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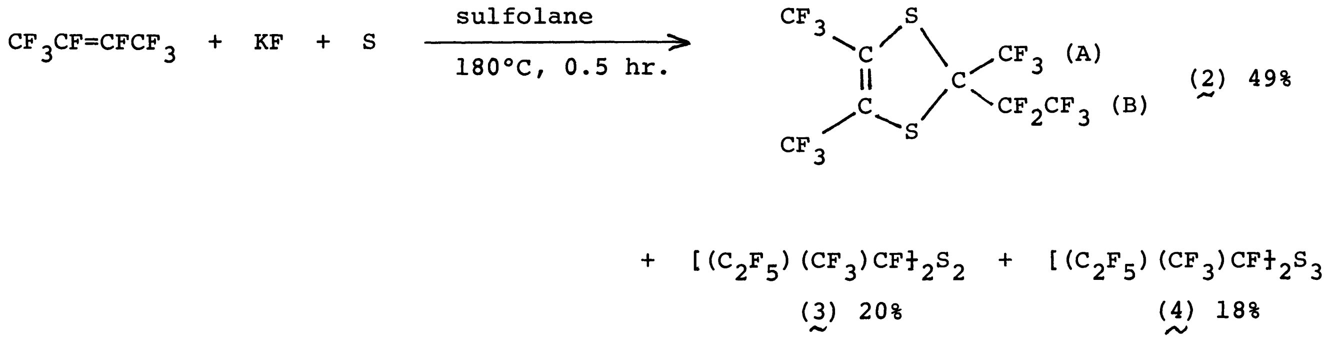
SYNTHESIS OF PERFLUORINATED 1,3-DITHIOLES FROM FLUOROOLEFINS

Donald J. BURTON and Yoshio INOUYE*
Department of Chemistry, The University of Iowa
Iowa City, Iowa 52240 U.S.A.
Department of Resources and Environment Science
The Tokai University, Hiratsuka, Kanagawa 259-12

In contrast to the formation of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane from hexafluoropropene, potassium fluoride, and sulfur, perfluoro-2-butene and perfluoro-pentenes react with potassium fluoride and sulfur to form perfluoro-1,3-dithioles via intermediate thioenolate anions.

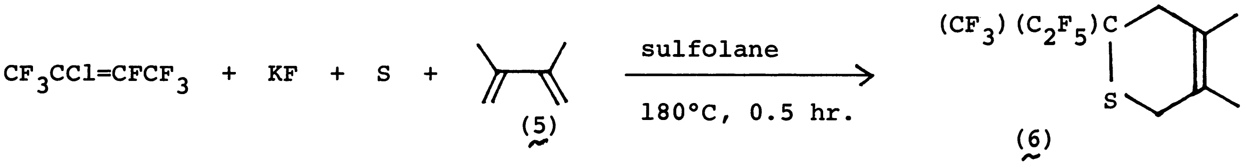
Hexafluorothioacetone (HFTA) has been prepared by a variety of synthetic methods.¹⁾ It rapidly dimerizes to 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (**1**) on standing or by reaction with a variety of bases.²⁾ Compound (**1**) can more conveniently prepared via the in situ formation of HFTA from hexafluoropropene, potassium fluoride and sulfur.²⁾ Recent reports have documented the synthetic utility of (**1**) as a synthetic precursor.^{3,4,5,6)}

Attempts to extend the Knunyants's methodology²⁾ to the formation of homologous dithietanes failed. The major product of the reaction of perfluoro-2-butene with potassium fluoride and sulfur was not a dithietane, but was perfluoro-2-ethyl-

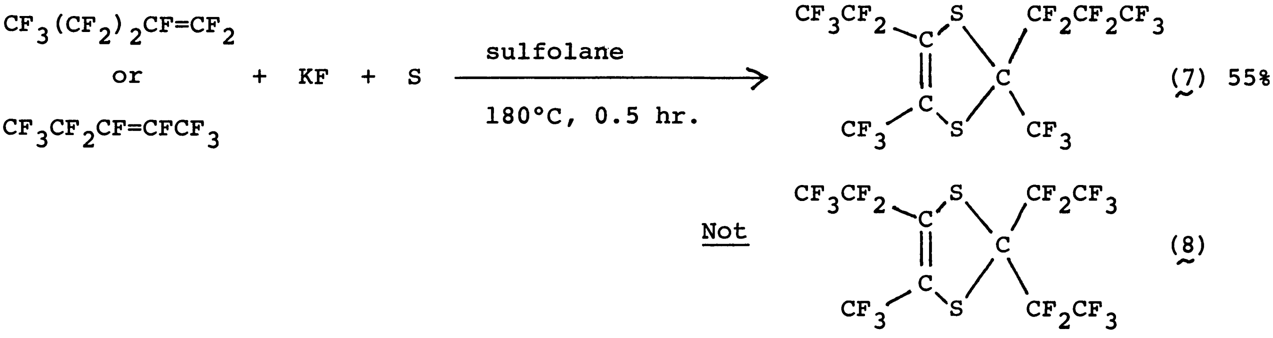


2,4,5-trimethyl-1,3-dithiole (2). Lesser amounts of the acyclic disulfide and trisulfide were obtained. Similar results were obtained with 2-chloro-heptafluoro-2-butene, potassium fluoride and sulfur.7) Compound (2) showed a parent ion in the mass spectrum at 425.9194 (calcd. 425.9217 for $C_8F_{14}S_2$) with major fragments at 356.9302 for loss of CF_3 (calcd. 356.9265) and 306.9319 for loss of C_2F_5 (calcd. 306.9297). The infrared spectrum showed a strong C=C absorption at 1625 cm^{-1}. The ^{19}F NMR spectrum showed a singlet at 56.2 ppm8) (6 F's, CF_3 groups attached to the olefinic carbons), a triplet of quartets at 72.5 ppm (3 F's CF_3 (A)), a quartet at 79.1 ppm (3 F's, CF_3(B)), and a quartet at 109.0 ppm (2 F's, CF_2). Similar data which were consistent with the assignments for the disulfide and trisulfide were obtained.

Confirmation of the thioketone as an intermediate in these reactions was obtained when the reaction was carried out in the presence of 2,3-dimethyl-1,3-butadiene (5). The formation of (2), the disulfide (3), and the trisulfide (4) was completely quenched and only a Diels-Alder adduct (6) of the thioketone was found.

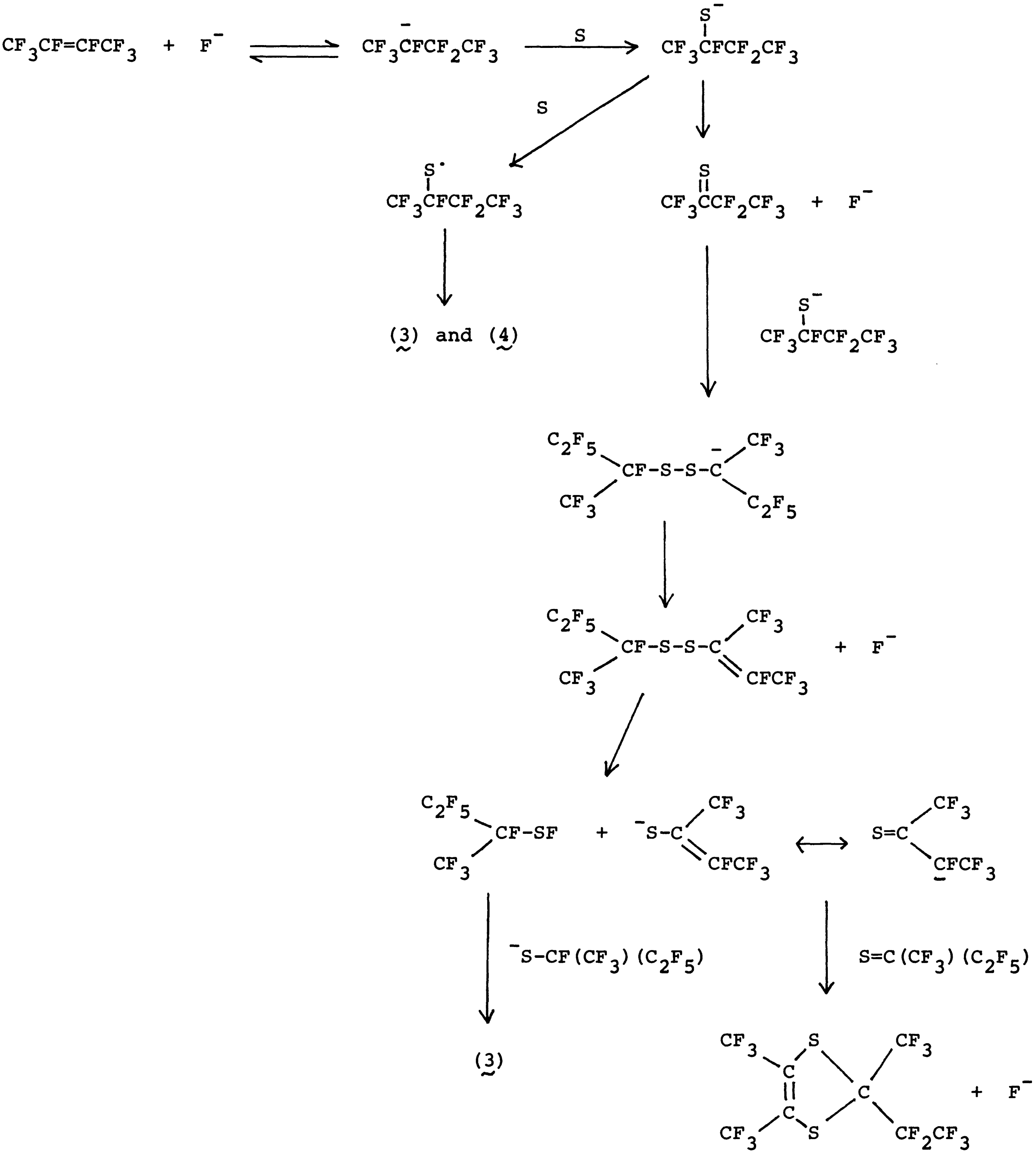


When either perfluoro-1-pentene or perfluoro-2-pentene was reacted under similar conditions, again dithiole was obtained.9) No evidence of dithietane formation was found. Surprisingly, only dithiole (7) from the 2-thioketone was isolated. None of the expected dithiole (8) from the isomeric 3-thioketone was observed.10)



We propose that the dithioles arise from the reaction of perfluoro-thioketone with thioenolate anion. The latter is formed by the cleavage of the disulfide, which is produced by the initial capture of perfluoro-mercaptide by thioketone.

Mechanistic scheme;



Evidence consistent with the cleavage of a disulfide linkage was obtained when the disulfide (3), by-product of the perfluoro-2-butene reaction, was reacted with potassium fluoride and (5). Since the Diels-Alder reaction described earlier demonstrates the formation of thioketone in the reaction sequence, the formation of (6) indicates the *in situ* generation of the thioketone with the cleavage of the disulfide linkage of (3) by potassium fluoride. This result suggests that the dithiole (2) was also formed from the disulfide (3). However, the mechanistic pathway on this route is not clear.

$$(C_2F_5)(CF_3)CF\text{-}S\text{-}S\text{-}CF(C_2F_5)(CF_3) + KF + (5) \longrightarrow (6) \quad 91\%$$

In conclusion, the formation of dithietane from hexafluoropropene, potassium fluoride and sulfur is a unique reaction - *not* a general reaction. Homologous fluorinated olefins do form an analogous intermediate thioketone; however, subsequent reaction of the thioketone gives 1,3-dithiole - *not* 1,3-dithietane.

Acknowledgement;

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7) 52% of (2), 11.5% of disulfide and 15% of trisulfide were obtained.

8) All the chemical shifts were calculated from $CFCl_3$ as an internal standard.

9) Perfluoro-1-pentene was isomerized to perfluoro-2-pentene prior to reaction with KF and S. All the spectroscopic data were consistent with the dithiole structure assignment.

10) It's not clear whether the 2-thioketone is selectively formed or whether the 2-thioketone reacts more rapidly in the subsequent steps.

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