

6.02, 6.17, 6.98, 7.75, 8.14, 8.30 μ ; nmr τ -2.11 (s, 1, enol H), 6.28 (s, 3, COOCH₃), 9.12 (s, 3, tertiary CH₃), 9.12 (d, 3, J = 6.5 Hz, secondary CH₃).

Anal. Calcd for C₁₄H₂₂O₈: C, 70.56; H, 9.30. Found: C, 70.84; H, 9.30.

(±)-Fukinone (1).—To a stirred solution of the carbomethoxy decalone 10 (200 mg, 0.841 mmol) in 2 ml of dry ether at 0° was added 20 mg (0.841 mmol) of sodium hydride. The reaction mixture was stirred for 10 min and 2.15 ml (5.05 mmol) of 2.35 M ethereal methylolithium was added over a period of 5 min. The resulting solution was refluxed for 2 hr, diluted with 15 ml of dry ether and then poured into 35 ml of rapidly stirred water. The ether layer was separated, washed with brine, dried (MgSO₄), and concentrated to afford 160 mg (80%) of the keto alcohol 11, ir (film) 2.90, 5.85 μ . The crude alcohol was dissolved in 10 ml of dry pyridine at 0°, 100 μ l of thionyl chloride was added, and the resultant solution was stirred for 15 min. The solvent was removed under reduced pressure at 0° and the residual material was taken up in benzene. The benzene solution was washed with water and brine, dried (MgSO₄), and concentrated to afford 134 mg of a pale yellow oil. The latter, as shown by glc analysis (column C, 170°, 90), contained mainly (±)-isofukinone (12) and exhibited ir (film) absorptions at 5.85, 6.10, and 11.27 μ . A solution of this dehydration product in 15 ml of dry benzene containing a trace of *p*-toluenesulfonic acid was refluxed for 20 hr. The solution was washed with 10% aqueous sodium bicarbonate and brine, dried (MgSO₄), and concentrated. Glc analysis (column C, 200°, 85) showed that the residual oil (125 mg) contained approximately 70% (±)-fukinone (1), 20% of the decalone 9, and 10% of an unidentified component. An analytical sample of (±)-fukinone (1) was obtained by preparative glc (column D, 230°, 180) and exhibited uv max 251 m μ (ϵ 6640); ir (film) 5.95, 6.17 μ ; nmr τ 8.08 (s, 3, vinyl CH₃), 8.24 (s, 3, vinyl CH₃), 9.04 (s, 3, tertiary CH₃), 9.16 (d, 3, J = 6.5 Hz, secondary CH₃). These spectral data are in complete agreement with the spectra data reported² for the natural product (+)-fukinone.

Anal. Calcd for C₁₅H₂₄O: mol wt, 220.183. Found (high resolution mass spectrometry): mol wt, 220.181.

Registry No.—(±)-1, 25828-19-7; (±)-3, 25828-20-0; (±)-4, 25828-21-1; (±)-5, 25828-22-2; (±)-6, 25828-23-3; (±)-7, 25828-24-4; (±)-8, 25828-25-5; (±)-9, 25828-26-6; (±)-10, 25828-27-7.

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Catalytic Decomposition of α -Haloalkyl Esters

LEONARD O. MOORE

Research and Development Department,
Chemicals and Plastics, Union Carbide Corporation,
South Charleston, West Virginia 25303

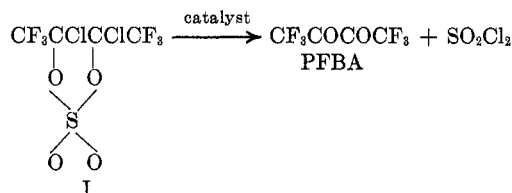
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The preparation of perfluorobiacetyl (PFBA) results in the formation of 2,3-dichloro-1,1,1,4,4,4-hexafluorobutane-2,3-diol cyclic sulfate (I) as a coproduct.¹ This material is of little interest of itself; so conversion to PFBA was of interest. This would double the overall yield of PFBA from 2,3-dichloro-1,1,1,4,4,4-hexafluoro-2-butene.

The compound I was not soluble enough in water for hydrolysis to occur at any reasonable rate, but use of a

cosolvent, dimethylformamide or dimethyl sulfoxide, resulted in complete hydrolysis. The product was PFBA hydrate. PFBA could then be obtained by dehydration with either fuming sulfuric acid or phosphorous pentoxide. This procedure involves two steps and the best yield obtained was 75%.

It has now been found that I will decompose in the presence of various catalysts to PFBA and sulfur

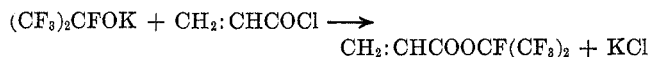


chloride in high yield. Compounds which catalyze this reaction are nitrogen or phosphorous derivatives with an unshared pair of electrons which can complex the sulfate. The results of a series of screening runs are given in Table I. In addition, water, alcohols, ethers, esters, and ketones have been in contact with I with no evidence of catalytic decomposition. Dimethylformamide, DMF, was also shown to be an effective catalyst. The use of more than a catalytic amount of DMF allowed the PFBA formed to distill from the solvent free from chlorine and sulfur dioxide.

All of the effective catalysts have an unshared pair of electrons, being nitrogen or phosphorous derivatives. Related compounds which do not have a pair of electrons available for complexation, ammonium chloride and heptafluorobutyramide, do not act as catalysts, and aromatic amines are poor catalysts.

Compounds with active hydrogens, in particular N-H, undergo side reactions apparently forming amine salts which are inactive. Ammonium hydroxide, *tert*-butylamine, and ethanalamine exemplify this behavior.

A reaction of this type has also been observed in the preparation of perfluoroisopropyl acrylate. The preparation of this acrylate has been reported previously with the comment that dimethylformamide would be



the best solvent.² This recommendation was based on gas chromatographic analysis of the crude reaction mixture. Attempts at this laboratory to use dimethylformamide as the solvent resulted in poor yields. The difficulty was traced to decomposition during distillation with small amounts of DMF in the still kettle. Acrylyl fluoride and hexafluoroacetone were formed.

This reaction, which may be quite general, provides a means of recovering PFBA from I, but solvents such as DMF and *N*-methylpyrrolidone should be avoided in the preparation and use of α -haloalkyl esters.

Experimental Section

Hydrolysis of I in a Water-Organic Mixture.—To 33 g of I was added 20 g of water and 8 g of dimethyl sulfoxide (DMSO). The mixture was heated at 70° for 1.5 hr until the second phase disappeared. Extraction with ether left, after evaporation of the solvent, 26 g of PFBA hydrate and DMSO. No effort was

(1) L. O. Moore and J. W. Clark, *J. Org. Chem.*, **30**, 2472 (1965).

(2) A. G. Pittman, D. L. Sharp, and R. E. Lundin, *J. Polym. Sci., Part A-1*, **4**, 2637 (1966).

TABLE I
 CATALYTIC DECOMPOSITION OF I

No.	Compd	Temperature of initial reaction, °C	Time to completion, hr	Yield of PFBA, %	Comments
1	(C ₆ H ₅) ₃ P	25	1.0	~90	Smooth reaction
2	NH ₄ OH	25		0	Solids formed
3	(CH ₃) ₃ CNH ₂	25		0	Solids formed
4	(C ₄ H ₉) ₃ N	40	1.25	~90	Smooth reaction
5	(CH ₂) ₄ CONCH ₃	40	Not determined	~80	Smooth reaction
6	(C ₆ H ₅ O) ₃ P	40	Not determined	~90	Smooth reaction
7	C ₆ H ₅ N	42	2.0	~90	Smooth reaction
8	HOCH ₂ CH ₂ NH ₂	50		0	Brown tarry material formed
9	<i>p</i> -HOC ₆ H ₄ NH ₂	150	Slow reaction	~30	Some solids forming
10	(CH ₃) ₂ SO	150	No reaction	0	
11	C ₆ H ₇ CONH ₂	150	No reaction	0	
12	NH ₄ Cl	150	No reaction	0	

made to separate these at this point. The yield of PFBA hydrate was 78% as determined by formation of 2,3-bis(trifluoromethyl)quinoxaline, mp 118°, from a weighed portion and excess *o*-phenylenediamine.¹

The reaction was repeated with 8 g of dimethylformamide (DMF) in place of the DMSO and it was noted that some yellow color developed when the DMF came in contact with I even at 25°, but with water present the color disappeared rapidly. The second phase had disappeared in only 0.25 hr and extraction, followed by stripping of the ether, gave 25 g of PFBA hydrate and DMF. The yield of PFBA hydrate was 73%, determined as above.

Dehydration of PFBA Hydrate.—The two portions above were combined and 9 g of the mixture was heated with 40 g of 20% fuming sulfuric acid to 70° for 2.5 hr. Yellow vapors evolved and were trapped in a Dry Ice cooled trap. The melting point, -20°, and boiling point, 20°, indicated that this was nearly pure PFBA. The overall yield was about 75% based on I.

The dehydration was repeated but using 10 g of P₂O₅ in place of the fuming sulfuric acid. Evolution of yellow vapors had stopped after 1.25 hr and the yield was 2 g (39%).

Reaction of I with Excess Dimethylformamide.—A mixture of 43 g of I and 19.7 g of DMF was heated in a 150-cc flask from 30 to 145° over 1.25 hr. There was an immediate reaction and the product, 27 g, which collected in Dry Ice cooled traps, was found to be nearly pure PFBA. The yield was quantitative.

The mixture in the kettle was not identified, but there was no evidence for either SO₂ or Cl₂ evolution. The residue dissolved in water and gave strong sulfate and chloride tests.

Catalytic Preparation of PFBA from I.—DMF (1 g) and 33 g of I were stirred together in a 200-cc flask. Evolution of a yellow vapor was immediately evident and continued as the temperature was raised over 6 hr to 158°. At the end of this time the reaction kettle contained two layers of 1 g each. One was a water soluble material, apparently unreacted DMF, and the other was I.

Distillation of the material collected in a Dry Ice cooled trap gave 5 g of Cl₂, 3 g of SO₂, and 18 g of PFBA. The distillation residue, 4 g, contained 43% of sulfuryl chloride and the remainder was starting material.

Catalyst Screening.—Several compounds were examined as possible catalysts by adding 0.1 g of each to 5 g of I and then heating the mixture to 70° till the reaction was complete. The results are summarized in Table I, no. 1, 4, and 7.

Similarly, several other compounds were evaluated on a smaller scale by mixing 0.01–0.05 g of the test compound with 0.5 g of I and then, when necessary, heating either till a smooth reaction proceeded or to a maximum of 150°. The results of these experiments are summarized in Table I, no. 2, 3, 5, 6, and 8–11. In each case the volatile PFBA was collected in a Dry Ice cooled trap and identified by comparison to known material.¹

Heptafluoroisopropyl Acrylate. Preparation in Diglyme.—To 300 ml of diethylene glycol dimethyl ether, diglyme, in a 500-cc flask was added 19.2 g of anhydrous KF; the mixture was cooled to -20° with vigorous stirring. Hexafluoroacetone, 54 g, was then added and the suspended salt dissolved. This mixture was

allowed to warm to 20–23° and 29 g of acrylyl chloride was added slowly to maintain the temperature. A precipitate formed as the acrylyl chloride was added which was shown to be KCl. The mixture was then stripped to a kettle temperature of 50° (20 mm) to give 56 g of colorless liquid. Distillation separated 40 g of crude product and fractionation gave 25 g (33%) of heptafluoroisopropyl acrylate, bp 85°, *n*_D²⁰ 1.3128.² In an earlier run, some difficulty had been encountered from polymerization so that the distillation was carried out using a slow purge of air to the kettle and hydroquinone was added to the kettle and the receiver. With these precautions no polymerization was observed.

Heptafluoroisopropyl Acrylate. Preparation in Dimethylformamide.—The above procedure was followed but with the use of DMF in place of the diglyme. The reaction appeared to proceed identically in all respects until the distillation. When the material which had been stripped off was heated to distill the final product, a low boiling material was stripped out which was identified as hexafluoroacetone and then acrylyl fluoride was distilled, bp 32.5°, *n*_D²⁰ 1.3465. The acrylyl fluoride structure was confirmed by its mass spectrum and the formation of an anilide derivative, mp 103–104°.³

This reaction was repeated using half the quantities used above but a water wash was used to remove DMF from the crude product. Distillation gave 7 g (18%) of heptafluoroisopropyl acrylate.

Registry No.—I, 722-89-4.

(3) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed, Wiley, New York, N. Y., 1948, p 222.

Improved Procedure for Oxidations with the Chromium Trioxide-Pyridine Complex

RONALD RATCLIFFE¹ AND RONALD RODEHORST

Department of Chemistry, University of California, Berkeley, California 94720

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In 1948, Sisler, Bush, and Accountius reported the isolation of a brick-red complex, with the empirical composition CrO₃·2C₅H₅N, from the reaction of anhydrous chromium trioxide with pyridine.² Poos,

(1) National Institutes of Health Predoctoral Fellow, 1967–1970. Author to whom correspondence should be addressed: Merck Sharp & Dohme Research Laboratories, Rahway, N. J. 07065.

(2) H. H. Sisler, J. D. Bush, and O. E. Accountius, *J. Amer. Chem. Soc.*, **70**, 3827 (1948).