

ORGANIC AND BIOLOGICAL CHEMISTRY

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The Chemistry of Carbonyl Fluoride. I. The Fluorination of Organic Compounds

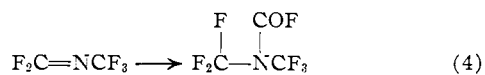
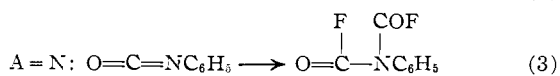
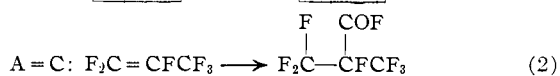
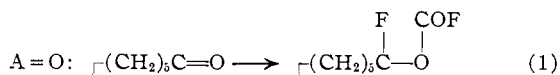
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Carbonyl fluoride is a versatile intermediate to organic fluorine compounds. Its reaction with carbonyl compounds such as cyclohexanone, benzaldehyde and benzophenone gives the *gem*-difluorides, while *N,N*-dimethylformamide yields α,α -difluorotrimethylamine. Metal fluoride-catalyzed addition at the ethylenic bond in perfluoroolefins forms perfluoroacyl fluorides, while the C—N unsaturated compounds $\text{CF}_3\text{N}=\text{CF}_2$, $\text{C}_6\text{H}_5\text{N}=\text{CO}$ and $\text{CF}_3\text{C}\equiv\text{N}$ give, respectively, $(\text{CF}_3)_2\text{NCOF}$, $\text{C}_6\text{H}_5\text{N}(\text{COF})_2$ and $\text{CF}_3\text{CF}_2\text{NCO}$.

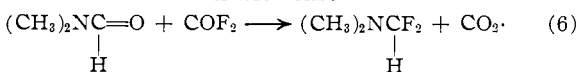
The principal reactions reported for carbonyl fluoride are those in which it behaves as an acyl fluoride,¹ and those in which its oxygen is replaced by halogen.²⁻⁴

Our explorations now being reported have led to a convenient laboratory synthesis of carbonyl fluoride and have demonstrated the utility of this fluoride in the preparation of fluoroorganic compounds. Carbonyl fluoride is easily synthesized in good conversions by introduction of liquefied phosgene into a suspension of sodium fluoride in acetonitrile at 35°. Reactions of carbonyl fluoride leading to organic fluorides follow the general pattern of addition of the F- and -COF units across an unsaturated system $-\text{C}=\text{A}$, where A is O, C or N as in eqs. 1 to 5 inclusive. Reaction with a



carbonyl compound proceeds further in certain instances with the elimination of carbon dioxide to convert a $-\text{C}=\text{O}$ group to a $-\text{CF}_2$ group.⁵

N,N-Dimethylformamide, for example, undergoes this transformation with ease



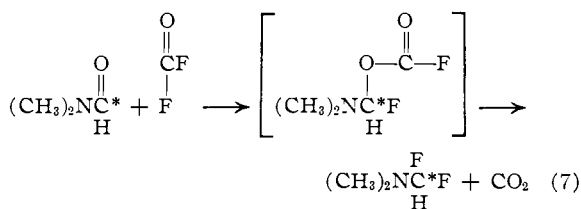
Reactions with Carbonyl Compounds.—As indicated in eqs. 1 and 6, carbonyl fluoride and a car-

(1) H. J. Emeleus and J. F. Wood, *J. Chem. Soc.*, 2183 (1948).(2) O. Ruff and S.-C. Li, *Z. anorg. u. allgem. Chem.*, **242**, 272 (1939).

(3) Donald D. Coffman and C. W. Tullock, U. S. Patent 2,757,213, July 31, 1956.

(4) R. N. Haszeldine and H. Iserson, *J. Am. Chem. Soc.*, **79**, 5801 (1957).(4a) Cf. also R. S. Porter and G. H. Cady, *ibid.*, **79**, 5625, 5628 (1957).(5) Similar transformations of a carbonyl compound have been effected by reactions with phosgene; see, for example, H. Staudinger, *Ber.*, **42**, 3976 (1909); H. Eilingsfeld, M. Seefelder and H. Weidinger, *Angew. Chem.*, **72**, 836 (1960).

bonyl compound may yield a fluoroalkyl fluoroformate or may give the *gem*-difluoride and carbon dioxide. With *N,N*-dimethylformamide at 25° the fluoroformate was not isolated. However, the novel α,α -difluorotrimethylamine, a reactive distillable liquid,⁶ was obtained in 82% conversion. *N,N*-Dimethylformamide containing a C¹⁴-tagged carbonyl group gave difluorotrimethylamine that retained essentially all the C¹⁴-carbon, and the carbon atom of the carbonyl fluoride appeared as carbon dioxide.



Cyclohexanone, however, in the presence of a catalytic amount of *N,N*-dimethylformamide or of pyridine, yielded the distillable adduct 1-fluorocyclohexyl fluoroformate in 64% conversion. This fluoroformate ester underwent cleavage of carbon dioxide on treatment with boron trifluoride etherate to form 1,1-difluorocyclohexane in 54% conversion. Other examples of carbonyl fluoride additions to carbonyl compounds are the conversion of hexafluorocyclobutanone to heptafluorocyclobutyl fluoroformate, of biacetyl to 1,2-difluoro-1,2-dimethylethylene carbonate, and of 2,3-pentanedione to 1,2-difluoro-1-ethyl-2-methylethylene carbonate which was isolated in the *cis* and *trans* forms.

Reactions of carbonyl fluoride with the carbonyl compounds listed in Table I gave *gem*-difluorides under the conditions used. Benzaldehyde at 25° gave 58% conversion to benzylidene difluoride, while with pyridine or *N,N*-dimethylformamide as catalysts comparable conversions were obtained at 150°. Similar catalysis was observed with pyridine and with cesium fluoride in the conversion of benzophenone to difluorodiphenylmethane. In contrast, benzoyl fluoride gave α,α,α -trifluorotoluene in very low conversions.

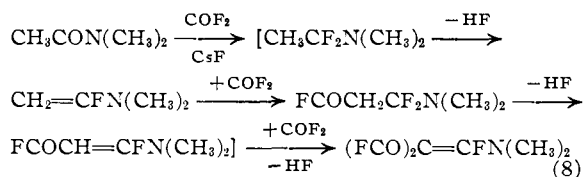
(6) In contrast, the analogous chlorine compound, $\left[\begin{array}{c} \text{H} \\ | \\ \text{(CH}_3\text{)}_2\text{NCCl} \end{array} \right]^+ \text{Cl}^-$, is a hygroscopic nonvolatile solid; Z. Arnold, *Chem. Listy*, **52**, 2013 (1958).

TABLE I
REPLACEMENT OF CARBONYL OXYGEN BY FLUORINE USING
CARBONYL FLUORIDE

Carbonyl compound (>CO)	Temp., °C.	Derived difluoride (>CF ₂)	Conver- sion, %
C ₆ H ₅ COC ₆ H ₅	250	C ₆ H ₅ CF ₂ C ₆ H ₅	62
C ₆ H ₅ CHO	150	C ₆ H ₅ CHF ₂	80
HCON(CH ₃) ₂	25	HCF ₂ N(CH ₃) ₂	82
C ₆ H ₅ CON(CH ₃) ₂	50	C ₆ H ₅ CF ₂ N(CH ₃) ₂	39
(CH ₃) ₂ NCON(CH ₃) ₂	150	(CH ₃) ₂ NCF ₂ N(CH ₃) ₂	10
HCONHCH ₃	75	HCF ₂ N(CH ₃)COF	6
		HCON(CH ₃)COF	34
CH ₃ CONHCH ₃	125	CH ₃ CF ₂ N(CH ₃)COF	20
		CH ₃ CON(CH ₃)COF	42
(CH ₂) ₃ CONH	50	[(CH ₂) ₃ CON] ₂ CO	15
		(CH ₂) ₃ CONCOF	47
(CH ₂) ₃ CONH	125	(CH ₂) ₃ CONCOF	23
		(CH ₂) ₃ CF ₂ NCOF	17

In comparing carbonyl fluoride and sulfur tetrafluoride⁷ for their efficacy in oxygen replacement, carbonyl fluoride is more effective with amides, is considerably less reactive with acids to form the CF₃ group, is susceptible to catalysis by bases, and gives isolable intermediates in specific instances. On the other hand, sulfur tetrafluoride is more reactive in forming CF₃ compounds from acids, and its reactions are catalyzed by acids. In the use of carbonyl fluoride for replacement of carbonyl oxygen, the fluorine-free carbon dioxide coproduct is formed while sulfur tetrafluoride in similar reactions forms thionyl fluoride as coproduct.

Reactions with N,N-Disubstituted Amides.—N,N-Disubstituted amides devoid of hydrogen alpha to the carbonyl group react with carbonyl fluoride to form α,α-difluoroamines as shown in Table I. When α-hydrogens are present, however, more complex reactions may occur. Thus, equimolar amounts of N,N-dimethylacetamide and carbonyl fluoride at 25° in the presence of cesium fluoride formed 1-(dimethylamino)-1-fluoro-2,2-bis-(fluoroformyl)-ethylene in 19% conversion based on the amide. This ethylene is formed presumably by replacement of carbonyl oxygen by fluorine and successive eliminations of hydrogen fluoride and additions of carbonyl fluoride (eq. 8). For identi-



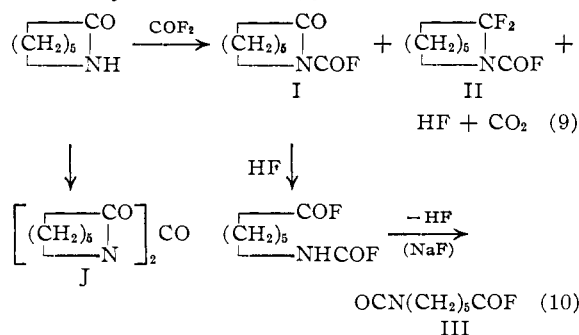
fication the substituted ethylene was hydrolyzed to N,N-dimethylmalonic acid. 1-Methyl-2-pyrrolidone in the presence of cesium fluoride similarly gave the analogous 2-fluoro-3-fluoroformyl-1-methyl-4,5-dihydropyrrole in very low conversion (ca. 4%) but moderate yield.

Hydrogen fluoride in combination with carbonyl fluoride led to cleavage reactions; N,N-dimethylacetamide at 100–175° yielded N,N-dimethyl-

carbamoyl fluoride (17% conv.) along with considerable acetyl fluoride.

Reactions with N-Monosubstituted Amides.—Amides having only one N-substituent react with carbonyl fluoride in three principal ways: by N-acylation, by replacement of oxygen with fluorine, and by cleavage. Acylation of the nitrogen appears to be the initial reaction. Table I lists examples of N-acylation and oxygen replacement. These reactions and also cleavage are illustrated by the transformations of caprolactam.

Caprolactam and carbonyl fluoride in equimolar amounts at 75° yielded N-fluoroformylcaprolactam (I) in 30% conversion and the ureide carbonyl N,N-di-(caprolactam) (J) in 25% conversion, but very little N-fluoroformyl α,α-difluoro-hexamethylenimine (II). With a larger proportion of carbonyl fluoride at 75–125° (and sodium fluoride treatment during work-up), however, ω-fluoroformylpentyl isocyanate (III), an isomer of I, was isolated in 34% conversion, and II was obtained in 19% conversion. In the presence of cesium fluoride, an acceptor for hydrogen fluoride, some I (19%) was obtained, but the principal product was the gem-difluoride II (37%). Separate experiments showed that I in the presence of hydrogen fluoride at 75–125° gave a product which, after treatment with sodium fluoride to remove hydrogen fluoride, yielded III in 40% conversion.



Reactions with Fluoroolefins.—As indicated in eq. 2 carbonyl fluoride has been found to add to perfluoroolefins to give the perfluoroacyl fluorides listed in Table II. The addition is accomplished

TABLE II
PERFLUOROACYL FLUORIDES DERIVED FROM COF₂ AND
PERFLUOROÖLEFINS

Fluoroolefin	Fluoroacyl fluoride	Conver- sion, %
CF ₃ CF=CF ₂	(CF ₃) ₂ CFCOF	80
CF ₃ CF=CFCF ₃	CF ₃ CF ₂ CF(CF ₃)COF	62
CH ₃ OCF=CF ₂	CH ₃ OCF ₂ CF ₂ COF	62
CF ₂ CF	CF ₃ CF ₂	
CF ₂ CF	CF ₃ CFCOF	54
CF ₂ =CF ₂	CF ₃ CF ₂ COF	13

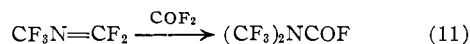
readily in a polar non-protonic medium such as acetonitrile using excess carbonyl fluoride at 100–150°. High proportions of hexafluoropropene under similar conditions lead to the formation of bis-(perfluoroisopropyl) ketone.⁸ Cesium fluoride,

(7) W. R. Hasek, W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

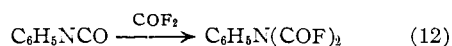
(8) R. D. Smith, F. S. Fawcett and D. D. Coffman, *ibid.*, **84**, 4285 (1962).

potassium fluoride or bifluoride, or tetraethylammonium fluoride, which have low lattice energies, are catalysts. The acyl fluorides undergo the usual transformations of an acyl halide such as hydrolysis and amidation.

Reactions with Compounds with C-N Multiple Bonds.—Carbonyl fluoride has been found capable of adding to bonds containing carbon doubly and triply linked to nitrogen (eqs. 3, 4 and 5) to form carbamoyl fluoride derivatives or isocyanates. Thus, pentafluoro-2-azapropene with carbonyl fluoride and cesium fluoride catalyst in acetonitrile at 150° gave, in 56% conversion, N,N-bis-(trifluoromethyl)-carbamoyl fluoride (eq. 11). Also,



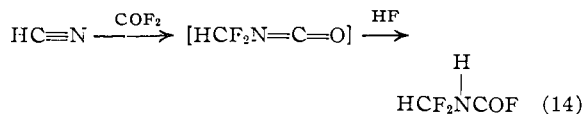
carbonyl fluoride and phenyl isocyanate gave N,N-bis-(fluoroformyl)-aniline.



The fluoride ion-catalyzed addition of carbonyl fluoride to the carbon-nitrogen triple bond proceeded less readily. Thus, trifluoroacetonitrile at 200–300° gave pentafluoroethyl isocyanate in only low conversions, presumably *via* the transitory

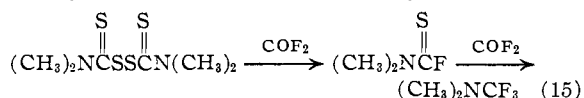


$\text{CF}_3\text{CF}=\text{NCOF}$. Hydrogen cyanide with carbonyl fluoride and hydrogen fluoride at ordinary temperatures gave difluoromethylcarbamoyl fluoride in high conversions (eq. 14), possibly by addition of



hydrogen fluoride to the intermediate isocyanate which was not isolated. The carbamoyl fluoride appeared to undergo dehydrofluorination when stored over sodium fluoride, forming a water-reactive solid product.

Other Transformations.—Carbonyl fluoride has also been found to cleave disulfide links and to replace thiono sulfur by fluorine. Thus, tetramethylthiuram disulfide gave both N,N-dimethylthiocarbamoyl fluoride and α,α,α -trifluorotrimethylamine. In a separate synthesis, α,α,α -



trifluorotrimethylamine was obtained in 55% conversion from N,N-dimethylthiocarbamoyl fluoride and carbonyl fluoride under conditions found to bring about cleavage of the thiuram disulfide. This facile conversion of a thiocarbonyl fluoride group to a trifluoromethyl group is in striking contrast to the difficult conversion of the fluoroformyl group to the trifluoromethyl group by use of carbonyl fluoride. For example, the N,N-bis-(trifluoromethyl)-carbamoyl fluoride was formed in reactions of carbonyl fluoride with perfluoro-2-azapropene but perfluorotrimethylamine, the further fluorination product, was not observed. Also, very vigorous conditions were necessary to prepare α,α,α -trifluorotoluene from benzoyl fluoride or

from benzoic acid, and the major product from phenyl isocyanate was N,N-bis-(fluoroformyl)-aniline formed at elevated temperature; N,N-bis-(trifluoromethyl)-aniline was not observed.

Tetramethylthiourea gave difluorobis-(dimethylamino)-methane in 80% conversion.

Mechanisms.—These reactions suggest certain possibilities for the addition of carbonyl fluoride

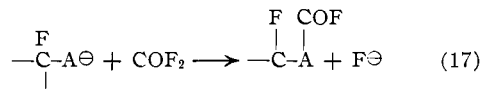
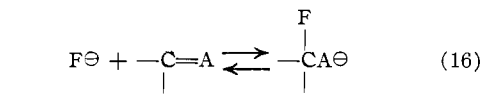
to $-\text{C}=\text{A}$ systems. In general, the reactions appear to occur *via* (I) reversible formation of a nucleophilic anion $\text{C}-\text{A}^\ominus$, either (a) by addition of a fluoride ion at the adjacent carbon atom

($\text{F}-\text{C}-\text{A}^\ominus$), (b) by similar coordination of a basic

catalyst B at that site ($\text{B}^\oplus-\text{C}-\text{A}^\ominus$), or (c) by in-

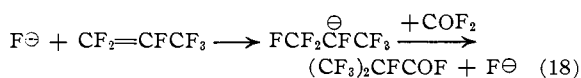
herent polarization of the unsaturated reactant [$(\text{CH}_3)_2\ddot{\text{N}}-\text{C}=\text{O}$], and (II) reaction of this anion

$-\text{A}^\ominus$ with carbonyl fluoride at the highly electrophilic carbon atom to displace fluoride ion. The



adduct with a carbonyl compound may undergo loss of carbon dioxide.

In the addition of carbonyl fluoride to fluoroolefins, it is presumed that a fluoride ion adds to the fluoroolefin⁹ to form an intermediate fluorocarbanion which reacts with carbonyl fluoride.



Brehm and co-workers¹⁰ and also Wiley¹¹ have described reactions which evidently involve the addition of a fluorocarbanion to a fluoroolefin or to a carbonyl compound. Pentafluoro-2-azapropene, an analog of hexafluoropropene, presumably reacts similarly *via* the $(\text{CF}_3)_2\text{N}^\ominus$ anion.

The especially high reactivity of N,N-dimethylformamide and similar amides, on the other hand, seems to be due to the inherently highly polarized character of the carbonyl group¹²: $(\text{CH}_3)_2\ddot{\text{N}}-\text{C}=\text{O}$.

The C¹⁴ tracer experiment shows clearly that the carbon atom of the carbon dioxide is derived from carbonyl fluoride. The decarbonation step also would be expected to be aided by the adjacent $(\text{CH}_3)_2\ddot{\text{N}}-$ group of the amides, accounting for the facile conversion directly to the *gem*-difluoride.

(9) W. T. Miller, Jr., J. H. Fried and H. Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).

(10) W. J. Brehm, K. G. Bremer, H. S. Eleuterio and R. W. Meschke, U. S. Patent 2,918,501 (1959).

(11) D. W. Wiley, U. S. Patent 2,988,537 (1961).

(12) H. K. Hall, Jr., *J. Am. Chem. Soc.*, **78**, 2717 (1956). G. Fraenkel and C. Niemann, *Proc. Natl. Acad. Sci.*, **44**, 688 (1958).

Introduction of the second acyl group to form RN(COF)COR lowers the basicity of the nitrogen and the reactivity of the carbonyl groups.

With carbonyl compounds such as cyclohexanone, benzaldehyde or benzophenone, the anionic inter-

mediate $B-C-O^{\ominus}$ may originate through catalysis by fluoride ion (*e.g.*, from COF_2 -pyridine complex) or by other basic catalysts. The elimination of carbon dioxide from alkyl fluoroformates has been reported to be facilitated by pyridine.¹³ The presence of the electronegative fluorine in benzoyl fluoride evidently deactivates the carbonyl group for reaction with carbonyl fluoride.

Acknowledgment.—We are indebted to Dr. W. D. Phillips and Mr. C. B. Matthews for the measurement and interpretation of the n.m.r. spectra; to Miss Naomi Schlichter for the measurement and interpretation of the infrared spectra; and to Mr. W. M. Kipp for the mass spectral data. Many discussions with Dr. D. W. Wiley have been helpful.

Experimental

Caution! Carbonyl fluoride and many products derived from it are toxic. Suitable safety precautions must be observed in working with these materials.

The reactions with carbonyl fluoride were carried out under autogenous pressure in pressure vessels of Hastelloy construction, arranged for either shaking or rocking, except where otherwise stated. The pressure equipment was provided with safety relief disks and was barricaded. Liquid or solid reactants were placed in the vessel in an atmosphere of nitrogen, the head was assembled, the vessel was cooled to solid carbon dioxide temperature, evacuated, and gaseous reactants (COF_2 , etc.) were condensed into it. After being heated for the specified period under autogenous pressure, the reactor was allowed to cool. In cases where the gaseous products were of interest, these were condensed into a previously evacuated stainless steel cylinder at liquid nitrogen temperature; otherwise, excess COF_2 and volatile by-products were vented. Liquid or solid products recovered from the vessel were purified by the usual procedures of distillation, recrystallization and sublimation generally in glass equipment.

Infrared spectra were determined with a Perkin-Elmer model 21 double-beam spectrometer. Nuclear magnetic resonance (n.m.r.) spectra were measured with a Varian high resolution nuclear magnetic resonance spectrometer and associated electromagnet. The measurements for fluorine were made at either 40 or 56.4 Mc. using as a reference standard either trifluoroacetic acid contained in a capillary in the sample tube or 1,2-difluorotetrachloroethane added directly to the liquid sample. The spectra were calibrated by measuring the displacement in cycles per second (c.p.s.) from the reference compound as indicated, and for uniformity were converted to the common basis of parts per million (p.p.m.) of field strength with reference to CF_3COOH . The proton magnetic resonance spectra were similarly measured at 56.4 or 60 Mc. using as a reference either water in a capillary or tetramethylsilane directly in the liquid sample. The results were converted to p.p.m. values with reference to tetramethylsilane. Negative p.p.m. values refer to the low field side of the reference compound and positive values to the high field side. Conversion factors used were 1,2-difluorotetrachloroethane = 444 c.p.s. to low field side of trifluoroacetic acid at 40 Mc., and water = 298 c.p.s. to low field side of tetramethylsilane at 56.4 Mc.

A. Preparation of Carbonyl Fluoride.—A 2-l., 4-necked glass flask was provided with a thermometer, a 500-ml. dropping funnel equipped with a pressure-equalizing side tube, a Tru-bore stirrer with a paddle of Teflon polytetrafluoroethylene, a heater, and two reflux condensers mounted

vertically one above the other. The lower condenser, which was cooled with cold water (or with coolant at -30 to -35°), had an aperture vertically aligned so that refluxing liquid from the upper condenser fell directly through to the reactor. The upper condenser was an efficient coolant-in-coil type with circulating coolant at -70 to -78° (a cold finger-type condenser filled with solid carbon dioxide-acetone mixture can be used). The top of the upper condenser was connected by means of Tygon tubing to one or more efficient traps cooled in solid carbon dioxide-acetone slush and then to a large receiver cooled in liquid nitrogen. The exit from the system was protected by an atmosphere of helium maintained by means of a bubbler tube. The apparatus, thoroughly dried before use, was protected from the ingress of moisture.

In the flask were placed 380 g. (9.0 moles) of finely divided sodium fluoride and 1 l. of acetonitrile, and the mixture was stirred and heated to $30-35^{\circ}$. In the funnel were placed 300 ml. of acetonitrile and 350 g. (3.5 moles) of phosgene (conveniently condensed as liquid in a solid carbon dioxide-cooled trap and thence poured into the acetonitrile in the funnel). The phosgene solution was added dropwise to the stirred slurry at $30-40^{\circ}$. Refluxing occurred at the upper condenser (also at the lower one if coolant at *ca.* -30° was used) during the addition which required 1-2 hr. When the addition of phosgene had been completed, the reaction mixture was stirred at $30-45^{\circ}$ for an additional 15-30 min. The carbonyl fluoride (*ca.* 165-190 g., 70-80% conversion) was collected as a solid in the liquid nitrogen-cooled receiver. It was transferred under reduced pressure to a stainless steel cylinder for storage (for room temperature storage, never more than 200 g. of COF_2 was condensed in a 500-ml. cylinder, and the cylinder was equipped with a rupture assembly for 1400-1600 p.s.i.). The spent reaction mixture was decomposed cautiously by treatment with aqueous ammonium hydroxide until basic and was discarded after dilution with a large volume of water.

The COF_2 prepared in this way was of *ca.* 95 mole % purity as determined by infrared¹⁴ or mass spectrometry. Carbon dioxide was the major impurity, *ca.* 4 to 5%, with traces of phosgene and carbonyl chlorofluoride; COF_2 has b.p. -83° and f.p. -114° .¹⁵ It is thus not conveniently condensed as a liquid at atmospheric pressure. Other laboratory syntheses of COF_2 include the reaction of carbon monoxide with silver(II) fluoride^{16,16} and treatment of phosgene with antimony(III) fluoride plus chlorine.⁴

B. Reactions of COF_2 with Ketones, Aldehydes and Acids. 1-Fluorocyclohexyl Fluoroformate.—Cyclohexanone (40 g.), 4.0 ml. of *N,N*-dimethylformamide (DMF) and 65 g. of COF_2 were heated in a 240-ml. pressure vessel at 50° for 12 hr. to give 70 g. of liquid product. Two distillations yielded 52 g. (78% conversion) of 1-fluorocyclohexyl fluoroformate, b.p. $63-64^{\circ}$ (27 mm.). Pyridine as catalyst gave similar results. An analytical sample fractionated with a spinning band column had b.p. 62° (27 mm.), n_D^{25} 1.3393; infrared spectrum: strong 5.40 (CO of COF), 3.39 and 3.48 μ (satd. CH).

Anal. Calcd. for $C_7H_{10}F_2O_2$: C, 51.20; H, 6.14; F, 23.15. Found: C, 51.74; H, 6.11; F, 22.81.

The fluorine n.m.r. showed two peaks of comparable area, one singlet at -68.7 p.p.m. (COF) and one fivefold centered at $+32.5$ p.p.m. (CF). The proton n.m.r. showed a doublet attributed to the four hydrogens on C_2 and C_6 and a larger singlet attributed to the remaining six hydrogens.

The fluoroformate (10 g.) with 20 g. of *p*-chloroaniline in ether gave 16 g. of crude solid *p*-chloroanilide. Recrystallization from ethylene chloride-pentane yielded 11.5 g., m.p. $101-102^{\circ}$, and further recrystallization raised the m.p. to $105-105.5^{\circ}$. The n.m.r. in acetonitrile solution showed a fivefold resonance (CF) like the original fluoroformate.

Anal. Calcd. for $C_{13}H_{16}ClNO_2F$: F, 7.0; Cl, 13.1. Found: F, 6.85; Cl, 12.95.

(14) A. H. Nielsen, T. G. Burke, P. J. H. Woltz and E. A. Jones, *J. Chem. Soc.*, 596 (1952).

(15) O. Ruff and G. Miltschitzky, *Z. anorg. u. allgem. Chem.*, **221**, 154 (1934).

(16) M. W. Farlow, E. H. Man and C. W. Tullock, in E. G. Rochow, Editor-in-Chief, "Inorganic Syntheses," Vol. VI, McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 155.

(13) S. Nakanishi, T. C. Myers and E. V. Jensen, *J. Am. Chem. Soc.*, **77**, 3099, 5033 (1955).

1,1-Difluorocyclohexane.—A solution of 17 g. of 1-fluorocyclohexyl fluorofornate in 50 ml. of hexane was treated with 4.8 g. of boron trifluoride etherate.¹³ The liquid mixture, which contained a small lower layer (etherate), was stirred under reflux while connected to a gas bubbler tube to indicate the evolution of gas. On heating at 45°, gas evolution began and continued with gentle reflux as the mixture was heated in the range 45–70° over a period of 3 hr. The mixture was cooled, and the upper layer was separated and treated with sodium fluoride. Filtration and distillation gave 6.5 g. (54% conversion) of 1,1-difluorocyclohexane, b.p. 101–107°, n_D^{20} 1.3900–1.3895.¹⁷ The infrared and fluorine n.m.r. spectra agreed with those of a sample of 1,1-difluorocyclohexane prepared from cyclohexanone and sulfur tetrafluoride.⁷

Anal. Calcd. for $C_6H_{10}F_2$: F, 31.62. Found: F, 31.41.

Heptafluorocyclobutyl Fluoroformate.—Hexafluorocyclobutanone (14 g.), cesium fluoride (1.5 g.) and 25 g. of COF_2 were heated in a 240-ml. pressure vessel at 150° for 3 hr. and 175° for 12 hr. Distillation gave 12.4 g. (64% conversion) of the perfluoro ester, b.p. 46.5–47°; infrared spectrum 5.31 (CO of COF), 8.15, 8.52, 9.92, 10.28 and 10.91 μ . The fluorine n.m.r. spectrum consisted of four peaks, all measured relative to 1,2-difluorotetrachloroethane as reference: one of unit area at –60.2 p.p.m. (COF), one of unit area at +64.1 p.p.m. (CF), one of two units area at +54.7 p.p.m. (CF_2) and one of four units area at +53.4 (two equivalent CF_2 groups). This spectrum is consistent with the above structure even in the absence of splitting, which is sometimes observed. Gas chromatography using 20% Silicone 703 on Columpak showed a major peak of about 95 area %. The fluorine analysis was satisfactory, although the carbon analysis was high.

Anal. Calcd. for $C_4F_8O_2$: C, 24.60; F, 62.27. Found: C, 26.35, 26.79; F, 61.56, 61.86, 62.03.

Difluorodiphenylmethane.—Benzophenone (27 g.), 2.0 ml. of pyridine and 38 g. of COF_2 were heated in a 240-ml. pressure reactor at 150° for 2 hr., 200° for 2 hr. and 250° for 10 hr. The recovered black liquid in pentane solution was treated with sodium fluoride to remove hydrogen fluoride and was filtered and distilled to obtain 19.1 g. (62% conversion) of difluorodiphenylmethane, b.p. 100–101° (2.5 mm.), n_D^{20} 1.5360–1.5368. The fluorine n.m.r. spectrum showed a singlet peak in the CF region like that for an authentic specimen of difluorodiphenylmethane.^{7,18} After passage through a column of 28–200 mesh silica gel using ethanol eluant to remove traces of ketone, the refractive index was n_D^{20} 1.5349.

Use of 2.0 g. of cesium fluoride in place of the pyridine gave 13.5 g. (40% conversion) of difluorodiphenylmethane; with no added catalyst 0.6 g. (3% conversion) of difluorodiphenylmethane was obtained.

Reaction of COF_2 with Biacetyl; 1,2-Difluoro-1,2-dimethylethylene Carbonate.—Biacetyl (20 g.), 2.0 ml. of pyridine and 54 g. of COF_2 were heated at 50° for 2 hr., 75° for 2 hr. and 100° for 10 hr. to give 36 g. of brown liquid product. A preliminary distillation gave 27 g. which on fractionation through a spinning band column gave 17.9 g. (50% conversion) of 1,2-difluoro-1,2-dimethylethylene carbonate, b.p. 54–57° (28 mm.); infrared spectrum: 5.29 and 5.39 μ (CO in five-membered ring carbonate¹⁹), 3.32 and 3.38 μ (satd. CH) and 7.13 μ (possibly C– CH_3). The fluorine n.m.r. spectrum centered at +26.4 p.p.m. and the proton n.m.r. spectrum at –1.8 p.p.m. and both consisted of complex symmetrical patterns.

Anal. Calcd. for $C_6H_6F_2O_3$: C, 39.48; H, 3.9; F, 24.98. Found: C, 40.53, 39.71, 40.07; H, 4.24, 4.39, 4.34; F, 24.85.

From the analysis of the $A_3XX'A_3$ system reported by Anet,²⁰ values of $J_{FF} = 25.1$, $J_{HF} = 18.5$ and $J_{HF'} = 3.5$ c.p.s. were obtained by inspection of the proton spectrum.

(17) F. Cuthbertson and W. K. R. Musgrave, *J. Appl. Chem.*, **7**, 99 (1957), report b.p. 100.5°, n_D^{20} 1.3906; ref. 7, b.p. 98–99°, n_D^{20} 1.3890.

(18) A. L. Henne and H. M. Leicester, *J. Am. Chem. Soc.*, **60**, 864 (1938), report b.p. 125° (10 mm.), n_D^{20} 1.5379; ref. 7 reports b.p. 114–115° (7.5 mm.), n_D^{20} 1.5351.

(19) J. L. Hales, J. I. Jones and W. Kynaston, *J. Chem. Soc.*, 618 (1957).

(20) F. A. L. Anet, *J. Am. Chem. Soc.*, **84**, 747 (1962); A. A. Bothner-By and C. Nair-Colin, *ibid.*, **84**, 743 (1962).

These J -values were used to calculate the theoretical spectra which showed good agreement with the observed spectra in both line positions and intensities. In the methyl spectrum 12 of the calculated 14 lines were observed with the remaining two being of very low calculated intensity. All of the 28 calculated lines were accounted for in the fluorine spectrum. We are indebted to Dr. Walter Mahler of Explosives Department, E. I. du Pont de Nemours and Co., for these calculations.

Reaction of COF_2 with 2,3-Pentanedione. 1-Ethyl-2-methyl-1,2-difluoroethylene Carbonate.—A mixture of 25 g. of 2,3-pentanedione, 2.0 ml. of pyridine and 55 g. of COF_2 was heated at 50° for 2 hr., 75° for 2 hr. and 100° for 10 hr. The recovered brown liquid (41 g.) was flash distilled *in vacuo*. The distillate was filtered through sodium fluoride and redistilled through a Vigreux still head to obtain 20.2 g. of colorless distillate, b.p. 60–73° (15 mm.). Fractionation with a spinning band column yielded (A) 15 g. (37% conversion) of colorless product, b.p. 58–59° (16 mm.) and (B) 3.9 g. (9% conversion) of colorless product, b.p. 65–68° (5 mm.). These products were identified as the two isomers of 1,2-difluoro-1-ethyl-2-methylethylene carbonate. Both isomers showed strong infrared bands at 5.37–5.4 μ (CO, negatively substituted).¹⁹

The fluorine n.m.r. spectrum of A showed two resonances of equal size, one centered at +29.4 p.p.m. (split into doublet 22 c.p.s., quadruplet 16 c.p.s., triplet 2 c.p.s.) and the other at +38.0 p.p.m. (split three times into doublets, 24, 20 and 18 cps., and into quadruplets 3.5 c.p.s.). The hydrogen n.m.r. spectrum of A showed three resonances: one for CH_3 centered at –1.8 p.p.m. (split into doublet 19 c.p.s., doublet 3.7 c.p.s.), one for CH_3 of ethyl group at –1.1 p.p.m. (triplet, 7 c.p.s.), and a broad multiplet for CH_2 centered near –2.1 p.p.m. that overlapped the –1.8 p.p.m. resonance.

The fluorine n.m.r. spectrum of B showed two resonances of equal size, one centered at +35.0 p.p.m. (split into doublet 9 c.p.s., quadruplet 20 c.p.s.) and the other centered at +47.6 p.p.m. (split three times into doublets, 8.5, 21 and 17 c.p.s., with further unresolved fine splitting). The hydrogen n.m.r. spectrum of B showed three resonances: one centered at –1.8 p.p.m. (split into doublet 19.5 c.p.s., doublet 1 c.p.s.), one for CH_3 of ethyl group at –1.1 p.p.m. (triplet, 7 c.p.s.) and a broad multiplet for CH_2 centered near –2.1 p.p.m. that overlapped the –1.8 p.p.m. resonance.

From the above spectra the coupling constants summarized in Table III were obtained.

TABLE III
APPROXIMATE COUPLING CONSTANTS FOR CYCLIC

J	Ethyl-methyl		
	Isomer A ^b	Isomer B	Dimethyl ^a
F_2F_3	23	9	25
F_2H_1	18	20	18.5
$F_3H_4^c$	18	17	
	20	21	3.5
F_2H_4	2	0–1	
F_3H_3	3.6	1	
H_4H_5	7	7	
H_1H_4	0	0	

^a The CH_2 protons are non-equivalent, being adjacent to the asymmetric carbon of the ring, and evidently split F_3 individually to give two doublets; P. M. Nair and J. D. Roberts, *J. Am. Chem. Soc.*, **79**, 4565 (1957). ^b The values for J_{FF} suggest that these compounds are the *trans* forms.

Anal. Calcd. for $C_6H_8O_3F_2$: C, 43.39; H, 4.85; F, 22.88; mol. wt., 166.1. Found: (A) C, 43.54; H, 4.96; F, 23.39; mol. wt., 163, 163 (f.p., benzene). (B) C, 43.91; H, 4.84; F, 23.10; mol. wt., 167, 168 (f.p., benzene).

Benzylidene Difluoride.—Benzaldehyde (27 g.), 1.0 ml. of *N,N*-dimethylformamide (DMF) (6 mole %, on aldehyde) and 33 g. of COF_2 were heated in a 240-ml. pressure vessel at 100° for 2 hr. and 150° for 10 hr., to give 30 g. of brown liquid product. Two distillations gave 26 g. (80% conversion) of benzylidene difluoride²¹ b.p. 55–62° (50 mm.), n_D^{20} 1.4575–1.4605. The fluorine n.m.r. spectrum (doublet in CF_2 region) agreed with that of an authentic sample,⁷ as did the infrared spectrum of a portion that had been passed through a column of 28–200 mesh silica gel using ethanol eluant to remove a trace of benzaldehyde.

Anal. Calcd. for $\text{C}_7\text{H}_6\text{F}_2$: F, 29.65. Found: F, 29.72.

Under otherwise identical conditions but in the absence of DMF catalyst, the conversion to benzylidene difluoride was 18%. With pyridine catalyst the conversion was 58%. In an experiment at 180° for 2 hr. and 250° for 5 hr. without added catalyst, benzylidene difluoride was isolated in 58% conversion. By infrared analysis of the recovered gaseous product from this experiment, carbon dioxide was identified as a co-product formed in greater than 60% conversion based on aldehyde charged.

α,α,α -Trifluorotoluene.—Benzoic acid (20 g.), 5 g. of hydrogen fluoride and 40 g. of COF_2 were heated in a 240-ml. pressure vessel at 350° for 10 hr. to give 22.5 g. of fuming black liquid. The product in ethereal solution was treated with sodium fluoride, filtered, and distilled to obtain 2.7 g., b.p. 40–50° (101 mm.), that was shown to contain α,α,α -trifluorotoluene²² by the presence of a singlet fluorine n.m.r. resonance the same as that of an authentic sample.⁷ Further fractions amounting to 13 g., b.p. 83–93° (100 mm.), were identified as benzoyl fluoride,²³ the major product, by the presence of a singlet fluorine n.m.r. peak the same as that of an authentic sample. Use of boron trifluoride catalyst gave similar results.

C. Addition of COF_2 to Fluoroolefins. Heptafluoroisobutyryl Fluoride.—Acetonitrile (30 ml.), 2 g. of granular anhydrous potassium fluoride, 25 g. of hexafluoropropene and 20 g. of COF_2 were heated in a 240-ml. pressure vessel at 50° for 2 hr., 75° for 2 hr. and 100° for 5 hr. The volatile product (44 g.) was recovered in a stainless steel cylinder cooled in liquid nitrogen and then distilled to give 30 g. (80% conversion) of colorless heptafluoroisobutyryl fluoride, b.p. –2 to +4°. The product reacted vigorously with water or alcohol to form an acidic solution. Qualitative gas chromatography with a column packed with Silicone 200-on-firebrick showed a small minor early peak and the one major component with a retention time very nearly equal to, but not identical with, that for a reference sample of perfluoro-*n*-butyryl fluoride. The fluorine n.m.r. spectrum was consistent with the structure $(\text{CF}_3)_2\text{CF}-\text{COF}$, consisting of three peaks: one peak centered at –108 p.p.m. attributed to COF , interpreted as split into a doublet by a single fluorine and then each in turn split sevenfold by the two CF_3 groups, with overlapping to give the observed eightfold pattern with 5–6 c.p.s. separation between adjacent peaks. A second peak attributed to CF_3 groups appeared as a triplet centered at –1.0 p.p.m. with 6 c.p.s. separation between adjacent peaks interpreted as two overlapping doublets. The third peak attributed to the C–F group centered at +105 p.p.m. appeared as an eightfold pattern as did the COF peak (above). The proton n.m.r. spectrum showed the absence of hydrogen in the compound. Infrared and mass spectral data were consistent with the above structure. The infrared showed strong absorption at 5.30 μ (CO of COF), a strong band at 7.8 μ (CF), major absorption in the 8 μ region (CF) as well as prominent bands at 7.58, 7.82, 8.39, 8.66 and 10.01 μ .

Anal. Calcd. for $\text{C}_4\text{F}_8\text{O}$: F, 70.36. Found: F, 71.10, 71.10.

Essentially the same yield of heptafluoroisobutyryl fluoride was obtained using an equimolar ratio of hexafluoropropene and COF_2 or when a more soluble fluoride, tetraethylammonium fluoride, was used instead of potassium fluoride. Use of cesium fluoride catalyst without sol-

vent at 200° for 10 hr. gave a 46% conversion to the acyl fluoride.

Nonafluoro-(methylethylacetyl) Fluoride.²⁴—A mixture of 200 g. (1.0 mole) of octafluoro-2-butene, 100 g. (1.5 moles) of COF_2 , 12.5 g. of cesium fluoride and 175 ml. of acetonitrile was heated in a 1-l. pressure vessel at 150° for 12 hr. The gaseous product (318 g.) was collected in a stainless steel cylinder cooled in liquid nitrogen, and then distilled to give, after a forerun of unreacted octafluoro-2-butene and COF_2 , 215 g. (80% conversion) of nonafluoro-(methylethylacetyl) fluoride, b.p. 23–26°.

The acyl fluoride in ether was treated with excess aniline, the aniline hydrofluoride was removed by filtration, and the filtrate was washed with 10% hydrochloric acid and water and then was dried over Drierite. Evaporation of the ether left the anilide of nonafluoro-(methylethylacetyl) acid, which was crystallized from ethanol-water; m.p. 80.5–81.5°.

Anal. Calcd. for $\text{C}_{11}\text{H}_6\text{F}_9\text{NO}$: C, 38.95; H, 1.78; F, 50.42; N, 4.13. Found: C, 39.72; H, 1.96; F, 50.76; N, 4.15.

The fluorine n.m.r. spectrum of the acyl fluoride with 1,2-difluorotetrachloroethane reference consisted of a peak at –111 p.p.m. attributed to the COF group, a doublet at –5.6 p.p.m. and +2.6 p.p.m. attributed to CF_3 groups, two peaks at +41.9 p.p.m. and +43.4 p.p.m. for CF_2 and a peak at +102 p.p.m. for CF.

β -Methoxytetrafluoropropionyl Fluoride.—A mixture of 19 g. of methyl trifluorovinyl ether,²⁵ 25 ml. of benzonitrile, 5 drops of a sirupy preparation of tetraethylammonium fluoride and 25 g. of COF_2 was heated in a 240-ml. pressure vessel at 50° for 3 hr., 100° for 3 hr. and 125° for 10 hr. The volatile product (42 g.) was collected in a stainless steel cylinder cooled in liquid nitrogen and then distilled to give 18.7 g. (62% conversion) of β -methoxytetrafluoropropionyl fluoride, b.p. 48–51°; infrared spectrum (gas): 5.29 μ (CO of COF), 3.30, 3.35 and 3.47 μ (satd. CH) and strong absorption at 8–10 μ .

Anal. Calcd. for $\text{C}_4\text{H}_3\text{F}_6\text{O}_2$: C, 26.96; H, 1.70; F, 53.32. Found: C, 26.99; H, 2.09; F, 53.70.

The proton n.m.r. spectrum showed one singlet peak at –3.7 p.p.m. for $-\text{OCH}_3$. Three fluorine n.m.r. peaks were observed, one at –98.8 p.p.m. (COF) that showed fivefold splitting, while the other two at +15.1 and +44.6 p.p.m. (CF_2 's) each showed fourfold splitting. Additional evidence for the structure was obtained by conversion as follows to the known methyl ester.

Methyl β -Methoxytetrafluoropropionate.—To methanol (2 ml.) was added dropwise during 10 min. 5.75 g. of β -methoxytetrafluoropropionyl fluoride with ice-bath cooling. The mixture was then kept at room temperature for 30 min. Ether and 2.5 g. of finely divided sodium fluoride (to absorb hydrogen fluoride) were added, and the mixture was filtered and distilled with a small spinning band column to give 3.50 g. (60% conversion) of methyl β -methoxytetrafluoropropionate¹¹ as three fractions, b.p. 130–136°, n_D^{20} 1.3368–1.3371. The fluorine n.m.r. spectra for the three fractions consisted of two peaks, each split into triplets, at +14.2 and at +43.9 p.p.m., while the proton n.m.r. spectrum consisted of two peaks at –4.1 and at –3.9 p.p.m. The n.m.r. (fluorine and proton) spectral and infrared data for this propionate were identical with those of the compound previously prepared.¹¹

A 0.7-g. higher-boiling fraction, n_D^{20} 1.3605, showed an additional fluorine n.m.r. peak (singlet, located between the above two fluorine peaks), and infrared examination showed it to be a mixture of the above ester and dimethyl difluoromalonate, a probable product of partial hydrolysis of the ester.¹¹

Heptafluorocyclobutanecarbonyl Fluoride.²⁴—A mixture of 24 g. (0.15 mole) of hexafluorocyclobutene, 15 g. (0.23 mole) of COF_2 , 3g. of cesium fluoride and 30 ml. of acetonitrile was heated in a 240-ml. pressure vessel at 125° for 4 hr. and at 150° for 5 hr. The liquid product was distilled to give 18.6 g. (54% conversion) of heptafluorocyclobutanecarbonyl fluoride, b.p. 35–39°. The fluorine n.m.r. spectrum was consistent with the acyl fluoride structure. There were CF_2 peaks at +51.8, +52.3, +54.6 p.p.m., a CF peak at +108 p.p.m. and a peak for COF at –111 p.p.m.

(24) We are indebted to Dr. R. D. Smith for these experiments.

(25) S. Dixon, U. S. Patent 2,917,548 (1959).

(21) F. Swarts, *Bull. Acad. roy. Belg.*, 414 (1900), (*Chem. Zentr.*, **71**, II, 667 (1900)) reports b.p. 133.5°. F. Swarts, *J. chim. phys.*, **20**, 65 (1922), reports n_D^{20} 1.45775.

(22) H. S. Booth, H. M. Elsey and P. E. Burchfield, *J. Am. Chem. Soc.*, **57**, 2066 (1935), report b.p. 102.3°.

(23) C. E. Entemann, Jr., and J. R. Johnson, *ibid.*, **55**, 2900 (1933), report b.p. 151° (736 mm.).

The acyl fluoride (2 g.) dissolved in 20 ml. of dry ether was treated with 5 g. of aniline with stirring at 0°. The mixture was allowed to warm to room temperature, and the aniline hydrofluoride was removed by filtration. The filtrate was washed with 10% hydrochloric acid and water and then was dried over Drierite. Evaporation of the ether left the anilide of heptafluorocyclobutanecarboxylic acid, which was crystallized from ethanol-water; m.p. 137.5–138°.

Anal. Calcd. for $C_{11}H_5F_7NO$: C, 43.87; H, 2.01; F, 44.16; N, 4.65. Found: C, 44.47; H, 2.15; F, 44.28; N, 4.85.

Pentafluoropropionyl Fluoride.²⁴—A mixture of 26 g. (0.26 mole) of tetrafluoroethylene, 17 g. (0.26 mole) of COF_2 , 2 g. of cesium fluoride and 27 ml. of acetonitrile was heated in a well barricaded 240-ml. pressure vessel at 100° for 4 hr. and at 150° for 5 hr. Low-temperature distillation of the gases bled from the cooled tube afforded 5.7 g. (13%) of pentafluoropropionyl fluoride,²⁶ b.p. -28 to -23°. N.m.r. spectroscopy indicated the presence of octafluorocyclobutane as an impurity.

The pentafluoropropionyl fluoride (4 g.) was bubbled into a solution of 5 g. of aniline in 30 ml. of dry ether at -30°. The mixture was stirred and allowed to warm to room temperature, then the aniline hydrofluoride was removed by filtration. The filtrate was washed with 10% hydrochloric acid and water and then was dried over Drierite. Evaporation of the ether left a solid residue of pentafluoropropionanilide, which was crystallized from ethanol-water; m.p. 99.5–100°.

Anal. Calcd. for $C_9H_5F_5NO$: C, 45.20; H, 2.53; F, 39.72; N, 5.86. Found: C, 46.14; H, 2.55; F, 39.03; N, 5.95.

D. Addition of COF_2 to Unsaturated Carbon-Nitrogen Compounds. Addition of COF_2 to Pentafluoro-2-azapropene.—Pentafluoro-2-azapropene (18 g.), 25 g. of COF_2 , 30 ml. of acetonitrile and 1.8 g. of cesium fluoride were heated in a 240-ml. pressure vessel at 50° for 2 hr., at 100° for 2 hr., and at 150° for 10 hr. Volatile product (42 g.) was collected in a stainless steel cylinder cooled in liquid nitrogen and then distilled to give 15 g. (56% conversion) of colorless N,N-bis-(trifluoromethyl)-carbamoyl fluoride, b.p. 12–17°,²⁷ infrared spectrum: 5.30 μ (CO of COF). The fluorine n.m.r. spectrum consisted of a large doublet peak with two components of equal area centered at -19.5 p.p.m. with 20 c.p.s. separation (CF_2) and another smaller peak in the COF region at -79.5 p.p.m. (COF) which was split sevenfold (19 c.p.s.).

A mixture of 20 g. of bis-(trifluoromethyl)-amine, 1.50 g. of cesium fluoride and 25 g. of carbonyl fluoride was heated at 200° for 2 hr., 250° for 2 hr. and 300° for 12 hr. The gaseous product (42 g.) was stored at room temperature and autogenous pressure over 42 g. of powdered sodium fluoride to obtain 39 g. of unabsorbed gas. Infrared examination of the latter showed the presence of bis-(trifluoromethyl)-carbamoyl fluoride.

N,N-Bis-(fluoroformyl)-aniline.—Phenyl isocyanate (20 g.), 30 g. of COF_2 and 2.9 g. of cesium fluoride were heated in a 240-ml. pressure vessel at 100° for 2 hr., 125° for 2 hr. and 150° for 8 hr. After cooling and venting gaseous materials, there was obtained 30 g. (95% conversion) of white solid. Recrystallization from chloroform gave white crystals of N,N-bis-(fluoroformyl)-aniline, m.p. 90.5–94°. An analytical sample recrystallized again from the same solvent melted at 93.5–95.5°.

Anal. Calcd. for $C_8H_5F_2NO_2$: C, 51.89; H, 2.72; N, 7.57; F, 20.52; mol. wt., 185. Found: C, 52.58; H, 2.59; N, 8.29 (D); F, 20.51; mol. wt., 184.

The fluorine n.m.r. spectrum (in chloroform or acetonitrile) consisted of one singlet peak in the COF region at -81.0 p.p.m.; infrared spectrum (KBr wafer): 5.30 and 5.46 μ (CO's of $N(COF)_2$), 3.26 μ (aromatic =CH), 6.28 and 6.70 μ (C=C), 13.15 and 14.35 μ (monosubstituted aromatic).

In certain instances, experiments at 150° gave lower conversions but raising the temperature to 200° generally gave conversions of 60–75% of recrystallized product. N,N-Bis-(fluoroformyl)-aniline was also obtained in 68% conversion when phenyl isocyanate dimer was treated with

COF_2 in the presence of CsF at 100° for 2 hr., 125° for 2 hr. and 150° for 8 hr. Treatment of aniline with COF_2 in the presence of sodium fluoride (to absorb hydrogen fluoride) at 150° also gave N,N-bis-(fluoroformyl)-aniline. Reaction of aniline with COF_2 to form fluoroformanilide has been reported in the literature.¹ This compound has also been obtained by addition of hydrogen fluoride to phenyl isocyanate. The conversion of aniline in one operation to N,N-bis-(fluoroformyl)-aniline may possibly proceed via fluoroformanilide followed by either a second substitution of hydrogen or an elimination of hydrogen fluoride to form phenyl isocyanate with subsequent addition of COF_2 .

Pentafluoroethyl Isocyanate.²⁸—Trifluoroacetonitrile (20 g.), 30 g. of COF_2 and 1.5 g. of cesium fluoride were heated in a 240-ml. pressure vessel at 200° for 2 hr., 250° for 2 hr. and 300° for 10 hr. Distillation of the volatile product gave 6 g. (18% conversion) of pentafluoroethyl isocyanate, b.p. -4 to -3°;²⁹ infrared spectrum (gas): 4.40 μ (strong) and 6.79 μ (isocyanate bands),³⁰ strong bands at 7.39, 8.08, 8.73 and 9.50 μ (CF). The fluorine n.m.r. spectrum showed two singlet peaks, one at +9.6 p.p.m. and another larger one at +11.5 p.p.m. in agreement with this structure.

Difluoromethylcarbamoyl Fluoride.—Hydrogen cyanide (62 g.), 20 g. of cesium fluoride, 46 g. of hydrogen fluoride and 160 g. of COF_2 were rocked at 25° for 2.5 days in a 1-l. pressure reactor. The volatile products (56 g.) comprised 75% COF_2 , 10% HCN, 5–10% CO_2 , <5% SiF_4 and small amounts of an unknown material that contained C-F and NCO as judged by the infrared spectrum. A portion (60 g.) of the 219 g. of crude liquid product recovered from the reactor was evaporated at 1 mm. for 40 min. The 51 g. (70% conversion) of liquid volatilized was shown to be difluoromethylcarbamoyl fluoride. Mass spectrometric analysis showed major peaks at 113, 112, 95, 51 and 47, and the infrared spectrum showed major absorption at 3.01 (NH), 5.45 (CO of COF), 6.55 (amide II band), 7.61, 8.10, 8.55, 9.02, 9.18, 9.95 and 13.07 μ . The fluorine n.m.r. spectrum showed two types of fluorine in a 1:2 ratio, the former being in the -COF region and the latter, a doublet, was in the - CF_2 - region. The proton n.m.r. spectrum showed two different hydrogens in a 1:1 ratio, both being triplets. A test portion was distilled at 41–44° (51 mm.). Considerable loss resulted from the formation of a water-reactive solid, and there was some etching of the glass container.

Anal. Calcd. for $C_2H_2F_3NO$: F, 50.40. Found: F, 49.48.

A portion (44 g.) of the crude unvolatilized HCF_2NHCOF and 50 g. of pelleted NaF were placed in a stainless steel pressure reactor cooled in solid carbon dioxide-acetone and then removed from the cooling bath; there was a mild spontaneous warm-up near 25°. On opening the reactor the sodium fluoride pellets were found to be coated with a brown, water-reactive solid not further characterized.

In contrast to the behavior of tertiary amides, primary carboxamides such as acetamide and benzamide reacted readily with COF_2 at 25–50° under autogenous pressure to yield, after storage over sodium fluoride at room temperature to remove HF, a variety of products including acyl fluorides, acyl isocyanates, carbonitriles, N-fluoroformyl anides and α,α -difluoroisocyanates. These reactions in general did not give high yields of a single product under the conditions examined.

E. Synthesis of α,α -Difluoroamines from N,N-Disubstituted Carboxamides. α,α -Difluorotrimethylamine.—N,N-Dimethylformamide (113 g.) and COF_2 (100 g.) were shaken at 25° for 20 hr. in a 500-ml. pressure vessel. The gaseous products (73 g.) were vented (in other similar experiments, the gas was at least 90% carbon dioxide), and the liquid (136 g.) was immediately distilled through a 4' Vigreux column to obtain 117 g. (82% conversion) of colorless liquid α,α -difluorotrimethylamine, b.p. 49–51°, which fumed strongly in air. Mass spectrometric analysis showed the presence of major peaks at 95, 94, 80, 76, 60, 51, 50, 44, 43, 42, 41, 40, 33, 32, 31, 29, 28, 27, 15, 14, 13 and 12. The n.m.r. spectrum showed the presence of two different kinds of hydrogen in about a 6:1 ratio, with the

(28) We are indebted to Drs. R. D. Lipscomb and W. C. Smith for suggestions concerning the reaction of carbonyl fluoride with $C\equiv N$ compounds.

(29) A. H. Ahlbrecht and D. R. Husted, U. S. Patent 2,617,817 (1952), report b.p. -9° (742 mm.).

(30) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 3428 (1956).

(26) W. C. Francis and R. N. Haszeldine, *J. Chem. Soc.*, 2151 (1955).

(27) J. A. Young, T. C. Simmons and F. W. Hoffmann, *J. Am. Chem. Soc.*, **78**, 5637 (1956), report b.p. 13–15° for $(CF_2)_2NCOF$.

smaller hydrogen peak being a triplet; only one type of fluorine was present and it was a doublet. The infrared spectrum (liquid) showed major absorption at 3.33, 3.37, 3.58 (satd. CH), 6.70, 6.82, 7.17, 7.43, 7.57, 8.19, 8.60, 9.17, 9.44, 10.75 (broad) and 11.56 μ .

Anal. Calcd. for $C_2H_7F_2N$: F, 40.00; N, 14.74. Found: F, 39.42; N, 15.37.

A mixture of dimethylformamide (34.5 g.) and dimethylformamide (2.0 g.), having the carbonyl carbon tagged with carbon 14,³¹ together with COF_2 (36 g.) was stored in a 300-ml. stainless steel pressure vessel at 25° for 21 hr. under autogenous pressure. The 24 g. of recovered CO_2 , which was condensed by liquid nitrogen after prior passage through a trap cooled in solid carbon dioxide-acetone slush, contained only 0.41% of the radioactivity originally added. Half the 44 g. of crude liquid product was distilled, yielding 19 g. of α, α -difluorotrimethylamine, b.p. 48–49°. This indicated that 80% of the dimethylformamide had been converted to the difluoroamine. A count of the radioactive disintegrations/min. of a test portion of the difluoroamine distillate showed the entire distilled product to contain 82.5% of the radioactivity originally added.³²

N,N-Dimethylformamide (90 g.) was added to a 500-ml. gas wash bottle provided with a fritted disk inlet; COF_2 (28 g.) was bubbled through the dimethylformamide over a period of 50 minutes. The exit gas (14 g.) was shown by infrared analysis to contain 55% COF_2 and 20% CO_2 . The product was removed from the wash bottle by subjecting the liquids to 1–2 mm. pressure. Distillation of the liquid so removed yielded 6 g. of the difluoroamine, b.p. 48–53°, corresponding to a 24% conversion based on COF_2 .

α, α -Difluorobenzyl dimethylamine.³³—*N,N*-Dimethylbenzamide (40 g.) and COF_2 (25 g.) were heated with rocking in a 500-ml. pressure vessel at 50°/1 hr. The 20 g. of gaseous product was shown by infrared analysis to contain 50–55% COF_2 and 35–45% carbon dioxide. Distillation of the liquid product yielded 18 g. of α, α -difluorobenzyl dimethylamine, b.p. 55–59° (12 mm.) (39% conversion), and 5 g. of unreacted *N,N*-dimethylbenzamide. The fluorine n.m.r. spectrum of the product showed the presence of one type fluorine in the $-CF_2-$ region.

Anal. Calcd. for $C_9H_{11}F_2N$: F, 22.22. Found: F, 21.64.

Difluorobis-(dimethylamino)-methane.—Tetramethylurea (58 g.), 66 g. of COF_2 and 11 g. of cesium fluoride were heated with rocking in a 500-ml. pressure reactor at 150° for 2 hr. The 50 g. of gaseous product was shown by infrared analysis to contain 80% COF_2 and 15–20% CO_2 . The non-volatile liquids (65 g.) removed from the reactor were subjected to reduced pressure (1–2 mm.) for several minutes; the 10 g. of product removed was distilled through a spinning band column, yielding 7 g. of difluorobis-(dimethylamino)-methane, b.p. 97° (10% conversion). The product was characterized by proton and fluorine n.m.r. spectra, which showed the presence of one type hydrogen and one type fluorine, and by infrared analysis (liquid) which showed major absorption at 3.31, 3.37, 3.46, 3.50, 3.55 (satd. CH), 6.75, 7.45, 8.21, 8.74, 9.40, 10.24 (broad), 10.92 and 13.95 μ .

Anal. Calcd. for $C_8H_{12}F_2N_2$: F, 27.54. Found: F, 26.76, 27.07.

In another experiment³⁴ tetramethylthiourea (26.4 g.), 20 g. of COF_2 and 10 g. of sodium fluoride were heated with rocking in a 100-ml. pressure reactor at 75° for 6 hr. The liquid product was washed from the reactor with methylene chloride; distillation yielded 20.6 g. (80% conversion) of the difluorodiamine, b.p. 97°.

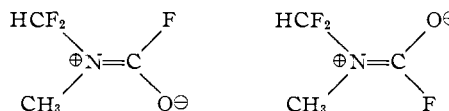
F. Synthesis of *N*-Fluoroformyl- α, α -difluoroamines, *N*-Fluoroformylamides and Ureides from *N*-Monosubstituted Carboxamides and Lactams. *N*-Fluoroformyl- α, α -difluorodimethylamine (A) and *N*-Fluoroformyl-*N*-methylformamide (B).—*N*-Methylformamide (30 g.), 33 g. of COF_2 and 42 g. of sodium fluoride were heated in a 500-ml. pressure vessel at 50° for 2 hr. and 75° for 2 hr. The 12 g. of gaseous product was shown by infrared analysis to contain 50% COF_2

and 30–40% CO_2 . The non-volatile product was warmed to 30° (2–3 mm.), and the 25 g. of liquid so recovered was distilled to give 3 g. (6% conversion) of (A) $HCF_2N(CH_3)COF$, b.p. 78°, and 17.5 g. (34% conversion) of (B) $HCON(CH_3)COF$, b.p. 127–128°.

Compound A was identified by infrared analysis (liquid phase) which showed major peaks at 3.34 (satd. CH), 5.49 (CO of COF), 7.00, 7.40, 7.48, 7.76, 7.86, 8.57, 9.19, 9.56, 9.97, 12.02, 13.27 and 14.30 μ ; by n.m.r. spectra which showed two different types of fluorine in a 2:1 ratio and two different types of hydrogen in a 3:1 ratio; and by elemental analysis.

Anal. Calcd. for (A) $C_3H_4F_3NO$: C, 28.35; H, 3.16; F, 44.88; N, 11.02. Found: C, 28.95; H, 4.13; F, 45.36; N, 10.47.

The fluorine resonance peaks in A indicate the presence of the forms



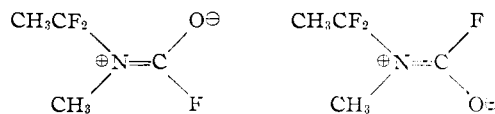
The infrared spectrum for compound B showed major peaks at 3.35 (satd. CH), 5.46 (CO of COF), 5.83 (CO of CHO), 6.65, 6.81, 7.00, 7.26, 7.44, 7.56, 7.70, 8.90, 9.05, 9.88, 12.08, 13.20 and 14.1 μ ; the n.m.r. spectra showed one type of fluorine and two different types of hydrogen in a 3:1 ratio.

Anal. Calcd. for (B) $C_3H_4FNO_2$: C, 34.29; H, 3.81; F, 18.10; N, 13.33. Found: C, 34.95; H, 4.27; F, 17.99; N, 13.08.

N-Fluoroformyl- α, α -difluoroethylmethylamine (C) and *N*-Fluoroformyl-*N*-methylacetamide (D).—*N*-Methylacetamide (36 g.), 66 g. of COF_2 and 42 g. of sodium fluoride were heated in a 500-ml. pressure reactor at 75° for 2 hr. and 125° for 2 hr. The 38 g. of gaseous product contained 70% COF_2 and 20–30% CO_2 . The non-volatile product was warmed to 50° (1 mm.), and the 42 g. of liquid thus recovered was distilled through a spinning band column, yielding 5 g. (20% conversion) of (C), $CH_3CF_2N(CH_3)COF$, b.p. 97–100°, and 13 g. (42% conversion) of crude (D), $CH_3CON(CH_3)COF$, b.p. 120–138°; redistillation gave a D heart cut, b.p. 136–138°.

The infrared spectrum of *N*-fluoroformyl- α, α -difluoroethylmethylamine (C) showed major peaks at 3.40 (satd. CH), 5.51 (CO of COF), 6.98, 7.13, 7.33, 7.87, 8.30, 8.76, 9.17, 9.30, 10.04, 10.31, 10.73, 11.28 and 13.22 μ .

The fluorine n.m.r. spectrum showed two types of fluorine in a 2:1 ratio, the larger peak at higher field being a quintuplet and the smaller peak a triplet, suggesting that the following forms might be present.



Anal. Calcd. for (C) $C_4H_6F_3NO$: F, 40.45. Found: F, 40.44.

Compound D was identified as *N*-fluoroformyl-*N*-methylacetamide by analysis; by its infrared spectrum which showed major absorption at 3.35 (satd. CH), 5.47 (CO of COF), 5.76 (CO of CH_3CO), 6.95, 7.27, 7.51, 7.76, 7.90, 8.73, 9.02, 9.58, 9.98, 10.20, 10.42, 10.63 and 13.20 μ ; and by its n.m.r. spectrum which showed one type fluorine in the COF region and two types of hydrogen in a 1:1 ratio.

Anal. Calcd. for (D) $C_4H_6FNO_2$: F, 15.97. Found: F, 15.91.

N-Fluoroformylbutyrolactam (E), Carbonyl *N,N'*-Di-(butyrolactam) (F) and *N*-Fluoroformyl- α, α -difluorotetramethylenimine (G).—Butyrolactam (85 g.) and 60 g. of COF_2 were heated at 50° for 2 hr. in a 500-ml. pressure reactor. The 137 g. of liquid product, after storage at room temperature over sodium fluoride, yielded on distillation 62 g. (47% conversion) of (E) *N*-fluoroformylbutyrolactam, b.p. 71–72° (0.3 mm.), and 15 g. (15% conversion) of (F) carbonyl-*N,N'*-di-(butyrolactam), b.p. 147–150° (0.7 mm.). An analytically pure sample of (F) was obtained by sublimation at 97–113° (<1 mm.), m.p. 105–107°.

(31) The C^{14} tagged *N,N*-dimethylformamide was obtained from Nuclear Research Chemicals, Inc., Orlando, Fla. A sample of 0.1 g. showed 77,000 disintegrations/min.

(32) We are indebted to R. S. Blake for the radioactive C^{14} counts.

(33) This compound (b.p. 70–71° (15 mm.)) has been prepared in 17% yield by the reaction of sulfur tetrafluoride with *N,N*-dimethylbenzamide; see ref. 7.

(34) We are indebted to Dr. H. E. Winberg for this experiment.

The infrared spectrum of E, identified as N-fluoroformylbutyrolactam, showed major absorption peaks at 3.34 and 3.42 (satd. CH), 5.40, 5.52 and 5.65 (C=O), 7.30, 7.61, 8.48, 9.76, 9.86, 10.50, 10.69, 11.90, 13.19 and 14.90 μ . The fluorine n.m.r. spectrum showed one type of fluorine in the -COF region.

Anal. Calcd. for (E) $C_5H_8FNO_2$: F, 14.50; N, 10.68. Found: F, 14.37; N, 10.82.

Compound F was identified as carbonyl-N,N'-di-(butyrolactam). The infrared spectrum (KBr wafer) showed major absorption peaks at 3.35 and 3.43 μ (satd. CH), 5.68, 5.93 μ (C=O), 6.82, 7.06, 7.27, 7.52, 7.96, 8.51, 9.29, 9.78, 10.58, 12.17 and 12.87 μ .

Anal. Calcd. for (F) $C_8H_{12}N_2O_3$: C, 55.10; H, 6.13; N, 14.30. Found: C, 55.17; H, 6.25; N, 14.03.

Butyrolactam (43 g.) and 110 g. of COF_2 were heated in a 500-ml. pressure reactor at 75° for 1 hr. and 125° for 1 hr. The 57 g. of gaseous product contained 80% COF_2 and 20% CO_2 . The 79 g. of crude liquid product after storage at room temperature over sodium fluoride was distilled through a spinning band column, yielding 13 g. of a liquid (G), b.p. 33-37.5° (3 mm.), and 15 g. of (E) N-fluoroformylbutyrolactam, b.p. 70-72° (0.3 mm.), which was identified by comparison of its infrared spectrum with that of an authentic specimen.

Compound G could not be purified further by careful redistillation or by chromatography on alumina. The infrared spectrum (liquid) showed major absorption peaks at 3.33 and 3.41 μ (satd. CH), 5.48 (CO of COF), 6.91, 7.08, 7.20, 7.30, 7.56, 7.92, 8.17, 8.32, 8.91, 9.15, 9.91, 10.07, 10.24, 10.53, 10.75, 11.31, 11.82, 13.18 and 13.61 μ . Mass spectrometric analysis showed a strong parent peak at 153 which suggested the sample was chiefly N-fluoroformyl- α,α -difluorotetramethylenimine; other major peaks were present at 152, 134, 133, 132, 125, 112, 109, 104, 91, 90, 89, 86, 84, 79, 77, 76, 75, 74, 64, 59, 57, 56, 51, 47, 45, 42, 41, 40, 39, 38, 33, 31, 29, 28, 27, 26 and 15. The fluorine n.m.r. spectrum showed two peaks corresponding to two types of fluorine; in addition the spectrum showed two smaller fluorine peaks, the larger of these in the CF_2 region and the smaller in the -COF region. The sample was obviously impure.

Anal. Calcd. for (G) $C_8H_{10}F_3NO$: C, 39.20; H, 3.90; F, 37.30; N, 9.15. Found: C, 40.42; H, 4.11; F, 39.96; N, 9.77.

N-Fluoroformylcaprolactam (I), N-Fluoroformyl- α,α -difluorohexamethylenimine (II), Carbonyl N,N'-Di-(caprolactam) (J) and ω -Fluoroformylpentyl Isocyanate (III).— ϵ -Caprolactam (136 g.) and 66 g. of COF_2 were heated in a 500-ml. pressure reactor at 75° for 2 hr. The 194 g. of liquid product, after storage at room temperature over sodium fluoride to remove hydrogen fluoride, was distilled through a spinning band column to obtain compound I, 64 g. (30% conversion), b.p. 90-98° (0.1 to 0.3 mm.). Compound I later was shown to be chiefly N-fluoroformylcaprolactam contaminated by small amounts of N-fluoroformyl- α,α -difluorohexamethylenimine (II). Redistillation of I removed the more volatile N-fluoroformyl- α,α -difluorohexamethylenimine (II), yielding pure N-fluoroformylcaprolactam (I), b.p. 91-93° (0.6 mm.). The infrared (liquid) spectrum showed major absorption peaks at 3.38 and 3.46 μ (satd. CH), 5.40, 5.54 and 5.74 (C=O), 7.21, 7.30, 7.37, 7.44, 7.86, 8.21, 8.46, 8.62, 9.21, 10.06, 10.29, 11.25 and 13.12 μ . The fluorine n.m.r. spectrum showed one type of fluorine in the -COF region.

Anal. Calcd. for (I) $C_7H_{10}FNO_2$: F, 11.95. Found: F, 11.67.

The 59 g. of solid residue remaining from the preceding distillation was sublimed at 125-145° (0.2 mm.) to yield 38 g. (25% conversion) of (J) carbonyl N,N'-di-(caprolactam), m.p. 110-112°. Its infrared spectrum (KBr wafer) showed major absorption peaks at 3.39 and 3.46 μ (satd. CH), 5.83 and 5.94 (C=O), 7.17, 7.38, 7.48, 7.87, 7.94, 8.23, 8.51, 8.64 and 10.21 μ .

Anal. Calcd. for (J) $C_{15}H_{20}N_2O_3$: C, 61.90; H, 7.95; N, 11.11. Found: C, 62.19; H, 7.81; N, 11.09.

Caprolactam (113 g.) and 100 g. of COF_2 were heated in a 500-ml. pressure reactor at 75° for 1 hr. and 125° for 1 hr. The 30 g. of gaseous product recovered was shown to contain 30% COF_2 and 70% CO_2 . The 180 g. of liquid product after storage at room temperature over sodium

fluoride was distilled through a spinning band column to obtain the following fractions having the approximate composition indicated as determined by their fluorine n.m.r. spectra.

G.	Fractions		Approx. compn.	
	B.p., °C. (mm.)		II, %	III, %
(1)	12	59-70 (0.5)	90	10
(2)	22	55-69 (.35 to .70)	80	20
(3)	26	56 (.35)	50	50
(4)	20	51-52 (.42)	20	80
(5)	21	59-60 (.40)	100	

Fraction 5 was shown to be pure $OCN(CH_2)_5COF$ (III). The infrared spectrum showed strong absorption peaks at 3.40 and 3.48 (satd. CH), 4.40 (NCO), 5.44 (CO of COF), 6.82, 7.06, 7.36, 9.30 and 11.36 μ , and one fluorine peak in the -CF region was found in the fluorine n.m.r. spectrum.



Anal. Calcd. for III $C_7H_{10}FNO_2$: C, 52.83; H, 6.30; F, 11.95. Found: C, 53.26; H, 6.45; F, 11.92.

Fraction 1 was carefully redistilled to give a heart cut, b.p. 50° (0.3 mm.), of N-fluoroformyl- α,α -difluorohexamethylenimine (II). The infrared spectrum showed major absorption peaks at 3.41 and 3.50 μ (satd. CH), 5.54 (CO of COF), 7.08, 7.57, 7.78, 8.15, 8.32, 8.49, 9.26, 9.57 and 10.08 μ , and the fluorine n.m.r. spectrum showed two types of fluorine in a 2:1 ratio, the smaller peak being in the O=C-F region.

Anal. Calcd. for II $C_7H_{10}F_2NO$: F, 31.49; N, 7.74. Found: F, 30.96; N, 8.26.

The n.m.r. analysis of all the fractions obtained indicated approximately a 34% conversion of caprolactam to $OCN(CH_2)_5COF$ (III) and a 19% conversion to the difluoroimine II.

In an experiment in which caprolactam (40 g.), 66 g. of COF_2 and 18 g. of cesium fluoride were heated in a 500-ml. pressure vessel at 75° for 1 hr. and 125° for 1 hr., N-fluoroformylcaprolactam (I) was isolated in 19% conversion and N-fluoroformyl- α,α -difluorohexamethylenimine (II) was isolated in 37% conversion. Only a small amount of ω -fluoroformylpentyl isocyanate (III) was formed as judged by spectral analyses. It seems likely that the isocyanate may have resulted from a two-step reaction involving the conversion of N-fluoroformylcaprolactam (I) to $FOCNH(CH_2)_5COF$ by hydrogen fluoride. Storage of this intermediate over sodium fluoride could yield the isocyanate $OCN(CH_2)_5COF$ (III). In the experiment just cited, ring-opening did not occur probably because hydrogen fluoride as formed was absorbed by the cesium fluoride. Partial confirmation of this hypothesis is found in the following experiment. N-Fluoroformylcaprolactam (I) (48 g.) and hydrogen fluoride (15 g.) were heated in a 500-ml. pressure reactor at 75° for 1 hr. and 125° for 1 hr. The crude liquid product after storage over sodium fluoride pellets at room temperature for 2 days was then distilled to obtain 11 g. (40% conversion) of III, $OCN(CH_2)_5COF$, b.p. 72-75° (0.45 mm.). At this stage the oil-bath temperature inadvertently was raised from 130° to 170°, which resulted in the sudden transformation of the liquid residues to a solid product.

G. Synthesis of Tetrasubstituted Ethylenes from N,N-Disubstituted Carboxamides. 1-Dimethylamino-1-fluoro-2,2-bis-(fluoroformyl)-ethylene.—N,N-Dimethylacetamide (64 g.), 50 g. of COF_2 and 14 g. of cesium fluoride when shaken at 25° for 20 hr. in a 500-ml. pressure reactor gave 16 g. of gaseous product (90% CO_2 and 5% COF_2) and 99 g. of liquid product. The liquid was stored over sodium fluoride, filtered, and distilled through a 4" Vigreux column to yield 31 g. of liquid, b.p. 35-52° (3 mm.), chiefly unreacted dimethylacetamide, and 25 g. of yellow-orange solid, b.p. 138-148° (1 mm.), m.p. 75-77°. Redistillation of the solid gave a heart cut of 1-dimethylamino-1-fluoro-2,2-bis-(fluoroformyl)-ethylene, b.p. 143-145° (1 mm.), m.p. 75-77°; infrared spectrum (Nujol mull): 5.45, 5.56 and 5.73 μ (CO of COF), 6.04 (C=C) and 7.65, 9.96, 10.49, 11.00, 12.87, 13.84 and 14.08 μ . The fluorine n.m.r. spectrum revealed the presence of two different fluorines in a 2:1 ratio, with the smaller peak being a triplet and the larger peak, which was in the COF region, existing either

as a doublet or as two very similar peaks. The proton n.m.r. showed only one type of hydrogen.

Anal. Calcd. for $C_6H_5F_3NO_2$: F, 31.55; N, 7.73. Found: F, 31.28; N, 7.95.

This substituted ethylene frequently polymerized during attempted distillation to give a colored, water-soluble product. Sublimation of the solid at 105–110° (0.1 mm.) was a more satisfactory purification procedure.

N,N-Dimethylacetamide (88 g.) was placed in a 500-ml. glass gas washing bottle provided with a fritted disk inlet, and 28 g. of COF_2 was bubbled through the liquid over a period of 37 minutes with intermittent interruptions for cooling when the reaction mixture reached 40–45°. The exit gases (13 g.) contained 60–65% COF_2 and 25–30% CO_2 . The liquid product was distilled through a 4' Vigreux column to yield 10 g. of yellow-orange solid, b.p. 153–160° (0.4 to 0.5 mm.), which on sublimation at 105–110° (0.1 mm.) yielded 8 g. (4% conversion) of pale-yellow 1-dimethylamino-1-fluoro-2,2-bis-(fluoroformyl)-ethylene, identified by its fluorine n.m.r. spectrum.

In the presence of added hydrogen fluoride at higher temperatures, cleavage products were formed. N,N-Dimethylacetamide (44 g.), 40 g. of COF_2 and 40 g. of anhydrous hydrogen fluoride when treated at 100° for 1 hr. and then at 175° for 1 hr. gave 23 g. of gaseous product that was shown by infrared to contain largely COF_2 and CO_2 together with a considerable amount of acetyl fluoride. The liquid product from the reaction was stored over NaF, flash distilled, and then redistilled to obtain 8 g. of N,N-dimethylcarbamoyl fluoride, b.p. 127–129°. The n.m.r. spectra showed one type of fluorine in the COF region and one type of hydrogen.

Anal. Calcd. for C_5H_6FNO : F, 20.88. Found: F, 20.87.

N,N-Dimethylcarbamoyl fluoride was also prepared from 250 g. of N,N-dimethylcarbamoyl chloride, 200 g. of finely divided NaF and 500 ml. of tetramethylene sulfone by heating at atmospheric pressure gradually to 125° during 1.5 hr. and then at 125–135° for an additional 4 hr. Two distillations gave 146 g. (70% conversion) of N,N-dimethylcarbamoyl fluoride, b.p. 54–56° (51 mm.). The infrared spectrum of this preparation was identical with that of the compound isolated above.

The substituted ethylene (3 g.) and 25 ml. of water were mixed (reaction with bubbling) and allowed to stand in a polyethylene container at room temperature for 2 days. The bulk of the water was evaporated at room temperature, and the sirupy residue was dried *in vacuo* over phosphorus pentoxide for 5 days to give white solid N,N-dimethylmalonic acid; infrared spectrum: strong 6.2 (CO of amide), 5.75 μ (CO of COOH).

Anal. Calcd. for $C_5H_6NO_3$: C, 45.80; H, 6.87; N, 10.69; neut. equiv., 131. Found: C, 46.12; H, 6.94; N, 10.65; neut. equiv., 129.

2-Fluoro-3-fluoroformyl-1-methyl-4,5-dihydropyrrole.—N-Methyl- α -pyrrolidone (50 g.), 35 g. of COF_2 and 10 g. of cesium fluoride were rocked at 25° for 20 hr. under autogenous pressure. The 16 g. of recovered gas contained 60% COF_2 and 30% CO_2 . The liquid product was decanted from the cesium fluoride and was distilled through a 4' Vigreux column to obtain 23 g. of liquid, b.p. 56–66° (2 mm.). Infrared analysis indicated this to be chiefly starting material plus hydrogen fluoride, possibly in the form of a salt. There was also obtained 3 g. of yellow liquid 2-fluoro-3-fluoroformyl-1-methyl-4,5-dihydropyrrole, b.p. 75–83° (2 mm.), that solidified on cooling; infrared spectrum (CCl_4 solution): 3.41 and 3.48 (satd. CH), 5.72 (CO of COF), 6.25 (conj. C=C, cyclic) and 7.07, 7.24, 7.66, 7.88, 8.21, 10.15, 13.15, 13.62 and 14.18 μ . The fluorine n.m.r. spectrum showed two fluorines in a 1:1 ratio, one in the -COF region and the other in the C-F region.

Anal. Calcd. for $C_5H_7F_2NO$: F, 25.85. Found: F, 25.52.

H. Conversion of Carboxylic Acids to Acyl Fluorides by COF_2 . **Benzoyl Fluoride from Benzoic Acid.**³⁵—A 1-l. pressure vessel was charged with 224 g. (2 moles) of benzoic acid, 160 g. (2.4 moles) of COF_2 and 100 g. of sodium fluoride pellets. The vessel was heated for 10 hr. at 175° with shaking. The vessel was cooled, and the non-vola-

tile reaction products were rinsed with 150 ml. of dry pentane into a glass receiver. The pentane was evaporated, and the residue was distilled under reduced pressure to obtain 155 g. (62% yield) of benzoyl fluoride, b.p. 65–67° (30 mm.).^{23,36}

Trifluoroacetyl Fluoride.³⁵—Into a 500-ml. pressure vessel were placed 100 g. (0.87 mole) of trifluoroacetic acid and 75 g. (0.87 mole) of COF_2 . The mixture was heated and mechanically agitated at 150° for 6 hr. The vessel was cooled to 25°, and the gaseous products were transferred to a previously evacuated 500-ml. stainless steel cylinder cooled in liquid nitrogen. There was no residue in the reaction vessel. The gaseous products were transferred, by passage over sodium fluoride pellets, to a liquid nitrogen-cooled distillation flask. Low-temperature fractional distillation of the products gave 79 g., b.p. -79° to -55°, and 57 g., b.p. -55° to -50°,³⁷ chiefly trifluoroacetyl fluoride (56% yield). The lower boiling fraction comprised carbon dioxide, COF_2 and an additional small amount of trifluoroacetyl fluoride.

Benzoyl Fluoride from Methyl Benzoate.—Methyl benzoate (25 g.), 35 g. of COF_2 and 2 g. of N,N-dimethylformamide were heated in a 240-ml. pressure vessel at 200° for 2 hr., 250° for 3 hr. and 300° for 10 hr. The liquid product (25 g.) was poured into a slurry of 20 g. of powdered sodium fluoride in 100 ml. of dry pentane. Filtration and distillation gave 12 g. (55% yield) of crude benzoyl fluoride boiling over the range 47–58° (20 mm.).^{23,36}

2-(Fluoroformyl)-ethyl Fluoroformate from β -Propiolactone.—A 240-ml. Hastelloy-lined pressure reactor was charged with 15 g. of β -propiolactone and 20 ml. of acetonitrile. Pyridine (1.5 ml.) was placed in a glass ampule with a bent tip such that shaking of the reactor would break the ampule. After cooling and evacuating, 40 g. of COF_2 was added, and the mixture was agitated and heated at 50° for 2 hr., 75° for 2 hr. and 100° for 8 hr. After cooling, there was obtained 47 g. of brown liquid product. A preliminary distillation gave 13 g. of colorless distillate, b.p. ca. 45° (1–2 mm.), which was filtered through powdered sodium fluoride and distilled with a spinning band column to obtain 10.3 g. (36% conversion) of 2-(fluoroformyl)-ethyl fluoroformate, b.p. 43–47° (5 mm.), n_D^{20} 1.3642–1.3650. The fluorine u.m.r. spectrum showed two triplet resonances of equal size, one centered at -58.9 p.p.m. (OCOF) and the other centered at -121 p.p.m. (COF). The proton magnetic resonance spectrum showed two resonances of equal size centered at -2.8 p.p.m. and at -4.2 p.p.m., each showing approximately fivefold splitting (triplets, further split but incompletely resolved). The infrared spectrum showed absorption at 5.45 μ with a shoulder at 5.40 (two C=O's, OCOF and COF), at 3.34 (satd. CH) and 8–9 μ (CF and/or C-O).

Anal. Calcd. for $C_4H_4F_2O_3$: C, 34.8; H, 2.92; F, 27.5. Found: C, 35.22; H, 3.09; F, 27.03.

Perfluorobutyryl Fluoride.³⁵—A mixture of 208 g. (0.97 mole) of perfluorobutyric acid, 85 g. (1.29 moles) of carbonyl fluoride and 60 g. (1.43 moles) of sodium fluoride pellets was heated under autogenous pressure at 150° for 15 hr. in a 1-l. vessel. The product was collected in an evacuated, stainless steel cylinder cooled in liquid nitrogen. The products from two identical runs were combined and distilled in a low-temperature still to obtain 9.0 g. of forerun, b.p. -18 to +4°, and 328 g. (78% conversion) of perfluorobutyryl fluoride, b.p. 4–6°.

I. Replacement of Thiono Sulfur by Fluorine. **α,α,α -Trifluorotrimethylamine.**³⁸—Tetramethylthiuram disulfide (72 g.) and 80 g. of COF_2 were heated with rocking at 50° for 1 hr., 75° for 1 hr. and 85° for 1 hr. in a 500-ml. pressure vessel. The volatile product (117 g.) was distilled through a low-temperature column to obtain 34 g. of carbon oxysulfide, distilling chiefly at -48° to -45°, and 28 g. of α,α,α -trifluorotrimethylamine, b.p. 15–20°. The material boiling below -48° was not collected but was probably chiefly unreacted

(36) A. I. Mashentsev, *J. Gen. Chem. (U.S.S.R.)*, **15**, 915 (1945); b.p. 155–156°, d_4^{18} 1.155, n_D^{20} 1.4983.

(37) N. Fukuhara and L. A. Bigelow, *J. Am. Chem. Soc.*, **63**, 783 (1941); the b.p. is reported as -59°, but the material contained some O_2F_2 . F. Swarts, *Bull. sci. acad. roy. Belg.*, **8**, 343 (1922); b.p. -50°.

(38) α,α,α -Trifluorotrimethylamine has been prepared in 45–75% conversion by reaction of sulfur tetrafluoride with tetramethylthiuram disulfide at 120°; R. J. Harder and W. C. Smith, *J. Am. Chem. Soc.*, **83**, 3422 (1961).

(35) We are indebted to Dr. E. K. Ellingboe for this experiment.

COF₂. The trifluoroamine was characterized by mass spectrometric analysis which showed major peaks at 113, 112, 94, 78, 76, 69, 60, 50, 44, 43, 42, 41, 40, 33, 31, 28, 15, 14, 13 and 12. The fluorine n.m.r. spectrum showed one type of fluorine in the CF₃ region.

Anal. Calcd. for C₃H₆F₃N: F, 50.50. Found: F, 49.09.

Since the low fluorine content probably resulted from hydrolysis by trace amounts of water, the compound was purified by gas chromatography (20% Silicone 703 on Columapak at 0°). The infrared spectrum (gas) of the purified sample showed major absorption at 3.29, 3.33, 3.42, 3.47 and 3.53 μ (satd. CH), 6.66, 6.70, 6.74, 6.82, 7.42, 7.82, 8.31, 9.17 and 10.26 μ.

The pressure reactor contained 7 g. of sulfur and 27 g. of dark-colored liquid which yielded on distillation 19 g.

(30% conversion) of (CH₃)₂NC-F, b.p. 42–42.5° (1.7 min.);

infrared spectrum (liquid): 3.39 (satd. CH), 6.39 (C=S of N-C₃FS), 7.10 (N-CH₃), 7.85, 8.53, 9.00, 9.48, 10.76 and 14.90 μ. The fluorine n.m.r. spectrum showed one type of fluorine in the S=C-F region.

Anal. Calcd. for C₃H₆FNS: C, 33.70; H, 5.60; F, 17.75; S, 29.90. Found: C, 33.97; H, 6.01; F, 17.92; S, 30.39.

In another experiment in which (CH₃)₂NC-F (16 g.) and 30 g. of COF₂ were heated with rocking at 75° for 1 hr. and 85° for 1 hr. in a 300-ml. pressure vessel, the trifluoroamine was obtained in 55% conversion; 6 g. of unreacted (CH₃)₂S=CN-F was recovered.

[CONTRIBUTION NO. 774 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON, 98, DEL.]

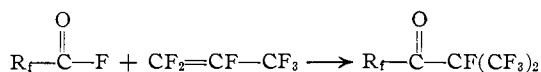
The Chemistry of Carbonyl Fluoride. II. Synthesis of Perfluoroisopropyl Ketones

By R. D. SMITH, F. S. FAWCETT AND D. D. COFFMAN

RECEIVED APRIL 27, 1962

A convenient synthesis of the new perfluoroisopropyl ketones, (CF₃)₂CF-CO-R_f, has been found in the fluoride ion-catalyzed addition of a fluoroacyl fluoride to hexafluoropropene. Diketones have been prepared by reaction of hexafluoropropene with oxalyl fluoride and with perfluoroglutaryl fluoride.

The addition of carbonyl fluoride to fluoroolefins in the presence of a fluoride ion catalyst and a polar non-protonic solvent to form fluoroacyl fluorides has been reported.¹ In some further studies, this reaction has been extended to the preparation of a family of fluoroketones containing the perfluoroisopropyl group by reaction of hexafluoropropene (HFP) with various fluoroacyl fluorides. In the conversion of carbonyl fluoride and HFP to perfluoroisobutyryl fluoride, bis-(perfluoro-



isopropyl) ketone is a co-product. This ketone is also obtained in 39% conversion through use of two moles of HFP with one of carbonyl fluoride. The bis-(perfluoroisopropyl) ketone is formed also from preformed perfluoroisobutyryl fluoride and HFP under the same conditions used for the HFP-carbonyl fluoride reaction. The ketones were obtained in conversions up to 75% as shown in Table I.

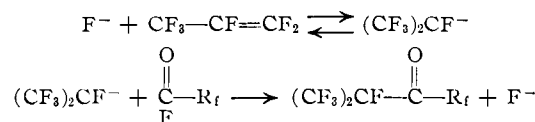
TABLE I
PERFLUOROISOPROPYL KETONES FROM HEXAFLUOROPROPENE AND FLUOROACYL FLUORIDES

Acyl Fluoride	RCCF(CF ₃) ₂ ketone; R	% Conv. to ketone
FCOF	(CF ₃) ₂ CF-	39
CF ₃ COF	CF ₃ -	75
<i>n</i> -C ₃ F ₇ COF	CF ₃ CF ₂ CF ₂ -	60
iso-C ₃ F ₇ COF	(CF ₃) ₂ CF-	38
H(CF ₂) ₄ COF	H(CF ₂) ₄ -	64
$\overline{\text{F}}$ COF	$\overline{\text{F}}$	8
FCO ₂ COF	(CF ₃) ₂ CFCO-	28
FCO(CF ₂) ₃ COF	(CF ₃) ₂ CFCO(CF ₂) ₃ -	75

(1) F. S. Fawcett, C. W. Tullock and D. D. Coffman, *J. Am. Chem. Soc.*, **84**, 4275 (1962).

In the reaction of trifluoroacetyl fluoride with HFP at 200°, use of cesium fluoride catalyst alone gave 65% conversion to trifluoromethyl perfluoroisopropyl ketone. Similarly, in the conversion of carbonyl fluoride and HFP at 200° to perfluoroisobutyryl fluoride, the use of cesium fluoride catalyst but no solvent gave 46% conversion, while without a catalyst either in the presence or absence of acetonitrile solvent no adduct was obtained. The combined use of a relatively polar solvent, such as acetonitrile, and a catalyst is beneficial, however, as illustrated by the higher conversions (70–75%) observed at lower reaction temperatures (100–125°) for both the carbonyl fluoride¹ and trifluoroacetyl fluoride additions to HFP. Other catalysts which have been found effective include potassium fluoride, potassium bifluoride and quaternary ammonium fluorides.

This ketone synthesis, which is similar to reactions of carbonyl fluoride with unsaturated systems,¹ presumably occurs *via* a fluorocarbanion intermediate that is formed by the reversible addition of a fluoride ion to the fluoroolefin. Reaction of this anion with the acyl fluoride at its highly electrophilic carbonyl group, either by direct displacement or by addition-elimination, would yield the fluoroketone and fluoride ion



The fluoroketones are thermally stable compounds that distil without decomposition. They are non-flammable and resistant to oxidation. They are soluble in diethyl ether and in petroleum ether, whereas the corresponding fluorocarbons are immiscible. Bis-(perfluoroisopropyl) ketone ap-