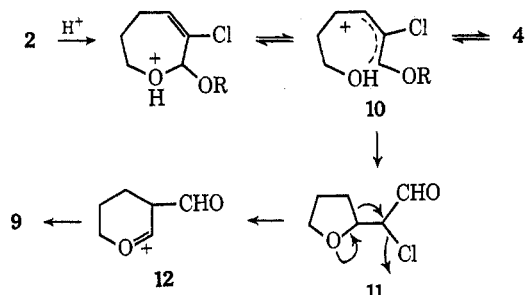


chemical shift of the olefinic proton in **8** should be shifted only slightly downfield as compared with cyclohexene; on the other hand a large (1.5–2.0 ppm) downfield shift would be expected for structure **9**, in agreement with observation. The following mechanistic scheme provides an explanation for the formation of **9**.



The protonation of **2** will result in the formation of the ring-opened allylic ion **10** which can either give the hydroxy aldehyde **4** or the tetrahydrofuran derivative **11**. The solvolysis of α -chloro aldehydes by an S_N1 mechanism would be expected to be quite slow; it is more reasonable to depict the reaction as an anchimerically assisted displacement of chloride ion on the aldehyde itself or on its hydrate. This would lead to the stabilized carbonium ion **12** and the observed product **9**. Cope and Graham¹⁰ and more recently Pasto¹¹ and coworkers have presented evidence for similar transformations in the solvolysis of α -halo ketones. One can think of other explanations for the formation of **9**, but it seems futile to elaborate further on this without more experimental results.

The reaction sequence represents a convenient route to the aldehyde **9**, particularly since the isolation of the intermediate oxepin derivative is not necessary.

Experimental Section¹²

3-Chloro-2-*t*-butoxy-2,5,6,7-tetrahydrooxepin (2).—To a solution of potassium *t*-butoxide from 8.6 g (0.22 g-atom) of potassium in 220 ml of *t*-butyl alcohol was added all at once 33.4 g (0.2 mol) of 7,7-dichloro-2-oxabicyclo[4.1.0]heptane.¹³ The mixture was heated under reflux for 24 hr; excess of *t*-butyl alcohol was distilled on a rotatory evaporator. The residue was added to water and the product extracted with ether. The extract was washed with water (containing some Na_2CO_3) and dried (Na_2CO_3 anhydrous). The ether was evaporated and the residue fractionated giving 32.2 g (79%) of **2**, bp 54–55° (0.5 mm), n_D^{20} 1.4670.

Anal. Calcd for $\text{C}_{10}\text{H}_{17}\text{ClO}_2$: C, 58.68; H, 8.37. Found: C, 58.62; H, 8.44.

The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate, mp 198° dec. When heated further, the compound solidified and remelted at 222° dec, uv λ_{max} (ethanol) 372 nm (ϵ 18,800), 247 (10,000), 283 inf (5700).

Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{ClN}_4\text{O}_5$: C, 43.84; H, 3.99; N, 17.05. Found: C, 43.91; H, 4.03; N, 17.03.

2H-3,4-Dihydropyran-5-carboxaldehyde (9).—A mixture of the acetal **2** (51.1 g, 0.25 mol), 20 ml of dioxane, and 100 ml of 2 *N* HCl was shaken mechanically at room temperature overnight (~12 hr). A homogeneous yellow-colored solution was obtained from which the product was isolated by continuous extraction with ether. The dried (MgSO_4) extract was evaporated and the liquid residue distilled to give 25.9 g (92%) of the aldehyde **9**:

(10) A. C. Cope and E. S. Graham, *J. Amer. Chem. Soc.*, **73**, 4702 (1951).

(11) D. J. Pasto and M. P. Serve, *ibid.*, **87**, 1515 (1965); D. J. Pasto, K. Garves, and M. P. Serve, *J. Org. Chem.*, **32**, 774 (1967).

(12) Melting points and boiling points are uncorrected. Infrared spectra were obtained with a Beckman IR 5 instrument. The nmr spectra were measured with a Varian A-60 instrument, using carbon tetrachloride as solvent and tetramethylsilane as internal standard.

(13) W. E. Parham, E. E. Schweizer, and S. A. Mierzwa, *Org. Syn.*, **41**, 76 (1961).

bp 68° (3 mm); n_D^{20} 1.5140; ν_{max} (liq) 2715, 1665 (–CHO), 1625 cm^{-1} (C=C); λ_{max} (heptane) 241.5 nm (ϵ 17,600), (methanol) 250 nm (ϵ 19,900).

Anal. Calcd for $\text{C}_6\text{H}_9\text{O}_2$: C, 64.27; H, 7.19. Found: C, 64.32; H, 7.40.

The 2,4-dinitrophenylhydrazone was recrystallized from chloroform, mp 239° dec, λ_{max} (ethanol) 391 nm (ϵ 17,100), 290 (6100), 258 (10,300).

Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{N}_4\text{O}_5$: C, 49.31; H, 4.14; N, 19.17. Found: C, 49.63; H, 4.17; N, 18.85.

Registry No.—**1**, 7556-13-0; **2**, 25090-31-7; **4** (2,4-dinitrophenylhydrazone), 15299-59-9; **9**, 25090-33-9; **9** (2,4-dinitrophenylhydrazone), 25111-11-9.

Pyrolysis of Heptafluorobutyric Anhydride

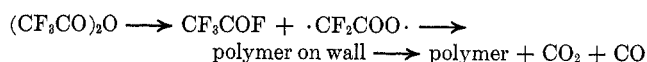
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Pyrolytic reactions of fluorocarbons containing functional groups have not been studied sufficiently that the mode of decomposition of a relatively simple compound such as heptafluorobutyric anhydride could be predicted. There is good precedent for radical decomposition followed by coupling. The pyrolyses of perfluoroacyl bromides¹ and perfluoroacyl hypobromites² give bromoperfluoroalkanes, the pyrolysis of trifluoroacetyl nitrite gives trifluoronitrosomethane,^{3,4} and the pyrolysis of pentafluoropropionic anhydride^{5a} and heptafluorobutyric anhydride^{5b} were reported to give perfluorobutane and perfluorohexane, respectively.

In contrast with these rather straightforward radical formation and coupling reactions, however, is the report that trifluoroacetic anhydride decomposes thermally to give trifluoroacetyl fluoride, carbon dioxide, and carbon monoxide.⁶ Mechanistically this was thought to involve first a dissociation to trifluoroacetyl fluoride and a difluoroacetoxy diradical.



At higher temperatures some tetrafluoroethylene was observed, probably from coupling of difluorocarbene arising from the diradical.

Related to this is the thermal decomposition of hexafluoroacetone⁷ which, at over 500°, produces trifluoroacetyl fluoride and difluorocarbene. At lower temperatures hexafluoroethane is formed, but mechanistic studies indicated that this reaction involved a first-order rearrangement rather than dissociation and coupling of radicals.

It has now been found that heptafluorobutyric anhydride decomposes by two pathways. The most prominent involves a fluoride transfer leading to hepta-

(1) J. D. Lazerte, W. H. Pearson, and E. A. Kauk, U. S. Patent 2,704,776 (May 22, 1955).

(2) M. Hudlicky, "Chemistry of Organic Fluorine Compounds," Macmillan, New York, N. Y., 1962, pp 182–185.

(3) J. Banus, *J. Chem. Soc.*, 3755 (1953).

(4) R. E. Banks, M. G. Barlow, R. N. Haszeldine, and M. K. Creath, *ibid.*, 1350 (1966).

(5) (a) R. N. Haszeldine and K. Leedham, *ibid.*, 1548 (1953); (b) A. D. Kirshenbaum, A. G. Streng, and M. Hauptschein, *J. Amer. Chem. Soc.*, **75**, 3141 (1953).

(6) J. P. Corbett and E. Whittle, *J. Chem. Soc.*, 3247 (1963).

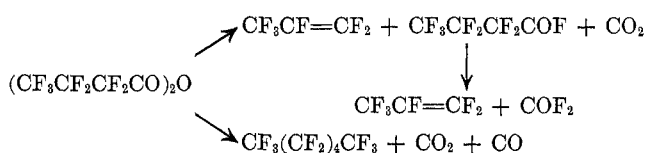
(7) W. Batey and A. B. Trentwith, *ibid.*, 1388 (1961).

TABLE I: CATALYTIC DECOMPOSITION OF HEPTAFLUOROBUTYRIC ANHYDRIDE

Catalyst	Temp, °C	Contact time, sec	Yield, mol % ^a				Ratio coupling/elim
			C ₂ F ₆	C ₃ F ₇ COF	C ₆ F ₁₄	(C ₃ F ₇ CO) ₂ O	
Ag on Al ₂ O ₃ ^b	150	200	0.8	0.8	0	99.2	0
Ag on Al ₂ O ₃	250	200	16.0	27.6	4.4	76.3	0.20
Ag on Al ₂ O ₃	300	100	80.2	39.8	10.6	29.3	0.18
Ag on Al ₂ O ₃	350	100	171.0	0.0	8.4	5.6	0.10
Al ₂ O ₃	300	100	21.0	16.4	0	81.7	0
Pt on Al ₂ O ₃ ^c	230	100	6.8	7.4	0	92.9	0
Pt on Al ₂ O ₃ ^d	230	100	84.6	79.9	0	4.0	0

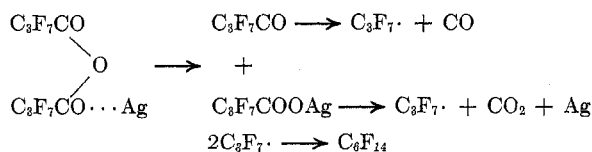
^a Yields were estimated using some distillation and weighing and some gas chromatography assuming area per cent equal to weight per cent. The products were identified by their physical properties and mass spectra. ^b This catalyst was prepared from silver nitrate and Norton LA-956 alumina. It contained 6.7% of silver. ^c This catalyst was prepared from 3.13 g of hexachloroplatinic acid and 250 g of Norton LA-956 alumina. ^d This platinum catalyst was commercial Houdry, grade 100s, 0.5% platinum-on-alumina catalyst. The surface area was about 100 m²/g.

fluorobutyryl fluoride and carbon dioxide, and the second, observed only over a metallic silver catalyst, appears to be a radical decomposition followed by coupling to give perfluorohexane.



The first of these two routes is apparently the result primarily of thermal activation of the heptafluorobutyryl anhydride although it is catalyzed by alumina, platinum on alumina, as well as occurring in a bomb reactor, and it is the major reaction over metallic silver. Over silver at temperatures of 300° and above, the heptafluorobutyryl fluoride observed at lower temperatures is converted to carbonyl fluoride and hexafluoropropene. The reaction is similar to that observed for trifluoroacetic anhydride⁶ and hexafluoroacetone at higher temperatures.⁷

The second pathway of reaction is very similar to the decomposition of silver heptafluorobutyrate^{5,10} and of the reaction of heptafluorobutyric anhydride with silver oxide,^{5b} which gives in each case perfluorohexane, carbon oxides, and metallic silver. The present study does not start with silver(I) so the mechanism, although probably related, would not be the same.⁸ Silver apparently complexes with the anhydride in a way that alumina or platinum does not. A reasonable picture involves the silver complexing with oxygen inducing the loss of a heptafluorobutyryl radical and leaving silver heptafluorobutyrate. The loss of carbon monoxide from a perfluoroacyl radical is known to be fast,⁹ and the radical decomposition of the silver salts of perfluoro acids is well documented.^{5,10} The earlier work with silver oxide^{5b} probably involved a similar reaction, but with formation of only the silver salt.



(8) A 1,4 shift is needed for a first-order rearrangement. This is less likely than the 1,2 shift proposed for the hexafluoroacetone decomposition, and a free radical pathway seems more likely.

(9) The loss of carbon monoxide from perfluoroacyl radicals is best noted in photochemistry in which fluorinated ketones are used as a source for fluoroalkyl radicals. The absolute rate of decarbonylation has been determined. See, for example, J. C. Amplett and E. Whittle, *Trans. Faraday Soc.*, **63**, 80 (1967); J. S. E. McIntosh and G. B. Porter, *ibid.*, **64**, 119 (1968).

(10) M. Hudlicky, *ref 2*, p 271

Surprisingly, decomposition of heptafluorobutyric anhydride did not occur in open tubes of 0.75-in. diameter made of either tantalum or silver at temperatures up to 850° and contact times of 100 sec. It seems that surface contact is very important in this reaction and this may be the reason why it has not been noted before. It is expected that similar results will be found for other perfluoro acid anhydrides.

Experimental Section

Pyrolysis of Heptafluorobutyric Anhydride over a Catalyst.—A 0.75-in. × 5-ft silver-lined tube mounted vertically in a direct-wound furnace was packed with 200 cc of a silver-on-alumina catalyst¹¹ using supports to hold the catalyst in the high-temperature zone of the tube. Perfluorobutyric anhydride was fed from a buret at a rate to give a contact time of about 100 sec. The products were analyzed by gas chromatography and mass spectroscopy as well as by physical properties.

A series of experiments were made using a silver catalyst, two platinum catalysts, and a sample of the alumina support used for the silver and one of the platinum catalysts. The results are given in Table I.

Pyrolysis of Heptafluorobutyric Anhydride in a Titanium Bomb.—A 500-cc titanium bomb was charged with 57.4 g of heptafluorobutyric anhydride and heated to 350° for 12 hr. At temperature the pressure reached 2500 psig, and after cooling there was still 400 psig pressure in the bomb. The volatile components, 42 g, were condensed in Dry Ice-acetone cooled traps backed by a gas sample bottle, and an additional 4 g of black liquid was poured from the bomb. Distillation separated 13 g (62%) of hexafluoropropene, 17 g (56%) of heptafluorobutyryl fluoride, and 15 g (26%) of heptafluorobutyric anhydride. This accounts for only 86% of the starting material, and there were black carbon-like solids coating the bomb wall. There was, however, no evidence by gas chromatography or mass spectroscopy for any perfluorohexane.

Pyrolysis of Heptafluorobutyric Anhydride in an Open Tube.—A 0.75 in. × 5 ft tantalum tube was mounted in a direct-wound furnace and heated with a nitrogen purge to establish a series of temperature profiles. Heptafluorobutyric anhydride was then fed from a buret to the top of the tube at a rate to give a contact time of 100 sec. At both 350 and 450° there was no evidence of reaction.

The above procedure was repeated using the same size silver-lined stainless steel tube at 450, 550, 700, and 850°, all at 100-sec contact time. Again no reaction was observed, except that at 850° there was a small amount of black solids formed on the reactor wall near the outlet.

The experiment at 700° in the silver-lined tube was repeated with 0.1% by weight of iodine added as a possible radical initiating source. There was again no reaction.

Registry No.—Heptafluorobutyric anhydride, 336-59-4.

(11) The silver-on-alumina catalyst was prepared by impregnating 200 cc of 3/16 in. × 3/16 in. Norton LA-956 α -alumina with 30 g of silver nitrate in 40 ml of water under vacuum. The salt was converted to metallic silver by reduction using a flow of 5 l./hr of hydrogen as the catalyst was heated up to 700° over a 29-hr period.