787 (1955).
3. M. A. Dmitriev, G. A. Sokol'skii, and I. L. Knunyants, Izv. AN SSSR. Otd. Khim. Nauk (1960) p. 1035.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
