Journal of Fluorine Chemistry, 13 (1979) 159-162

Received: September 7, 1978

HIGHLY FLUORINATED HETEROCYCLES PART XIV. [1] THE CONVERSION OF 2,2,5,5-TETRAFLUORO-3-THIOLEN INTO 2,5-DIFLUOROTHIOPHEN: AN APPARENT EXAMPLE OF THE THERMAL ELIMINATION OF MOLECULAR FLUORINE.

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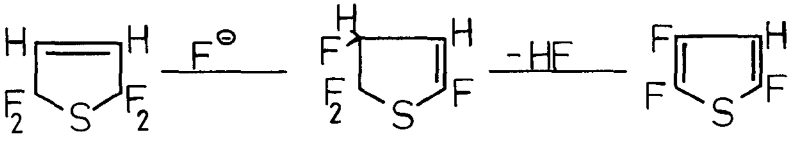
SUMMARY

Pyrolysis of 2,2,5,5-tetrafluoro-3-thiolen gives, as major product, 2,5-difluorothiophen. The possible importance of this observation is discussed.

INTRODUCTION

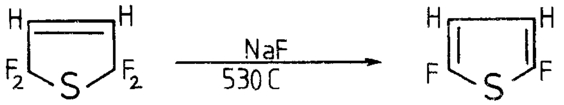
In the course of our continuing studies on the chemistry of polyfluorheterocycles [2] we have attempted to prepare 2,3,5-trifluorothiophen via the hoped-for rearrangement/ dehydrofluorination sequence shown, involving pyrolysis in glass.



I

apparatus of 2,2,5,5-tetrafluoro-3-thiolen (I) [3] over sodium fluoride, a reagent known [4] to promote such rearrangements.

However, this reaction did not occur at moderate temperatures (<480C), and above this (at 530C) a different reaction (Scheme 1) proceeded, giving a moderate yield of 2,5-difluorothiophen, [5] a compound whose synthesis by another route we have already reported. This observation gives the best example yet reported of the apparent loss of molecular fluorine from a molecule with no metal or metal oxide scavenger present. Presumably the sodium fluoride functions here as a heat exchanger only.



SCHEME 1

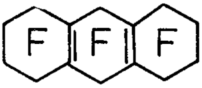
Earlier work carried out in these laboratories reveals similarities; thus studies by Stacey, Stephens and Tatlow, and by Rimmington [4] on the pyrolysis of cyclic polyfluoroolefines over sodium fluoride, previously cited [6] as establishing the order of preference in fluoride-ion-catalysed rearrangements of double bonds, show that apparent loss of F_2 from monohydroheptafluorcyclohexadienes is required in the production of pentafluorobenzene from the dehydrofluorination/rearrangement of various octafluorocyclohexenes, where pentafluorobenzene is prominent amongst the products, and is sometimes formed in greater amounts than the more easily explicable hexafluorobenzene.

It may be, of course, that these reactions are actually not simple losses of F_2 from the pyrolysed species, but rather exchange reactions of the type:

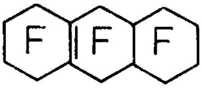
$$RF_2 + R' \longrightarrow R + R'F_2$$

Such a reaction has been observed in our laboratories in a study of the interconversion of the perfluorocyclohexadienes [7], where passage of perfluorocyclohexa-1,3-diene through an aged (i,e. surface fluorinated) hot metal tube gave, in addition to starting material and the 1,4-diene, the disproportionation products hexafluorobenzene and decafluorocyclohexene. Interestingly, an attempted defluorination of the 1,4-diene, using clean mild steel, is reported in the same paper as again giving a small (1%) yield of perfluorocyclohexene in addition to the other, expected, materials.

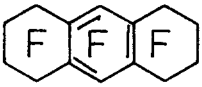
If this exchange reaction were general, it would afford an explanation of some points previously obscure; in particular fluorination of anthracene over potassium tetrafluorocobaltate (III) gives [8] II, and IV as principal products.



II



III



IV

The existing theories [6a,9] of fluorination mechanisms might permit an explanation of the route to II, but the difficulties relating to III and IV are more severe [6a,8]. However, an exchange between two molecules of II, giving one each of III and IV, would rationalise their formation, and is expected to be thermodynamically favoured because IV is aromatic.

Most of the literature results mentioned above can be plausibly interpreted in terms of disproportionation. However, the result which we report here is much less susceptible to such an interpretation, since disproportionation should lead to 3*H*,4*H*/-hexafluorothiolan (or its 3H/4H isomer?) and hence to 3*H*-pentafluoro-3-thiolen or tetrafluorothiophen. All of these are known compounds, and none of them was detected in the reaction mixture. It therefore seems that this is the first well authenticated example of a direct loss of F_2 from a molecule.

EXPERIMENTAL

2,2,5,5-Tetrafluoro-3thiolen (5·6g) was volatilised over 4 hours, in a stream of N_2 (3·5 cm^3/h), through a pyrex tube (25 x 1 cm) packed with sodium fluoride pellets, at a temperature between 530 - 540 C. Products (4·6g) were condensed in a glass trap cooled with liquid N_2, and allowed to come to room temperature before reweighing (2·7g). Ir analysis showed that the bulk of the material lost was

SiF_4. GLC analysis of the less volatile material showed, in addition to starting material, a single major product (50% of the material), isolation of which permitted its identification (i.r, n.m.r, mass spec.) as the known 2,5-difluorothiophen.

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