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UNEXPECTED REACTIONS OF PERFLUORO INNER OLEFINS WITH THIOLS

—— SUPPOSED 1,4-ELIMINATION OF RS-F ——

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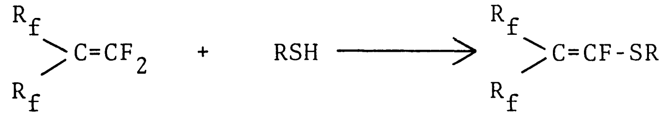
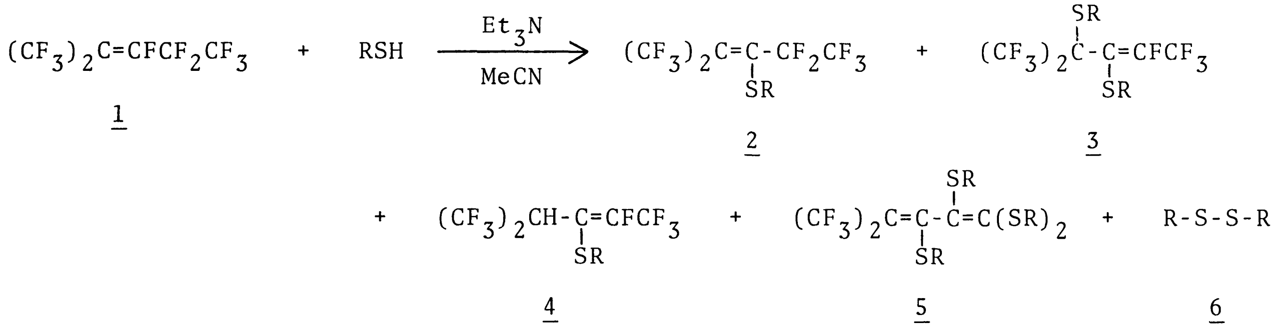
Reactions of perfluoro-2- and -4-methyl-2-pentenes with thiols were found to involve an oxidation-reduction system. 1,4-Elimination of sulfenyl fluorides from thio-substituted perfluoroolefins forming 1,3-dienes and disulfides is suggested as the reaction pathway.

Several examples of the nucleophilic reactions of thiols with perfluoro terminal olefins have been reported. Tetrafluoroethene, hexafluoropropene and 2-(trifluoromethyl)pentafluoropropene are known to be substituted by alkyl- or arylthio group at their terminal position.$^{1,2)}$


(R_f = F or CF_3)

However, no reports on the reactions of perfluoro inner olefins with S-nucleophiles have appeared in the literature. In a course of our studies on the nucleophilic reactions of the oligomers of hexafluoropropene, reactions between thiols and perfluoro-2-methyl-2-pentene [1], one of hexafluoropropene dimers, were examined. As a result, the expected thio-substituted perfluoroolefins [2, 3] and their reduced derivatives [4, 5] together with a considerable amount of disulfide [6] of the thiol, were found in the reaction products.



$$\underset{\underline{1}}{(CF_3)_2C{=}CFCF_2CF_3} + RSH \xrightarrow[MeCN]{Et_3N} \underset{\underline{2}}{(CF_3)_2C{=}\underset{SR}{C}{-}CF_2CF_3} + \underset{\underline{3}}{(CF_3)_2\overset{SR}{C}{-}\underset{SR}{C}{=}CFCF_3}$$

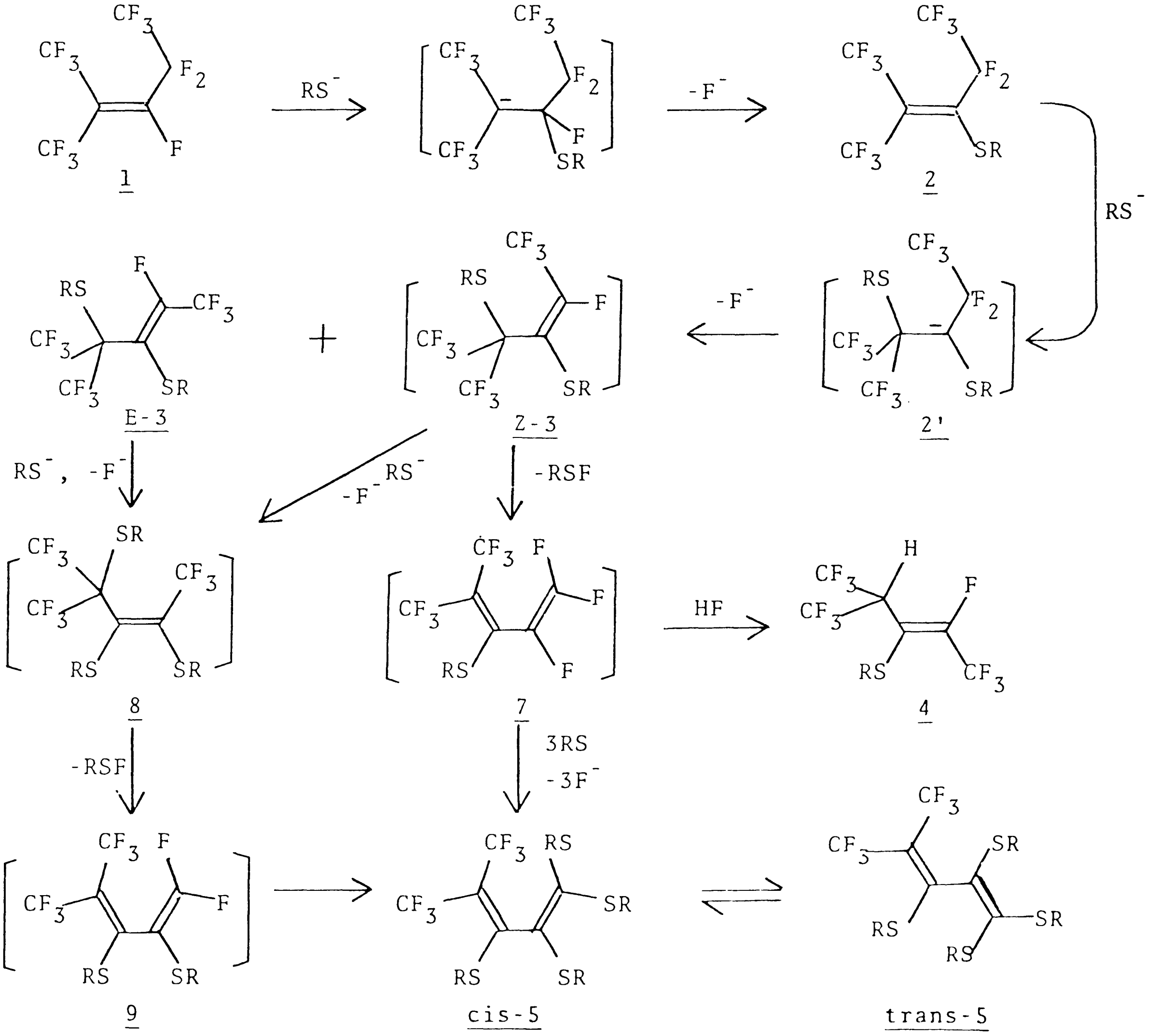
$$+ \underset{\underline{4}}{(CF_3)_2CH{-}\underset{SR}{C}{=}CFCF_3} + \underset{\underline{5}}{(CF_3)_2C{=}\underset{SR}{C}{-}\overset{SR}{C}{=}C(SR)_2} + \underset{\underline{6}}{R{-}S{-}S{-}R}$$

For example, when an equimolar amount of phenylmethanethiol was allowed to react with 1 in acetonitrile at 0 - 5 °C, in the presence of triethylamine, mono- and bis-(benzylthio)-substituted derivatives, 2 and 3, a hydrogen-containing derivative, 4, and dibenzyl disulfide, 6, were formed in a ratio shown in Table 1.$^{3)}$ These products were separated from each other by means of column chromatography or recrystallizations from suitable solvents, and were subjected to various analysis. The structures were established mainly from their ^{19}F and ^{1}H nmr spectra, by checking carefully the

Table 1 Yields of the products

RSH	Mol. ratio RSH / $\underline{1}$	Yields (%)[a)] $\underline{2}$	$\underline{E\text{-}3}$	$\underline{4}$	$\underline{5}$ cis	$\underline{5}$ trans	$\underline{6}$	Recovd. RSH
$PhCH_2SH$	1	59*	32*	3*	—	—	6*	—
//	2	8*	23*	16*	—	—	44*	—
//	10	—	—	—	23	3	15	45
PhSH	10	—	—	—	30	—	32	19

a) Yields are based on the thiol used. Figures with asterisk mean that they are calculated from the signal intensities of ^{19}F and ^{1}H nmr spectra.



$$[\mathrm{RSF}] + \mathrm{RS}^- \longrightarrow \underset{\underline{6}}{\mathrm{R\text{-}S\text{-}S\text{-}R}} + \mathrm{F}^-$$

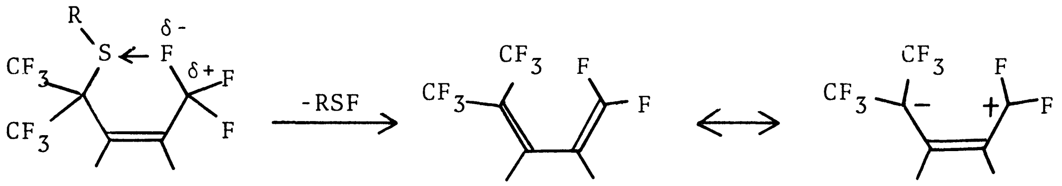
chemical shifts and the coupling constants.4) With two molar amounts of the thiol in the above reaction, 3 and 4 were formed as the major products, whereas with much more excess amount of the thiol, 5 was mainly obtained (63% based on 1). The formation of the mono-substituted derivative 2 was normally expected, because an analogous phenoxy compound was obtained in a good yield by the similar reaction of phenol with 1.5) The easier formation of bis-substituted derivative 3, compared with the case of the reaction with phenol, should be ascribed to the comparatively stable carbanion [2'] which is stabilized by the sulfur atom through its vacant 3d orbital.

The formation of 4, 5 and 6 suggests that an oxidation-reduction system is involved in the reaction. We ascertained experimentally that no oxidation of the thiol to 6 by the atmospheric oxygen occurs under these conditions, and that 1 is required for the oxidation.

The reaction pathway was speculated as shown in the scheme. At the disubstitution step, Z-3 should have been formed together with E-3, although the former was not detected in the reaction mixture. Model inspections show that the interatomic distance between S and F, mutually 1,6-positioned in Z-3, comes near 1.6 A, an average S-F bond length. This would make benzyl sulfenyl fluoride release easily from Z-3 affording a 1,3-diene [7], which could be converted either into 4 by 1,4-addition of hydrogen fluoride, or into 5 by substitution of fluorines for RS's. Released sulfenyl fluoride must have reacted immediately with thiol to give 6 and HF.

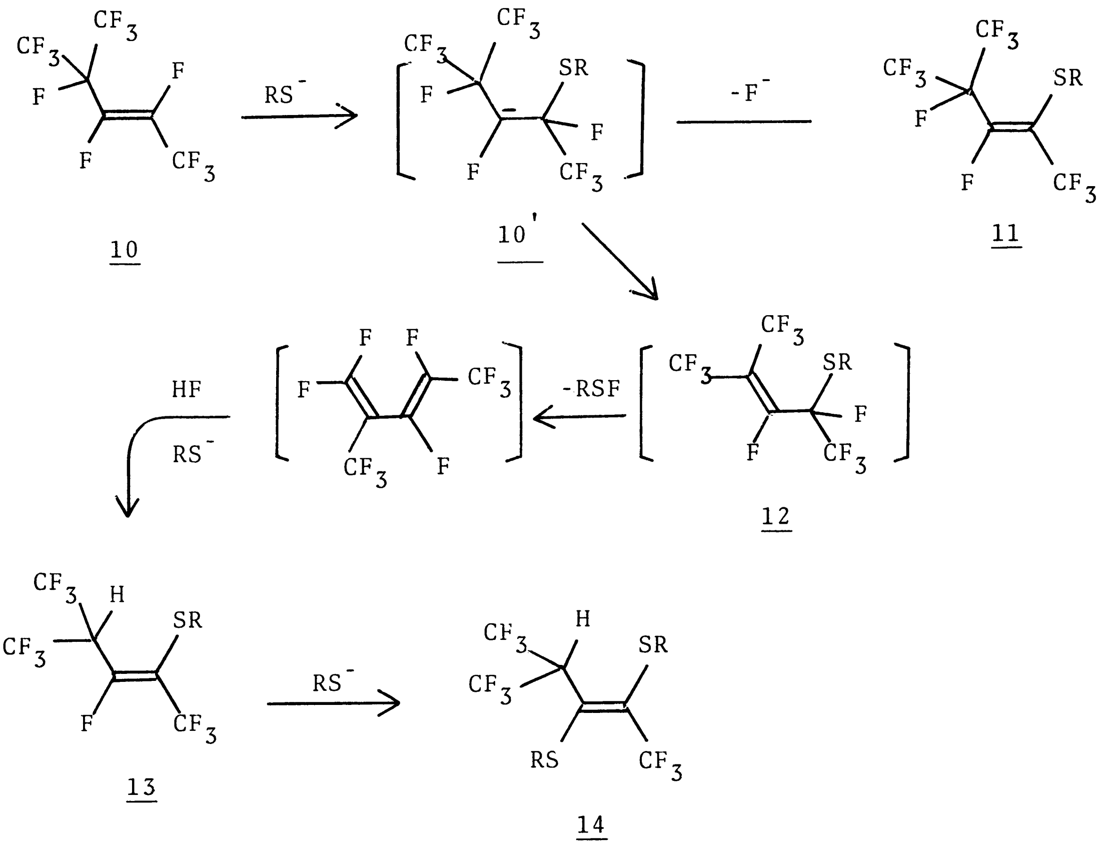
There is another possible route from 3 to 5. By an additional nucleophilic attack with RS^- on 3 (E or Z), the tri-RS-substituted product [8] would be formed. From this compound, 1,4-RSF-elimination would occur again, forming another 1,3-diene [9]. Further nucleophilic attack on 9 results in the formation of 5. We confirmed experimentally that E-3 is converted into 5 in the reaction with five molar amounts of the thiol. The 1,3-diene 5 thus obtained has expectedly a cis-form, and was converted into the more stable trans-isomer by heating it in a solvent such as xylene.

Thus, the reaction pathway can be well explained only by assuming 1,4-elimination of RSF. Although this kind of elimination is unknown so far in the polyfluoroolefin series, it would have taken place with high probability in the present case. Eliminations of RSF from the inner monoenes, Z-3 and 8, leave respectively conjugated dienes, 7 and 9, which are both sterically more released from the crowd of substituents than are the monoenes. Further, 7 and 9 are stabilized by two electron-attractive trifluoromethyl groups at one end and by two electron-donative fluorine atoms at the other.



When benzenethiol was used instead of phenylmethanethiol, more complex products were formed. The reaction with a large excess of benzenethiol, however, gave tetra-(phenylthio)-substituted diene, cis-5 (R = Ph), in a yield of 75% based on 1, together with diphenyl disulfide.

Perfluoro-(E)-4-methyl-2-pentene [10], another dimer of hexafluoropropene, also reacted with phenylmethanethiol under the similar conditions. When an equimolar amount of phenylmethanethiol was used, the products obtained were 11, 13, 14 and 6 in a ratio 4 : 5 : 28 : 52. Although the reaction is more complicated than that with 1, seemingly because of an S_N2'-like mechanistic process, the reaction pathway involving 1,4-elimination can also be proposed as follows.



References and notes

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2) S. R. Sterlin, V. M. Izmailov, V. L. Isaev, A. S. Shal, R. N. Sterlin, B. L. Dyatkin, and I. L. Knunyants, Zh. Vses, Khim. Obshch., 18, 710 (1973).
3) Reaction analysis was most easily performed in those with phenylmethanethiol, because the characteristic nmr signal for its CH_2 protons was useful for chasing the reactions.
4) The details of the establishment of structures will be published elsewhere.
5) Nobuo Ishikawa and Akira Nagashima, Bull. Chem. Soc. Jpn., 49, 502 (1976).

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