many samples of the urea. Vacuum sublimation at *ca.* 60° can be used to reduce these inclusions.[28]

Reaction of Tris(difluoramino)methyl Isocyanate with Pyridine.—The 18-ml reactor had two arms, one of which was attached by means of a special ring joint and a Viton-A O ring.[29] Pyridine (0.31 mmol) was dissolved in *ca.* 0.5 ml of anhydrous acetonitrile, which was added by vacuum transfer. The isocyanate (0.64 mmol) was then condensed in at −196°, and the mixture was stirred for 1.5 hr at 0°. The excess isocyanate and acetonitrile were removed under vacuum at −23°, and the residue was sublimed at room temperature into the detachable arm in 94% yield, calculated for a 1:1 adduct, $\nu_{max}^{mineral\ oil}$ 1770 cm^{-1} (C=O). The product was stored at −80° and handled in a dry atmosphere, since it is very hygroscopic and discolors at room temperature.

Anal. Calcd for $C_7H_5F_6N_5O$: F, 39.43. Found: F, 37.95.

Another reaction between pyridine and a 100% excess of isocyanate was run without solvent at −23°. Intermittent mixing was effected by transfers of the reaction mixture back and forth between the two arms of the above reactor and by periodic condensation of the unchanged isocyanate onto the solid product. The infrared spectrum of the solid product was the same as that of the product prepared in acetonitrile solution.

^{19}F nmr spectra of the following samples in acetonitrile solution were obtained: the isocyanate (−30.6 ppm); various mixtures of the isocyanate and pyridine after reaction for 2.25 hr at −23° without solvent (0.11 mol pyridine per mol isocyanate) (−29.7 ppm), 0.20 (−29.6 ppm), 0.49 (−28.5 ppm); the 1:1 adduct (−26.7 ppm) prepared in acetonitrile from 0.6 mmol of isocyanate and 0.5 mmol of pyridine followed by removal of the excess isocyanate and solvent under vacuum at −23°. Acetonitrile and nmr standards were added by vacuum transfer to the above samples.

***N*,*N*-Dimethyl-*N'*-tris(difluoramino)methylformamidine (8).**—A 6-ml reactor was charged in a glove bag under a nitrogen atmosphere with 73 μl (0.94 mmol) of dimethylformamide. The dimethylformamide had been distilled twice in a dry apparatus from phosphorus pentoxide at atmospheric pressure. The reactor was then cooled to −196° and evacuated, and 0.94 mmol of tris(difluoramino)methyl isocyanate was added by vacuum transfer. The liquid nitrogen bath was removed and, as soon as the frost on the outside of the reactor had melted, magnetic stirring was started. The reaction mixture was stirred for 2.5 hr and allowed to stand at room temperature for an additional 21 hr.

A fraction which was volatile at room temperature was removed from the reactor by vacuum transfer. It amounted to 0.88 mmol and was 95% carbon dioxide (0.84 mmol, 89% of theory) according to mass spectrometric analysis.

The residue remaining in the reactor consisted of a liquid and a small amount of white solid. A solution of the liquid in 1.5 ml of reagent grade carbon tetrachloride was washed three times with 0.5-ml portions of deionized water. Centrifugation helped separate the liquid layers, and the bottom (carbon tetrachloride) layer was withdrawn by pipette. The carbon tetrachloride solution was dried with anhydrous sodium sulfate, and the sodium sulfate was rinsed with 0.2 ml of carbon tetrachloride. The formamidine was obtained as a colorless liquid residue by removal of the more volatile carbon tetrachloride, ν_{max} 1639 cm^{-1} (C=N),[9a] ^1H nmr 2.04 (1 H, somewhat broadened, −N=CH−), 6.91 and 6.97 (6 H, overlapping, nonequivalent methyl groups).

Anal. Calcd for $C_4H_7F_6N_5$: F, 47.67. Found: F, 47.62.

Registry No.—**3,** 37950-73-5; **4,** 37950-74-6; **6,** 37950-75-7; **7,** 37950-76-8; **8,** 37950-77-9; methyl tris(difluoramino)methylcarbamate, 37950-78-0; ethylene *N*,*N'*-bis[tris(difluoramino)methyl]dicarbamate, 37950-79-1; allyl tris(difluoramino)methylcarbamate, 37950-80-4; 2,3-epoxypropyl tris(difluoramino)methylcarbamate, 37950-81-5; tris(difluoramino)methylurea, 37950-82-6; tris(difluoramino)methylurea perchlorate, 37950-83-7; adduct of pyridine and tris(difluoramino)methyl isocyanate, 37950-84-8; **1,** 37950-70-2.

Acknowledgment.—It is a pleasure to acknowledge the contributions of the following persons: Dr. J. E. Lancaster and Mrs. M. Neglia determined the nmr spectra; Mr. J. H. Deonarine and staff carried out the elemental analyses; Mr. R. C. Bell and staff prepared the isocyanate; Dr. V. P. Wystrach provided helpful consultations.

---

[28] Work done by A. J. Fanelli, R. F. Phillips, and E. J. Schriffert of these laboratories.

[29] Delmar Scientific Laboratories, Inc., Maywood, Ill.

Fluorinations in the Presence of Sodium Fluoride. Preparation of Tetrakis(difluoramino)methane

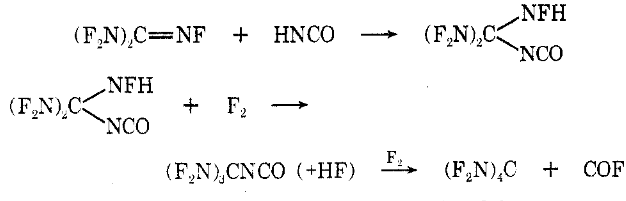
WILLIAM C. FIRTH, JR.,* SIMON FRANK, AND M. D. MEYERS

American Cyanamid Company,[1] Central Research Division, Stamford, Connecticut 06904

Received September 26, 1972

Fluorination of bis(difluoramino)fluoraminomethyl isocyanate, $(F_2N)_2C(NFH)NCO$, with elemental fluorine in the presence of sodium fluoride gave tetrakis(difluoramino)methane. In the absence of sodium fluoride the product was tris(difluoramino)methyl isocyanate. Sodium fluoride similarly induced fluorinations of isocyanic acid and pentafluoroguanidine. Tetrakis(difluoramino)methane is a liquid, bp 40.2°, mp −13°. The ir spectrum, mass spectrum, vapor pressure, heat of fusion, and density are also reported.

As part of a program on the synthesis of CNF_2 oxidizers, we wished to synthesize tetrakis(difluoramino)methane, $(F_2N)_4C$, because of its extraordinarily high content of NF_2 oxidizing groups and unusual carbon tetranitrogen skeleton. Our synthetic approach was to add isocyanic acid to pentafluoroguanidine and then fluorinate the adduct.[2]



$$(F_2N)_2C{=}NF + HNCO \longrightarrow (F_2N)_2C(NFH)(NCO)$$

$$(F_2N)_2C(NFH)(NCO) + F_2 \longrightarrow (F_2N)_3CNCO\ (+HF) \xrightarrow{F_2} (F_2N)_4C + COF_2$$

In the fluorination, liquid pentafluoroguanidine–isocyanic acid adduct at 0° was entrained by a stream of fluorine diluted with helium and passed in the vapor phase through sodium fluoride pellets to remove the expected hydrogen fluoride. The products were condensed at −196°, separated by fractional codistillation,[3] and analyzed by infrared spectroscopy. Both

---

[1] This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, with monitoring by the Bureau of Naval Weapons, RMMP, under Contract NOrd 18728.

[2] W. C. Firth, Jr., S. Frank, and E. J. Schriffert, *J. Org. Chem.*, **38**, 1080 (1973). Tetrakis(difluoramino)methane has also been synthesized by addition of ammonia to pentafluoroguanidine followed by fluorination: C. D. Wright and J. L. Zollinger, *J. Org. Chem.*, **38**, 1075 (1973).

[3] G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

tetrakis(difluoramino)methane and tris(difluoramino)methyl isocyanate were formed in this reaction.

Subsequently it was discovered that formation of tetrakis(difluoramino)methane depended upon the presence in the fluorination apparatus of sodium fluoride. If sodium fluoride was omitted, fluorination stopped with formation of tris(difluoramino)methyl isocyanate. This effect of sodium fluoride can be used to control the fluorination to give either the isocyanate or tetrakis(difluoramino)methane to the essential exclusion of the undesired product, as shown in Table I.

TABLE I

FLUORINATIONS

Compd, mmol	NaF	Time, min	Yield, %	
			$(F_2N)_3NCO$	$(F_2N)_4C$
$(F_2N)_2C(NFH)NCO$, 2.4–2.9	No	45–50	75–88	0
$(F_2N)_2C(NFH)NCO$, 1.4	Yes	30	0	92
$(F_2N)_3CNCO$, 0.5	Yes	17		80

The effect of NaF on the course of this fluorination suggested the idea of fluorinating isocyanic acid by the new technique. Surprisingly, no reaction occurred in the absence of NaF pellets. However, when fluorine gas (14% in He) was passed over liquid HNCO (at −78°) and then through NaF pellets at 25°, smooth fluorination gave the expected end products.

$$HN{=}C{=}O \xrightarrow{F_2\text{–}He} [N.R.] \xrightarrow[25°]{NaF} NF_3 + F_2C{=}O + HF \text{ (as } SiF_4)$$

Another example of this catalytic effect of NaF in these vapor-phase fluorinations was the successful fluorination of pentafluoroguanidine, otherwise not reactive to fluorine, to give an 82% yield of tris(difluoramino)fluoromethane.[4]

$$(F_2N)_2C{=}NF \xrightarrow[24°]{27\%\ F_2/NaF} (F_2N)_3CF + \text{small amounts of } CF_4,\ NF_3$$

Tetrakis(difluoramino)methane, the perfluoro analog of tetranitromethane, is a colorless liquid, stable to storage in glass, and unreactive at room temperature with mercury, water, anhydrous calcium sulfate, or mineral oil. The compound was unchanged after 4 hr at 70° in the liquid phase in a glass capillary. Its physical properties are summarized in Table II.

The fluorine nmr signal at ϕ^{*5} −29.5 is in the expected region.[6]

The mass spectrum does not show the parent m/e 220 peak. Instead the largest mass corresponds to the parent peak after loss of NF_2, a common situation with CNF_2 compounds.

TABLE II

PHYSICAL PROPERTIES OF TETRAKIS(DIFLUORAMINO)METHANE

^{19}F nmr: single, broad peak at ϕ^* −29.5

Ir spectrum: 1120 (m), 1060 (w), 980 (s), 950 (s), and 910 cm^{-1} (s)

Mass spectrum (most abundant m/e's): 168, 97, 64, 52

Vapor pressure: $\log P\,(\text{mm}) = 6.8640 - 1096.1/(234.7 + T, °\text{C})$ (0–70°)

Boiling point: 40.2°

$\Delta H°_{vap}$: 6.61 kcal/mol at 25°

$\Delta S°_{vap}$: 18.68 cal/mol deg at 25°

Melting point: −13°

ΔH_{fusion}: 850 cal/mol

Density: $\rho = 1.8053 - 1.9815 \times 10^{-3}\,T - 13.9275 \times 10^{-6}\,T^2 + 6.623 \times 10^{-8}\,T^3$ (T in °C over the range 0–60°); 1.748 g/ml at 25°

The five main infrared absorptions are reasonable for a compound of this type. Probable assignments based upon comparison with difluorocyanamide[7] are NF_2 out-of-phase stretching at 910 cm^{-1}; NF_2 in-phase stretching plus CN stretching at 950, 980, and 1060 cm^{-1}; and NCN out-of-phase stretching at 1120 cm^{-1}.

Experimental Section

Caution.—The NF compounds are extremely sensitive explosives and strong oxidizing agents. Further details on the handling of these compounds and the general experimental techniques used have been described elsewhere.[2]

Fluorination of Bis(difluoramino)fluoraminomethyl Isocyanate.—The fluorinations were conveniently carried out by passing a stream of F_2 (16 cc/min) diluted with He (50 cc/min) into a simple glass reaction train consisting of three 70-ml U tubes and a cold trap connected in series. The first U tube contained liquid bis(difluoramino)fluoraminomethyl isocyanate and was cooled in a 0° bath. The second U tube was left empty or filled with NaF pellets, depending on whether tris(difluoramino)methyl isocyanate or tetrakis(difluoramino)methane, respectively, was desired. The product was trapped out in the third U tube at −196°.

After a simple vacuum line fractionation to remove by-products such as SiF_4 and COF_2, which can be volatilized at −78°, the products were purified by fractional codistillation.[3] The purification and properties of the isocyanate are described elsewhere.[2,6]

Anal. Calcd for CN_4F_8: C, 5.46; N, 25.46; F, 69.08. Found: C, 5.4; N, 25.0; F, 68.6.

Registry No.—Tetrakis(difluoramino)methane, 17125-65-4.

Acknowledgment.—We wish to thank Dr. J. E. Lancaster and Mrs. M. Neglia for the nmr spectrum, Mr. J. H. Deonarine and staff of our Research Service Department for the elemental analyses, Dr. R. S. Kolat and Dr. J. J. Keavney for determinations of physical properties, and Mr. N. B. Colthup for assistance in the interpretation of the ir spectrum. The encouragement of Dr. V. P. Wystrach is appreciated.

---

[4] R. J. Koshar, D. R. Husted, and C. D. Wright, *J. Org. Chem.*, **32**, 3859 (1967).

[5] G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

[6] W. C. Firth, Jr., and S. Frank, *J. Org. Chem.*, **38**, 1083 (1973).

[7] N. B. Colthup, *Spectrochim. Acta, Part A*, **23**, 2167 (1967).