dinitrophenylhydrazone, m. p. 121–122°[26]; acetophenone (7.6 g., 32% yield), b. p. 198–201°; benzoylacetone (15.6 g., 24% conversion), b. p. 141–144° at 19 mm., m. p. 54–58°[27]; and from the residue was obtained after recrystallization from methanol, 0.8 g. (2% yield) of dibenzoylmethane, m. p. 75–77° and mixed m. p. with a known sample of 76–78°.[35]

Acylation of Ketone Enol Esters with Anhydrides by Boron Fluoride.—A mixture of the anhydride and ketone enol ester (1.5:1 molar ratio) was saturated with boron fluoride at 0–20° for one to two hours and then hydrolyzed with sodium acetate solution and worked up as described for the self-acylations of enol esters. The results are summarized in Table III.

Acylations with Acetyl Chloride.—A mixture of the enol acetate of methyl n-amyl ketone and acetyl chloride (0.15 mole each) was saturated with boron fluoride for one hour at 10–20°. On working up the reaction mixture, there was obtained 16.2 g. (69% conversion) of n-butylacetylacetone, b. p. 103–105° at 20 mm., m. p. of copper complex 184–185°.[10]

A mixture of 43.6 g. (0.2 mole) of the enol benzoate of methyl n-amyl ketone and 15.7 g. (0.2 mole) of acetyl chloride on saturation with boron fluoride at 0–20° for one

hour, yielded 5.8 g. (25% conversion) of methyl n-amyl ketone, b. p. 148–154°,[32] 9.9 g. (32% yield) of n-butylacetylacetone, b. p. 102–105° at 20 mm. (copper complex, m. p. 184–185°),[10] and 8.4 g. (19% conversion) of n-butylbenzoylacetone, b. p. 148–152° at 5 mm.

Summary

1. Evidence has been obtained that the thermal conversion of ketone enol esters to β-diketones involves an intramolecular rearrangement and that the conversion by boron fluoride at low temperatures consists of an intermolecular acylation of one molecule by another.

2. Ketone enol esters have been acylated with enol esters, acid anhydrides and acid chlorides by means of boron fluoride to form β-diketones.

3. Certain new enol esters have been prepared and the structure of enol esters of unsymmetrical methyl-methylene ketones were determined by ozonolysis.

SOUTH CHARLESTON 3, W. VA.
DURHAM, N. C.   RECEIVED JANUARY 20, 1950

(35) Levine, Conroy, Adams and Hauser, THIS JOURNAL, 67, 1510 (1945).

Reactions of Polyfluoro Olefins. I. Preparation of Sulfides and Sulfones[1,2]

BY KARL E. RAPP, ROY L. PRUETT, JOHN T. BARR, CARL T. BAHNER, J. DONALD GIBSON AND ROBERT H. LAFFERTY, JR.

The reactions of chlorotrifluoroethylene, 1,1-dichloro-2,2-difluoroethylene and hexafluorocyclobutene with compounds containing a thiol group were investigated as a part of a study of the reactions of polyfluoro olefins. Hanford[3] has reported that ethanethiol reacted with tetrafluoroethylene on heating eight hours at 110° in the presence of benzoyl peroxide to form a mixture of liquid and solid products believed to have the general formula $H(CF_2CF_2)_nC_2H_4SH$, where n ranges from 1 to 25. The principal product boiled at 84–86° and the analytical data agreed with the above formula where n = 1. Catalysts mentioned included "organic and inorganic peroxy compounds, basic catalysts, various acid catalysts, oxygen, ozone and iodine." Hanford stated further, "No appreciable reaction is obtained below 75° and it is usually necessary to heat the reaction mixture to 100° or higher in order to obtain a substantial reaction in a reasonable time." These observations are especially interesting in view of the fact that polyfluoro olefins were found to react readily with thiols near room temperature under the influence of basic catalysts to form polyfluoro sulfides.

The reactions of thiols with polyfluoro ethylenes was one of simple addition. Although addition to chlorotrifluoroethylene could result in the formation of two isomers, only one was indicated by the distillation curve of $C_2H_5SC_2F_3ClH$ using a seven-foot column packed with glass helices. A mass spectrograph scan[4] of this distilled material showed an ion with a mass to charge ratio corresponding to an SCF_2 fragment and one corresponding to $C_2H_5SCF_2$, but none corresponding to either an $SCFCl$ or a C_2H_5SCFCl fragment. On the other hand, lower peaks were found at mass to charge ratios corresponding to both $CFClH$ and CF_2H fragments. In view of the fact that the last fragment easily could be a result of recombination, it appears that the reaction produces only the α,α-difluoro sulfide. This is in agreement with analogous reactions with alcohols to form polyfluoro ethers.[5]

2-Mercaptoethanol, having both an –OH and an –SH group, provided a means of determining whether an alcohol or a thiol would add preferentially to a polyfluoro olefin. The product formed with chlorotrifluoroethylene did not have the

(1) Presented at the 116th Meeting of the American Chemical Society, Atlantic City, New Jersey, September, 1949.

(2) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Corporation at Oak Ridge, Tennessee.

(3) Hanford, U. S. Patent 2,443,003 (1948); cf. E. I. du Pont de Nemours and Company, British Patent 583,874 (1947).

(4) Mass spectrograph scan by Miss Jeanne Pemberton and Mr. W. G. Schwab of the Mass Spectrometer Section of the Physical Research Department.

(5) Hanford and Rigby, U. S. Patent 2,409,274 (1946); Miller, Fager and Griswold, THIS JOURNAL, 70, 431 (1948); Park, Vail, Lea and Lacher, ibid., 70, 1550 (1948); Hurwitz and Miller, "Reactions of Chlorofluoro Olefins with Anionic Reagents," Abstracts of Papers, American Chemical Society, Washington, D. C., August, 1948, p. 4L; Young and Tarrant, ibid., 71, 2432 (1949).

characteristic thiol odor and failed to give a precipitate with silver nitrate, mercuric chloride or lead acetate. These tests show that the formula of the product must be $HOC_2H_4SC_2F_3ClH$ rather than $HSC_2H_4OC_2F_3ClH$. Probably one factor favoring the formation of the former product was the presence of a higher concentration of $-SC_2H_4-OH$ than $-OC_2H_4SH$ ions in the solution as a result of the greater acidity of the thiol group.

Hexafluorocyclobutene appeared to be more active than chlorotrifluoroethylene in reacting with thiols. The reaction was complicated by the elimination of hydrogen fluoride, permitting compounds to be formed with both one and two sulfide linkages.

A mechanism analogous to that proposed by Park, Sharrah and Lacher[6] for alcohols would involve substitution
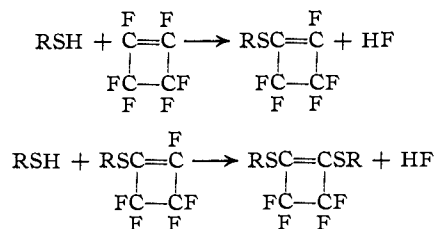
An alternative hypothesis, involving addition rather than substitution, is proposed which more readily accounts for the products obtained
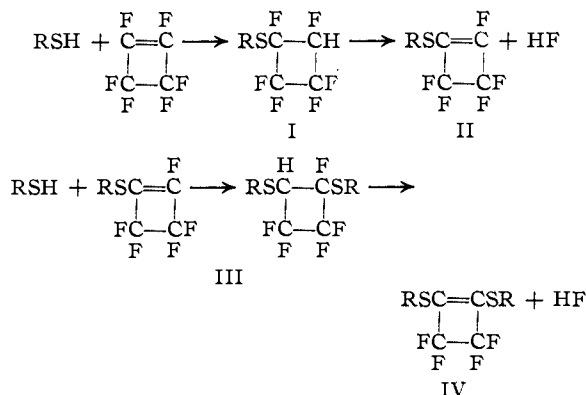
Compounds corresponding to formulas II, III and IV were isolated and analyzed.[7]

If the former hypothesis is accepted, the appearance of a compound corresponding to type formula III would have to be explained by the addition of HF to the corresponding compound of type IV. It seems extremely unlikely, however, that such an addition would occur under the conditions of these experiments. In fact, a spontaneous evolution of HF occurred during distillation of one of the products, resulting in a mixture consisting only of compounds corresponding to types II and IV.

(6) Park, Sharrah and Lacher, THIS JOURNAL, **71**, 2337 (1949).

(7) The structure proof of type compound IV will be presented in paper IV of this series.

Oxidation of the alkyl sulfides with potassium permanganate in aqueous acetic acid took place in the expected manner to form the corresponding sulfones in good yields. The contrast between these and non-fluorinated sulfones is brought out by comparison of diethyl sulfone, m. p. 73–74°, readily soluble in water, with ethylsulfonylchlorotrifluoroethane, m. p. −18°, insoluble in water. The latter compound was found to be miscible with chlorotrifluoroethylene liquid polymer above 48°.

Experimental

Materials.—All thiols used in these experiments were obtained from Eastman Kodak Company, except mercaptoethanol which was a product of Carbide and Carbon Chemicals Corporation and ethanethiol which was purchased from Mallinckrodt Chemical Company. Chlorotrifluoroethylene was supplied by the Fluorothene Plant at K-25.

1,1-Dichloro-2,2-difluoroethylene was prepared by dechlorination of 1,1,1,2-tetrachloro-2,2-difluoroethane as has been reported.[8]

Hexafluorocyclobutene was prepared by dechlorination of 1,2-dichlorohexafluorocyclobutane, which had been prepared by thermal dimerization of chlorotrifluoroethylene.[9] Almost quantitative conversion of chlorotrifluoroethylene to the cyclic dimer was obtained by heating about 1200 g. of the former in a 1-l. high pressure bomb twenty-four hours at 200°. The maximum pressure attained was about 3000 p. s. i. This decreased rapidly to about 500 to 600 p. s. i. at the end of the reaction time. It was found that as good yields could be obtained without encountering such high initial pressures by beginning the reaction at 125°, and gradually raising the temperature to a maximum of 200° as the pressure fell, maintaining a pressure of about 1000 p. s. i. until the maximum temperature was reached. Reaction times of twenty-four to thirty hours gave 95% yields. Dechlorination was carried out most conveniently by placing 300 g. of 1,2-dichlorohexafluorocyclobutane, 300 ml. of absolute ethanol and 175 g. of 30-mesh zinc in a flask equipped with a reflux condenser to act as a dephlegmator and connected through a calcium chloride tube to a metal trap chilled in Dry Ice to condense and hold the product. The flask was heated to 45–50° to initiate the reaction, which caused spontaneous refluxing for about one hour. Refluxing was continued for three hours by external heating. Unreacted dimer was recovered by adding an equal volume of water to the alcohol–zinc chloride solution. Conversions and yields were in the range of 90 to 95%. Equal conversions and yields were obtained when 500 ml. of 95% ethanol was substituted for the absolute ethanol, provided that the reaction time was increased to seven to eight hours.

General Method of Procedure.—The sulfides were prepared by treating a thiol or substituted thiol with a polyfluoro olefin in the presence of an alkaline catalyst. Since the polyfluoro olefins used were gases at room temperature and atmospheric pressure, the reactions were carried out in steel pressure vessels. A reactor equipped with a valve was evacuated and charged with a mixture of thiol and catalyst, then cooled in a slush of Dry Ice and trichloroethylene and re-evacuated. While the reactor was still at this temperature, the polyfluoro olefin was introduced. The charging tube was replaced by a "T"

(8) Miller, THIS JOURNAL, **62**, 993 (1940); Henne and Weist, *ibid.*, **62**, 2051 (1940).

(9) Harmon, U. S. Patent 2,404,374 (1946); Henne and Ruh, THIS JOURNAL, **69**, 279 (1947); Henne and Zimmersheid, *ibid.*, **69**, 281 (1947); Harmon, U. S. Patent 2,436,142 (1948); Miller, "The Use of Perfluoro- and Chloroperfluoro-olefins in the Synthesis of Fluorocarbon Materials," Technical Information Division, Atomic Energy Commission, MDDC-1177, (declassified May 28, 1949); Scherer, "Fluorderivate des Propans und Butans," I. G. Res. Lab., U. S. Dept. of Commerce, Office of Technical Services P. B. 776.

TABLE I

REACTIONS OF THIOLS WITH POLYFLUORO ETHYLENES

Reactants				Catalyst		Products	Reaction Temp., °C.	Time, hr.	Yield, %	Boiling point, °C.	Mm.	n^{25}D	d^{25}_4
C₂H₅SH	1	CF₂=CFCl	1.25	Triton B	0.02	C₂H₅SC₂F₃ClH	26	48	95	69.1	100	1.4079	1.3212
n-C₄H₉SH	1	CF₂=CFCl	1.12	Triton B	0.02	C₄H₉SC₂F₃ClH	23	16	95	71.6	25	1.4196	1.2224
n-C₄H₉SH	1	CF₂=CCl₂	1.13	Triton B	0.02	C₄H₉SC₂F₂Cl₂H	44	72	90	43.0	1	1.4545	1.2707
HSCH₂COOH	1	CF₂=CFCl	2.38	(C₂H₅)₃N	2.03	HOOCCH₂SC₂F₃ClH	45	24	48ᵃ	85ᵇ·ᶜ	<0.01	1.4470	1.5847
HOC₂H₄SH	1	CF₂=CFCl	2.25	NaSC₂H₄OH	0.05	HO(CH₂)₂SC₂F₃ClH	25	96	87	62.5	0.5	1.4426	1.4793

ᵃ This yield of necessity refers to distilled material while the others refer to washed product before distillation. ᵇ Maximum temperature of Hickman alembic molecular still. ᶜ M. p. 19°.

TABLE II

REACTIONS OF THIOLS WITH HEXAFLUOROCYCLOBUTENE

Reactants				Catalyst		Products	Reaction Temp., °C.	Time, hr.	Yield,ᵃ %	Melting point, °C.	Boiling point, °C.	Mm.	n^{25}D	d^{25}_4
n-C₄H₉SH	1	Cyclo-C₄F₆	1.12	Triton B	0.02	(C₄H₉S)₂C₄F₆H	44	168	30	-31.5	50ᵇ	<0.01	1.4810	1.1588
n-C₄H₉SH	1	Cyclo-C₄F₆	1.10	(C₂H₅)₃N	1.10	C₄H₉SC₄F₆	46	48	23ᶜ		61.7	18	1.4086	1.2555
						(C₄H₉S)₂C₄F₄			33ᵈ	-41	45ᵇ	<0.01	1.4701	1.1615
HSCH₂COOH	1	Cyclo-C₄F₆	1.88	Triton B	2.03	(HOOCCH₂S)₂C₄F₄	26	72	23	116-117				
2-C₁₀H₇SH	1	Cyclo-C₄F₆	2.16	(C₄H₉)₃N	0.52	(C₁₀H₇S)₂C₄F₄	25	72	70	90-91				

ᵃ These yields of necessity refer to distilled or crystallized material. ᵇ Maximum temperature of Hickman molecular still. ᶜ,ᵈ Part of these yields are thought to have been present originally as C₄H₉SC₄F₆H and (C₄H₉S)₂C₄F₅H, respectively.

tube carrying a pressure gage and valve to allow the gage and line to be evacuated. The pressure observed as soon as the reactor had been shaken and warmed to room temperature was taken as the initial reading. The reactor was shaken occasionally by hand or steadily by mechanical shaker and the pressure read from time to time. When a temperature above that of the room was desired, the reactor was warmed by a warm water-bath or a thermostatically controlled electric heater. It is interesting that in some cases no pressure change was noted even though the reaction was found to have gone practically to completion when the reactor was opened.

Because of the extremely unpleasant odor of the thiols, care was taken to ensure complete reaction before the reactor was opened. For this reason an excess of the polyfluoro olefin was used and the time and temperature employed were greater than considered necessary for complete reaction.

The liquid products were washed with water and dried over anhydrous sodium carbonate. The more volatile compounds were distilled at reduced pressure through a column packed with glass helices. Liquids which had very low vapor pressures were distilled in a Hickman alembic molecular still[10] using Dry Ice in the condensing cone. While this operation did not permit determination of accurate distillation temperatures and pressures, it was possible to follow the progress of the distillation by observing the refractive index of the distillate from time to time.

Reactions of Polyfluoro Ethylenes.—The physical properties of five sulfides prepared by reaction of thiols with polyfluoro ethylenes are shown in Table I. Experimental details of selected representative reactions are described below:

Ten milliliters of Triton B (a 40% aqueous solution of benzyltrimethylammonium hydroxide) was mixed with 84.5 g. of ethanethiol in the reactor and 198 g. of chlorotrifluoroethylene was added. The mixture was shaken by hand and allowed to stand in the air of a room at 23.5°. The heat of reaction had raised the temperature of the reactor to about 45° at the end of three hours, at which time it was cooled in cold water and set in the open air again. After thirty minutes it had become warm to the hand once more and was returned to the water-bath. The following morning the gage reading on the bomb was 23 p. s. i. as compared with an initial reading of 55 p. s. i. The pressure did not change on standing six hours longer. The unreacted chlorotrifluoroethylene was allowed to escape

(10) Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1938, p. 120.

and it was noted that the mercaptan odor was practically absent. After the liquid remaining in the bomb was washed three times with water, it weighed 234 g. This product was dried over calcium chloride and distilled at 107 mm. pressure. The very narrow boiling range of the distillation indicated that the colorless mobile liquid, which had an ethereal odor, was almost pure ethylthiochlorotrifluoroethane.

For comparison, runs were made using two other catalysts. When 2 g. of sodium hydride was dissolved in 125 g. of ethanethiol to form the sodium derivative of the latter and the addition reaction was carried out in nearly the same manner as when Triton B was used as catalyst, 278 g. of product was obtained. On the other hand, when 10 g. of tributylamine was used as catalyst with 102 g. of ethanethiol and the reaction mixture was kept nine days at room temperature, eight hours at 40 to 60° and twelve hours at 60 to 65°, the reaction was still incomplete, as only about 30 g. of the ethylthiochlorotrifluoroethane was found upon distillation.

This sulfide was attacked slowly by boiling alcoholic potassium hydroxide. In contrast to ordinary alkyl sulfides it did not add bromine in benzene, nor did it form a sulfonium salt on standing thirty days with methyl iodide.

Reactions of Hexafluorocyclobutene.—The properties of five products obtained by reaction of 1-butanethiol, 2-naphthalenethiol, and mercaptoacetic acid with hexafluorocyclobutene are shown in Table II.

1-Butanethiol reacted with hexafluorocyclobutene to yield several different products. When 1-butanethiol, hexafluorocyclobutene and Triton B were mixed in the molar ratio of 1:1.12:0.02 and kept one week at about 44°, the reaction mixture was found to have become strongly acid. After the second day of the above period, the reaction mixture was heated to 65° for thirty minutes, but no change in pressure was noted upon cooling. Upon working up the mixture, a 30% yield of product was obtained by molecular distillation, m. p. -31.5°, n^{25}D 1.4810, d^{25}_4 1.1588. Analytical data indicated that this compound was 1,2-bis-(butylthio)-1,3,3,4,4-pentafluorocyclobutane. Probably the failure to obtain a larger yield was due to the fact that the hydrogen fluoride split out during the reaction had neutralized the basic catalyst. Evidently at least part of the addition had taken place even after the mixture became acidic. In another experiment the reaction mixture consisted of 1-butanethiol, hexafluorocyclobutene and triethylamine in the molar ratio 1:1.1:1.1. There was evidence that the reaction took place even while the reactor was still chilled in Dry Ice. After removal of the triethylamine, the liquid

water-insoluble products were subjected to steam distillation and then redistilled through a column packed with glass helices. Both the low-boiling distillate and the higher-boiling material left in the still-pot gave off large amounts of hydrogen fluoride on standing overnight. The formation of hydrogen fluoride at this point is more readily explained by the addition mechanism outlined above. The products were rewashed and redistilled. The more volatile fraction, obtained in 23% yield, was concluded to be 1-butylthio-2,3,3,4,4-pentafluorocyclobutene, probably formed by splitting off hydrogen fluoride from 1-butylthio-1,2,3,3,4,4-hexafluorocyclobutane. The less volatile fraction, obtained in 23% yield, was concluded to be 1,2-bis-(butylthio)-3,3,4,4-tetrafluorocyclobutene, probably formed by splitting off hydrogen fluoride from 1,2-bis-(butylthio)-1,3,3,4,4-pentafluorocyclobutane.

Preparation of Sulfones.—Several of the sulfides were oxidized to sulfones by use of potassium permanganate in aqueous acetic acid solution. The sulfide was dissolved in glacial acetic acid and cooled to 5° by an ice-bath. An oxidation equivalent of potassium permanganate dissolved in warm water was added slowly with vigorous stirring, keeping the temperature below 20°. Stirring was con-

TABLE III
POLYFLUOROALKYL SULFONES

Sulfone	Yield, %	M. p., °C.	B. p., °C.	Mm.	$n^{25}D$	d^{25}_4
$C_2H_5SO_2C_2F_3ClH$	86	−18	99	22	1.4144	1.5009
$C_4H_9SO_2C_2F_3ClH$	88	−15	95	0.2	1.4218	1.3635
$C_4H_9SO_2C_2F_2Cl_2H$	88	−0.5 to +0.5	70[a]	0.01	1.4517	1.3953

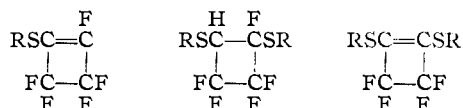[a] Maximum temperature of Hickman alembic molecular still.

determinations by the combustion method were good, but determination of sulfur and chlorine by Carius method was less satisfactory. In some cases sulfur and chlorine were determined by a peroxide fusion method. Results of all analyses are recorded in Table IV.

Conclusions

Polyfluoroalkyl sulfides can be prepared easily in excellent yields by reaction of thiols with polyfluoro olefins at or near room temperature in the presence of basic catalysts. The sulfides so prepared are relatively stable toward most reagents.

The addition of hydroxy thiols to polyfluoro olefins involves the –SH group in preference to the –OH group partially because of the greater acidity of the former group.

Hexafluorocyclobutene is more active than chlorotrifluoroethylene in reaction with thiols. Several types of products have been obtained, represented by the formulas

$$\begin{array}{ccc} & \text{F} & & \text{H} \quad \text{F} & & \\ \text{RSC}{=}\text{C} & & \text{RSC}{-}\text{CSR} & & \text{RSC}{=}\text{CSR} \\ | \quad | & & | \quad | & & | \quad | \\ \text{FC}{-}\text{CF} & & \text{FC}{-}\text{CF} & & \text{FC}{-}\text{CF} \\ \text{F} \quad \text{F} & & \text{F} \quad \text{F} & & \text{F} \quad \text{F} \end{array}$$

Polyfluoroalkyl sulfones can be prepared easily in excellent yields by the oxidation of polyfluoroalkyl sulfides with potassium permanganate in aqueous acetic acid. These products are stable and have unusual properties.

TABLE IV
ANALYSIS OF REACTION PRODUCTS

Compound	Carbon, % Calcd.	Found	Hydrogen, % Calcd.	Found	Sulfur, % Calcd.	Found	Chlorine, % Calcd.	Found	Mol. wt. Calcd.	Found
$C_2H_5SC_2F_3ClH$	26.90	26.56	3.39	3.39	17.95	17.69	19.85	19.74	178.6	179.5
$C_4H_9SC_2F_3ClH$	34.87	34.87	4.88	5.09	15.51	15.45	17.15	17.23		
$C_4H_9SC_2F_2Cl_2H$	32.31	32.54	4.52	4.32	14.35	13.97	31.79	31.54	223.1	220.9
$(C_4H_9S)_2C_4F_5H$	44.69	44.30	5.93	5.82	19.89	19.22			232.2	232.8
$C_4H_9SC_4F_5$	41.38	41.44	3.91	4.14	13.81	13.85				
$(C_4H_9S)_2C_4F_4$	47.66	47.80	6.00	5.72	21.21	21.77			302.4	305.6
$HOOCCH_2SC_2F_3ClH$	23.03	23.02	1.93	1.96	15.37	15.43	17.00	16.76		
$(HOOCCH_2S)_2C_4F_4$	31.37	31.76	1.97	1.94	20.94	21.14			306.2	304.8
$HOCH_2CH_2SC_2F_3ClH$	24.69	24.75	3.11	3.05	16.47	16.51	18.22	17.72		
$(2-C_{10}H_7S)_2C_4F_4$	65.16	65.48	3.19	3.20	14.47	14.31				
$C_2H_5SO_2C_2F_3ClH$	22.82	23.07	2.87	3.12	15.20	15.42	16.84	17.00	210.6	218.9
$C_4H_9SO_2C_2F_3ClH$	30.20	30.42	4.22	4.07	13.41	13.38	14.86	14.70		
$C_4H_9SO_2C_2F_2Cl_2H$	28.25	28.59	3.95	3.77	12.55	12.42	27.80	27.62		

tinued from one to three hours during which time the solution was allowed to come to room temperature. The manganese dioxide was destroyed by addition of sodium bisulfite and more water was added to cause the sulfone to separate as a lower layer. The product was washed with water, dried over anhydrous sodium carbonate and distilled. The yields of washed sulfones were about 86 to 88%. In this manner the sulfones shown in Table III were prepared from the corresponding sulfides. These sulfones were colorless mobile liquids of pleasant odor, insoluble in water but soluble in the ordinary organic solvents, neutral in reaction and stable toward heat.

Analyses.—A variety of analytical methods were used.[11] The precision and consistency of the carbon and hydrogen

(11) Analyses were performed by Clark Microanalytical Laboratories, Urbana, Illinois, Miss Frances Ball and Mr. R. R. Rickard of the Microchemical Group of the Analytical Research Section and Mr. R. E. Millspaugh of the Special Analyses Group of the Works Laboratory.

Summary

Thiols in the presence of an alkaline catalyst reacted readily at or near room temperature with polyfluoro olefins such as chlorotrifluoroethylene, 1,1-dichloro-2,2-difluoroethylene and hexafluorocyclobutene. Benzyltrimethylammonium hydroxide or sodium ethyl sulfide catalyst produced high yields of ethylthiochlorotrifluoroethane from ethanethiol and chlorotrifluoroethylene, while tributylamine produced a lower yield because of slower reaction. Mercaptoacetic acid and 2-mercaptoethanol reacted as did simple alkane thiols. Sulfones were prepared by oxidation of polyfluoroalkyl sulfides with potassium permanganate in aqueous acetic acid.

Reactions of hexafluorocyclobutene with thiols were complicated by the elimination of hydrogen fluoride to produce unsaturated sulfides which were capable of further reaction. 1-Butylthio-2,3,3,4,4-pentafluorocyclobutene, 1,2-bis-(butyl-thio)-1,3,3,4,4-pentafluorocyclobutane and 1,2-bis - (butylthio) - 3,3,4,4 - tetrafluorocyclobutene were obtained from the reaction of hexafluorocyclobutene and 1-butanethiol.

OAK RIDGE, TENN.　　RECEIVED NOVEMBER 9, 1949

Reactions of Polyfluoro Olefins. II.[1] Reactions with Primary and Secondary Amines[2]

BY ROY L. PRUETT, JOHN T. BARR, KARL E. RAPP, CARL T. BAHNER, J. DONALD GIBSON AND ROBERT H. LAFFERTY, JR.

Diethylamine has been treated with aluminum chloride and tetrafluoroethylene at 90° to obtain an unidentified liquid boiling at 176–177° and 761 mm.[3] Rigby and Schroeder[4] have treated polyfluoroölefins, such as tetrafluoroethylene and chlorotrifluoroethylene, with primary and secondary amines in the presence of borax and at temperatures of 50–150°. By that method they obtained N-substituted difluoro- and chlorofluoroacetamides. Hurwitz and Miller[5] have reported that secondary amines react "readily under mild conditions" with polyfluoro ethylenes "to yield saturated products having exclusively α,α-difluoro structures."

An investigation of the reactions of primary and secondary amines, both aliphatic and aromatic, with chlorotrifluoroethylene and hexafluorocyclobutene has been conducted. The results of this investigation show that a catalyst is unnecessary for the addition of either primary or secondary amines to take place under mild conditions and that, using a different concentration of the secondary amine, a compound other than the saturated α,α-difluoro addition product is obtained as the principal reaction product.

The reaction between primary aliphatic amines and chlorotrifluoroethylene, as illustrated by n-butylamine, produced a mixture of N-n-butyl-α-chloro-α-fluoroacetimidyl fluoride (II) and N,N'-di-n-butyl-α-chloro-α-fluoroacetamidine (III).

The imidyl fluoride structure for (II) was indicated by its hydrolysis to the N-n-butyl-α-chloro-α-fluoroacetamide (IV) and by reaction with additional amine to produce a compound identical in composition and refractive index with (III).

By analogy with previously reported reactions of chlorotrifluoroethylene with anionic rea-

$$n\text{-}C_4H_9NH_2 + ClCF=CF_2 \longrightarrow [CHClFCF_2NHC_4H_9] \quad (I)$$

(III) $CHClFC\underset{\diagdown NHC_4H_9}{\overset{\diagup NC_4H_9}{}}$ $\xleftarrow{\;n\text{-}C_4H_9NH_2\;}$ $CHClFCF=NC_4H_9$ (II)

(IV) $CHClF\overset{O}{\overset{\diagdown}{C}}\!-\!NHC_4H_9$ $\xleftarrow{\quad H_2O \quad}$

gents[1,5,6] it is believed that the imidyl fluoride (II) was formed by loss of hydrogen fluoride from the unstable primary addition product (I).

Aromatic amines reacted in a manner similar to aliphatic amines, although the reaction was much slower. When aniline reacted with chlorotrifluoroethylene, the only product isolated was N,N'-diphenyl-α-chloro-α-fluoroacetamidine. The failure to produce any of the imidyl fluoride intermediate may have been due to difference in reaction conditions. The structure of the amidine was proved by hydrolyzing it to the corresponding amide. The amidine appeared to form a crystalline association compound with dioxane, with a ratio of 1.5 moles of dioxane per mole of amidine.

When secondary amines were treated with chlorotrifluoroethylene, the first reaction was one of addition to form a tertiary amine containing an α,α-difluoro structure. However, when an excess of amine was used, and the reaction conditions modified somewhat, further reaction occurred. It is believed that this reaction proceeded in several definite steps. In the first step, which occurred rapidly and with evolution of heat, the secondary amine added to the olefin. The following steps were much slower and, according to this hypothesis, were alternate losses of HX and addition of dialkyl amine to the resulting olefins. This process continued until all the halogen was removed and

(1) The previous paper in this series is: Rapp, Pruett, Barr, Bahner, Gibson and Lafferty, THIS JOURNAL, 72, 3642 (1950).
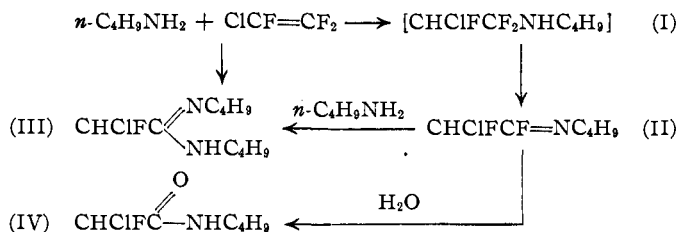
(2) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Corporation at Oak Ridge, Tennessee.

(3) E. I. du Pont de Nemours and Company, British Patent 583,874; C. A., 41, 5141 (1947).

(4) Rigby and Schroeder, U. S. Patent 2,409,315 (1946).

(5) Hurwitz and Miller, "Reactions of Chlorofluoro Olefins with Anionic Reagents," Abstracts of Papers, 114th Meeting, American Chemical Society, Washington, D. C., August, 1948, p. 4L.

(6) Hanford and Rigby, U. S. Patent 2,409,274 (1946); Miller, Fager and Griswold, THIS JOURNAL, 70, 431 (1948); Park, Vail, Lea and Lacher, ibid., 70, 1550 (1948).