

ADDITION REACTIONS OF TETRAFLUOROETHYLENE

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The unusual reactivity of the carbon—carbon double bond of tetrafluoroethylene brings about the participation of this versatile fluoroolefin in vinyl polymerization (1), cycloalkylation (2), and addition reactions (3). This paper reports further transformations of tetrafluoroethylene involving the addition of active hydrogen compounds, halogen, and analogous reactants.

An important addition reaction is that of an alcohol with tetrafluoroethylene to obtain the corresponding alkyl ether.

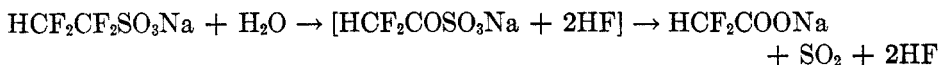


A variety of ethers prepared in this way are listed in Table I in the Experimental Section. It is of interest that tetrachloroethylene does not react (3c) under similar conditions but chlorotrifluoroethylene does (3b, c, e).

In some reactions of active hydrogen compounds with tetrafluoroethylene, for example, with amines, derivatives of difluoroacetic acid are obtained rather than the tetrafluoroethane compound. The mechanism of this unexpected transformation was revealed when it was found that reactions with sodium bisulfite gave both types of products, namely, sodium tetrafluoroethanesulfonate and sodium difluoroacetate.



The difluoroacetic acid derivative apparently results from the lability of the fluorine atoms which are removed from the α -carbon atom by hydrolysis.



Sodium tetrafluoroethanesulfonate, the free acid, and selected derivatives including various ammonium salts (Table II) are described below.

With amines and tetrafluoroethylene, a similar reaction apparently occurs *via* the intermediate $\alpha, \alpha, \beta, \beta$ -tetrafluoroamines (not isolated) (3b) which are hydrolyzed to N-substituted difluoroacetamides.

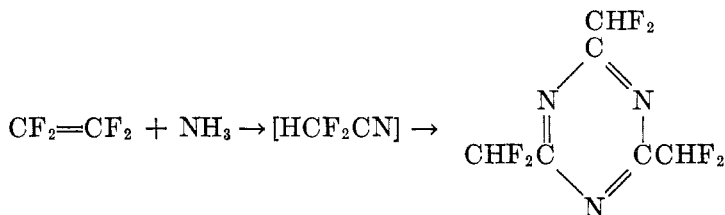


N-Substituted difluoroacetamides from tetrafluoroethylene and a number of amines are described in the Experimental Section (see Table III). With ammonia, the reaction is similar but involves the formation of difluoroacetonitrile which

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trimerizes immediately so that the product is 2,4,6-tris(difluoromethyl)-s-triazine.



The first step is analogous to the reaction of ammonia with asymmetrical dichlorodifluoroethylene to form dichloroacetonitrile, which, however, does not trimerize (10).

An intermediate containing labile fluorine atoms is also formed in the acid-catalyzed reaction of formaldehyde with tetrafluoroethylene. The reaction yields α,α -difluorohydracrylic acid.

$$\text{CF}_2=\text{CF}_2 + \text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow [\text{HOCH}_2\text{CF}_2\text{CF}_2\text{OH}] \rightarrow \text{HOCH}_2\text{CF}_2\text{COOH}$$

This reaction is analogous to the synthesis of α,α -dichlorohydracrylic acid from tetrachloroethylene (8).

In addition reactions with halogens and analogous reactants, the tetrafluoroethanes are formed. Thus, iodine yields tetrafluoroethylene diiodide, a dense, distillable liquid. In contrast, iodine does not add to tetrachloroethylene (5). Reaction of tetrafluoroethylene with nitrogen tetroxide gives 1,2-dinitro-1,1,2,2-tetrafluoroethane (13), analogous to the formation of 1,2-dinitro-1,1,2,2-tetrachloroethane from tetrachloroethylene (6).

EXPERIMENTAL

Caution. Information is not available concerning the toxicity of the various fluorine-containing products described. Accordingly, the products should be regarded with suspicion and handled with appropriate care.

1,1,2,2-Tetrafluoroethyl alkyl ethers. The preparation of the tetrafluoroethyl ethers (3a) is illustrated by the etherification of ethanol and of ethylene glycol as described in the following paragraphs. The properties of the various 1,1,2,2-tetrafluoroethyl alkyl ethers prepared from ethanol, *n*-dodecanol, *n*-octadecanol, cyclohexanol, and ethylene glycol are listed in Table I.

1,1,2,2-Tetrafluoroethyl ethyl ether. A stainless steel-lined shaker tube was charged with 90 ml. of absolute ethyl alcohol and 0.5 g. of sodium. The tube was swept with nitrogen, evacuated, and charged with 75 g. of tetrafluoroethylene. The tube was placed in a shaker box and heated at 50° under autogenous pressure for eight hours. At the end of this time, the pressure was released through a carbon dioxide-acetone cooled trap in which 2 ml. of liquid collected. The product from the tube was combined with the contents of the trap, and the tube was washed out with absolute alcohol. The combined material was distilled through a precision column, and the fraction boiling at 54° collected. The fraction weighed 101.7 g. which amounts to a 93% yield based on tetrafluoroethylene. This product appeared to contain a small amount of ethanol. As a final means of purification, the crude ether was washed three times with distilled water. After drying over sodium sulfate, the 1,1,2,2-tetrafluoroethyl ethyl ether was distilled, and found to boil constantly at 57.5° at atmospheric pressure.

1,1,2,2-Tetrafluoroethyl ethers of ethylene glycol. A mixture of 65 g. of ethylene glycol,

50 ml. of anhydrous ether, and 0.5 g. of metallic sodium was heated with 50 g. of tetrafluoroethylene in a shaker tube at 75° for eight hours under autogenous pressure. Distillation of the product gave a small foreshot (10 g.) boiling at 37–80°/100 mm. which appeared to contain some of the di-ether. The main product boiled from 86–95°/100 mm., and amounted to 49.7 g. Redistillation gave two fractions, the lower-boiling one being the di-ether and the other the monoether. The *bis(tetrafluoroethyl)ether* of ethylene glycol (23.7 g.) boiled constantly at 86°/100 mm. The *tetrafluoroethyl β-hydroxyethyl ether* boiled at 94°/100 mm.

Tetrafluoroethanesulfonic acid (?). Sodium 1,1,2,2-tetrafluoroethanesulfonate. A silver-lined, high-pressure shaker tube was charged with 100 g. of sodium sulfite and 200 g. of distilled water, and was evacuated to remove air. A sodium bisulfite solution buffered to pH 6–7 with borax or disodium phosphate can also be employed with satisfactory results. The tube was then charged with tetrafluoroethylene so that the pressure was 350 lb./sq. in. when the tube was heated at 120°, and was repressured to 350 lb./sq. in. with tetrafluoroethylene whenever the pressure dropped to about 325 lb./sq. in., due to absorption. The

TABLE I
1,1,2,2-TETRAFLUOROETHYL ALKYL ETHERS

ETHER	YIELD, %	B.P., °C.	n_D^{25}	d_4^{25}	MR _D		ANALYSIS FLUORINE, %	
					Calc'd ^b	Found ^c	Calc'd	Found
HCF ₂ CF ₂ OC ₂ H ₅	93	57.5	1.294	1.1978	22.3	22.4	52.0	51.97
HCF ₂ CF ₂ OC ₁₂ H ₂₅	99	105/4 mm.	1.3968	0.9831	68.5	69.8	26.5	25.5
HCF ₂ CF ₂ OC ₁₈ H ₃₇ ^a	80	170/6 mm.	1.4144	0.9530	96.2	97.1	20.5	20.7
HCF ₂ CF ₂ OC ₆ H ₁₁	99	86/100 mm.	1.3848	1.1526	38.6	40.7	38.0	37.3
(HCF ₂ CF ₂ OCH ₂ —) ₂	9	86/100 mm.	1.3202	1.4726	33.2	35.3	58.0	53.4
HCF ₂ CF ₂ OCH ₂ CH ₂ OH	15	94/100 mm.	1.3418	1.4159	23.8	24.1	46.9	46.3

^a M.P., 20–23°.

^b Calculated employing 1.1 as the atomic refraction (AR_F) of fluorine.

^c Based on the formula of Lorenz and Lorentz. See Shriner and Fuson, "The Systematic Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., (1948), p. 45.

reaction proceeded smoothly, and there was a total pressure drop of about 1500 lb. over a period of nine hours at 120°. The reaction mixture was filtered to remove 17 g. of sodium fluoride. The filtrate was evaporated to dryness on a steam-bath, and the solid residue was extracted with hot absolute alcohol. The alcohol extract was evaporated on a steam-bath to obtain a mixture of salts (177 g.), which melted on the Maquenne block at 175°.

1,1,2,2-Tetrafluoroethanesulfonic acid monohydrate. The above reaction product (165 g.) was acidified with 135 ml. of 35% sulfuric acid, and the solution was filtered to remove the precipitated sodium sulfate. The filtrate was extracted several times with ether, the extract was dried, and the ether was removed. The residue was distilled under reduced pressure. After removing the low-boiling material which consisted of water and difluoroacetic acid, the tetrafluoroethanesulfonic acid monohydrate (75 g.) was found to distill at 112–114.5°/5 mm. The acid solidified (m.p. 54°) in the receiver, and was very hygroscopic.

Anal. Calc'd for C₂H₄F₄O₄S: F, 38.0; S, 16.0; Neut. equiv., 200.

Found: F, 39.74; S, 16.10; Neut. equiv., 198.8.

1,1,2,2-Tetrafluoroethanesulfonic acid. Tetrafluoroethanesulfonic acid monohydrate (40 g.) was treated with 35 ml. of thionyl chloride in a 125-ml. Claisen flask fitted with a reflux condenser. The compound was not soluble in thionyl chloride, and on warming gently on a steam-bath two layers were formed. After about an hour, the evolution of sulfur dioxide and hydrogen chloride ceased and only one layer remained. The product was distilled under

reduced pressure to obtain a nearly quantitative yield of the anhydrous 1,1,2,2-tetrafluoroethanesulfonic acid boiling at 90–92°/3.5 mm.

Anal. Calc'd for $C_2H_2F_4O_3S$: Neut. equiv., 182. Found: Neut. equiv., 183.

Ammonium salts of 1,1,2,2-tetrafluoroethanesulfonic acid. Reaction of the anhydrous acid with amines, or of the monohydrate with an appropriate isocyanate, gave the corresponding ammonium tetrafluoroethanesulfonates listed in Table II.

The monohydrate or anhydrous tetrafluoroethanesulfonic acid with aniline gave a colorless solid melting at about 235° on the Maquenne block. The salt was soluble in water, ethanol, ethyl acetate, and dioxane but was insoluble in ether and petroleum ether.

TABLE II
SALTS OF 1,1,2,2-TETRAFLUOROETHANESULFONIC ACID WITH AMINES

AMINE	M.P., °C. ^a	EMPIRICAL FORMULA	ANALYSIS				NEUT. EQUIV.	
			N		S		Calc'd Found	
			Calc'd	Found	Calc'd	Found		
Aniline	235	$C_8H_9F_4NO_3S$	—	—	11.64	11.66	275	273.3 274.3
α -Naphthylamine	225	$C_{12}H_{11}F_4NO_3S$	4.31	4.05	9.85	9.18	325	322.5 326.5
Ammonia	198	$C_2H_7F_4NO_3S$	6.57	6.55				
Methylamine	119–120.5							
Dodecylamine	155							

^a Maquenne block.

TABLE III
PROPERTIES OF N-SUBSTITUTED DIFLUOROACETAMIDES

AMIDE	YIELD, %	B.P., °C/MM.	n_D^{25}	d_4^{25}	ANALYSIS					
					MR _D		N, %		F, %	
					Calc'd ^b	Found	Calc'd	Found	Calc'd	Found
$HCF_2CONHC_6H_5^a$	71	114/5			—	—	8.32	8.32	22.20	22.75
$HCF_2CON(CH_2)C_6H_5$	51	104/4	1.5036	1.2305	44.0	44.5	7.57	8.23	20.55	20.87
$HCF_2CONHC_4H_9-n$	90	113/30	1.4112	1.1029	33.3	34.0	9.26	9.44	25.20	24.49
$HCF_2CON(C_4H_9)_2-n$	62	107/10	1.4270	1.0158	52.2	52.2	6.75	6.71	18.30	18.52

^a M.P., 58°.

^b See Table I, footnotes ^b and ^c.

A similar salt was obtained on treating the acid monohydrate with an excess of phenyl isocyanate.

Reaction of tetrafluoroethanesulfonic acid with α -naphthylamine gave a solid, which after recrystallization from water, melted at about 225° on the Maquenne block. An identical product was obtained by reacting tetrafluoroethanesulfonic acid monohydrate with α -naphthyl isocyanate.

1,1,2,2-Tetrafluoroethanesulfonyl chloride. Anhydrous tetrafluoroethanesulfonic acid (81 g.) was added slowly to 100 g. of phosphorus pentachloride. The tetrafluoroethanesulfonyl chloride, b.p. 92–92.5° was separated from the phosphorus oxychloride by fractional distillation.

Anal. Calc'd for $C_2HClF_4O_2S$: F, 37.9; Cl, 17.7.

Found: F, 40.2; Cl, 18.3.

N-Substituted difluoroacetamides. These derivatives were prepared by the reaction of tetrafluoroethylene with aniline, *N*-methylaniline, *n*-butylamine, and di-*n*-butylamine (9). The properties of the amides are listed in Table III. A typical preparation involving the reaction of tetrafluoroethylene and aniline follows.

Difluoroacetanilide. A stainless steel-lined shaker tube was charged with 93 g. of freshly distilled aniline and 15 g. of borax ($Na_2B_4O_7 \cdot 10H_2O$). The tube was swept with nitrogen, closed, cooled in carbon dioxide-acetone, and charged with 50 g. of tetrafluoroethylene. The mixture was heated with shaking at 130° for eight hours. The product was washed with a saturated solution of potassium carbonate, dried over potassium carbonate, and distilled. The distillate consisted of 51.4 g. of recovered aniline, and 61.6 g. (71% yield) of difluoroacetanilide boiling at 90°/1 mm. and at 114°/5 mm. The difluoroacetanilide melted at 58°. Difluoroacetanilide has been reported (12) as boiling at 259.8° and melting at 52.4°.

Difluoroacetonitrile trimer. When tetrafluoroethylene is allowed to react with ammonia under anhydrous conditions at room temperature, an exothermic reaction occurs with the formation of a bright red product which can be separated into a white solid (ammonium fluoride) and an ether-soluble portion shown to be 2,4,6-tris-(difluoromethyl)-*s*-triazine. When the reaction between tetrafluoroethylene and ammonia is not moderated by copper acetate, the reaction may become violently exothermic.

A stainless steel-lined shaker tube was charged with 100 ml. of ether and 0.1 g. of copper acetate. The bomb was blanketed with nitrogen, cooled, evacuated, and charged with 50 g. of anhydrous ammonia and 75 g. of tetrafluoroethylene. The mixture was kept at room temperature for six hours with shaking. The gas was released through a carbon dioxide-acetone cooled trap in which about 30 ml. of bright red liquid collected. The shaker tube contained a bright pink solid weighing about 130 g. The pink solid and red liquid were combined with the bomb washings, and extracted in a Soxhlet apparatus with anhydrous ether. The ether extract was fractionated. The principal product boiled at 75°/10 mm. and corresponded in composition to the trimeric form of difluoroacetonitrile. It amounted to 47.1 g. or an 82% yield. When redistilled, the colorless product boiled at 73°/9 mm., melted at 24.5°, and had the following physical properties: n_D^{25} 1.3999; d_4^{25} 1.5973.

Anal. Calc'd for $(C_2HF_2N)_3$: F, 49.4; N, 18.2; Mol. wt., 231.

Found: F, 47.0; N, 18.09 (K), 17.81 (D); Mol. wt., 213 (ebullioscopic method in benzene).

The trimeric product does not react with bromine in carbon tetrachloride, with dilute aqueous permanganate, or with very dilute nitrous acid.

Hydrolysis of 2,4,6-tris(difluoromethyl)-s-triazine (11). The hydrolysis of 2,4,6-tris(difluoromethyl)-*s*-triazine (22 g.) was carried out by refluxing with 70 ml. of 4 *N* sodium hydroxide for four hours. Ammonia was evolved during the reaction. After separation of unreacted triazine, the aqueous phase was acidified by the addition of 30 ml. of 50% sulfuric acid, and was then extracted with 100 ml. of ether. Fractional distillation of the dried ether extract gave 6 g. of difluoroacetic acid (22% yield) boiling at 131°.

2,4,6-Tris(difluoromethyl)-*s*-triazine (50 g.) was refluxed in water (75 ml.) for fifty hours. The water-insoluble material was separated, washed, dried, and distilled to recover 7 g. of unchanged triazine. Evaporation of the aqueous reaction solution gave 50 g. of salt presumed to be ammonium difluoroacetate. This salt dissolved in hot aqueous sodium hydroxide with the liberation of ammonia. When an aqueous solution of the salt was acidified with conc'd sulfuric acid and extracted with methylene chloride, distillation of the extract gave a liquid identified by boiling point (132°) and neutral equivalent [94] as difluoroacetic acid.

α,α -Difluorohydracrylic acid (14). Paraformaldehyde (15 g.), 150 ml. of conc'd sulfuric acid, and 50 g. of tetrafluoroethylene were heated in a silver-lined shaker tube at 80° for fifteen hours. The product, which evolved fumes of hydrogen fluoride, was poured on 375 g. of ice. After separation of a small amount of oily material and filtration, the mixture was

extracted with four 100-ml. portions of ether, the ether was washed with 50 ml. of water, then extracted with 180 ml. of water containing 20 g. of sodium hydroxide. To the alkaline extract was added with cooling 36 ml. of 50% sulfuric acid. The acidified solution was extracted with four 50-ml. portions of ether. The ether was evaporated, and the syrupy residue was heated under vacuum at 60° for several hours. The weight of the hygroscopic syrup was 16 g. Fluorine analysis and neutral equivalent indicated that it was 80% α, α -difluoroacrylic acid. Since the material darkened and increased in viscosity without distilling when heated at 250°/8 mm., it was esterified for purification. The syrup (15 g.), absolute alcohol (23 g.), and 60 g. of anhydrous copper sulfate were heated under reflux on a steam-bath for eleven hours. Distillation of the liquid gave 7.9 g. (n_D^{25} 1.3830) of a pleasant-smelling ester, ethyl α, α -difluoroacrylate; b.p. 58–61°/6 mm., 181°/760 mm.

Anal. Calc'd for $C_6H_8F_2O_2$: C, 38.97; H, 5.23; F, 24.66.

Found: C, 39.53; H, 5.83; F, 23.1.

The α, α -difluoroacrylic acid obtained upon hydrolysis of the ester melted at 49–53°.

Tetrafluoroethylene diiodide (4). A silver-lined shaker tube was charged with 100 g. of iodine in 150 ml. of ether. The tube was maintained under 300–370 lb./sq. in. of tetrafluoroethylene pressure at 60° for fifteen hours. The product was filtered, washed with sodium thiosulfate solution, then with water, and dried. When distilled it gave tetrafluoroethylene diiodide, b.p. 112–113°, 51°/110 mm., and 23°/14 mm. The product was deeply colored with iodine when distilled at ordinary pressure; when distilled at 14 mm., it had only a faint color. Further discoloration was minimized by storage at temperatures near zero. The yield was 103 g. or 74% based on iodine. It had the following physical properties: n_D^{25} 1.4895; d_4^{25} 2.6293.

Anal. Calc'd for $C_2F_4I_2$: F, 21.48; I, 71.74; MR_D , 37.0.

Found: F, 22.3; I, 68.86; MR_D , 40.3.

1,2-Dinitro-1,1,2,2-tetrafluoroethane. This compound was prepared in glass apparatus at 0° under a few pounds pressure. The apparatus consisted of a 500-ml. filter flask, the side arm of which was connected to an open-end mercury manometer through a T-tube. The remaining end of the T-tube was connected to the tetrafluoroethylene supply through capillary tubing. Connections were made with "Tygon" tubing, since rubber is rapidly attacked by nitrogen tetroxide. A rubber stopper for the flask was coated with sodium silicate, dried, and the lower part covered with aluminum foil. The flask was surrounded with ice and charged with 57 g. of nitrogen tetroxide which had been distilled from phosphorus pentoxide. It is necessary that the nitrogen tetroxide be dry. After flushing the flask with tetrafluoroethylene, the stopper was wired on and the flask was pressured to 7 lb./sq. in. a total of 27 times during three eight-hour periods. Absorption of gas became slow at this point and a permanent pressure developed in the system, caused by the presence of permanent gases from side reactions. The reaction flask was deeply etched. The contents of the flask were poured onto ice, and the liquid (8.8 g.) which separated was washed with water. The yield, based on nitrogen tetroxide, was 7.5%. After drying over magnesium sulfate, the liquid distilled at 58–59°. The colorless 1,2-dinitro-1,1,2,2-tetrafluoroethane so obtained had the following physical properties: n_D^{25} 1.3265; d_4^{25} 1.6024.

Anal. Calc'd for $C_2F_4N_2O_4$: C, 12.51; F, 39.57; MR_D , 22.7.

Found: C, 13.32; F, 38.7; MR_D , 24.2.

The patent literature (13) records the following properties: b.p., 57–58°/750 mm.; sp. gr. (20°) 1.595; n_D^{25} 1.348; MR_D , 25.76.

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SUMMARY

A number of new fluorine-containing compounds including several tetrafluoroethyl ethers, tetrafluoroethanesulfonic acid, certain difluoroacetamides, a

tris(difluoromethyl)-s-triazine, difluorohydracrylic acid, and tetrafluoroethylene diiodide have been synthesized by reactions of tetrafluoroethylene with alcohols, sodium bisulfite, amines, ammonia, formaldehyde, and iodine. In reactions with these agents, tetrafluoroethylene is appreciably more reactive than tetrachloroethylene.

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