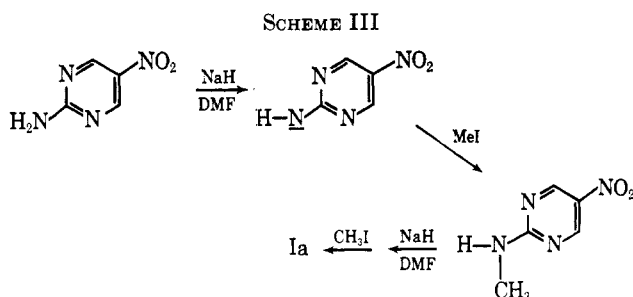


Figure 3.—Mass spectrum of III.

synthesis," proving that methylation of the exocyclic nitrogen had occurred (Scheme III).



The synthesis of III was readily accomplished by the catalytic reduction of Ia to 5-amino-2-dimethylaminopyrimidine and reaction of the latter with benzenesulfonyl chloride in pyridine solution.

### Experimental Section

Spectra were taken on an Atlas CH<sub>4</sub> mass spectrometer at an ionization potential of 70 eV and ionizing current of 20  $\mu$ A. Samples were introduced by the direct inlet system. Melting points were determined on a Fischer hot stage and are uncorrected. Thin layer chromatography (tlc) was carried out on fluorescent silica gel (D<sub>5</sub>F-Fluka).

6-Dimethylaminopurine (II) was obtained from "Calbiochem," Los Angeles, Calif., and is their "Grade A."

**2-Dimethylamino-5-nitropyrimidine (Ia).** Method A.—A solution of 8.4 g (31 mmoles) of 1,1-dimethylguanidine sulfate, 5 g (31 mmoles) of sodium nitromalondehyde,<sup>17</sup> 3.2 g (31 mmoles) of sodium carbonate, and a few drops of piperidine in 35 ml of water was allowed to stand at ambient temperatures. The precipitate was collected, dried, and subjected to Soxhlet extraction with benzene. A 33% yield (1.73 g) of light yellow needles, sensitive to air and light, was obtained: mp 222° (lit.<sup>9</sup> mp 222°); tlc,  $R_f$  0.60 using methanol-benzene (1:9, v/v);  $\lambda_{\text{max}}^{\text{MeOH}}$  223 m $\mu$  ( $\epsilon$  7000), 345 (14,300).

**Method B.**—2-Amino-5-nitropyrimidine (0.5 g, 3.5 mmoles) was added with stirring and in a dry nitrogen atmosphere to a suspension of 0.168 (7 mmoles) of sodium hydride (a 50% suspension in mineral oil was used) in 10 ml of dimethylformamide. After the reaction subsided, 0.99 g (7 mmoles) of methyl iodide was added and stirring was continued for 24 hr. The solvent was removed *in vacuo* and the residue rinsed with pentane to remove mineral oil and with 8 ml water to remove sodium iodide. Crystallization from methanol yielded 0.49 g (85%) of light yellow needles of Ia, identical in all respects with the product obtained by method A.

**2-Di(trideuteriomethyl)amino-5-nitropyrimidine (Ib)** was prepared by method B using 7 mmoles of CD<sub>3</sub>I (obtained from Yeda Inc., Rehovot, Israel).

**2-Dimethylamino-5-benzenesulfonamidopyrimidine (III).**—A suspension of 0.35 g (2.1 mmoles) of 2-dimethylamino-5-nitropyrimidine<sup>11</sup> in 100 ml of methanol was hydrogenated catalytically in a Parr low-pressure hydrogenation apparatus, using 0.1 g of platinum oxide. The catalyst was removed by filtration and the solvent evaporated under reduced pressure. The 5-amino-2-dimethylaminopyrimidine thus obtained (tlc,  $R_f$  0.52 using isopropyl alcohol-benzene, 1:1, v/v) was very sensitive to air oxidation and was therefore immediately thoroughly dried under vacuum (oil pump), dissolved in 10 ml of dry pyridine (under nitrogen), and treated with 0.5 g of benzenesulfonyl chloride. The mixture was stirred at ambient temperatures for 3.5 hr. After partial removal of solvent under vacuum (oil pump), the product was precipitated by the addition of ice water and adjustment of pH to 6. The product was collected, washed with cold water, dried, and recrystallized from methanol: yield, 0.3 g (60%); mp 178°; tlc,  $R_f$  0.72 using isopropyl alcohol-benzene (1:1, v/v);  $\lambda_{\text{max}}^{\text{MeOH}}$  224 m $\mu$  ( $\epsilon$  9900), 257 (19,100), 332 (1800).

*Anal.* Calcd for C<sub>15</sub>H<sub>14</sub>N<sub>4</sub>SO<sub>2</sub>: C, 51.79; H, 5.07; N, 20.14; S, 11.50. Found: C, 52.01; H, 5.16; N, 20.39; S, 11.68.

**Registry No.**—Ia, 14233-44-4; Ib, 14233-45-5; II, 1128-06-7; III, 14233-47-7.

(17) P. E. Fanta, "Organic Syntheses," Coll. Vol. IV, N. Rabjohn Ed., John Wiley and Sons, Inc., New York, N. Y., 1963, p 844.

## Organic Fluoronitrogens. VII.<sup>1a</sup> Tris(difluoramino)fluoromethane and Related Compounds<sup>1b</sup>

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The direct fluorination of guanylurea sulfate yields tris(difluoramino)fluoromethane (II), pentafluoroguanidine (III), tetrafluoroformamide (IV), 3,3-bis(difluoramino)perfluoro-2-azapropionyl fluoride (V), bis(difluoramino)fluoromethyl isocyanate (VI), and the previously described bis(difluoramino)difluoromethane (I). The fluorination of guanylurea yields I-IV. Some of the physical and chemical properties of these nitrogen-fluorine compounds are presented. The compounds, especially II-IV, are shock sensitive and explosive.

The synthesis of bis(difluoramino)difluoromethane (I), the first reported compound having more than one difluoramino group bonded to a single carbon atom,

(1) (a) Preceding paper in this series: R. L. Rebertus, J. J. McBrady, and J. G. Gagnon, *J. Org. Chem.*, **32**, 1944 (1967). (b) Presented in part at the International Symposium on Fluorine Chemistry, Estes Park, Colo., July 1967. Note: Pentafluoroguanidine was also prepared by another route which was very recently reported by R. A. Davis, J. L. Kroon, and D. A. Rausch, *J. Org. Chem.*, **32**, 1662 (1967). (c) Deceased, Aug 5, 1965.

was recently disclosed in a previous paper<sup>2</sup> in this series and by Englin and co-workers.<sup>3</sup> This paper describes the direct fluorination of guanylurea and guanylurea sulfate which resulted in the synthesis

(2) R. J. Koshar, D. R. Husted, and R. A. Meiklejohn, *J. Org. Chem.*, **31**, 4232 (1966).

(3) M. A. Englin, S. P. Makarov, S. S. Dubov, and A. Ya. Yakubovich, *Zh. Obshch. Khim.*, **35**, 1416 (1965).

of tris(difluoramino)fluoromethane (II) having three difluoramino groups bonded to a carbon atom, pentafluoroguanidine<sup>1b</sup> (III) and tetrafluoroformamidine (IV) containing the fluorimino group,  $-C(=NF)NF_2$ , and two additional *gem*-bis(difluoramino) compounds.

### Results and Discussion

The direct fluorination of guanylurea sulfate at  $-10^\circ$  with 10% by volume of fluorine in nitrogen gave 1–5% yields of  $CF_2(NF_2)_2$  (I),  $CF(NF_2)_3$  (II),  $(F_2N)_2C=NF$  (III),  $F_2NCF=NF$  (IV),  $(F_2N)_2CFNFCOF$  (V), and  $(F_2N)_2CFNCO$  (VI).<sup>4</sup> The yields of I, II, and III were 5, 3, and 3%, respectively. Fluorination of guanylurea under similar conditions gave I–IV; the yields of II and III were about 5%. Extensive carbon–nitrogen bond cleavage also occurred during these fluorinations to yield carbonyl fluoride, nitrogen trifluoride, and other low molecular weight products. The nitrogen–fluorine compounds were isolated by gas chromatography and their structures were determined by elemental analyses, molecular weight, and various spectroscopic analyses such as infrared, fluorine nuclear magnetic resonance (nmr), and mass spectroscopy. The fluorine nmr shielding values are presented in Table I.

TABLE I  
F<sup>19</sup> NMR SPECTRA<sup>a</sup>

Compound	Group	$\phi^{*b}$
$CF(NF_2)_3$ (II)	NF <sub>2</sub>	-23.2
	CF	138.7
$(F_2N)_2C=NF$ (III)	NF <sub>2</sub>	-46.8
	NF <sub>2</sub>	-42.3
	=NF	-20.3
$F_2NCF=NF$ (IV)	NF <sub>2</sub>	-42.6
	=NF	21.4
	CF	83.8
$(F_2N)_2CFNFCOF$ (V)	NF <sub>2</sub>	-23.6
	NF	72.4
	CF	132.9
	COF	9.6
$(F_2N)_2CFN=C=O$ (VI)	NF <sub>2</sub>	-25.6
	CF	112.2

<sup>a</sup> Trichlorofluoromethane was used as the internal reference.  
<sup>b</sup> For the definition of  $\phi^*$ , see G. Filipovich and G. V. D. Tiers, *J. Phys. Chem.*, **63**, 761 (1959).

**Tris(difluoramino)fluoromethane (II).**—The physical properties of tris(difluoramino)fluoromethane (II) are summarized in Table II. Various spectroscopic analyses gave support for the structure of II. The infrared spectrum exhibits an absorption at  $7.78 \mu$  (s) assigned to the CF-stretching vibration and a complex absorption pattern having maxima at  $10.13$  (vs),  $10.45$  (vs), and  $10.91 \mu$  (vs) which are attributed mainly to the NF-stretching vibration. The fluorine nmr spectrum exhibits a broad NF<sub>2</sub> peak at  $\phi^* -23.2$  and a singlet at  $\phi^* 138.7$  which is assigned to the single fluorine attached to carbon. The peak area ratio is about 6:1. The mass spectrum shows a base peak at a mass ( $m/e$ ) of 64 which is assigned to the ion,  $CNF_2^+$ , and the significant highest mass at 135 (13%), which is attributed to the ion,  $(F_2N)_2CF^+$ .

Tris(difluoramino)fluoromethane was found to re-

(4) The authors wish to thank Dr. F. A. Fleming for his contributions relating to VI.

TABLE II  
PHYSICAL PROPERTIES OF  
TRIS(DIFLUORAMINO)FLUOROMETHANE (II)

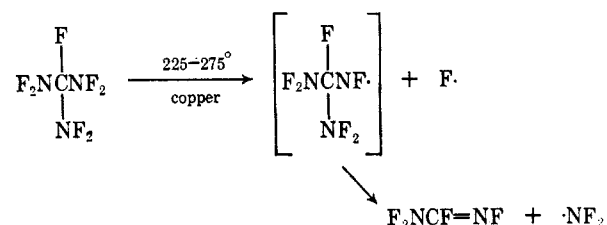
Formula	$CF(NF_2)_3$
Boiling point, $^\circ C^a$	$5.6 \pm 1$
Melting point, $^\circ C$	-137 to -132
Vapor pressure <sup>b</sup>	$\log P_{mm} = 7.6484 - (1328.8/T)$
Heat of vaporization, kcal mole <sup>-1</sup> <sup>c</sup>	6.08
Trouton's constant	21.8
Liquid density (g/cc) <sup>d</sup>	$d_t = 1.622 - 30.020 \times 10^{-4}t -$ $1.701 \times 10^{-6}t^2 - 9.732 \times 10^{-8}t^3$
	$d_{25} = 1.56$
Critical properties	$T_c = 143^\circ$ <sup>e</sup> $d_c = 0.609$ g/cc <sup>f</sup> $V_c = 307$ cc/mole <sup>f</sup> $P_c = 28.6$ atm <sup>g</sup>

<sup>a</sup> Extrapolated from the vapor pressure curve. <sup>b</sup> Temperature range, 190–310°K. <sup>c</sup> Calculated from the vapor pressure curve. <sup>d</sup> Temperature range,  $-40$  to  $80^\circ$ . The standard deviation was  $\pm 0.004$  g/cc. <sup>e</sup> Meniscus disappearance method. <sup>f</sup> Hakala extrapolation (*Chem. Eng. News*, **37**, (11), 43 (1959)). <sup>g</sup> Meissner-Redding extrapolation.

sist hydrolytic attack by dilute aqueous alkaline or acidic media at room temperature. Thus,  $CF(NF_2)_3$  as well as  $CF_2(NF_2)_2$  can be freed from the various unsaturated components, *e.g.*, III–VI, by passage of crude fluorination product through 5–10% aqueous sodium hydroxide. Tris(difluoramino)fluoromethane has shown no evidence of reaction when the liquid was contacted for 2 months with concentrated sulfuric acid at room temperature.

Tris(difluoramino)fluoromethane appeared to be thermally stable at temperatures below  $200^\circ$ . Differential thermal analysis<sup>5</sup> in a sealed Monel cup revealed a slow exotherm beginning at  $250^\circ$  with inflections at about  $270$  and  $278^\circ$ ; decomposition products were mainly carbon tetrafluoride, nitrogen trifluoride, and nitrogen. A 25% by weight sample of II in trichlorofluoromethane was heated in a borosilicate glass ampoule at  $200^\circ$  for 12 hr without noticeable change. Under similar conditions at  $225^\circ$  for the same period, nearly complete degradation occurred. Gas samples of II have been stored at room temperature in glass for several months without evidence of decomposition.

The reactivity of tris(difluoramino)fluoromethane with various metals was investigated. The initial studies carried out in borosilicate glass ampoules revealed no appreciable reaction at room temperature with metals such as mercury, copper, or aluminum. In the presence of copper in glass at  $125^\circ$  for 72 hr, II gave a 55% conversion to  $CO_2$ ,  $N_2O$ ,  $SiF_4$ ,  $NO_2$ ,  $CF_4$ ,  $CF_2(NF_2)_2$ , and  $F_2NCF=NF$ ; the latter two products were formed in very low yield. Passage of 22% by volume



of II in nitrogen through a brass tube containing copper turnings at  $225^\circ$  gave a 10% conversion to a

(5) R. L. Bohon, *Anal. Chem.*, **33**, 1451 (1961).

mixture of  $F_2NCF=NF$ ,  $CF_2NF_2$ ,  $CF_4$ , and  $NF_3$ . At  $275^\circ$  under similar conditions, the conversion was 60% and the yield of  $F_2NCF=NF$  was 6%. The formation of  $F_2NCF=NF$  is proposed to result from II by the initial abstraction of one of the fluorine atoms attached to nitrogen followed by the facile elimination of  $NF_2$  radical from the resulting intermediate radical.

**Pentafluoroguanidine, Tetrafluoroformamidine, and Other Products.**—The synthesis of N-fluorimino compounds has been reported by several investigators. Some of the methods used for the preparation of these compounds include the direct fluorination of nitrogenous compounds,<sup>6-9</sup> the reaction of nitrogen trifluoride with fluoro olefins,<sup>10</sup> free-radical reactions of difluoramino radicals with polyhalogenated compounds,<sup>11</sup> and the reductive defluorination of compounds containing a terminal difluoramino group.<sup>12</sup> Fluorimino compounds, such as III and IV, containing the  $C(=NF)NF_2$  moiety have not been reported previously.<sup>1b</sup>

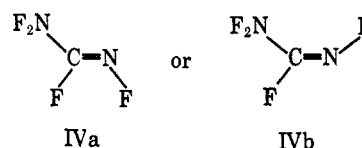
Some of the physical properties of pentafluoroguanidine (III) are summarized in Table III. Infrared, fluorine nmr, and mass spectral analyses gave support for the structure of III. The infrared spectrum exhibits a very weak carbon–nitrogen unsaturation absorption at  $6.14 \mu$  and prominent strong absorptions (complex) at  $10.10$  (s),  $10.67$  (s), and  $11.04 \mu$  (vs) in the region assigned to the  $NF$ -stretching vibration. The fluorine nmr spectrum shows two equal, broad peaks at  $\phi^* -46.8$  and  $-42.3$  assigned to the fluorines of the two geometrically nonequivalent  $NF_2$  groups and at  $\phi^* -20.2$  assigned to the fluorine of the  $=NF$  group. The peak area ratio is 2:2:1. The mass spectrum of pentafluoroguanidine exhibits a base peak at a mass ( $m/e$ ) of 97 which is ascribed to the ion  $F_2NC^+=NF$ . Another high intensity peak (83%) is found at a mass of 78 which is assigned to the ion,  $CN_2F_2^+$ .

TABLE III  
PHYSICAL PROPERTIES OF PENTAFLUOROGUANIDINE (III)

Formula	$F_2N$ $F_2N > C=NF$
Boiling point, $^\circ C^a$	$-2.3 \pm 1$
Melting point, $^\circ C$	$-148$ to $-146$
Vapor pressure <sup>b</sup>	$\log P_{mm} = 7.322 - (1203/T)$
Heat of vaporization, kcal mole <sup>-1</sup> <sup>c</sup>	5.50
Trouton's constant	20.3
Critical temperature, $^\circ C^d$	132

<sup>a</sup> Extrapolated from the vapor pressure curve. <sup>b</sup> Temperature range,  $100$ – $253^\circ K$ . <sup>c</sup> Calculated from the vapor pressure curve. <sup>d</sup> The meniscus disappearance method was used. Some decomposition occurred in borosilicate glass above  $110^\circ$ .

Tetrafluoroformamidine, a more volatile fluorimino compound boiling at about  $-30^\circ$ , can exist in either the *syn* (IVa) or *anti* (IVb) configuration shown below.



The formation of only one geometric form of IV has been indicated by fluorine nmr, infrared, and chromatographic analyses. The nmr spectrum consists of only three resonance peaks at  $\phi^* -42.6$  ( $NF_2$ ),  $21.4$  ( $=NF$ ), and  $83.8$  (CF) in the area ratio of 2:1:1. The  $\phi^* 83.8$  peak appears as a quadruplet which is interpreted as an overlapping double triplet. The coupling constant between the fluorine attached to carbon and the fluorine of  $=NF$  is 12 cps. Although a definite assignment of the configuration of IV cannot be made at this time, the small coupling constant between fluorine atoms on carbon and the imino nitrogen suggests the *syn* configuration (IVa). This tentative assignment is based partly on the work carried out by Dybvig<sup>11</sup> which presents the interpretation of the fluorine nmr spectra of  $CF_2=NF$  and the isomers of  $CFBr=NF$ . The *syn*-fluorine atoms were found to display coupling constants (cycles per second) of 22.1 for  $CF_2=NF$  and 17.6 for  $CFBr=NF$  which are in the vicinity obtained for IV while the *anti*-fluorine atoms showed coupling constants of greater magnitude, *i.e.*, 184 and 218, respectively.

The infrared spectrum of tetrafluoroformamidine shows prominent absorptions at  $5.86 \mu$  (s) due to the carbon–nitrogen unsaturation,  $7.73 \mu$  (s) assigned to the CF-stretching vibration, and two strong absorptions at  $10.61$  and  $11.23 \mu$  in the region for the  $NF$ -stretching vibration. The mass spectrum of IV exhibits a base peak ( $m/e$ ) at 64 assigned to the fragment  $CNF_2^+$ . A peak at a mass of 116 (1.8%) is believed to be due to the parent ion,  $CN_2F_1^+$ .

In contrast to the hydrolytic stability of  $CF_2(NF_2)_2$  and  $CF(NF_2)_3$  at room temperature, both  $(F_2N)_2C=NF$  and  $F_2NCF=NF$  were found to hydrolyze readily, especially in alkaline media.<sup>13</sup> Hydrolysis occurred also at a significant but slower rate in acidic or neutral media at  $25^\circ$ . Under acidic conditions, the fluorimino compounds yielded varying amounts of carbon dioxide, fluoride ion, difluoramine, and other products. During the isolation and storage of these fluorimino compounds, precautions were taken to prevent their decomposition by the exclusion of even trace amounts of moisture.

Differential thermal analyses<sup>5</sup> of pentafluoroguanidine and tetrafluoroformamidine in sealed Monel cups indicated a lower stability than either of the saturated compounds, I and II. Pentafluoroguanidine was found to undergo a rapid exothermic decomposition at  $243^\circ$ . Under similar conditions, tetrafluoroformamidine gave a sharp exotherm at about  $208^\circ$ . With each compound, carbon tetrafluoride, nitrogen trifluoride, and nitrogen were obtained as major products. Both compounds have been heated at  $100^\circ$  for several hours in the vapor phase in stainless-steel cylinders without major decomposition. Gas samples of III and IV have been stored in dry borosilicate glass storage bulbs at room temperature for several months without appreciable decomposition. A chro-

(13) The hydrolytic reactions of these fluorimino compounds will be reported in a forthcoming paper in this series by R. L. Rebertus and B. W. Nippoldt.

(6) R. N. Haszeldine, *Research* (London), **4**, 338 (1951).

(7) J. A. Cuculo and L. A. Bigelow, *J. Am. Chem. Soc.*, **74**, 710 (1952).

(8) J. A. Attaway, R. H. Groth, and L. A. Bigelow, *ibid.*, **81**, 3599 (1959).

(9) B. C. Bishop, J. B. Hynes, and L. A. Bigelow, *ibid.*, **86**, 1827 (1964).

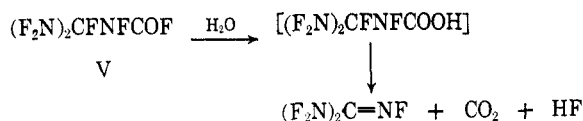
(10) R. D. Dresdner, F. N. Tlumac, and J. A. Young, *ibid.*, **82**, 5831 (1960).

(11) D. H. Dybvig, *J. Inorg. Chem.*, **5**, 1795 (1966).

(12) R. A. Mitsch, *J. Am. Chem. Soc.*, **87**, 328 (1965).

matographically pure sample of pentafluoroguanidine analyzed 98%, by chromatography, after storage for 3 months under these conditions.

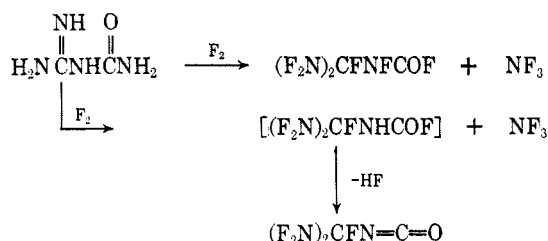
The N-fluorocarbonyl fluoride,  $(F_2N)_2CFNFCOF$ , was found to undergo rapid hydrolysis in neutral or slightly acidic media to give initially a high yield of pentafluoroguanidine and carbon dioxide. Prolonged contact of V with water (36 hr) resulted in extensive degradation to yield mainly tetrafluorohydrazine, nitrous oxide, and carbon dioxide. Formation of pentafluoroguanidine presumably occurs by the initial formation of the unstable acid intermediate,  $(F_2N)_2CFNFCOOH$ , followed by decarboxylation and dehydrofluorination.



**Formation of Products.**—The direct fluorination of guanylurea and its sulfate salt involves replacement of hydrogen, accompanied by various degrees of carbon-nitrogen cleavage and addition of fluorine to imino bonds. Several independent reactions are indicated. The formation of pentafluoroguanidine, for example, is proposed to occur by the following route which involves carbon-nitrogen cleavage only at the carbonyl-carbon site with the retention of the imino group.



Tris(difluoramino)fluoromethane would be expected to result by a similar process accompanied by addition of fluorine to the imino group of guanylurea or intermediates. Relatively minor cleavage also occurs during the fluorination of guanylurea sulfate under the conditions used to yield  $(F_2N)_2CFNCO$  and  $(F_2N)_2CFNFCOF$ . Formations of these compounds by the following routes are proposed.



**General Comments.**—Certain safety precautions were found necessary when handling the crude fluorination mixtures or isolated compounds. Most of the compounds, particularly tris(difluoramino)fluoromethane and pentafluoroguanidine, are shock sensitive and explode violently. The compounds appear to be especially hazardous when undergoing phase transitions. Details concerning the safety precautions are found in the Experimental Section of this paper. All of the nitrogen-fluorine compounds are strong oxidizers and react rapidly with potassium iodide solutions, liberating iodine.

### Experimental Section

**Precautions.**—The nitrogen-fluorine compounds described in this paper are explosive under certain conditions. Suitable protective equipment should be used during all phases of the

work, including manipulations during spectroscopic and elemental analyses. We have operated within a quantity limit of 1 g in Pyrex, using poly(methyl methacrylate) shielding and wearing heavy-duty face shields, leather jackets, ear plugs, and reinforced gauntlets. For quantities greater than 1 g, remote handling is recommended. Liquid samples confined in metal containers are potentially even more hazardous and adequate barricades should be provided, *e.g.*, concrete or heavy steel, to protect the operator from metal fragments which could result from an explosion.

Compounds II-IV are especially shock sensitive and explosive, particularly in the liquid state and during phase transitions. For example,  $(F_2N)_2C=NF$  has exploded when cooled or warmed rapidly near its melting point or when a frozen sample was inadvertently contacted with air. Although liquid nitrogen and liquid air have been used as coolants for the transfer of small amounts of these compounds under vacuum, the use of nonflammable slush baths maintained above the melting point of the compound or mixture are preferred. Contact of the crude fluorination products or compounds with air is to be avoided. All of the fluoronitrogen compounds can be stored conveniently in closed borosilicate glass containers in the vapor phase at room temperature or as 10-15% solutions in inert fluorochemicals, *e.g.*, perfluorotributylamine.

**Materials.**—Guanylurea sulfate was obtained from the American Cyanamid Co. The guanylurea sulfate was mixed with the desired amount of powdered sodium fluoride and the mixtures stored in a desiccator. Guanylurea (mp 105-107°) was prepared by treatment of the sulfate with an ethanolic solution of sodium hydroxide. Fluorine was obtained from the General Chemical Division of the Allied Chemical Corp. Several fluorochemicals were used for the preparation of the various chromatographic columns. The fluorosilicone fluid, FS-1265, was obtained from the Dow Corning Corp. The fluorochemical FC-43 and the fluorochemical FX-45<sup>14</sup> are products from the Minnesota Mining and Manufacturing Co. Dry acid-washed Chromosorb P (mesh 30-60) obtained from Johns-Manville was used as the inert support for the chromatographic columns.

**Methods of Analyses and Isolation of Products.**—The infrared spectra were recorded by means of a Perkin-Elmer double-beam spectrophotometer, Model 21, using 2.5-cm gas cells equipped with sodium chloride windows. The fluorine nmr shielding values ( $\phi^*$ ) were obtained with trichlorofluoromethane as the internal reference using dilutions of 20-30% by volume, according to methods previously described.<sup>15</sup> A Varian V-4300-2 instrument operating at 40.0 Mc was used. Perfluoroacetic acid is  $\phi^* 76.5$  on the above scale. Ultraviolet measurements were carried out with a Cary recording spectrophotometer, Model 11, using 10-cm cells with quartz windows. A Consolidated Electroynamics Corp. Model 21-103-C mass spectrometer was used to obtain the mass spectra and to determine the molecular weights by effusion rate studies. An ionization potential of 70 v and an ionization chamber temperature of 250° were employed.

The gas chromatographic analyses and isolation of compounds were carried out with a Perkin-Elmer vapor fractometer, Model 154-D, equipped with a thermistor detector and modified gas sampling and backflush valves. For preparative scale separations, columns of 15-24 ft  $\times$  0.5 in. were used. Gas samples of less than 2 mmoles were usually condensed into a barricaded 25-ml stainless-steel coil and then allowed to warm to ambient temperature prior to introduction into the column. Dry helium at flow rates of about 50-300 cc/min was used as the carrier gas. The various nitrogen-fluorine compounds eluting from the column were condensed into flame-dried borosilicate glass traps cooled with liquid nitrogen or appropriate nonflammable slush baths. Table IV gives the retention times of the compounds relative to air and either trichlorofluoromethane or dichlorodifluoromethane as reference compounds (100).

**Fluorination of Guanylurea Sulfate.**—A mixture of 1.0 g (3.3 mmoles) of guanylurea sulfate and 4.0 g of powdered sodium fluoride was placed in a 650-ml capacity rectangular brass reactor fitted at the bottom with a 2  $\times$  10 in. porous Monel plate. The reactor was equipped with a gas inlet located below the plate and a gas outlet at the top. The outlet was connected to a borosilicate glass trap which was cooled with liquid oxygen and opened at the other end to a nitrogen atmosphere.

(14) FX-45 is a polyfluorinated oil having a boiling range of about 100-140° at 1 mm.

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

TABLE IV

RELATIVE RETENTION TIMES OF FLUORONITROGEN COMPOUNDS

Compound	Retention times		
	Column A <sup>a</sup>	Column B <sup>b</sup>	Column C <sup>c</sup>
CF <sub>2</sub> (NF <sub>2</sub> ) <sub>2</sub>	8	138	36
F <sub>2</sub> NCF=NF	19	104	30
CF(NF <sub>2</sub> ) <sub>3</sub>	27		136
(F <sub>2</sub> N) <sub>2</sub> C=NF	43		94
(F <sub>2</sub> N) <sub>2</sub> CFNCO	126		
(F <sub>2</sub> N) <sub>2</sub> CFNFCOF	206		

<sup>a</sup> Column (15 ft × 0.5 in.) was composed of 20% by weight of FS-1265 on Chromosorb P operated at 20°. Values are relative to trichlorofluoromethane as 100. <sup>b</sup> Column (10 ft × 0.5 in.) composed of 33% by weight of FC-43 on Chromosorb P operated at -19°. Values are relative to dichlorodifluoromethane as 100. <sup>c</sup> Column (24 ft × 0.5 in.) composed of 33% by weight of FX-45 on Chromosorb P operated at 23°. Values are relative to trichlorofluoromethane as 100.

The reactor was closed and cooled to an inside temperature of -10°, measured at the plate, and the system was flushed with nitrogen (200 cc/min) to expel air. A gas mixture of 10% by volume of fluorine in nitrogen was metered into the reactor from a 2.3-l. stainless-steel cylinder having an initial pressure of 150 psig. Approximately 80 mmoles of fluorine was delivered over a period of 5.5 hr. During the fluorination, the flow rate of the fluorine-nitrogen mixture was increased from 50 (1 hr) to 85 cc/min (2.3 hr) and finally to 110 cc/min (2.2 hr). After completion of the introduction of fluorine, the reactor was allowed to warm to room temperature and flushed with nitrogen for 15 hr.

The collection trap<sup>16</sup> was attached to a high-vacuum manifold and the nitrogen was removed by evacuation. The products were then allowed to warm to room temperature and the mixture was separated by distillation condensation at 1 mm employing traps cooled at -135 and -196°. The -196° cooled trap contained 3.7 mmoles of a mixture of carbonyl fluoride (major component), carbon dioxide, nitrogen trifluoride, as well as small amounts of I-IV.

The various components in the -135° trap (1.6 mmoles) were isolated by gas-liquid partition chromatography (glpc) at 24° employing a 15 ft × 0.5 in. column composed of 20% by weight of the fluorosilicone fluid, FS-1265, on Chromosorb P. Helium at a flow rate of about 55 cc/min was used. About 0.3 mmole of F<sub>2</sub>NCF<sub>2</sub>NF<sub>2</sub>, 0.05 mmole of F<sub>2</sub>NCF=NF, 0.22 mmole of CF(NF<sub>2</sub>)<sub>3</sub>, 0.22 mmole of (F<sub>2</sub>N)<sub>2</sub>C=NF, and 0.21 mmole of a mixture of (F<sub>2</sub>N)<sub>2</sub>CFN=C=O and (F<sub>2</sub>N)<sub>2</sub>CFNFCOF were isolated. The mixture of the isocyanate and N-fluorocarbonyl fluoride (1:2 mole ratio) was separated by employing the FS-1265 column at 24° using a helium flow rate of 200 cc/min.

The order of elution and approximate retention times relative to trichlorofluoromethane are given in Table IV.

**Fluorination of Guanyurea.**—Using procedures similar to those described above, 1.0 g (10 mmoles) of guanyurea was contacted with 6% fluorine in nitrogen at -3 to 0° over a period of 7 hr. A total of about 0.2 mole of fluorine was delivered. The effluent from the reactor passed through a metal tube containing sodium fluoride pellets (25°) and was collected in a trap cooled with liquid oxygen.

The product in the trap was separated into two fractions by distillation condensation at 1 mm, using traps cooled to -135 and -196°. There was obtained 8.1 mmoles (-196° trap) of a mixture consisting of mainly carbonyl fluoride, nitrogen trifluoride, and carbon tetrafluoride. About 1.4 mmoles of a mixture of I-IV was collected in the -135° trap. Chromatographic analysis and isolation of components of this fraction indicated the composition CF<sub>2</sub>(NF<sub>2</sub>)<sub>2</sub> (5%), F<sub>2</sub>NCF=NF (2%), CF(NF<sub>2</sub>)<sub>3</sub> (44%), and (F<sub>2</sub>N)<sub>2</sub>C=NF (25%).

**Tris(difluoramino)fluoromethane (II).**—Tris(difluoramino)fluoromethane was isolated by chromatography employing either column A or C (Table IV). Another method was as follows. The crude fluorination product, which was collected in the -135° trap by the method described above, was diluted with nitrogen and allowed to pass through a bubbler containing 10% aqueous sodium hydroxide. Attached to the exit of the bubbler was a CaSO<sub>4</sub> drying tube followed by a trap cooled at -140°. The

effluent, which collected in the trap, contained mainly CF(NF<sub>2</sub>)<sub>3</sub> and CF<sub>2</sub>(NF<sub>2</sub>)<sub>2</sub>. CF(NF<sub>2</sub>)<sub>3</sub> was then separated by glpc.

The mass spectrum fragmentation pattern of tris(difluoramino)fluoromethane is presented in Table V. The molecular weight, determined by mass effusion rate studies using *m/e* of 52, 64, and 69, was 187, 185, and 189, respectively (calcd 187).

TABLE V

MASS SPECTRUM OF TRIS(DIFLUORAMINO)FLUOROMETHANE

<i>m/e</i> <sup>a</sup>	Cation	Rel pattern, <sup>b</sup> %
14	N	3.6
26	CN	2.4
31	CF	27.8
33	NF	16.2
45	CNF	8.9
50	CF <sub>2</sub>	4.3
52	NF <sub>2</sub>	40.3
64	CNF <sub>2</sub>	100.0
69	CF <sub>3</sub>	7.0
83	CNF <sub>3</sub>	30.4
116	CN <sub>2</sub> F <sub>4</sub>	3.9
135	CN <sub>2</sub> F <sub>5</sub>	13.0

<sup>a</sup> *I*<sub>m</sub> = 0.258 and 0.538 (*m/e* 83-135). <sup>b</sup> Mass values (*m/e*) of less than 2% are not given.

The infrared spectrum of tris(difluoramino)fluoromethane exhibited prominent absorptions ( $\mu$ ) at 7.78 (s), 8.76 (m), 9.59 (m), 10.13 (vs), 10.45 (vs), 10.91 (vs), and 14.80 (m). The absorptions at 10.13, 10.45, and 10.91 in the region for the NF vibration were complex. The ultraviolet spectrum exhibited end absorption ( $\lambda$ ) at 237 m $\mu$  ( $\epsilon$  1).

The physical properties of tris(difluoramino)fluoromethane are given in Table II and the fluorine nmr shielding values ( $\phi^*$ ) are found in Table I.

*Anal.* Calcd for CF<sub>7</sub>N<sub>3</sub>: C, 6.4; F, 71.1; N, 22.5. Found: C, 6.5; F, 71.8; N, 22.1.

**Pentafluoroguanidine (III).**—A high-purity sample of III can be obtained by chromatography using column A and then column C (Table IV). The mass spectrum fragmentation pattern for pentafluoroguanidine is summarized in Table VI. The molecular weight, determined by mass effusion rate studies using *m/e* of 52, 64, and 97, was 148, 145, and 148, respectively. The molecular weight by gas density was 148 (calcd 149).

TABLE VI

MASS SPECTRUM OF PENTAFLUOROGUANIDINE

<i>m/e</i> <sup>a</sup>	Cation	Rel pattern, <sup>b</sup> %
14	N	14.7
26	CN	18.7
28	N <sub>2</sub>	13.1
31	CF	84.5
33	NF	71.9
40	CN <sub>2</sub>	13.8
45	CNF	10.0
50	CF <sub>2</sub>	12.7
52	NF <sub>2</sub>	59.8
59	CN <sub>2</sub> F	22.7
64	CNF <sub>2</sub>	39.1
78	CN <sub>2</sub> F <sub>2</sub>	82.7
97	CN <sub>2</sub> F <sub>3</sub>	100.0

<sup>a</sup> *I*<sub>m</sub> = 0.258. <sup>b</sup> Mass values (*m/e*) less than 5% are not given.

The infrared spectrum of pentafluoroguanidine exhibited prominent absorptions ( $\mu$ ) at 6.14 (vw), 9.46 (w), 10.10 (s), 10.67 (s), 11.04 (vs), 12.78 (w), and 14.20 (w). The absorptions in the range of 10-11 were complex. The ultraviolet spectrum showed end absorption ( $\lambda$ ) at about 290 m $\mu$  ( $\epsilon$  1) with an inflection at 222 m $\mu$ .

The physical properties of pentafluoroguanidine are given in Table III and the fluorine nmr shielding values ( $\phi^*$ ) are found in Table I.

*Anal.* Calcd for CF<sub>5</sub>N<sub>3</sub>: C, 8.1; F, 63.7; N, 28.2. Found: C, 8.3; F, 62.2; N, 28.2.

**Tetrafluoroformamidine (IV).**—Isolation of IV in high purity

(16) The trap was closed, maintained at -183°, and transported to various locations in a heavy steel carrier equipped with 3-ft extension handles.

is best accomplished by chromatography using column A and then column B (Table IV). The mass spectrum fragmentation pattern for  $F_2NCF=NF$  is presented in Table VII. The molecular weight determined by mass effusion rate studies of  $m/e$  64 and gas density was 116 and 117, respectively (calcd 116).

TABLE VII  
MASS SPECTRUM OF TETRAFLUOROFORMAMIDINE

$m/e^a$	Cation	Rel pattern, <sup>b</sup> %
14	N	5.2
19	F	3.6
26	CN	3.5
28	N <sub>2</sub>	2.8
31	CF	33.6
33	NF	12.5
40	CN <sub>2</sub>	1.5
45	CNF	14.7
50	CF <sub>2</sub>	7.7
52	NF <sub>2</sub>	13.8
59	CN <sub>2</sub> F	1.0
64	CNF <sub>2</sub>	100.0
69	CF <sub>3</sub>	1.2
83	CNF <sub>3</sub>	1.4
97	CN <sub>2</sub> F <sub>3</sub>	4.4
116	CN <sub>2</sub> F <sub>4</sub>	1.8

<sup>a</sup>  $I_m = 0.258$ . <sup>b</sup> Mass values ( $m/e$ ) less than 1% are not given.

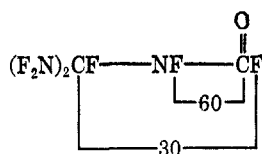
The infrared spectrum of tetrafluoroformamidine exhibited prominent absorptions ( $\mu$ ) at 5.86 (s), 7.73 (s), 10.10 (m), 10.61 (s), 11.23 (s), and 13.20 (m). The ultraviolet spectrum showed end absorption ( $\lambda$ ) at about 250 ( $\epsilon$  1). The fluorine nmr absorptions are given in Table I. The CF peak ( $\phi^*$  83.8) was a quadruplet with splittings of 12 cps.

*Anal.* Calcd for  $CF_4N_2$ : C, 10.3; F, 65.5; N, 24.2. Found: C, 10.5; F, 64.5; N, 24.0.

**3,3-Bis(difluoramino)perfluoro-2-azapropionyl Fluoride (V).**—The mass spectrum of V exhibited a base peak ( $m/e$ ) at 47 ( $COF^+$ ) and the second highest intensity peak was at 31 ( $CF^+$ , 12%). A peak at 163 ( $C_2N_2F_3O^+$ ) was also present. The molecular weight determined by mass effusion rate studies using  $m/e$  of 163 was 216 (calcd 215).

The infrared spectrum exhibited prominent absorptions ( $\mu$ ) at 5.29 (s, C=O), 7.75 (s), 8.05 (m), 8.35 (m), 9.22 (m), 9.66 (w), 10.39 (m), 10.72 (m), 11.04 (s), 12.85 (w), 13.64 (m), and 14.44 (w). The absorptions at 10.39, 10.72, and 11.04 were in the region for the NF-stretching vibration.

The fluorine nmr spectrum exhibited peaks ( $\phi^*$ ) at -23.6 ( $NF_2$ ), 9.6 ( $COF$ , doublet), 72.4 ( $NF$ ), and 132.9 ( $CF$ ) which appeared as a triplet. The approximate coupling constants ( $J$ , cycles per second) are given below.



**Bis(difluoramino)fluoromethyl Isocyanate (VI).**—The mass spectrum of VI exhibited prominent mass peaks ( $m/e$ ) which

correspond to the fragments  $CF^+$ ,  $NF^+$ ,  $CNO^+$ ,  $CNF^+$ ,  $CNFO^+$ ,  $CF_2^+$  (base peak),  $C_2NFO^+$ ,  $C_2NF_2O^+$ ,  $C_2N_2F_2O^+$ , and  $C_2N_2F_3O^+$ . The molecular weight based on mass effusion rate studies of  $m/e$  61 ( $CNFO^+$ ) and 73 ( $C_2NFO^+$ ) was 177 and 176, respectively (calcd 177).

The infrared spectrum exhibited absorptions ( $\mu$ ) at 4.37 (vs, N=C=O), 6.76 (s), 8.12 (s), 8.31 (s), 8.79 (m), 9.87 (m), 10.54 (s), and 11.09 (s). The fluorine nmr spectrum consisted of two peaks ( $\phi^*$ ) at -25.6 ( $NF_2$ ) and 112.2 ( $CF$ ) in a 4:1 ratio.

**Hydrolysis of 3,3-Bis(difluoramino)perfluoro-2-azapropionyl Fluoride.**—The N-fluorocarbonyl fluoride (0.04 mmole) was charged under vacuum into a 20-ml tube at -196° containing 0.15 ml of water. The tube was closed and allowed to warm gradually to room temperature (0.5 hr). The volatile product (0.07 mmole) contained mainly  $CO_2$  and  $(F_2N)_2C=NF$  (50 mole %), by infrared analysis. The volatile products were recondensed into the tube and allowed to remain in contact with the aqueous phase for 36 hr. Infrared analysis of the volatile products indicated mainly  $N_2F_4$ ,  $CO_2$ , and  $N_2O$ .

**Pyrolysis of Tris(difluoramino)fluoromethane.**—The pyrolysis was carried out in a 46-cm, brass tube (1.9-cm diameter) which was contacted with a high concentration of fluorine prior to its use in these experiments. The pyrolysis tube was packed with 12 g of copper turnings located at the center in a 6-in. zone. The  $CF(NF_2)_3$  was injected from a barricaded 3-ml stainless-steel cylinder and was diluted with nitrogen. The products from the pyrolysis were condensed by means of a borosilicate glass trap cooled with liquid air. The trap was protected from atmospheric moisture by means of a  $CaSO_4$  drying tube.

The results of the pyrolysis at 225, 250, and 275° are summarized in Table VIII.

TABLE VIII  
PYROLYSIS OF TRIS(DIFLUORAMINO)FLUOROMETHANE

CF(NF <sub>2</sub> ) <sub>3</sub> , mmole	Temp, °C	Product, mmole	Distribution of products, % <sup>b</sup>			CF <sub>4</sub> and NF <sub>3</sub>
			CF(NF <sub>2</sub> ) <sub>2</sub>	F <sub>2</sub> NCF=NF	CF <sub>2</sub> NF <sub>2</sub>	
0.74	225	0.5	92	2	0.4	4.5
0.6	250	0.35	58	8.5	4.5	22.5
0.45	275	0.3	40	6.5	2.1	28

<sup>a</sup> Contact period, 90 sec,  $N_2:CF(NF_2)_3$  volume ratio, 3.5:1.

<sup>b</sup> The percentages are area per cent by chromatography. Column A was used. The components from the pyrolysis at 275° were isolated and identified by infrared analysis.

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