tion under reduced pressure, and the green powder was suspended in 10 ml. of dry petroleum ether (b.p. 60–68°). To this was added 1.0 ml. (0.003 mole) of uranium(VI) ethoxide. The green solid slowly disappeared and a brown solution was formed. After removal of the petroleum ether by evaporation, the residual brown liquid was distilled giving 2.5 g. (78% yield) of uranium(V) ethoxide identified by boiling point and analysis.

AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

Reactions of Perfluoronitriles. I. Synthesis of Derivatives of Perfluoroamidines, N-Substituted Perfluoroamidines and Perfluorothioamides[1,2]

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Trifluoroacetonitrile, pentafluoropropionitrile and heptafluorobutyronitrile react with alkyl amines to produce N-alkyl perfluoroamidines and with hydrogen sulfide to give perfluorothioamides. Perfluoroamidines, which result from the reaction of perfluoronitriles with ammonia, react with silver oxide or mercuric oxide to form salts and also with hydrogen sulfide to give perfluorothioamides.

The strong electronegative effect of the fluorocarbon group in the perfluoronitriles has been found to increase considerably the reactivity at the carbon to nitrogen unsaturated linkage in these compounds, presumably by increasing the positive character of the carbon site. This condition has produced a reactivity different from that of organic nitriles that do not contain a fluorocarbon group and the products of several types of reactions have properties that are not found in the organic analog.

This paper describes the reactions of three perfluoronitriles with primary and secondary amines to produce N-alkyl perfluoroamidines and with hydrogen sulfide to produce perfluorothioamides. Modification of the procedure reported by Husted[3] for the preparation of the free perfluoroamidines is presented with some derivatives formed by these unusual compounds.

N-Alkyl substituted perfluoroamidines were prepared from the perfluoronitriles with primary and secondary alkyl amines. The properties of these compounds are shown in Table I. Although the primary and secondary alkyl amines reacted rapidly with the perfluoronitriles at the reflux temperature of the mixture, aromatic amines, for example, aniline, did not react even at a higher temperature. This indicates that the basicity of the amine is an important consideration in this reaction. Aniline, being a weaker base than either ammonia or alkyl amines, would furnish a relatively poor anionoid nitrogen to take part in the formation of the substituted amidine.

The perfluoroamidines are sufficiently acidic to form certain metallic salts. The silver and mercury salts shown in Table I are white crystalline solids that decompose on heating. The perfluoroamidines appear to function as monoprotic acids since in no case did the analyses indicate that more than one hydrogen was replaced by silver or mercury.

Basic properties are shown by the perfluoroamidines in their ability to form salts with inorganic, organic and perfluoroacids in anhydrous organic solvents. Salts prepared by reaction of perfluoroamidines with acetic and heptafluorobutyric acids are shown in Table I.

Acylation of the perfluoroamidines proceeds readily to form the N-acyl derivatives. Two tautomeric products are possible from this reaction

$$R_FC(:NH)NH_2 + RCOCl \longrightarrow \begin{cases} R_FC(=NH)NHC(O)R & \text{I} \\ R_FC(NH_2)=N-C(O)R & \text{II} \end{cases}$$

The complete structure of the acylated product has not been defined. Structure I might be expected to be acidic and to hydrolyze to the secondary amide III while Structure II would probably be a very weak acid or neutral molecule and

$$R_FC(:O)NHC(:O)R \quad \text{III} \qquad R_FC(:O)NH_2 + RC(:O)NH_2 \quad \text{IV}$$

hydrolyze to a mixture of amides IV. Actually, the N-benzoyl derivative of perfluorobutyramidine is a neutral compound insoluble in aqueous alkali. The acetyl derivative of $C_3F_7C(NH)NH_2$ was easily hydrolyzed by aqueous base to form perfluorobutyramide and acetamide. These properties suggest that even if a tautomeric equilibrium is operative, structure II is the reactive form in basic hydrolysis.

Perfluorothioamides were prepared by the reaction of hydrogen sulfide with either the perfluoronitrile or the perfluoroamidine and are shown in Table I. The reaction of the perfluoronitriles with hydrogen sulfide at room temperature was vigorous; in the synthesis of perfluorothioacetamide from perfluoroacetonitrile and hydrogen sulfide, the reactants were maintained at 0° to prevent charring. Preparation of the perfluorothioamides from the respective amidines was carried out in ethyl ether with good yields. These com-

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(2) This work was supported by the Office of Naval Research under Contract Nonr580(03); NR 356-333 with the University of Florida.

(3) D. Husted, U. S. Patent 2,676,985 (April, 1954).

TABLE I

Compound	B.p., °C.	M.p., °C.	d^{25}	$n^{25}D$	Nitrogen, % Calcd.	Nitrogen, % Found	Calcd.	Found
$CF_3C(:NH)NHCH_3$	47–48 (21 mm.)		1.2909	1.3919	22.20	21.85		
$CF_3C(:NH)N(CH_3)_2$	92		1.1795	1.3812	20.01	19.72		
$C_2F_5C(:NH)NHCH_3$	126		1.4258	1.3664	15.91	15.63		
$C_2F_5C(:NH)N(CH_3)_2$	110		1.2969	1.3678	14.75	14.43		
$C_3F_7C(:NH)NHCH_3$	137		1.5140	1.3561	12.37	12.02		
$C_3F_7C(:NH)N(CH_3)_2$	120		1.4242	1.3548	11.66	11.41		
$CF_3C(:NH)NHAg$		200 dec.			12.71	12.28	48.78[a]	48.40
$C_2F_5C(:NH)NHAg$		240 dec.			10.36	10.27	40.02[a]	40.38
$C_3F_7C(:NH)NHAg$		277 dec.			8.74	8.50	33.60[a]	32.86
$(C_2F_5C(:NH)NH)_2Hg$		159 dec.			10.65	10.22	38.38[a]	38.20
$(C_3F_7C(:NH)NH)_2Hg$		178 dec.			9.00	8.42	32.31[a]	32.60
$CF_3C(:NH)NH_2\cdot CH_3COOH$		Subl.			16.29	15.94	172[b]	174
$CF_3C(:NH)NH_2\cdot C_3F_7COOH$		Subl.			8.58	8.80	326[b]	323
$C_3F_7C(:NH)NH_2\cdot CH_3COOH$		Subl.			10.20	10.26	272[b]	277
$C_3F_7C(:NH)NH_2\cdot C_3F_7COOH$		Subl.			6.58	6.43	426[b]	420
$CF_3C(:S)NH_2$	40 (2 mm.)				10.82	10.85	24.78[c]	25.13
$C_2F_5C(:S)NH_2$	60 (23 mm.)	39–40			7.82	7.53	17.88[c]	18.18
$C_3F_7C(:S)NH_2$	69 (21 mm.)	47–48			62.1	6.01	13.97[c]	13.90

[a] Silver (mercury), %. [b] Neut. equiv. [c] Sulfur, %.

pounds are pale yellow solids or liquids and may be stored in sealed vials without decomposition.

Experimental

Trifluoroacetonitrile, Pentafluoropropionitrile and Heptafluorobutyronitrile.—These compounds were prepared by dehydration of the perfluoroamides as described by Swarts[4] and by Gilman and Jones.[5]

N-Methylperfluoroacetamidine.—Into an 80-ml. cylindrical glass flask immersed in a Dry Ice–acetone bath and fitted with a delivery tube and Dry Ice cooled reflux condenser was condensed 11.2 g. (0.1 mole) of trifluoroacetonitrile; 6.2 g. (0.2 mole) of methylamine was added and the mixture allowed to reflux under a Dry Ice condenser for one hour. Excess amine was distilled from the mixture and the remaining high boiling liquid fractionated under reduced pressure to yield 14 g. of N-methylperfluoroacetamidine, b.p. 35–36° at 11 mm.

The other N-alkyl perfluoroacetamidines shown in Table I were prepared in the same manner and in comparable yields. All of this series could be fractionated at atmospheric pressure with the exception of the N-methyltrifluoroacetamidine as described above.

Trifluoroacetamidine.[3]—Trifluoroacetonitrile, 17.0 g. (0.18 mole), was condensed in an apparatus similar to that described above for the preparation of N-methylperfluoroamidine. A large excess of anhydrous ammonia was condensed in the reaction vessel, the Dry Ice–acetone bath removed, and the mixture of ammonia and nitrile allowed to reflux for one hour. Excess ammonia was then removed by distillation and the product fractionated under reduced pressure in a small column packed with glass helices to yield 17.5 g. of trifluoroacetamidine, b.p. 35–36° (11 mm.), $n^{25}D$ 1.3801, d^{25} 1.4940.

Pentafluoropropionamidine and heptafluorobutyramidine were produced by this same procedure in 95 and 75% yields, respectively. These compounds are low melting solids and were recrystallized from an ethyl ether–petroleum ether mixture. They were found not to be hygroscopic if completely free of ammonia.

Silver Salts of Trifluoroacetamidine.—Silver oxide, 4.60 g. (0.020 mole), was added slowly to 5 g. (0.044 mole) of trifluoroacetamidine dissolved in 15 ml. of anhydrous ethyl ether. An immediate evolution of heat was noted with the formation of an insoluble white solid. The mixture was stirred vigorously to break up any lumps of silver oxide. When the black silver oxide was consumed, the white solid was filtered, washed with ethyl ether and dried to give slightly less than a quantitative yield of the silver salt of trifluoroacetamidine, $CF_3C(NH)NHAg$. This salt decomposed on heating at 200° (Table I).

Silver salts of pentafluoropropionamidine and of heptafluorobutyramidine were prepared in the same manner.

Mercury Salt of Heptafluorobutyramidine.—In a test-tube immersed in an oil-bath was placed an intimate mixture of 10 g. (0.046 mole) of heptafluorobutyramidine, $C_3F_7C(NH)NH_2$ and 5 g. (0.023 mole) of mercuric oxide. The mixture was heated to 110° to melt the amidine, then stirred vigorously. The formation of the white mercury salt could be noted and was essentially complete in 2 hours. The melt was cooled and unreacted amidine removed by continuous extraction with ethyl ether. Unreacted mercuric oxide was removed by centrifugation of a suspension of the powdered reaction product in ethyl ether. The heavier mercuric oxide settled first leaving the upper layer as essentially the mercury salt of the amidine. A number of centrifugations produced a low yield of the pure mercury salt of heptafluorobutyramidine, $(C_3F_7C(NH)NH)_2Hg$, a white solid that decomposed on heating at 178° (Table I).

The mercury salt of pentafluoropropionamidine was prepared by this same procedure. Trifluoroacetamidine could not be used in this reaction since it was not sufficiently stable at elevated temperatures.

The Trifluoroacetic Acid Derivative of Heptafluorobutyramidine.—To 15 ml. of trifluoroacetic acid was added 5.3 g. (0.025 mole) of heptafluorobutyramidine, $C_3F_7C(NH)NH_2$. The clear solution was allowed to stand one hour; the excess trifluoroacetic acid was then removed under reduced pressure. The remaining white solid was purified by sublimation to give 6.8 g. of the acid derivative of heptafluorobutyramidine, $C_3H_7C(NH)NH_2\cdot CF_3COOH$ (Table I.).

The other organic and perfluoro acid derivatives were prepared by a similar procedure in 75–85% yields.

N-Benzoylheptafluorobutyramidine.—A solution of 24.6 g. (0.174 mole) of benzoyl chloride in ether was placed in a flask protected from atmospheric moisture by drying tubes. The contents of the flask were cooled to 0° and a solution of 37 g. (0.174 mole) of heptafluorobutyramidine in ether was slowly added with stirring. Evolution of hydrogen chloride was noted and this produced a white precipitate of heptafluorobutyramidine hydrochloride. The flask was allowed to warm to room temperature and 23 g. of the hydrochloride removed by filtration. Dilution of the ethereal solution with petroleum ether and cooling precipitated 20 g. of N-benzoylheptafluorobutyramidine. After recrystallization from ethyl ether–petroleum ether, this product melted at 63°.

Anal. Calcd. for $C_{11}F_7H_7N_2O$: N, 8.86. Found: N, 8.58.

Heptafluorothiobutyramide.—A. From Heptafluorobutyronitrile.—Into an evacuated heavy walled Pyrex glass tube of approximately 60-ml. capacity, previously constricted for sealing, was condensed 6.8 g. (0.035 mole) of perfluorobutyronitrile, C_3F_7CN, and 3.4 g. (0.10 mole) of hydrogen sulfide. The tube was sealed, allowed to

(4) F. Swarts, *Bull. class. sci. acad. roy. Belg.*, [5] **12**, 692 (1926).

(5) H. Gilman and R. G. Jones, THIS JOURNAL, **65**, 1458 (1943).

remain at room temperature overnight, then opened and the volatile material removed. The remaining product was a pale yellow solid that was recrystallized from ether–petroleum ether to yield 6.3 g. of heptafluorothiobutyramide, $C_3F_7C(S)NH_2$, m.p. 49° (Table I).

Pentafluorothiopropionamide was prepared in the same manner from pentafluoropropionitrile and hydrogen sulfide at room temperature. For preparation of trifluorothioacetamide the reaction was moderated by cooling to 0° to prevent charring. This reaction could also be moderated by the use of ethyl ether as a solvent but reaction time was increased to 125 hours.

Heptafluorothiobutyramide.—B. From Heptafluorobutyramidine.—In a flask fitted with a delivery tube and protected by drying tubes was placed 15 g. (0.071 mole) of heptafluorobutyramidine dissolved in 25 ml. of ethyl ether. The solution was saturated with hydrogen sulfide and allowed to stand one hour. The ether was removed under reduced pressure and the remaining high boiling liquid fractionated under reduced pressure to yield 12 g. of a distillate that crystallized on cooling. Recrystallization from ether–petroleum ether gave heptafluorothiobutyramide, $C_3F_7C(S)NH_2$, yellow needles, m.p. 47–48°.

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[CONTRIBUTION FROM THE ILLINOIS STATE GEOLOGICAL SURVEY]

Aromatic Fluorine Compounds. VII. Replacement of Aromatic –Cl and $-NO_2$ Groups by –F[1,2]

BY G. C. FINGER AND C. W. KRUSE

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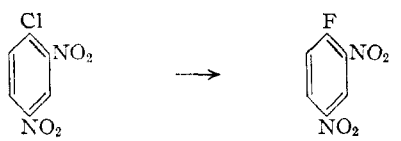
Replacement of –Cl by –F in aryl chlorides with potassium fluoride has been extended from 2,4-dinitrochlorobenzene to less activated halides by the use of non-aqueous solvents, especially dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). Also replacement of $-NO_2$ by –F in substituted nitrobenzenes was studied in DMF. As a direct result of this study, many aromatic fluorine compounds can now be obtained by a relatively simple synthetic route.

Unactivated aryl halides do not undergo Swarts-type organic halide–inorganic fluoride exchange reactions which are common with aliphatic and acyl halides.[3,4] Activation by at least two nitro groups has generally been considered necessary for exchange between aryl halides and fluoride ion.[5a] An outstanding example of such an exchange is the replacement of chlorine by fluorine in 2,4-dinitrochlorobenzene with anhydrous potassium fluoride at 190–205° in nitrobenzene solvent.[6,7]



A preliminary experiment has shown that even without a solvent the above reaction takes place at 200–230°. However, solvent studies with other non-aqueous solvents show a significant increase in reaction rate. The preceding reaction proceeds quite smoothly at steam-bath temperature in dimethylformamide (DMF) or dimethyl sulfoxide (DMSO). The accelerating effect of various solvents upon aryl halide–fluoride ion exchanges is emphasized by Table I. The decreasing reaction rates, as reflected by the longer time and higher temperatures, parallel the decreased activation from 2,4-dinitrochlorobenzene to 4-nitrochlorobenzene. Thus, aromatic halogen exchange reactions have been extended from the highly activated dinitrohalobenzenes to the moderately activated mononitrohalobenzenes by the solvent studies.

TABLE I

REPLACEMENT OF AROMATIC –Cl BY –F

Reactant[a] (subst. $C_6H_3NO_2$)	Solvent	Time, hr.	Temp., °C.	Yield, % of fluoro analog	Expt. ref.
	$C_6H_5NO_2$	4	195–210	76	I-1
	No solvent	0.5	200–230	62[b]	I-2
	C_6H_5CN	2	150–170	57[b]	I-3
3-NO_2-**4**-Cl–	$(CH_2CN)_2$	0.5	125–140	81[b]	I-4
	DMF	0.5	140–150	77	I-5
	DMF	13	95–100	77	I-6
	DMSO	2.5	95–100	78	I-7
3-CF_3-**4**-Cl–	DMF	4	160	81	II
2-Cl-5-CF_3–	DMF	3.5	160	76	III
2-Cl-5-CH_3OCO–	DMF	4	155	67	IV
2,4,6-Cl_3–	DMSO	2	175–180	10	V
2,5-F_2-**4**-Cl–	DMSO	2	170–175	45	VI
2,3,4-Cl_3–	DMSO	4	180–190	23	VII
2,4-Cl_2–	DMSO	6	180	47	VIII
2-Cl–	DMF	163	170	40[c]	IX-1
	DMSO	4.5	185	38	IX-2
4-Cl–	DMSO	14	190	72	X

[a] Group replaced is set in bold type. [b] Contaminated with chloro isomer. Vacuum fractionation was ineffective for the separation of these isomers, therefore yields were estimated by index of refraction which was found to have a near linear relationship for mixtures of 2,4-dinitrochloro- and 2,4-dinitrofluorobenzenes. Values determined from known mixtures for weight-per cent. of chloro isomer *vs.* $n^{20}D$ were 80.4%-1.5952, 54.9%-1.5866 and 23.12%-1.5764. [c] Estimated.

Brown fumes and traces of lower boiling products observed in the 2,4-dinitrohalobenzene studies suggested the possibility of some $-NO_2$ replacement. Earlier investigators[6,7] make no mention of such observations. Such a reaction appeared reasonable as properly activated nitro groups can be replaced by other nucleophilic reagents, as, for example, the replacement of $-NO_2$ by $-OCH_3$ in 2,3,5,6-tetrachloronitrobenzene.[8] Conclusive evi-

(1) Presented in part before the Organic Division, 129th Meeting of the American Chemical Society, April, 1956, Dallas, Texas. This research was supported in part by the United States Air Force under Contract No. AF 18(600)-985, monitored by the AF Office of Scientific Research of the Air Research and Development Command.

(2) Published by permission of the Chief of the Illinois State Geological Survey.

(3) "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, Ch. 2, p. 49.

(4) F. L. M. Pattison, *Nature*, **174**, 740 (1954).

(5) (a) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 277 (1951); (b) p. 315.

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(8) V. S.F. Berckmans and A. F. Holleman, *Rec. trav. chim.*, **44**, 851 (1925).