

THE FLUORIDE ANION CATALYZED SULFUR TRANSFER REACTIONS OF ELEMENTAL SULFUR (S₈) WITH THIOKETONES

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It is well known that thiocarbonyl compounds such as aryl, hetaryl or cycloaliphatic thioketones (R₂C=S) are important building blocks, widely applied for preparation of sulfur heterocycles with diverse ring size. Their superior ability to react with 1,3-dipoles or dienes via the C=S group brought them into prominence as ‘superdipolarophiles’ and ‘superdienophiles’ in [3+2] and [4+2] cycloadditions reactions, respectively [1,2]. Sulfurization of the C=S bond leads to so called “thiosulfines” (thiocarbonyl *S*-sulfides). They are considered as a class of elusive 1,3-dipoles that *in situ* undergo further conversions. The evidence of their supposed existence was unambiguously demonstrated in 1987 by R. Huisgen and J. Rapp [3-5]. The sulfur transfer reaction involving elemental sulfur (S₈) as a sulfur source, require its activation via homolytic or heterolytic cleavage of the S–S bond. Various chemical species are known to activate the S₈ ring, however one of the unorthodox but only little-known approaches is the usage of the fluoride anion F[−] as a catalyst.

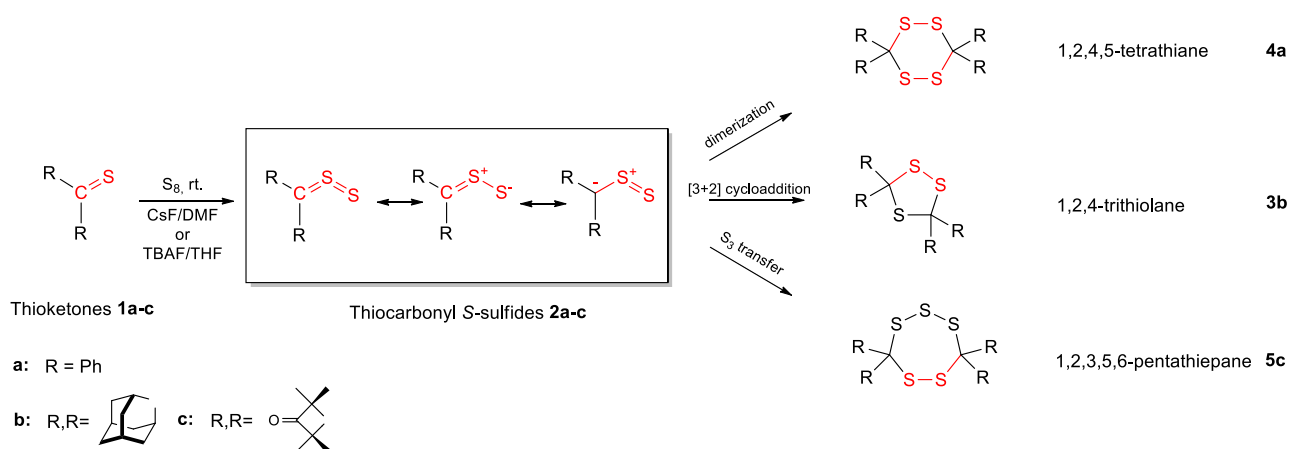


Fig. 1. *In situ* generation of thiocarbonyl *S*-sulfide with the use of fluoride anion and its further pathway conversation to heterocyclic compounds.

In our ongoing research, we found that sulfurization of aryl and cycloaliphatic thioketones **1a-c** by treatment with elemental sulfur (S₈) in the presence of cat. amounts of fluoride anion (cesium fluoride (CsF) or tetra-*n*-butyl ammonium fluoride (TBAF)), leads to formation of thiocarbonyl *S*-sulfides **2a-c** that *in situ* undergo further conversions. We also found that, depending on thioketone type, the product can be formed as 5-, 6- or 7-membered heterocyclic ring with four (1,2,4,5-tetrathiane) **4a**, three (1,2,4-trithiolanes) **3b**, or five (1,2,3,5,6-pentathiepanes) **5c** sulfur atoms. A novel, unique and efficient method for the *S*-transfer to the C=S bond *via* activation of S₈ with fluoride anion as well as mechanisms of the formation of sulfur rich heterocycles **3-5** will be discussed.

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