[CONTRIBUTION FROM THE CHEMICAL WARFARE LABORATORIES, ARMY CHEMICAL CENTER, AND THE DEPARTMENT OF CHEMICAL ENGINEERING, UNIVERSITY OF FLORIDA]

Fluorocarbon Nitrogen Compounds. I. Perfluorocarbamic Acid Derivatives, Amides and Oxazolidines[1]

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Bis-(trifluoromethyl)-carbamyl fluoride has been obtained by electrochemical fluorination of several compounds, among which $(CH_3)_2NCOCl$ gives the best yield. Although the acid fluoride and esters are stable, the free carbamic acid cannot be isolated. Use of homologous carbamyl chlorides in the process results in cyclization and consequent production of substituted oxazolidines which are thermally and chemically of much greater stability than their organic analogs. The perfluorocarbamyl fluoride pyrolyzes to give an excellent yield of perfluoro-2-azapropene, $CF_3N{=}CF_2$. Perfluoroamides have been obtained in low yield from N,N-dimethyl amides by the electrochemical process.

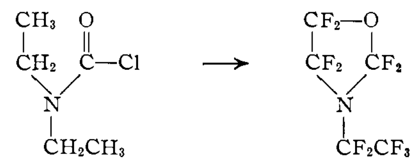
In work done independently at the two above-named laboratories it has been found that bis-(trifluoromethyl)-carbamyl fluoride can be synthesized by electrochemical fluorination of several different compounds, the yield obtainable being dependent on choice of starting material and conditions during the reaction. Six compounds which have given $(CF_3)_2NCOF$ as a product are $(CH_3)_2NCOCl$, $HCON(CH_3)_2$, $(C_2H_5)_2NCOCl$, $CH_3CON(CH_3)_2$, $CF_3CON(CH_3)_2$, $O(CH_2CH_2)_2NCOCl$ and $(CH_3)_2NCON(CH_3)_2$. These six different compounds have in common the structure $(RCH_2)_2N$–CO–M where R is hydrogen or alkyl and M is hydrogen, halogen or nitrogen, and it is probable that any starting material containing this arrangement will give the carbamyl fluoride as one product. With all these compounds there is considerable fragmentation, the best yield of the perfluoro carbamyl fluoride (37%) being obtained from dimethylcarbamyl chloride under conditions of minimum concentration and voltage (see Table I).

The free carbamic acid, $(CF_3)_2NCOOH$, appears to share the instability of its organic analog and only the esters of this acid have been found to be stable under ordinary conditions. Attempted acidolysis of the esters was unsuccessful, while ammonolysis and saponification resulted in complete destruction of the trifluoromethyl groups and production of fluoride ion.

Bis-(trifluoromethyl)-carbamyl fluoride resists hydrolysis when passed through water at room temperature, but reacts destructively with aqueous base, or with water at elevated temperatures. It does not undergo simple halogen exchange with $AlCl_3$, $SnCl_4$ or $SiCl_4$. On pyrolysis at 500–600°, COF_2 is eliminated and almost quantitative yields of both COF_2 and perfluoro-2-azapropene, $CF_3N{=}CF_2$, can be obtained.

Extension of the electrochemical synthesis to higher carbamyl chlorides does not give the homologous perfluoro carbamyl fluorides. Cyclization takes place, the carbonyl oxygen is incorporated into the ring, and a substituted oxazolidine is formed.

The five-membered ring structure has been fully substantiated, by nuclear magnetic resonance studies, for the perfluoro-3-ethyloxazolidine; however, the possibility of a six-membered ring for the 3-butyl compound has not been completely eliminated.



The perfluoro oxazolidines are colorless liquids very inert to chemical attack, as can be shown by the normal purification procedure, which consists of refluxing the compound successively with 50% aqueous alkali and concentrated sulfuric acid. Perfluoro-3-ethyl oxazolidine is thermally very stable, undergoing only about 10% decomposition at 650° with a contact time of nine minutes. This behavior may be contrasted with that of the organic oxazoles and oxazolidines which are basic in nature and generally susceptible to hydrolysis, oxidation or thermal decomposition.

It was hoped that use of the N,N-disubstituted amides in the electrochemical process would lead to the analogous perfluoro amides and, although $(CF_3)_2NCOF$ was the major product in the two runs of this nature, small amounts of the perfluoroamides were indeed obtained. Perfluoro-N,N-dimethylacetamide, $CF_3CON(CF_3)_2$, and perfluorotetramethylurea, $(CF_3)_2NCON(CF_3)_2$, whose structures have been confirmed by NMR spectrum, are the first reported amides to contain no hydrogen in either the acid or the amine moiety. It is of interest that these compounds, although their molecular weights are almost three times as high, have boiling points well over a hundred degrees lower than those of their organic analogs.

Experimental

Since the electrochemical apparatus and procedures for these runs were generally similar to those used by other workers,[3] this section describes only methods used for the identification of the products.

$(CH_3)_2NCOCl$ **Run.**—Fractionation of the cell product gave two flats, 70% of the crude product boiling at 13–15° and 13% at 38–41°.

The 13–15° cut, mol. wt. 201, showed an infrared absorption band at 5.35 μ, attributable to –COF. $(CF_3)_2NCOF$ has mol. wt. 199. Reaction with methanol gave the ester, b.p. 76°, n^{25}_D 1.2997.

(1) This material was presented in part at the September, 1954, Meeting of the American Chemical Society in New York. Much of the work was carried out on Project NR 356-333 between the Office of Naval Research and the University of Florida. Reproduction in whole or in part is permitted for any purpose of the United States Government.

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(3) (a) J. H. Simons and co-workers, *J. Electrochem. Soc.*, **95**, 47 (1949); (b) A. F. Clifford, H. K. El-Shamy, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 2372 (1953).

TABLE I

EXPERIMENTAL CONDITIONS FOR ELECTROCHEMICAL FLUORINATIONS

Organic starting material	Initial mole % organic	Total organic used	Potential applied (volts)	Average amperage	Faradays	Products: Compound	Products: Wt., g.
$HCON(CH_3)_2$	5.0	1139	5.2	24.1	198	$(CF_3)_2NCOF$	170
$(CH_3)_2NCOCl$[a]	3.5	1423	5.0–5.3	49	249	$(CF_3)_2NCOF$	154
	0.5	2175	5.0–5.3	55	452	$(CF_3)_2NCOF$	965
$(C_2H_5)_2NCOCl$	3.0	810	5.2–5.4	18.8	100	$CF_2OCF_2CF_2NC_2F_5$ (cyclic)	273
	5.5	595	4.6–4.8	8	125	$(CF_3)_2NCOF$	40
						$CF_2OCF_2CF_2NC_2F_5$ (cyclic)	241
$(C_4H_9)_2NCOCl$	2.2	1176	5.2–5.4	25.3	184	$(CF_3)_2NCOF$	[b]
						$CF_2OCF(C_2F_5)CF_2NC_4F_9$ (cyclic)	211
$O(CH_2CH_2)_2NCOCl$	1.1	604	4.8–5.0	10	170	$(CF_3)_2NCOF$	34
						$O(CF_2CF_2)_2NCOF$	30
$CF_3CON(CH_3)_2$	...	569	4.8–5.2		...	CF_3COF	65
						$(CF_3)_2NCOF$	137
						$(CF_3CON(CF_3)_2$	48
$(CH_3)_2NCON(CH_3)_2$	1.1	196	4.6–4.9	8	56	$(CF_3)_2NCOF$	46
						$(CF_3)_2NCON(CF_3)_2$	10

[a] The highest yield of the perfluorocarbamyl fluoride (37% of theory) was obtained from a smaller run, in which 256 g. (2.38 moles) of $(CH_3)_2NCOCl$ gave 174 g. of $(CF_3)_2NCOF$. This particular run, which was made in a smaller (rated 20 ampere) cell, gave no indication of the distillation flat at 38–40° discussed below, and the carbamyl fluoride was essentially the only product boiling above Dry Ice temperatures. [b] Not recorded.

Anal. Calcd. for $C_4H_3F_6NO_2$: C, 22.7; H, 1.4; N, 6.6; mol. wt., 211. Found: C, 22.4; H, 1.5; N, 6.5; mol. wt., 211.

The 38–41° cut has not yet been identified. Its low molecular weight (213) and low fluorine content (53%), as well as the fact that it gives smaller but definite yields of $(CF_3)_2NCOOCH_3$ on treatment with methanol, indicate that it may be a mixture rather than a pure compound.

$HCON(CH_3)_2$ Run.—The crude cell product was found to boil almost completely (170 of 172 g.) at 15°. This material, mol. wt. 197, showed an absorption band at 5.36 μ. The NMR spectrum agreed with the proposed structure, $(CF_3)_2NCOF$. Reaction with ethanol gave the ester, b.p. 89°, $n^{25}D$ 1.3118.

Anal. Calcd. for $C_5H_5F_6NO_2$: C, 26.7; H, 2.2; F, 50.7; N, 6.2. Found: C, 27.5; H, 2.4; F, 48.0; N, 6.5.

$(C_2H_5)_2NCOCl$ Run.—The fraction of the crude cell product boiling at 43–48° represented 82% of the Dry Ice condensate; however, considerable fluorocarbon material was isolated also from the cell drainings, and had a boiling range as high as 200°. If this material is included in the material balance, the crude product weighed 730 g., of which 33% boiled at 46–48° and 5% at 14–17°, no other flats in the distillation curve being observed.

The 46–48° fraction, mol. wt. 299–302, showed no –COF band in the infrared spectrum and did not react with alcohols, 20% KOH or concd. H_2SO_4. After this treatment it had b.p. 47.5°, $n^{25}D$ 1.2590, d_{25} 1.685. The NMR spectrum agreed with the proposed oxazolidine structure, $CF_2OCF_2CF_2NC_2F_5$ (cyclic).

Anal. Calcd. for $C_5H_{11}NO$: C, 20.0; F, 69.7; N, 4.7; *MR*D, 28.6. Found: C, 20.0; F, 69.7; N, 3.6; *MR*D, 28.6 (using 1.1 as atomic refraction of F).

$(C_4H_9)_2NCOCl$ Run.–The weight of the crude cell drainings was 614 g., of which 39% had b.p. 128–135°. No attempt was made to isolate $(CF_3)_2NCOF$, which would have appeared in the cell overhead rather than in the drainings. The 128° fraction, after treatment with 25% aqueous base, had b.p. 132.5°, $n^{25}D$ 1.2851, d_{25} 1.809. The NMR spectrum was complex and indicated, as well as the expected CF_3, CF_2 and CF peaks, the presence of smaller amounts of CF_3N and/or NF_2 groups. A possible impurity is $(C_4F_9)_2NCF_3$, estimated b.p. 134°. Either a five- or six-membered ring is concordant with the results; the oxazolidine structure is preferred because of analogy with the perfluoro-3-ethyloxazolidine.

Anal. Calcd. for $C_9F_{19}NO$: C, 21.6; F, 72.4; N, 2.8; *MR*D, 49.18. Found: C, 21.9; F, 70.7; N, 2.8; *MR*D, 48.23.

$O(CH_2CH_2)_2NCOCl$ Run.—Seven hundred and fifty grams of crude product was obtained, divided equally in three parts: (A) overhead product, b.p. <25°, [B] overhead product, b.p. >25°, and (C) cell drainings. Distillation of C gave no flats and the b.p. rose slowly from 70 to 240°. The distillate reacted with aqueous alkali. Fractionation of A and B gave very poor results, with two-phase distillates and lack of b.p. constancy. The best flats were those at 13–14.5° and 45–48°.

The 13–21° fraction, mol. wt. 188–220, was allowed to react with methanol to give mainly the ester $(CF_3)_2NCOOCH_3$, b.p. 75–76°, mol. wt. 212, $n^{25}D$ 1.3014; values for known ester are b.p. 76°, mol. wt. 211, $n^{25}D$ 1.2997.

The 45–48° fraction showed the –COF absorption band at 5.35 μ, and was assumed to be $O(CF_2CF_2)_2NCOF$. The average value for nitrogen analysis agreed with theory but individual determinations were very erratic.

Anal. Calcd. for $C_5F_9O_2N$: F, 61.7; mol. wt., 277. Found: F, 61.6; mol. wt., 275.

$CF_3CON(CH_3)_2$ Run.—The crude cell product, 379 g., gave only the following flats on fractionation; b.p. < –25°, 17%; b.p. 11–13.5°, 36%; b.p. 25–26°, 13%.

The fraction of b.p. < –25°, mol. wt. 109–113, was thought to be CF_3COF, b.p. –59°, mol. wt. 116. Treatment with ethanol gave an ester having b.p. 58–62°, mol. wt. 144. $CF_3COOC_2H_5$ has b.p. 62°, mol. wt. 142.

The 25–26° fraction, b.p. on refractionation 29.5–30°, showed no –COF absorption band but did show that of —C=O, 5.56 μ. An NMR spectrum substantiated the proposed structure, $CF_3CON(CF_3)_2$.

Anal. Calcd. for C_3F_9ON: F, 68.7; mol. wt., 249. Found: F, 68.6 ± 0.2; mol. wt., 249.

$(CH_3)_2NCON(CH_3)_2$ Run.—Of the 147 g. of crude product, 110 g., or 75%, was contained in the 15–20° fraction. There was also a small flat at 60–63°.

The 15–20° fraction, mol. wt. 194–200, gave an infrared spectrum identical with that of known $(CF_3)_2NCOF$, mol. wt. 199.

The 60–63° fraction (flat 61°), $n^{25}D$ 1.2668, showed the infrared absorption band for —C=O but not for –COF. An NMR spectrum substantiated the proposed structure, $(CF_3)_2NCON(CF_3)_2$.

Anal. Calcd. for $C_5F_{12}ON_2$: C, 18.1; F, 68.7; mol. wt., 332. Found: C, 19.0; F, 68.0; mol. wt., 325–332.

Pyrolysis of $(CF_3)_2NCOF$.—The carbamyl fluoride was allowed to expand out of a pressure vessel and bubbler into a vacuum-dried and nitrogen-flushed 1″ nickel tube filled with nickel protruded packing and heated at 575° over a 12″ length. The flow rate was about 0.04 mole/hour. The effluent gases were condensed in successive Dry Ice–acetone and liquid air traps, the Dry Ice trap being made of copper since the COF_2 formed is very corrosive toward glass at elevated temperatures. When all the carbamyl fluoride had been run through, the system was flushed with dry nitrogen for several hours. Fractionation of the Dry Ice condensate gave $CF_3N{=}CF_2$, b.p. −33 to −31°, in 96% yield and 89% conversion. The liquid air condensate and forerun from the fractionation amounted to 97% of the theoretical COF_2. Both products gave the correct mol. wt. and the $CF_3N{=}CF_2$ showed the C=N absorption band at 5.53 μ. Haszeldine reports b.p. −33° and the C=N band at 5.54 μ for this compound.[4]

(4) D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 2532 (1955).

Acknowledgment.—Much credit is due to those who investigated the NMR spectra of these compounds, as such studies, where possible, constitute the most reliable method for unequivocal assignment of structure. With the exception of $CF_3CON(CF_3)_2$, which was done by Dr. H. S. Gutowsky of the University of Illinois, all NMR spectra were taken and analyzed by Norbert Muller and George F. Svatos.

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Perfluoroacrylonitrile and its Derivatives[1]

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The carbon–carbon double bond in $CF_2{=}CFCN$ has been found to be very susceptible to attack. Hydrolysis with sulfuric acid yielded monofluoromalonic acid rather than perfluoroacrylic acid. Almost complete conversion of the fluorine in the molecule to fluoride ion occurred in the presence of aqueous base. Methanol added across the double bond in the absence of a catalyst to yield CH_3OCF_2CFHCN. When $CF_2{=}CFCN$ was heated in the presence of a catalyst, a dimer was formed. Butadiene-1,3 and $CF_2{=}CFCN$ reacted to yield $C_7H_6F_3N$. Bromination of $CF_2{=}CFCN$ give a high yield of $CF_2BrCFBrCN$. Many of the classical reactions of the nitrile group could be carried out if the C=C was protected by the prior addition of bromine.

Earlier publications from these laboratories have reported on the chemical reactivity of perfluoroolefins, $CF_2{=}CF{-}R_f$,[3,4] and the fluorohaloölefins, $CF_2{=}CFX$.[5,6] The compound perfluoroacrylonitrile contains the $CF_2{=}CF{-}$ structure conjugated with the nitrile group. This unsaturated nitrile has been prepared and the chemistry of both the $CF_2{=}CF{-}$ and $-CN$ molecular groupings investigated.

Chaney[7] had prepared this monomer *via* a sequence of reactions which began with the conversion of $CF_2ClCF{=}CCl_2$ to $CF_2ClCFClCOCl$. He observed that the olefinic bond in $CF_2{=}CFCN$ was very susceptible to nucleophilic attack; alcohols added in the absence of a catalyst to yield R_HOCF_2CFHCN. Henne and Fox[8] prepared perfluoroacrylic acid from the same fluorochloropropene.

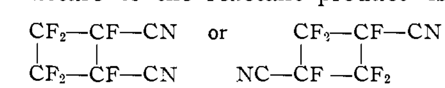
The methods of synthesis of perfluoroacrylonitrile emphasized in the present investigation used readily available starting materials. The following reaction sequence gave a 25% over-all yield

$$CF_2{=}CFCl + ICl \longrightarrow CF_2ClCFClI \xrightarrow{2C_2H_4} CF_2ClCFClCH_2CH_2I \xrightarrow{\text{base}} CF_2ClCFClCH{=}CH_2 \xrightarrow{KMnO_4} CF_2ClCFClCO_2H \longrightarrow$$

$$CF_2ClCFClCO_2C_2H_5 \longrightarrow CF_2ClCFClCONH_2 \longrightarrow CF_2ClCFClCN \longrightarrow CF_2{=}CFCN$$

Another method reported earlier[9] involved the conversion of CF_3CFHCN to $CF_2{=}CFCN$. The CF_3CFHCN was prepared by the addition of ammonia to perfluoropropene.[10]

Some reactions of $CF_2{=}CFCN$ left the nitrile group intact. A reaction with methanol occurred in the absence of any catalyst to give the ether, CH_3OCF_2CFHCN. Bromination of $CF_2{=}CF{-}CN$ took place under mild conditions to give $CF_2BrCFBrCN$. In the presence of catalytic amounts of Terpene B, dimerization of $CF_2{=}CFCN$ occurred. The structure of the reactant product is either



or a mixture of these two compounds. The dimer of perfluoroacrylonitrile and 1,3-butadiene was obtained by heating the two reactants under pressure. The structure of this dimer has not been determined.

Perfluoroacrylonitrile is decomposed in both aqueous base and aqueous acid. The bulk of the fluorine in $CF_2{=}CFCN$ was recovered as fluoride ion when this compound was sealed in an ampoule with aqueous base. In the presence of H_2SO_4, monofluoromalonic acid was formed. It is postulated that the compound $HOCF_2CFHFCO_2H$ is probably an intermediate in this reaction.

To obtain derivatives of $CF_2{=}CFCN$ it was found necessary to protect the olefinic bond during the conversion of the nitrile group. The dibromide was used successfully for this purpose. The amide, $CF_2BrCFBrCONH_2$, was prepared by hydrolyzing

(1) Presented before the Symposium on Fluorine Chemistry, 126th Meeting of the American Chemical Society, New York, N. Y., 1954.

(2) To whom requests for reprints should be sent: Fluorochemicals Division, Minnesota Mining and Manufacturing Co., St. Paul, Minn.

(3) T. J. Brice, J. D. LaZerte, L. J. Hals and W. H. Pearlson, THIS JOURNAL, **75**, 2698 (1953).

(4) J. D. LaZerte and R. J. Koshar, *ibid.*, **77**, 910 (1955).

(5) J. D. Park, D. K. Vail, K. R. Lea and J. R. Lacher, *ibid.*, **70**, 1550 (1948).

(6) J. D. Park, M. L. Sharrah and J. R. Lacher, *ibid.*, **71**, 2339 (1949).

(7) D. W. Chaney, U. S. Patents 2,439,505 (April 13, 1948), 2,443,-024 (June 8, 1948) and 2,456,768 (December 21, 1948).

(8) A. L. Henne and C. J. Fox, THIS JOURNAL, **76**, 479 (1954).

(9) J. D. LaZerte, W. H. Pearlson, J. L. Rendall and T. J. Brice, presented before the Fluorine Chemistry Symposium, 120th meeting of the American Chemical Society, New York, N. Y., 1951.

(10) J. D. LaZerte, U. S. Patent 2,704,769 (March 22, 1955).