

electronegative portion of the activated complex dipole requires solvation, and again that mixed acetic acid-trifluoroacetic acid dimer is less suited for this purpose than trifluoroacetic acid. The magnitude of the effect of acetic acid on reaction rate is then presumed to be related to the degree to which negative charge develops on activation; that is, the more polar is the activated complex, the more

acetic acid will depress the rate of reaction. Since, however, acetic acid in some instances produces little or no rate depression in these polar reactions this second explanation can be accepted only with considerable reservation.

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Fluorodienes. I. Synthesis from Cyclobutenes

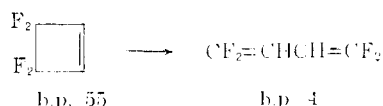
By J. L. ANDERSON, R. E. PUTNAM AND W. H. SHARKEY¹

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A number of fluorodienes have been prepared by pyrolysis of cyclobutenes and cyclobutyl acetates. Reactions of 1,1,4,4-tetrafluorobutadiene with chlorine, bromine, sodium ethoxide, sodium thiophenoxide and peroxytrifluoroacetic acid are described.

Thermal scission of the allylic carbon-carbon bond of cyclobutenes to give 1,3-dienes has been observed in a sufficient number of cases to suggest that it is a general reaction. A number of recently reported examples have been summarized by Vogel.² In contrast to the ease of cleavage noted in the hydrocarbon series, hexafluorocyclobutene is resistant to thermal isomerization. Thus, pyrolysis of hexafluorocyclobutene³ over active carbon at 600–700° has been reported to give a mixture of the cyclobutene and hexafluorobutadiene with a maximum diene concentration of only 12%. We have found that fluorocyclobutenes bearing hydrogens on the ethylenic carbons undergo ring opening upon pyrolysis to give 1,3-dienes in excellent yields.

When 3,3,4,4-tetrafluorocyclobutene was heated to 550–750°, it was converted almost quantitatively to 1,1,4,4-tetrafluorobutadiene.⁴ The reaction was carried out by addition of the cyclobutene to a hot tube packed with quartz rings as a heat transfer medium and kept at a pressure of 5–25 mm.



The product gases were rapidly quenched in a cold trap.

Identification of the product as 1,1,4,4-tetrafluorobutadiene was accomplished by spectral analysis and by the formation of derivatives. Infrared absorption at 1720 cm.⁻¹ confirmed the presence of difluorovinyl groups and absorption at 3120 cm.⁻¹ indicated vinyl hydrogens. Nuclear magnetic resonance (n.m.r.) spectra⁵ were most

unusual in showing a broad, unresolvable band in the range of –575 to –315 c.p.s. for the fluorine resonance. At temperatures of –120 to –80° the spectrum sharpened somewhat but not enough to be interpreted. Reaction of the diene with bromine gave 1,4-dibromo-1,1,4,4-tetrafluorobutene and the n.m.r. proton and fluorine spectra of this derivative were normal. In addition, an infrared spectrum of the dibromide showed the absence of a fluorinated double bond (no absorption at 1720–1750 cm.⁻¹). Oxidation of the dibromide produced bromodifluoroacetic acid.⁶ In contrast to its reaction with bromine, tetrafluorobutadiene formed a tetrachloride when treated with chlorine under mild conditions.

The cyclobutene used to prepare 1,1,4,4-tetrafluorobutadiene was readily obtained from tetrafluoroethylene and acetylene by reaction of equimolar amounts of these compounds in a shaker tube at 225°. Synthesis^{4a} of tetrafluorobutadiene directly from tetrafluoroethylene and acetylene has also been accomplished by passing a mixture of these compounds through a pyrolysis tube maintained at 600° and 1 atm. Undoubtedly the first product is the cyclobutene, which is cleaved to tetrafluorobutadiene at the high reaction temperature. Tetrafluorobutadiene has also been



prepared by pyrolysis of 1-acetoxy-2,2,3,3-tetrafluorocyclobutane, which is accessible from tetrafluoroethylene and vinyl acetate.⁷ Presumably, loss of acetic acid from the cyclobutane leads to

manufactured by Varian Associates, Palo Alto, Calif., operating at 40 Mc. and approximately 10,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (c.p.s.) from the proton resonance of H₂O and the F resonance of CF₃CO₂H. Negative frequency displacements indicate resonances occurring at higher field relative to the reference.

(6) E. L. Martin and W. H. Sharkey, *THIS JOURNAL*, **81**, 5256 (1959).

(7) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, *ibid.*, **71**, 490 (1948).

(1) To whom inquiries regarding this paper should be addressed.

(2) E. Vogel, *Fortschr. Chem. Forsch.*, **3**, 430 (1955).

(3) R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 3880 (1955).

(4) (a) J. L. Anderson, U. S. Patent 2,743,303 (April 24, 1956); (b) J. D. Park, J. Abrams, M. Hein, D. N. Gray and J. R. Lacher, *J. Org. Chem.*, **23**, 1661 (1958), have also prepared small amounts of 1,1,4,4-tetrafluorobutadiene from CF₂=CHI; they report a boiling point of –1.8° (584 mm.).

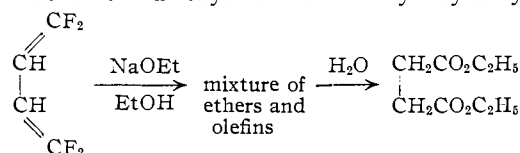
(5) Spectra were obtained by means of a high-resolution nuclear magnetic resonance spectrometer and associated electromagnet, both

tetrafluorocyclobutene, which isomerizes to the diene at the high temperatures (700–750°) employed.

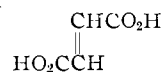
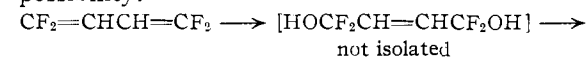
Pyrolysis of fluorocyclobutenes and fluorocyclobutyl acetates has been found to be applicable to the preparation of a variety of fluorodienes. The generality of the reaction is illustrated by the examples in Table I. In many cases, particularly those involving cyclobutenes with chlorine in the ring, much tar is formed. Other examples (notably 1-acetoxy-2,2,3,3-tetrafluorocyclobutane) pyrolyzed cleanly without charring.

Many of the cyclobutenes used were obtained directly by cycloalkylation of fluoroolefins with acetylenes. The structure of the products derived from tetrafluoroethylene was assumed from the nature of the reactants. The structures of the cyclobutenes derived from chlorotrifluoroethylene, 1,1-dichloro-2,2-difluoroethylene and methyl propiolate were assumed to be similar to the previously described products⁸ obtained from the same olefins and phenylacetylene. In the case of the cyclobutane prepared from vinyl acetate and chlorotrifluoroethylene, the structure of the product is presumed to be 1-acetoxy-2,2,3-trifluoro-3-chlorocyclobutane on the basis of its proton nuclear magnetic resonance spectrum. The spectrum contains a doublet for the methylene hydrogens and this fact is best explained by assuming the methylene group to be adjacent to the CClF group.

We have found 1,1,4,4-tetrafluorobutadiene to be a very reactive compound. With sodium ethoxide in ethanol it gave a product that was converted to diethyl succinate by hydrolysis.



NaHF₂ and diethyl ether were isolated as side products. Use of sodium thiophenoxide in place of sodium ethoxide gave CF₂=CHCH₂CF₂SC₆H₅ as the only product. Reaction of tetrafluorobutadiene with peroxytrifluoroacetic acid yielded fumaric acid. The route by which fumaric acid was formed is not known, but 1,4-addition of hydroxyl radicals followed by hydrolysis is a possibility.



Cycloalkylation reactions of 1,1,4,4-tetrafluorobutadiene are described in an accompanying paper.⁹

Experimental¹⁰

3,3,4,4-Tetrafluorocyclobutene.¹¹—To a 400-ml. stainless steel high-pressure bomb was added 3 drops of a terpene¹²

(8) J. D. Roberts, G. B. Kline and H. E. Simmons, Jr., *THIS JOURNAL*, **75**, 4765 (1953); E. J. Smutny and J. D. Roberts, *ibid.*, **77**, 3420 (1955).

(9) R. E. Putnam, J. L. Anderson and W. H. Sharkey, *ibid.*, **83**, 386 (1961).

(10) All melting points and boiling points are uncorrected.

(11) The authors are indebted to Dr. B. C. Anderson of this laboratory for preparation of tetrafluorocyclobutene by this method.

inhibitor. The bomb was cooled to –80° and charged, first with 80 g. of tetrafluoroethylene and then with 20 g. of acetylene. The bomb was closed and heated to 225° for 12 hours behind a barricade. The bomb was cooled to room temperature and tetrafluoroethylene, acetylene and octafluorocyclobutane were allowed to escape slowly. The liquid product that remained (36.4 g.) was distilled to yield 34 g. (35%) of 3,3,4,4-tetrafluorocyclobutene, b.p. 54–56°, *n*_D²⁵ 1.3086.

Anal. Calcd. for C₄F₄H₂: C, 38.11; H, 1.60; F, 60.29. Found: C, 38.57; H, 1.59; F, 60.13.

1-Chloro-3,3,4,4-tetrafluorocyclobutene.—1,1-Dichloro-2,2,3,3-tetrafluorocyclobutane⁷ (49 g.) was added to a solution of 40 g. of potassium hydroxide in 150 ml. of water and the mixture was heated to boiling. The product that distilled (b.p. 60–63°) was collected in a trap cooled with ice. Redistillation gave 17 g. (43%) of 1-chloro-3,3,4,4-tetrafluorocyclobutene, b.p. 59–60°, *n*_D²⁵ 1.3453.

Anal. Calcd. for C₄F₄HCl: C, 29.93; H, 0.63. Found: C, 29.56; H, 0.83.

1-Hydroxymethyl-3,3,4,4-tetrafluorocyclobutene.—In a 145-ml. stainless steel high-pressure tube were placed 40 g. of propargyl alcohol, 0.5 g. of hydroquinone and 3 drops of a terpene inhibitor. The bomb was cooled to –80°, evacuated, charged with 35 g. of tetrafluoroethylene and heated to 175° for 16 hours. The liquid product was distilled to yield 19 g. (35%) of 1-hydroxymethyl-3,3,4,4-tetrafluorocyclobutene, b.p. 74° (20 mm.), *n*_D²⁵ 1.3763.

Anal. Calcd. for C₅F₄H₅O: C, 38.48; H, 2.58. Found: C, 38.04; H, 2.97.

This procedure was used in preparing the cyclobutenes that follow.

1-Methoxycarbonyl-3,3,4,4-tetrafluorocyclobutene.—From 40 g. of tetrafluoroethylene containing 3 drops of a terpene inhibitor and 25 g. of methyl propiolate heated 16 hours at 190° there was obtained 18.5 g. (34%) of 1-methoxycarbonyl-3,3,4,4-tetrafluorocyclobutene, b.p. 140°, *n*_D²⁵ 1.3718.

Anal. Calcd. for C₆H₄F₄O₂: C, 39.14; H, 2.19. Found: C, 39.26; H, 2.51.

1-Phenyl-3,3,4,4-tetrafluorocyclobutene.—Phenylacetylene (40 g.), tetrafluoroethylene (40 g.) and a terpene inhibitor (3 drops) were heated 16 hours at 160°. Distillation of the reaction mixture gave 60 g. (73%) of 1-phenyl-3,3,4,4-tetrafluorocyclobutene, b.p. 88–89° (16 mm.), *n*_D²⁵ 1.4823.

Anal. Calcd. for C₁₀F₄H₆: C, 59.41; H, 2.99; F, 37.60. Found: C, 59.25; H, 3.14; F, 37.9.

1-Methoxycarbonyl-3,3-difluoro-4,4-dichlorocyclobutene.—1,1-Dichloro-2,2-difluoroethylene (50 g.) and methyl propiolate (35 g.) were heated 16 hours at 190°. From the reaction mixture there was obtained 26 g. (32%) of cyclobutene, b.p. 88° (22 mm.), *n*_D²⁵ 1.4446.

Anal. Calcd. for C₆H₄F₂Cl₂O₂: C, 33.28; H, 1.84; Cl, 17.53. Found: C, 33.20; H, 2.11; Cl, 17.5.

1-Methoxycarbonyl-3,3,4-trifluoro-4-chlorocyclobutene.—From 50 g. of chlorotrifluoroethylene and 40 g. of methyl propiolate heated at 190° for 16 hours there was obtained 30 g. (35%) of material of b.p. 64° (25 mm.), *n*_D²⁵ 1.4083.

Anal. Calcd. for C₆H₄F₃ClO₂: C, 35.93; H, 2.01; Cl, 17.68. Found: C, 36.29; H, 2.21; Cl, 17.97.















1-Acetoxy-1-methyl-2,2,3,3-tetrafluorocyclobutane.—A mixture of 140 g. of isopropenyl acetate, 40 g. of tetrafluoroethylene and three drops of a terpene inhibitor was heated to 190° for 3 hours. The product was distilled to give 32 g. (41%) of 1-acetoxy-1-methyl-2,2,3,3-tetrafluorocyclobutane, b.p. 137°, *n*_D²⁵ 1.3646.

Anal. Calcd. for C₇H₈F₄O₂: C, 42.01; H, 4.02. Found: C, 42.49; H, 4.60.

1-Acetoxy-2,2,3-trifluoro-3-chlorocyclobutane.—Vinyl acetate (140 g.) and chlorotrifluoroethylene (47 g.) were heated to 215° for 3 hours. The reaction mixture was distilled to obtain 30 g. (37%) of 1-acetoxy-2,2,3-trifluoro-3-chlorocyclobutane, b.p. 163–164°, *n*_D²⁵ 1.3921.

(12) Added to inhibit polymerization of the fluoroolefin. Tetrafluoroethylene should always be inhibited as otherwise it presents an explosion hazard. Terpenes that are effective include dipentene and terpinolene.

TABLE I
 PREPARATION OF DIENES

Diene	Starting material	Amount starting material, g.	Temp., °C.	Press., mm.	Yield, %	B.p., °C.		Ref. index n_D^{20}	Carbon, %		Hydrogen, %		Fluorine, %		Chlorine, %		Mol. wt.	
						°C.	mm.		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$\text{CF}_2=\text{CFCF}=\text{CF}_2^a$		0.5 ^d	700-900	1	10-14 ^b	6											
$\text{CF}_2=\text{CHCH}=\text{CF}_2$		56	700	10	~100	4											
$\text{CF}_2=\text{CHCH}=\text{CF}_2$		50	725	10	91	4											
$\text{ClFC}=\text{CHCH}=\text{CF}_2$		70	700	10	56	50-51		1.3870	33.72	33.50	1.42	1.09	39.98	39.63				
$\text{CF}_2=\text{C}(\text{Cl})-\text{CH}=\text{CF}_2$		37	700	10	38	45-46		1.3552	29.93	30.18	0.64	0.70			22.10	21.95	160	162
$\text{CF}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CF}_2$		160	700	10	57	39-40		1.3454	42.66	42.79	2.86	3.20	54.48	54.3			140	140
$\text{CF}_2=\text{C}(\text{CH}_2\text{OH})\text{CH}=\text{CF}_2$		15	650	1	50	67	16	1.3880	38.47	39.26	2.58	2.70	48.69	48.46			156	
$\text{CF}_2=\text{C}(\text{C}_6\text{H}_5)\text{CH}=\text{CF}_2$		15	700	10	60	43	5	1.4711	59.41	59.58	2.99	3.46	37.60	37.8			202	201
$\text{CF}_2=\text{C}(\text{CH}_2\text{Cl})\text{CH}=\text{CF}_2$		4	550	10	100	60	117	1.3632	34.41	34.48	1.73	1.96						
$\text{CF}_2=\text{C}(\text{CO}_2\text{CH}_3)\text{CH}=\text{CF}_2$		93	525	10	55	115		1.3809	39.14	38.77	2.19	2.28	41.28	41.2				
$\text{CCl}_2=\text{C}(\text{C}_6\text{H}_5)\text{CH}=\text{CF}_2$		40	700	10	40	72	4	1.5418	51.09	50.85	2.57	2.79	16.17	16.2	30.17	29.9		
$\text{CCl}_2=\text{C}(\text{CO}_2\text{CH}_3)\text{CH}=\text{CF}_2$		25	550	10	90	77	19	1.4642	33.28	33.29	1.84	2.06	17.53	17.4	32.75	32.73	218	214
$\text{CFCl}=\text{C}(\text{CO}_2\text{CH}_3)\text{CH}=\text{CF}_2$		25	550	2	80	60	20	1.4224	35.93	35.85	2.01	2.26			17.68	17.60		
$\text{CFCl}=\text{C}(\text{C}_6\text{H}_5)\text{CH}=\text{CF}_2$		20	750	5	60	86	7	1.5071	54.94	55.35	2.77	3.01			16.22	15.79	219	217

^a R. N. Haszeldine and J. E. Osborne, *J. Chem. Soc.*, 3880 (1955). ^b Higher yields obtained at higher temperatures. ^c Elemental analysis not obtained on diene; chlorination gave a tetrachloride. *Anal.* Calcd. for $\text{C}_4\text{F}_4\text{Cl}_4\text{H}_2$: C, 17.94; H, 0.75; F, 28.36; Cl, 52.95; mol. wt., 268. Found: C, 17.94; H, 1.16; F, 28.2; Cl, 52.68; mol. wt., 268. ^d Ml.

Anal. Calcd. for $C_4H_5F_3O_2Cl$: C, 35.57; H, 2.99. Found: C, 36.01; H, 3.30.

1-Chloromethyl-3,3,4,4-tetrafluorocyclobutene.—A mixture of 16 g. of 1-hydroxymethyl-3,3,4,4-tetrafluorocyclobutene, 50 ml. of ether and 10 drops of pyridine was heated under reflux and to it was added dropwise 12 g. of thionyl chloride in 50 ml. of ether. Heating under reflux was continued for 30 minutes. Distillation of the reaction mixture gave 15 g. (86%) of 1-chloromethyl-3,3,4,4-tetrafluorocyclobutene, b.p. 117°, n_D^{25} 1.3771.

Anal. Calcd. for $C_5F_4H_3Cl$: C, 34.41; H, 1.73; Cl, 20.32. Found: C, 34.56; H, 2.03; Cl, 20.47.

Preparation of Dienes from Cyclobutenes. 1,1,4,4-Tetrafluorobutadiene.—The following example is illustrative of the procedure used in the preparation of fluorodienes from cyclobutenes (see Table I).

The pyrolysis system used consisted of a dropping funnel attached to a vertical tube 2 feet long and 1 inch in diameter packed with pieces of 8-mm. quartz tubing cut into 0.25-inch lengths. A thermocouple well was introduced up the center of the tube, its end being located approximately at the center of the packing. The tube was heated by means of a Hevi Duty Electric Co. 110-volt electric furnace, type 70. The temperature at the center of the packing (also the center of the furnace) is the temperature that is specified in Table I. The lower end of the pyrolysis tube was connected in series to a solid carbon dioxide-cooled trap, a liquid nitrogen trap, a manometer, and an efficient vacuum pump. The material to be pyrolyzed was added dropwise at a rate of 0.5 to 1.0 ml. min.⁻¹.

Pyrolysis of 56 g. of 3,3,4,4-tetrafluorocyclobutene at 700° and 10 mm. in the above system gave a total of 55 g. of condensate divided equally between the two traps. The condensates were combined and distilled through a low-temperature still, all of the material boiling at 4–5°. Although elemental analyses of tetrafluorobutadiene were not obtained, they were obtained for the derivatives described subsequently.

Preparation of Dienes from Acetoxycyclobutenes. 1,1,4,4-Tetrafluorobutadiene.—The following procedure is illustrative of that employed in the preparation of fluorodienes from cyclobutyl acetates.

Fifty grams of 1-acetoxy-2,2,3,3-tetrafluorocyclobutane pyrolyzed in the above system at 725° and 10 mm. gave 48 g. of water-white condensate in the solid carbon dioxide-cooled trap. On warming to 28°, nearly all of the tetrafluorobutadiene distilled from the crude product. Purification by low-temperature distillation gave 31 g. (91%) of 1,1,4,4-tetrafluorobutadiene, b.p. 4°. Diene of 99.5% purity could also be obtained simply by passing the volatile material from the pyrolyzate through two towers of KOH pellets. The infrared and n.m.r. spectra of the diene were identical to those of diene prepared from 3,3,4,4-tetrafluorocyclobutene.

1,2,3,4-Tetrachloro-1,1,4,4-tetrafluorobutane.—Tetrafluorobutadiene (11 g.) and chlorine (9 g.) were sealed in a Vycor tube (22 mm. X 2 ft.). The tube was irradiated with an RS sun lamp for 0.5 hour during which time an exothermic reaction took place. Distillation of the tube contents gave 13 g. of material, b.p. 100–138°. Redistillation gave 7.7 g. (33%) of 1,2,3,4-tetrachloro-1,1,4,4-tetrafluorobutane, b.p. 51–53° (22 mm.), n_D^{25} 1.4094.

Anal. Calcd. for $C_4H_2F_4Cl_4$: C, 17.95; H, 0.75; F, 28.36; Cl, 52.94. Found: C, 17.94; H, 1.16; F, 28.20; Cl, 52.68.

1,4-Dibromo-1,1,4,4-tetrafluoro-2-butene.—Tetrafluorobutadiene (17 g.) was slowly added to a stirred solution of

30 g. of bromine in 75 ml. of chloroform. The mixture was stirred at room temperature for 5 hours. It was then distilled to give 32 g. (84%) of 1,4-dibromo-1,1,4,4-tetrafluorobutene, b.p. 105–107°, n_D^{25} 1.4183. The absence of 1,2-isomer was indicated by lack of infrared absorption at 1720–1750 cm.⁻¹ which is characteristic of a difluoro-vinyl group. The n.m.r. proton and fluorine spectra were normal. A single hydrogen peak occurred at 58.7 c.p.s. and a single fluorine peak occurred at –1270 c.p.s.

Anal. Calcd. for $C_4H_2F_4Br_2$: C, 16.81; H, 0.71; Br, 55.96. Found: C, 16.45; H, 0.91; Br, 56.26.

Reaction of 1,1,4,4-Tetrafluorobutadiene with Sodium Ethoxide.—A solution of sodium ethylate was prepared in a heavy-walled glass bottle by adding 2.3 g. of sodium to 50 ml. of ethanol. After cooling to –10°, 12.6 g. (0.1 mole) of tetrafluorobutadiene was added. The bottle was capped and heated on a steam-bath for 2 hours during which time a white solid separated. The solid was separated on a filter, washed with ether, and dried in vacuum at 65°. It was identified as sodium hydrogen fluoride (neutral equivalent calcd. 62 found 60), and the amount isolated (6 g.) corresponded to the removal of two equivalents of fluoride ion from the diene.

After distillation of the alcohol (5 g. of diethyl ether and much HF in forerun), the residual oil was treated with water and then extracted with ether. The ether extract was dried over sodium sulfate. Distillation gave 8 g. (47%) of diethyl succinate, b.p. 70–75° (4 mm.). The structure of the product was proved by comparison of its infrared spectrum with that of an authentic sample.

Phenyl 1,1,4,4-Tetrafluoro-3-butenyl Sulfide.—Sodium methoxide (6.4 g., 0.1 mole), anhydrous methanol (100 ml.) and thiophenol (11 g., 0.1 mole) were added to a heavy-walled glass bottle. The mixture was cooled to –80° and 12.6 g. (0.1 mole) of tetrafluorobutadiene was added. The bottle was capped and heated to 95° for 3 hours. The reaction mixture was distilled. As the solution was concentrated, the sodium fluoride that precipitated was removed by filtration. The fraction boiling at 57° (3 mm.) was collected (12 g., 51%). An infrared spectrum of the material showed it to be phenyl 1,1,4,4-tetrafluoro-3-butenyl sulfide. The spectrum had a strong band at 1755 cm.⁻¹ ($CF_2=C<$) and C–H stretching absorption bands at 3090 cm.⁻¹ (vinyl and aromatic H) and at 2890 cm.⁻¹ (H attached to a saturated C atom).

Anal. Calcd. for $C_{10}H_8F_4S$: C, 50.84; H, 3.42; S, 13.58. Found: C, 51.23; H, 3.44; S, 13.57.

Conversion of Tetrafluorobutadiene to Fumaric Acid.—Peroxytrifluoroacetic acid was prepared in a Carius tube from 2.5 ml. of methylene chloride, 0.3 ml. of 90% H_2O_2 and 1.8 ml. of trifluoroacetic anhydride.¹³ There was then added 6 ml. of perfluorodimethylcyclohexane, the tube was cooled to –80° and 8 g. of tetrafluorobutadiene was added. The tube was sealed and allowed to stand 20 hours at 28°. During this time, 0.3 g. of yellow solid precipitated. Sublimation at 200° and 5 mm. gave 0.15 g. of fumaric acid, identified by its infrared spectrum. The yield was 12% based on peroxytrifluoroacetic acid.

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(13) This reaction mixture presumably leads to an equilibrium mixture of H_2O_2 , CF_3CO_2H , CF_3CO_2H and $(CF_3CO)_2O$; W. D. Emmons, *THIS JOURNAL*, **76**, 3468 (1954).