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The Radiation-Induced Addition Reaction of Thiols to Chlorofluoroolefins

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The addition of thiols to chlorofluoroethylenes was carried out under γ-ray irradiation; chlorofluoroethyl alkyl sulfides were thus obtained. Chlorofluoroethyl alkyl sulfoxides and sulfones were prepared by the oxidation of the sulfides. The dehydrohalogenation of chlorofluoroethyl alkyl sulfides yielded chlorofluorovinyl alkyl sulfides, whose structure indicated that the thiyl radical attacked the difluoromethylene side of the asymmetrical dichlorodifluoroethylene. Chlorofluorovinyl sulfoxides and sulfones were also synthesized from the sulfides by oxidation with hydrogen peroxide.

The free radical addition of thiols to olefins[1] is well known, and a variety of sulfur-containing compounds, such as thiols[2] and hydrogen sulfide[3], have been added to fluoroolefins using peroxide, or under ultraviolet or X-ray irradiation. The base-catalyzed addition of thiols[4,5] to fluoroolefins has also been studied extensively.

In this paper, the addition of RSH, where R is methyl, ethyl, or isopropyl, to 1, 1, 2-trichloro-2-fluoroethylene, 1, 2-dichloro-1, 2-difluoroethylene, and 1, 1-dichloro-2, 2-difluoroethylene will be described. By the oxidation of 1 : 1 adducts (the chlorofluoroethyl alkyl sulfides), both the corresponding chlorofluoroethyl alkyl sulfoxides and sulfones were prepared. The chlorofluorovinyl alkyl sulfides, sulfoxides, and sulfones were also synthesized by the dehydrohalogenation of the 1 : 1 adducts, followed by oxidation.

The reactants were irradiated in a glass tube at a rate of 0.6—0.7 × 10^5 r./hr. for a period of 3—4 weeks at room temperature. The irradiation conditions of each run are listed in Table I, along with the yields as calculated on the basis of the amounts of olefins added. The addition to 1, 2-dichloro-1, 2-difluoroethylene and 1, 1-dichloro-2, 2-difluoroethylene gave mainly 1 : 1 adducts in appreciable yields. Since a mixture of thiols and chlorofluoroethylenes gave no products upon standing in a dark at room temperature for a month, the reactions under the radiation seem to be through a free-radical mechanism. The general reaction is:

$$\mathrm{RSH + CFX{=}CClX \xrightarrow{\gamma\text{-ray}} RSCFXCHClX}$$

where X=F or Cl; R=CH_3, C_2H_5, or i-C_3H_7.

TABLE I. IRRADIATION CONDITIONS IN ADDITION OF RSH TO CHLOROFLUOROOLEFINS

R	Molar ratio of RSH to olefin[a]	Total dose r.	Yield[b] of 1 : 1 adduct g.(%)	RSSR, g.	$(RS)_2C$=CFCl g.
		CFCl=CFCl			
C_2H_5	1.0	2.2 × 10^7	12.5(17.0)	3.8	2.0
C_2H_5	1.5	3.5 × 10^7	17.5(23.9)	3.5	10.5
i-C_3H_7	1.0	3.5 × 10^7	13.5(17.2)		2.0
		CF_2=CCl_2			
CH_3	1.0	2.2 × 10^7	48.2(71.0)	1.5	
C_2H_5	1.0	2.2 × 10^7	44.5(61.0)	2.5	
i-C_3H_7	1.0	3.5 × 10^7	57.5(73.3)		

a) Fifty grams of the olefin were used in each run.

b) Based on the amounts of olefin added.

The reaction of trichlorofluoroethylene and tetrachloroethylene with thiols gave no addition products, and the yields of the addition products with 1, 1-dichloro-2, 2-difluoroethylene were higher than those of 1, 2-dichloro-1, 2-difluoroethylene. These facts seem to indicate that asteric interference between the bulky sulfur and chlorine atom may have an effect on the reactivity of olefins. The physical properties of the 1 : 1 adducts are shown in Table II.

The alkyl disulfides, which were identified by a comparison of their infrared spectra and gas chromatogram with those of authentic samples, were generally formed as by-products. In the reaction of 1, 2-dichloro-1, 2-difluoroethylene with thiols, an appreciable amount of a viscous compound was obtained, together with the 1 : 1 adduct and alkyl disulfide. Further, the amount of the compound increased with an increase in the ratio of the thiol to the ethylene. From its infrared spectrum, molecular weight, and elemental analysis,

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[1] C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York (1957), p. 313.

[2] J. F. Harris, Jr., and F. W. Stacey, *J. Am. Chem. Soc.*, **83**, 840 (1961).

[3] J. F. Harris, Jr., and F. W. Stacey, ibid., **85**, 749 (1963).

[4] W. T. Miller, U. S. Pat. 2864867 (1958).

[5] I. L. Knunyants and A. V. Fokin, *Izv. Akad. Nauk SSSR, Otdel Khim. Nauk*, **1952**, 261; *Chem. Abstr.*, **47**, 3221 (1953).

TABLE II. CHLOROFLUOROETHYL ALKYL SULFIDES

R	B. p. °C(mmHg)	n_D^{20}	d_4^{20}	MR$_D$		Cl, %		F, %	
				Found	Calcd.	Found	Calcd.	Found	Calcd.
		$RSCF_2CCl_2H$							
CH_3	48—50(20)	1.4525	1.460	33.47	33.75	38.8	39.2	20.7	21.0
C_2H_5	61—62(20)	1.4531	1.372	38.43	38.37	35.7	36.4	19.3	19.5
i-C_3H_7	70—71(20)	1.4535	1.311	43.12	42.98	33.6	34.0	18.2	18.2
		RSCFClCFClH							
C_2H_5[a]	60—61(20)	1.4548	1.361	38.85	38.37	35.9	36.4	19.5	19.5
i-C_3H_7[b]	63—65(20)	1.4586	1.273	44.84	42.98				

a) Lit[5] b. p. 138°C, n_D^{20} 1.4612, d_5^{20} 1.425.

b) Though the gas chromatogram (column packed with Silicone DC-550 or PEG-400) showed a single peak, the compound seems to contain the disulfide as an impurity.

TABLE III. CHLOROFLUOROVINYL ALKYL SULFIDES

R	B. p. °C(mmHg)	n_D^{20}	d_4^{20}	MR$_D$		Cl, %		F, %		$\nu_{C=C}$ cm^{-1}
				Found	Calcd.	Found	Calcd.	Found	Calcd.	
		$RSCF{=}CCl_2$								
CH_3	45—46(20)	1.5062	1.427	33.53	33.20	43.7	44.1	11.9	11.8	1605
C_2H_5	52—54(20)	1.4458	1.337	38.24	37.82	40.1	40.6	10.6	10.9	1601
i-C_3H_7	67—68(20)	1.4896	1.269	43.03	42.44	37.2	37.6	9.6	10.1	1599
		$RSCF{=}CFCl$								
C_2H_5[a]	116—118	1.4455	1.255	33.65	33.03	22.1	22.4	23.7	24.0	1661
i-C_3H_7[b]	53—56(50)	1.4480	1.200	38.47	37.65	20.5	20.6	21.8	22.0	1658

a) Lit.[5] b. p. 106—107°C, n_D^{20} 1.4385, d_4^{20} 1.282.

b) Lit.[5] b. p. 135°C, n_D^{20} 1.4178, d_4^{20} 1.275.

TABLE IV. CHLOROFLUOROETHYL AND CHLOROFLUOROVINYL SULFOXIDES

R	B. p. °C(mmHg)	n_D^{20}	d_4^{20}	MR$_D$		Cl, %		F, %		$\nu_{S=O}$ cm^{-1}	$\nu_{C=C}$ cm^{-1}
				Found	Calcd.	Found	Calcd.	Found	Calcd.		
			$RSOCF_2CCl_2H$								
CH_3[a]						35.6	36.0	18.9	19.3		
C_2H_5	105—106(20)	1.4678	1.484	39.50	39.76	33.0	33.7	17.9	18.0	1030	
i-C_3H_7	75—77(3)	1.4676	1.423	43.93	44.38	31.1	31.6	16.4	15.9	1033	
			RSOCFClCFClH								
C_2H_5	93—94(15)	1.4711	1.483	39.78	39.76	32.8	33.7	17.6	18.0	1030	
i-C_3H_7	79—81(6)	1.4698	1.414	44.37	44.38	30.8	31.6	16.2	16.9	1033	
			$RSOCF{=}CCl_2$								
CH_3	115—117(15)	1.5224	1.565	34.51	34.59	39.7	40.1	10.3	10.7		1620
C_2H_5	101—103(15)	1.5107	1.472	38.86	39.21	36.6	37.2	9.4	10.0	1030	1620
i-C_3H_7	91—92(5)	1.5059	1.386	43.93	43.83	34.1	34.6	9.2	9.3	1033	1618
			$RSOCF{=}CFCl$								
C_2H_5	67—69(5)	1.4738	1.419	34.55	34.42	20.3	20.3	21.5	21.8	1030	1670
i-C_3H_7	70—73(3)	1.4509	1.409	39.08	39.61	17.2	17.4	18.3	18.6	1033	1669

a) M. p. 75—76°C.

the structure of the compound was determined to be $(RS)_2C{=}CFCl$. The formation of the compound is probably a result of the sequence of the radical dehalogenation. The radical dehalogenations from the intermediate radicals with bulky neighboring groups were often observed in radical-induced addition reactions, in, for example, those of polyhalobutene,[6] 1, 2-dichlorotetrafluorocyclobutene, and 1, 2-dichlorohexafluorocyclopentene.[7]

The direction of the attack of the thiyl radical on asymmetrical dichlorodifluoroethylene was determined by the dehydrohalogenation of the 1 : 1 adduct with potassium hydroxide; chlorofluorovinyl alkyl sulfide was thus yielded. The formation of

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[6] H. Muramatsu and P. Tarrant, *J. Org. Chem.*, **29**, 1796 (1964).

[7] H. Muramatsu and K. Inukai, ibid., **31**, 544, 2546 (1965).

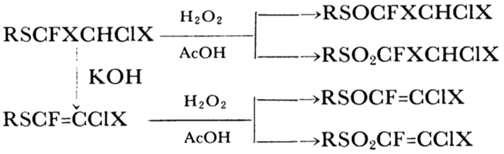
Table V. Chlorofluoroethyl and chlorofluorovinyl alkyl sulfones

R	B. p. °C(mmHg)	n_D^{20}	d_4^{20}	MR$_D$		Cl, %		F, %		ν_{SO_2} cm^{-1}	$\nu_{C=C}$ cm^{-1}
				Found	Calcd.	Found	Calcd.	Found	Calcd.		
				$RSO_2CF_2CCl_2H$							
CH_3	103—104(15)	1.4510	1.635	33.08	35.71	33.2	33.3	17.7	17.9	1162, 1352	
C_2H_5	103—105(15)	1.4548	1.541	39.96	40.33	31.1	31.3	16.7	16.7	1155, 1348	
i-C_3H_7	86—88(3)[a]					29.4	29.5	15.4	15.8	1149, 1345	
				$RSO_2CFClCFClH$							
C_2H_5	90—100(15)	1.4536	1.511	40.64	40.33	31.2	31.3	16.7	16.7	1150, 1350	
i-C_3H_7	86—88(3)	1.4568	1.465	44.80	44.95	28.7	29.5	15.3	15.8	1147, 1343	
				$RSO_2CF{=}CCl_2$							
CH_3	113—114(15)[b]					37.3	36.8	9.5	9.8	1166, 1348	1618
C_2H_5	106—108(15)	1.4896	1.526	39.20	39.78	34.2	34.3	9.1	9.2	1155, 1348	1610
i-C_3H_7	98—100(5)	1.4852	1.440	43.92	44.40	32.1	32.1	8.6	8.6	1148, 1345	1605
				$RSO_2CF{=}CFCl$							
C_2H_5	76—78(5)	1.4527	1.489	34.57	34.99	18.2	18.6	19.8	20.0	1142, 1350	1670
i-C_3H_7	70—73(3)	1.4509	1.409	39.08	39.61	17.2	17.4	18.3	18.6	1145, 1345	1662

a) M. p. 32—34°C. b) M. p. 44—46°C.

1-fluoro-2, 2-dichlorovinyl alkyl sulfides showed that the RS radical was added to the CF_2 side. If the thiyl radical would attack the CCl_2 side, 1-chloro-2, 2-difluorovinyl alkyl sulfides would be obtained. The physical properties of the chlorofluorovinyl alkyl sulfides prepared are shown in Table III.

The chlorofluoroethyl alkyl sulfoxides and sulfones were synthesized by the oxidation of the corresponding chlorofluoroethyl alkyl sulfides with hydrogen peroxide in acetic acid, at 40—45°C and at 75—80°C respectively. The oxidation of the chlorofluorovinyl alkyl sulfides run under similar conditions yielded the corresponding chlorofluorovinyl alkyl sulfoxides and sulfones.



Attempts to dehydrohalogenate the chlorofluoroethyl alkyl sulfoxides and sulfones were found to lead to the decomposition of the sulfoxides and sulfones. The physical properties of chlorofluoroethyl and chlorofluorovinyl alkyl sulfoxides and sulfones are listed in Tables IV and V respectively.

Experimental[8]

The Addition Reactions of Thiols to Chlorofluoroolefins.—A mixture of 23.5 g. (0.38 mol.) of ethanethiol and 50 g. (0.38 mol.) of 1, 1-dichloro-2, 2-difluoroethylene was sealed in a glass tube (ca. 300 ml. in capacity) and irradiated to a total dosage of 2.2×10^7 r. The contents of the tube were then washed out with a diluted solution of sodium hydroxide and extracted with ether. The distillation of the extract under reduced pressure gave 44.5 g. (0.22 mol., 61% yield) of 1, 1-difluoro-2, 2-dichloroethyl ethyl sulfide, b. p. 61—62°C/20 mmHg, and 2.5 g. of ethyldisulfide, which was identified by a comparison of its infrared spectra and gas chromatogram with those of an authentic sample.[9] The addition reactions of thiols to 1, 2-dichloro-1, 2-difluoroethylene were carried out under similar conditions. In these cases, appreciable amounts of the viscous compounds were obtained, together with the 1 : 1 adduct and alkyl disulfide. In the addition of ethanethiol, a compound with a b. p. of 87—89°C/10 mmHg, $\nu_{C=C}$ 1587 cm^{-1}, n_D^{20} 1.5215, d_4^{20} 1.207, was isolated using a preparative gas chromatograph. From its infrared spectrum, molecular weight, and elemental analysis, the structure was assumed to be $(C_2H_5S)_2C{=}CFCl$.

Found: MR$_D$ 50.64; F, 9.2; Cl, 18.2; mol. wt. 200.[10] Calcd. for $C_6H_{10}FClS_2$: MR$_D$ 49.99; F, 9.5; Cl, 17.7; mol. wt. 200.5.

The irradiation conditions and yields are summarized in Table I.

The Dehydrohalogenation of Chlorofluoroethyl Alkyl Sulfides.—A mixture of 30.0 g. (0.15 mol.) of 1, 1-difluoro-2, 2-dichloroethyl ethyl sulfide and 17.5 g. (0.31 mol.) of powdered potassium hydroxide in a 100 ml. flask equipped with a reflux condenser and a stirrer was heated at 120—125°C for 1.5 hr. The reaction mixture was then poured into water and extracted with ether. The extract was dried and distilled to give 22.0 g. (0.13 mol., 82% yield) of 1-fluoro-2, 2-dichlorovinyl ethyl sulfide, b. p. 52—54°C/20 mmHg.

In a similar manner, the other chlorofluoroethyl alkyl sulfides were treated with potassium hydroxide; they thus gave the corresponding halovinyl alkyl sulfides, whose physical properties are shown in Table III.

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[8] All temperature readings are uncorrected.

[9] E. Miller, F. S. Crossley and M. L. Moore, *J. Am. Chem. Soc.*, **64**, 2323 (1942).

[10] Determined by a mass spectrometer.

The Oxidation of Chlorofluoroethyl Alkyl Sulfides and Chlorofluorovinyl Alkyl Sulfides.—In a 100 ml. flask equipped with a stirrer and a reflux condenser were placed 12.0 g. (0.058 mol.) of 1, 1-difluoro-2, 2-dichloroethyl isopropyl sulfide and 8.0 g. (0.071 mol.) of hydrogen peroxide (30% aqueous solution) in acetic acid (50 ml.). The mixture was then stirred for 5 hr. at 40—45°C. After the acetic acid had been distilled off, the reaction mixture was washed with a sodium carbonate solution and extracted with ether. The extract was dried and distilled to give 11.5 g. (0.051 mol., 89% yield) of 1, 1-difluoro-2, 2-dichloroethyl isopropyl sulfoxide, b. p. 75—77°C/3 mmHg, ν_{SO} 1033 cm^{-1}.

Using the same procedure, the other chlorofluoroethyl and chlorofluorovinyl alkyl sulfides were oxidized to the corresponding sulfoxides in yields of about 70%.

In a 200 ml. flask there was placed 23.0 g. (0.11 mol.) of 1, 1-difluoro-2, 2-dichloroethyl isopropyl sulfide in acetic acid (20 ml.). Fifty grams (0.44 mol.) of hydrogen peroxide (30% aqueous solution) in 100 ml. of acetic acid were then added drop by drop over a period of 1 hr. After it had been continuously stirred for an additional 4 hr. at 75—80°C, the mixture was washed with an aqueous sodium carbonate solution and extracted with ether. The distillation of the extract gave 23.5 g. (0.098 mol., 92% yield) of 1, 1-difluoro-2, 2-dichloroethyl isopropyl sulfone, b. p. 86—88°C/3 mmHg; m. p. 32—34°C.

By the same procedure, the other chlorofluoroethyl and chlorofluorovinyl sulfides were oxidized to the corresponding sulfones in yields of about 80%.