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.

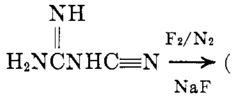
The molecular weight of I determined by gas density measurements was 157 and 159 (calcd 161). The boiling point was 18.4° determined from vapor pressure–temperature measurements.

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



	Relative amounts
$H_2N\overset{NH}{\overset{\|}{C}}NHC{\equiv}N \xrightarrow[NaF]{F_2/N_2} (F_2N)_2C{=}NF$	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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[1] O. Ruff and M. Giese, *Ber.*, **69**, 598, 604 (1936).

[2] R. A. Davis, J. L. Kroon, and D. A. Rausch, *J. Org. Chem.*, **32**, 1662 (1967).

[3] R. J. Koshar, D. R. Husted, and C. D. Wright, 4th International Symposium on Fluorine Chemistry, Estes Park, Colo., July, 1967.

-CF_2- doublet at +100.5 ppm coupled by 22.8 cps to the -NF- at +48.4 ppm are very reasonable for the F_2NCF_2NF- portion of the molecule and in good agreement for the same assignments made for F_2NCF_2-NFCN.

The highest boiling product obtained from the fluorination, N[(difluoroamino)difluoromethyl]-N,N′,N′,-N″,N″-1-hexafluoromethanetriamine, $(F_2N)_2CFNFCF_2NF_2$, is an explosive, colorless liquid boiling at 60°, extrapolated from vapor pressure–temperature measurements. The molecular weight found by gas density measurements was 267 (calcd 270).

The infrared absorption spectrum in the gas phase showed strong intensity bands in the CF region at 7.85, 8.10, and 8.32 μ. The 7.85-μ band had a shoulder at 7.65 μ. Strong bands at 10.45 and 10.95 μ, usually attributed to NF bonds, and weak bands at 9.45, 9.70, 9.95, 11.50, 11.75, 12.60, and 13.20 μ were also observed. The mass spectrum of $(F_2N)_2CFNFCF_2NF_2$ showed no parent peak. A peak observed at m/e of 218 was assigned to $C_2N_3F_8^+$ which results from loss of NF_2 from the parent molecule. Other major peaks observed which can be accounted for by the structure were at m/e of 147, 128, 135, 116, 102, 83, 69, and 64. The ^{19}F nmr spectrum ($CFCl_3$ as reference) showed five lines consistent with the structure as follows (peak, assignment, relation area): −23.5 ppm, $C(NF_2)_2$, 4; −19.2 ppm, CNF_2, 2; +90.0 ppm, -NF-, 1; +100.4 ppm, -CF_2-, 2; and 131.2 ppm, CF, 1.

Experimental Section

Caution! The products and various unidentified by-products from the fluorination of sodium dicyanamide and cyanoguanidine are extremely explosive in the gas, liquid, and solid state. They have been manipulated routinely in a mercury-free vacuum line with CF_2Cl_2 slush baths at −130 to −145°. It was standard practice to use adequate shielding and protective equipment and to keep the sample size below 0.5 g.

Fluorination of Cyanoguanidine.—Cyanoguanidine (5 g, 60 mmol) was mixed with 50 g of sodium fluoride which had been dried at 110°. The mixture was charged into a three-necked, 1-l. monel flask fitted with a stirrer and gas inlet and outlet. The flask was immersed in an ice bath and stirred while 20–40% fluorine diluted with nitrogen was introduced into the flask at a total gas flow rate of 200–400 ml/min for 60 min. The crude product was collected from the effluent stream in a glass U-trap cooled in a Dry Ice bath. When approximately 0.5 ml of crude product was collected in the U-trap, the trap was removed and additional product was collected in a second and third trap, etc.

Purification of the products was achieved by repeated codistillation[4] using a 10-mm copper column packed with fluorine-treated 40–60 mesh magnesium beads.

Fluorination of $NaN(CN)_2$.—Sodium dicyanamide (2 g, 20 mmol) and 20 g of magnesium fluoride were put into a 500-ml flask fitted with a stirrer, a fluorine inlet, and a gas outlet connected to a Dry Ice cooled trap. The rapidly stirred mixture was cooled in an ice bath and a 50:50 mixture of F_2–N_2 was passed through the flask at 200 cc/min for 60 min. During this time, about 1 cc of liquid was collected in the Dry Ice trap. The product was purified by codistillation.

The infrared data were obtained with a Perkin-Elmer Model 137B spectrophotometer. The cell had a 2.5-cm path length and NaCl windows. The vapor pressure was measured in a mercury-free system from −80 to −2°. The nuclear magnetic resonance spectrum was obtained on an instrument described by Baker and Burd.[5]

Registry No.—Sodium dicyanamide, 4615-74-1; cyanoguanidine, 461-58-5; $(F_2N)_2CFNFCF_2NF_2$, 16408-92-7; $F_2NC(=NF)NFCF_2NF_2$, 16408-93-8; I, 16408-94-9.

Acknowledgment.—This work was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by the Air Force Rocket Propulsion Laboratory, under Contact Nr. AF 33-(616)-6149.

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

[5] E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, **34**, 238 (1963); **28**, 313 (1957).

Effect of Fluorine on Photoelimination Reactions in Ketones

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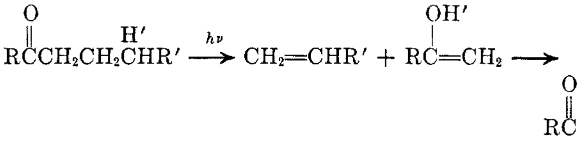
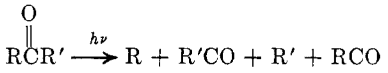
Considerable interest has been shown recently in the type II photolytic process in ketones. Wagner and Hammond[1] and Dougherty[2] have shown that both excited singlet and triplet species can be involved in solution while the work of Coulson and Yang[3] and Wagner[4] indicates that biradical species may also play a role. Earlier, it had been shown by Srinivasan,[5] by means of deuterium substitution, that the γ hydrogen is transferred to the carbonyl oxygen. The over-all process may be represented as



$$R\overset{\overset{O}{\|}}{C}CH_2CH_2\overset{H'}{C}HR' \xrightarrow{h\nu} CH_2{=}CHR' + R\overset{\overset{OH'}{|}}{C}{=}CH_2 \longrightarrow R\overset{\overset{O}{\|}}{C}CH_2H'$$

Nicol and Calvert[6] have carried out an extensive study of the effect of alkyl substitution on the vapor phase photolysis of a series of n-propyl ketones. Under these conditions the type I process is also important. Essentially no work has been carried out on the effect of substituents other than alkyl at the γ-carbon atom. For this reason we examined the effect of fluorine on the photolysis of 4,6,8,8,8-pentafluoro-3-octanone, $CF_3CH_2CHFCH_2CHFC(=O)CH_2CH_3$.



$$R\overset{\overset{O}{\|}}{C}R' \xrightarrow{h\nu} R + R'CO + R' + RCO$$

When irradiated either neat or in hydrocarbon solvents (0.2 M) four products could be detected by glpc. Only two of these could be separated in sufficient amount and purity for identification. 1-Fluoro-2-butanone was identified by comparison with a sample prepared independently from fluoroacetonitrile (Experimental Section). Glpc retention times, infrared, and H^1 and F^{19} nmr spectra were identical. 1,1,1,3,5-Pentafluoropentane was identified by comparison with a sample prepared from the 2:1 telomer of vinyl fluoride and trifluoromethyl iodide (Experimental Section).

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[1] P. J. Wagner and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 1245 (1966).

[2] T. J. Dougherty, *ibid.*, **87**, 4011 (1965).

[3] D. R. Coulson and N. C. Yang, *ibid.*, **88**, 4511 (1966).

[4] P. J. Wagner, *Tetrahedron Lett.*, **18**, 1753 (1967).

[5] R. Srinivasan, *J. Amer. Chem. Soc.*, **81**, 5061 (1959).

[6] C. H. Nicol and J. G. Calvert, *ibid.*, **89**, 1790 (1967).