the infrared spectrum was also shown to be identical with that of an authentic sample of $CF_3CF_2CF_2CF{=}NCF_3$.

Perfluoro-3-methyl-2-azabutene-1 did not isomerize when heated at 200° in the presence of dried cesium fluoride for 12 hr.

Registry No.—Perfluoro-2,3-diazabuta-1,3-diene, 692-73-9.

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The Synthesis of Saturated and Unsaturated α-Difluoramino Ethers

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In recent years, the syntheses of a variety of organic compounds containing the difluoramino grouping have been reported. Included are acyl difluoramines,[1] alkyl difluoramines,[2] perfluoroalkyldifluoramines,[3] and difluorourea.[4] In addition, the properties of a *vic*-difluoramino compound, 1,2-bisdifluoramino-4-methylpentane,[5] have been reported. Several review articles[6] emphasizing inorganic difluoramino compounds have also appeared.

For the most part the synthesis of difluoramino-containing molecules had been accomplished *via* fluorination of amines and thermal or photochemical reactions of tetrafluorohydrazine. A more recent publication[7] has disclosed the alkylation of difluoramine by various carbonium ions. As one of several reactions, Graham and Freeman reported the preparation of α-difluoraminopyran by reaction of dihydropyran and HNF_2 at room temperature. This appears to be the first indication that HNF_2 had any synthetically useful nucleophilic properties.

We now wish to report an additional synthetic utility of difluoramine. The reaction of acetals with HNF_2 now provides a new method for preparing α-difluoramino ethers. This reaction probably represents a fairly general mode of attack in that it occurs with saturated and unsaturated mono- and diacetals such as dimethyl acetal, acrolein acetal, tetramethoxypropane, tetramethoxybutene-2, and tetraethoxybutyne-2.[8] The only acetals tried that failed to react were two ketene acetals, specifically, the parent compound and dicyano ketene acetal. In all other examples, one alkoxide from each acetal grouping was replaced by $-NF_2$.

$$RCH(OR)_2 + HNF_2 \longrightarrow RCH(OR)NF_2 + ROH$$

The reaction conditions varied according to the starting material used. All reactions were carried out under an excess pressure of HNF_2 at temperatures ranging from ambient to 100° using standard vacuum line techniques. The appropriate alcohol (1 molar equiv) was isolated in each case and identified *via* infrared and gc. Tetramethoxypropane and tetraethoxybutyne-2 reacted similarly in that under the milder reaction conditions a mixture of the mono- and bisdifluoramino ether was isolated. On recycling this material with additional HNF_2 at a higher temperature the corresponding 1,3 or 1,4 product formed. On the other hand, tetramethoxybutene-2 reacted at room temperature in CCl_4 to give a nearly quantitative yield of high purity (92%) 1,4-bisdifluoramino ether. The integrated area ratio of 3:1:1 for methoxy, vinyl, and tertiary hydrogens and the nmr results listed in Table I are consistent with the proposed difluoramino ether. The reaction was also run in the absence of solvent (excess NHF_2) without affecting either the yield or purity of the bis ether. The work-up of the reaction mixture was greatly facilitated in the latter case.

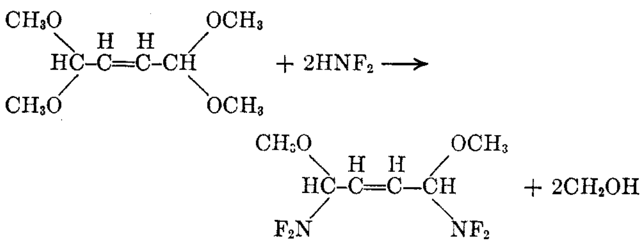

TABLE I

F^{19}	H^1
ϕ −25.5 (d) [$-CH(OR)NF_2$]	τ 3.91 (m) ($-CH{=}C$)
$J_{HF} \sim 18.5$ cps	τ 5.21 (dt) (tertiary H)
	$J_{HF} \sim 18.5$ cps
	τ 6.43 (s) ($-OCH_3$)

Experimental Section

Caution: Difluoramine should be handled with care. Explosions have occurred when HNF_2 was condensed at −196°.

Apparatus.—A heavy-wall glass pressure reactor[9] (15-ml capacity) fitted with a Teflon[10] valve was used in this experiment.

1,4-Bisdifluoramino-1,4-dimethoxybutene-2.—Tetramethoxybutene-2 (0.5 g, 0.0029 mol) was dissolved in 0.5 ml of CCl_4 and charged *via* a drawn-out medicine dropper to the bulb of the reactor. The reactor was then degassed three times and 0.700 g (0.013 mol) of HNF_2 was condensed in using a −126° bath (Freon-21 and liquid N_2). The reactor was allowed to warm to room temperature. Stirring (*via* magnetic stirrer) was continued for 24 hr. The volatile products were passed through a −78° (trichloroethylene–Dry Ice) and a −126° trap. The desired product remained behind as a colorless liquid. Bulb-to-bulb distillation of this liquid at 75° (0.5 mm) gave 0.607 g (98%) of the bis-α-difluoramino ether.

Anal. Calcd for $C_6H_{10}O_2N_2F_4$: C, 33.0; N, 12.85; F, 34.9; mol wt, 218. Found: C, 32.85; N, 13.02; F, 34.6; mol wt, 214.

1,4-Bisdifluoramino-1,4-diethoxybutyne-2.—The tetraethoxybutyne-2 (0.59 g, 0.0026 mol) was charged neat into a glass pressure reactor. The reactor was then degassed three times. The HNF_2 (0.50 g, 0.009 mol) was condensed in using a −126° bath. After reaching room temperature the reaction was stirred for 24 hr. Work-up in the usual manner (see reaction above)

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[10] Available from Fischer & Porter, Warminster, Pa., Catalog No. 795-609.

gave 0.61 g of a product which was composed of 70% mono- and 30% bisdifluoramino ether *via* nmr spectroscopy. Fresh HNF_2 was condensed into the reactor, and it was heated (oil bath) to 70° for 16 hr. Work-up gave 0.61 g of the bisdifluoramino ether as a colorless liquid.

Anal. Calcd for $C_8H_{12}O_2N_2F_4$: C, 39.67; N, 11.57; F, 31.40. Found: C, 39.4; N, 11.37; F, 30.8.

1,3-Bisdifluoramino-1,3-dimethoxypropane.—Tetramethoxypropane (0.500 g, 0.003 mol) was allowed to react with 0.420 g (0.008 mol) of HNF_2 in a glass pressure reactor at 50° for 3 days. The resulting liquid product was fractionated to give 0.53 g of a colorless liquid product.

Anal. Calcd for $C_5H_{10}O_2N_2F_4$: C, 29.12; N, 13.6; F, 36.9. Found: C, 29.3; N, 14.0; F, 36.6.

3-Ethoxy-3-difluoraminopropene-1.—Acrolein diethyl acetal (0.34 g, 0.0026 mol) and 0.35 g (0.006 mol) of HNF_2 were allowed to react in a glass pressure vessel and worked up as above to give 0.3 g of the title compound.

Anal. Calcd for $C_5H_9ONF_2$: C, 45.11; N, 10.2; F, 27.7. Found: C, 45.5; N, 10.13; F, 27.9.

Registry No.—1,4-Bisdifluoramino-1,4-dimethoxybutene-2, 16452-20-3; 1,4-bisdifluoramino-1,4-diethoxybutene-2, 16452-21-4; 1,3-bisdifluoramino-1,3-dimethoxypropane, 16462-48-9; 3-ethoxy-3-difluoramino-1-propene, 16452-22-5.

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Direct Fluorination of Sodium Dicyanamide and Cyanoguanidine

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Ruff and Giese[1] have reported that silver cyanide when diluted with fluorspar could be fluorinated with elemental fluorine to yield numerous products. Subsequently, we found that by using alkali metal fluorides as the diluent in place of fluorspar, guanidine could be fluorinated to pentafluoroguanidine.[2] In this Note, we report the extension of this technique to the direct fluorination of sodium dicyanamide and cyanoguanidine.

Sodium dicyanamide, $NaN(CN)_2$, mixed with a large amount of magnesium fluoride as diluent was fluorinated with 50% fluorine diluted with nitrogen. The low boiling product was collected in a Dry Ice trap. Fractionation of the light yellow liquid using codistillation indicated that it contained about 20 minor impurity components and a major component, $F_2NCF_2NFC{\equiv}N$ (I), representing about 90–95% of the over-all material.

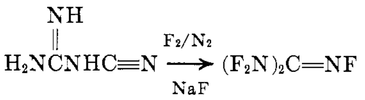
The molecular weight of I determined by gas density measurements was 157 and 159 (calcd 161). The boiling point was 18.4° determined from vapor pressure–temperature measurements.

The infrared absorption spectrum of I in the gas phase showed a sharp, weak intensity band at 4.45 μ assigned to C≡N stretch, strong bands at 6.7, 8.1, and 8.3 μ assigned to the CF_2 group, a strong broad band at 10.4–10.8 μ assigned to the NF bands, a medium strong band at 9.85 μ, and medium weak bands at 9.2, 12.45, and 14.2 μ.

The ^{19}F nmr spectrum ($CFCl_3$ as reference) showed a CF_2 doublet at 101.0 ppm due to coupling (J = 22.8 cps) with the –NF group, resulting in a NF triplet at 54.1 ppm and a NF_2 broad single peak at −20.55 ppm.

The fluorination of 5 g of cyanoguanidine diluted with a large amount of sodium fluoride resulted in 1.5 ml of material collected in a Dry Ice–acetone cooled trap. This crude liquid product contained five major components, three of which were identified by infrared and mass spectroscopy as the previously reported compounds $(F_2N)_2C{=}NF$[2], $(F_2N)_3CF$[3], and $F_2NCF_2NFC{\equiv}N$. The two higher boiling products were identified as $F_2NC({=}NF)NFCF_2NF_2$ and $(F_2N)_2CFNFCF_2NF_2$, both of which have the skeletal cyanoguanidine structure intact. Thus, the over-all reaction and the relative amounts of products obtained from the fluorination of cyanoguanidine may be illustrated as in Table I. 1-[(Difluoramino)difluoromethyl]-1,2,3,3-tetrafluoroguanidine, $F_2NC({=}NF)NFCF_2NF_2$, is an explosive, colorless liquid below its boiling point, 55°, obtained by extrapolation from vapor pressure–temperature measurements. The molecular weight found by gas density measurements was 229 (calcd 232). The mass spectrum showed no parent peak, which is common for many nitrogen–fluorine compounds. The largest mass peak at m/e 180 was assigned to $C_2N_3F_6^+$ which results from loss of NF_2 from the parent molecule. Other major peaks were at m/e of 161, 142, 128, 114, 109, 102, 97, 90, 83, 78, 69, and 64.

Table I



$$\overset{\text{NH}}{\overset{\|}{\text{H}_2\text{NC}}}\text{NHC}{\equiv}\text{N} \xrightarrow[\text{NaF}]{\text{F}_2/\text{N}_2} (\text{F}_2\text{N})_2\text{C}{=}\text{NF}$$

	Relative amounts
$(F_2N)_2C{=}NF$	1
$(F_2N)_3CF$	4.7
$F_2NCF_2NFC{\equiv}N$	Trace
$F_2NC({=}NF)NFCF_2NF_2$	3.5
$(F_2N)_2CFNFCF_2NF_2$	7

The infrared absorption spectrum of $F_2NC({=}NF)NFCF_2NF_2$ in the gas phase showed a weak intensity band at 6.15 μ assigned to C=N stretch, strong bands in the CF region at 7.70, 7.95, 8.15, and 8.50 μ, and strong bands in the NF region at 10.00, 10.50, and 11.20 μ. The 10.00-μ band had shoulders at 9.6 and 9.85 μ. In addition, a medium strong band at 11.65 μ and medium bands at 12.55 and 14.00 μ were observed. The ^{19}F nmr spectrum ($CFCl_3$ as reference) showed a NF_2 band at −41.0 ppm and the =NF band at −33.8 ppm. These are reasonable for the $-C({=}NF)NF_2$ portion of the molecule since it has been previously shown[1] that in the compound $(F_2N)_2C{=}NF$ the NF_2 groups came at −42.3 and −46.9 ppm and the =NF at −20.2 ppm. The NF_2 band at −19.7 ppm and the

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