to thank V. E. Wood and G. D. Green for help in conducting experiments; R. A. Meiklejohn, J. J. McBrady, H. L. Dinsmore, and S. Kulver for interpretation of infrared, nmr, and mass spectra; P. B. Olson and J. G. Gagnon for analytical determinations; R. L. Bohon for physical property measurements; and J. G. Erickson and R. A. Mitsch for their encouragement and helpful suggestions.

The Addition of Isocyanic Acid to Pentafluoroguanidine. Bis(difluoramino)fluoraminomethyl Isocyanate and Tris(difluoramino)methyl Isocyanate

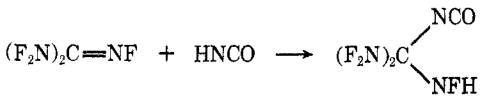
WILLIAM C. FIRTH, JR.,* SIMON FRANK, AND EDWARD J. SCHRIFFERT

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

Received September 26, 1972

Isocyanic acid and pentafluoroguanidine reacted in the presence of a catalyst to form a 1:1 adduct, bis(difluoramino)fluoraminomethyl isocyanate (**1**), and a 2:1 adduct (**2**). The products obtained from the reactions of **1** with ethyl alchol, water, isocyanic acid, and 100% sulfuric acid are described. Fluorination of **1** gave tris(difluoramino)methyl isocyanate (**3**) and tetrakis(difluoramino)methane.

In connection with a program on the synthesis of compounds with a high content of N–F bonds, the addition of isocyanic acid to pentafluoroguanidine[2,3] was investigated. The addition was successful,[4,5]



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

1

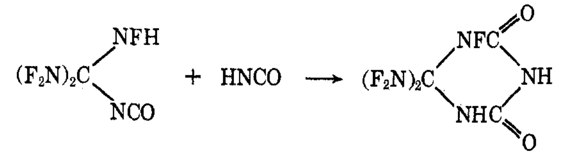
and the adduct proved to be a useful intermediate for the synthesis of a variety of new N–F compounds.

The low nucleophilicity of isocyanic acid and its rapid polymerization at room temperature operate against the desired addition to pentafluoroguanidine. Because of the low nucleophilicity of isocyanic acid, a basic catalyst, in this case urea, was added. When the catalyst was not used, erratic results were obtained. In order to minimize the polymerization reaction, a temperature of about −30° was used during the initial phase of the reaction. At this temperature isocyanic acid is quite stable, while at 0° it polymerizes readily.

The liquid 1:1 adduct (**1**) was separated from unchanged pentafluoroguanidine, isocyanic acid, and solid by-products by fractionation in a vacuum line.

The 1:1 adduct was assigned structure **1** on the basis of its infrared spectrum, proton and fluorine nmr spectra, and chemical reactions. Infrared absorptions at 3340 and 1410 cm^{-1} caused by the NH group in conjunction with a doublet of multiplets in the ^{19}F nmr spectrum at 125.0 ppm (J = 53 Hz) and a doublet at τ 1.59 (J = 53 Hz) in the ^{1}H nmr spectrum[6] establish the presence of an –NFH group. A broad, strong peak at −26.8 ppm was assigned to the difluoramino groups. Characteristic infrared absorptions at 2300 and 1480 cm^{-1} showed the presence of an isocyanate group.[8] The infrared spectrum is shown in Figure 1. Several reactions of **1** have established the presence of a carbon tetranitrogen skeleton and thus eliminated the possibility of a cyanate structure.

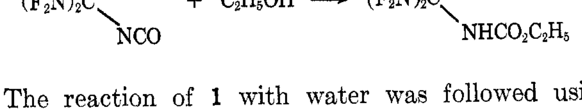
A 2:1 adduct (**2**) was extracted from the solid by-products formed during the preparation of **1**. It can also be prepared by the reaction of **1** with isocyanic acid.



1 **2**

The formulation of **2** as a cyclic compound is based upon the facts that the infrared and nmr spectra, respectively, show that the isocyanic acid has reacted with both the isocyanate and fluoramino groups, while its volatility (sufficient to allow vacuum sublimation at 50°) indicates that the compound is not a polymer. The question of whether the reaction occurs by initial reaction of the isocyanate or fluoramino group with isocyanic acid is not resolved.

The expected carbamate formed when **1** was treated with anhydrous ethyl alcohol.



$$(F_2N)_2C(NFH)(NCO) + C_2H_5OH \longrightarrow (F_2N)_2C(NFH)(NHCO_2C_2H_5)$$

The reaction of **1** with water was followed using fluorine nmr analysis. The results indicated that the amine which formed initially was unstable and lost difluoramine to form 1,1,2-trifluoroguanidine. Tri-

---

[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, and by the Bureau of Naval Weapons under Contract NOw 65-0277-c.

[2] R. A. Davis, J. L. Kroon, and D. A. Rausch, *J. Org. Chem.*, **32**, 1662 (1967); R. J. Koshar, D. R. Husted, and C. D. Wright, *ibid.*, **32**, 3859 (1967); R. J. Koshar and D. R. Husted, U. S. Patent 3,461,162 (1969).

[3] The pentafluoroguanidine was prepared by S. Frank, M. D. Meyers, and A. J. Fanelli, of these laboratories. An aqueous fluorination of guanidine hydrofluoride was used.

[4] A related addition of isocyanic acid to hexafluoroisopropylidenimine has been reported: W. J. Middleton and C. G. Krespan, *J. Org. Chem.*, **30**, 1398 (1965).

[5] Other adducts of pentafluoroguanidine have also been prepared: J. L. Zollinger, C. D. Wright, J. J. McBrady, D. H. Dybvig, F. A. Fleming, G. A. Kurhajec, R. A. Mitsch, and E. W. Neuvar, *ibid.*, **38**, 1065 (1973); C. D. Wright and J. L. Zollinger, *ibid.*, **38**, 1075 (1973).

[6] Fluorine and proton nmr spectra are reported in parts per million from trichlorofluoromethane and in τ values,[7] respectively.

[7] G. V. D. Tiers, *J. Phys. Chem.*, **62**, 1151 (1958).

[8] D. A. Barr and R. N. Haszeldine, *J. Chem. Soc.*, 3428 (1956).

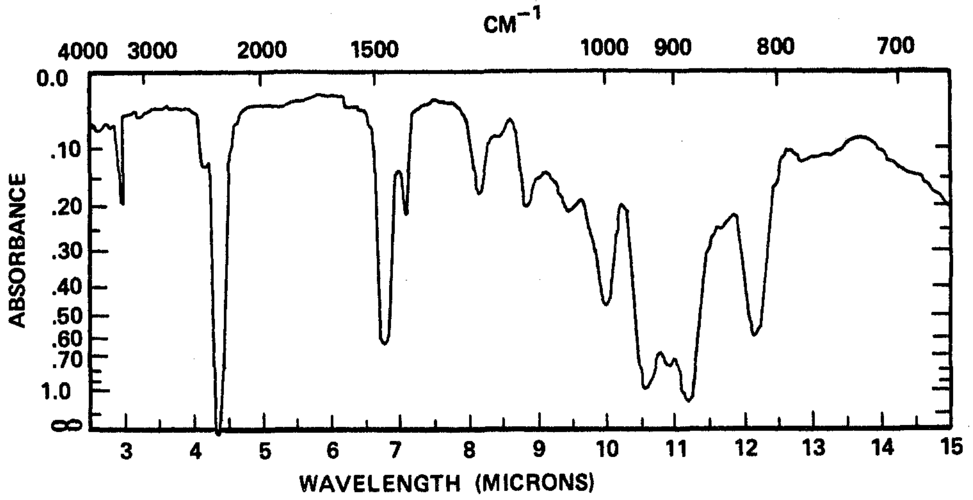


Figure 1.—Infrared spectrum of bis(difluoramino)fluoraminomethyl isocyanate (9 Torr in a 100-mm cell).

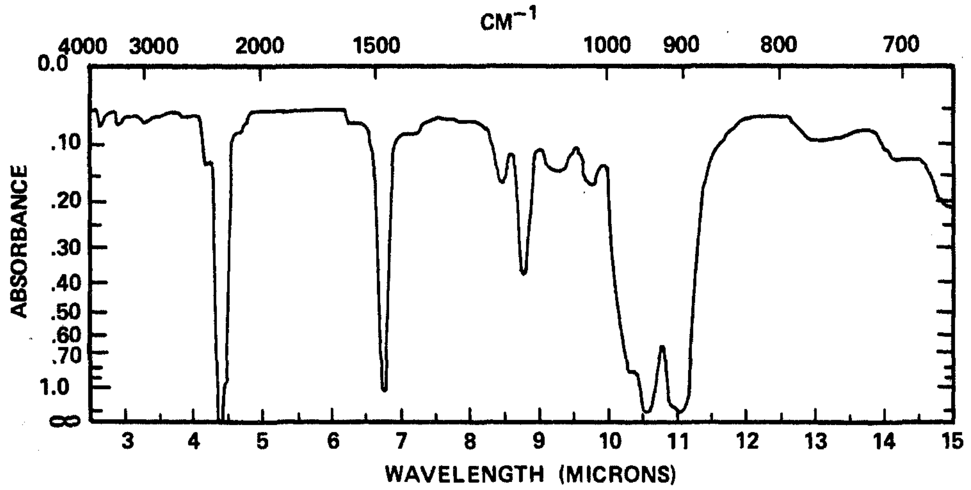
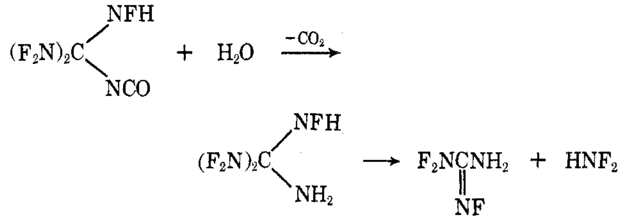


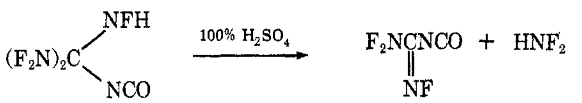
Figure 2.—Infrared spectrum of tris(difluoramino)methyl isocyanate (11 Torr in a 100-mm cell).

fluoroguanidine was isolated and identified on the basis of its infrared spectrum.



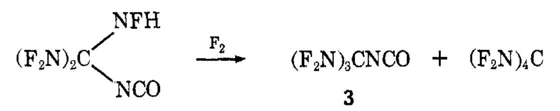
$$(F_2N)_2C(NFH)(NCO) + H_2O \xrightarrow{-CO_2} (F_2N)_2C(NFH)(NH_2) \longrightarrow F_2N\underset{\underset{NF}{\|}}{C}NH_2 + HNF_2$$

Trifluoramidino isocyanate[9] and difluoramine were formed when 1 was treated with 100% sulfuric acid.



$$(F_2N)_2C(NFH)(NCO) \xrightarrow{100\%\ H_2SO_4} F_2N\underset{\underset{NF}{\|}}{C}NCO + HNF_2$$

Mild fluorination of 1 gave a mixture of tris(difluoramino)methyl isocyanate (3) and tetrakis(difluoramino)methane. Sodium fluoride was present in the fluorination system as a hydrogen fluoride scavenger. It was later discovered that the sodium fluoride was necessary for formation of tetrakis(difluoramino)methane.[10] The conditions which have been developed for the preparation of either product in high yield will be described, together with the properties of tetrakis(difluoramino)methane, in another publication.[10] A scaled-up version of the process for the preparation of 3 was used to prepare samples for physical and chemical studies.[11] The isocyanate, a colorless liquid, bp 63°, was purified by fractional codistillation[12] or by treatment with sulfuric acid followed by fractionation in a vacuum line. The molecular weight, elemental analysis, infrared spectrum, and fluorine nmr spectrum were in good agreement with the proposed structure. The infrared spectrum is shown in Figure 2; band positions are given in the Experimental Section.



$$(F_2N)_2C(NFH)(NCO) \xrightarrow{F_2} \underset{\mathbf{3}}{(F_2N)_3CNCO} + (F_2N)_4C$$

---

[9] Trifluoramidino isocyanate was first prepared by T. H. Brownlee of these laboratories by the reaction of isocyanic acid with pentafluoroguanidine in sulfolane solution. We are grateful for permission to mention these results.

[10] S. Frank, W. C. Firth, Jr., and M. D. Meyers, *J. Org. Chem.*, **38**, 1088 (1973).

[11] We wish to thank the people of the Engineering Section of our department, under the direction of R. B. Wainright and R. C. Bell, for providing this material.

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

Experimental Section

Caution.—The compounds discussed in this paper which contain NF groups are very powerful explosives and extremely sensitive to impact, friction, and perhaps temperature changes! They are also strong oxidizing agents. Even quantities as small as 100 mg are regarded as dangerous. Therefore all work should be carried out with adequate protective clothing, equipment for remote manipulation of apparatus, and suitable barricades.[13]

Volatile reagents and products were manipulated in a Pyrex glass vaccum line. Joints and stopcocks were lubricated with Kel-F No. 90 grease. The reactions were carried out in Pyrex glass reactors made from Lab-Crest valves (Fisher and Porter Co.). Apparatus was routinely dried.

Fluorine and proton nmr spectra were obtained with a Varian DP-60 high-resolution spectrometer operating at 56.4 MHz. Chemical shifts are in parts per million from trichlorofluoromethane (internal standard or solvent), and a negative chemical shift means a deshielded ^{19}F nucleus compared to the standard. Proton spectra are given in τ values.[7]

Unless specified, infrared spectra were obtained with a Perkin-Elmer Model 137B instrument. The melting point data on solid compounds were obtained on a Fisher-Johns apparatus and are uncorrected.

Isocyanic acid was prepared by the procedure described in the literature,[14,15] with a few exceptions. Cyanuric acid (Eastman Kodak Co., Eastman Grade) was used without purification, but was dried at 200° *in vacuo*.[16] The isocyanic acid was dried with phosphorus pentoxide and distilled in a vacuum line. Treatment with silver oxide to remove hydrogen cyanide was unnecessary for our purposes and was omitted. The isocyanic acid could be stored indefinitely in a Dry Ice bath, and was handled as a gas at pressures of about 100 mm in a vacuum line. Above 140 mm polymerization may occur.[16]

Bis(difluoramino)fluoraminomethyl Isocyanate (1).—Equimolar amounts (1.5 mmol each) of pentafluoroguanidine and isocyanic acid were condensed into a dry reactor, which contained powdered urea (9.0 mg, 0.15 mmol) as a catalyst. The reaction was allowed to proceed at −30° for 3 hr and then for 1 hr at room temperature. The volatile products were fractionated in a vacuum line. A −45° trap retained **1** in generally 30–50% yield based on pentafluoroguanidine charged. Nmr spectra were determined on a dilute solution of **1** in trichlorofluoromethane, with tetramethylsilane as an internal proton standard.

The adduct **1** formed small amounts of difluoramine and a yellow syrup upon standing for 1 week in the liquid phase at room temperature, but was recovered essentially quantitatively after being heated as a liquid for 4 hr at 70°.

The −45° volatiles from the reaction consisted of unchanged isocyanic acid and pentafluoroguanidine. The reactor contained a white solid from which the 2:1 adduct **2** could be extracted with either anhydrous methanol or anhydrous ethyl ether. Either recrystallization or vacuum sublimation was used for purification. Another preparation is described below.

6,6-Bis(difluoramino)-5-fluorodihydro-*s*-triazine-2,4(1*H*,3*H*)-dione (2).—Equimolar quantities (1.0 mmol each) of **1** and isocyanic acid were vacuum transferred into a small, dry sublimation apparatus, which contained 0.1 mmol of urea. The same time-temperature program that was used for the preparation of **1** produced a 90–100% conversion to **2**. In a similar reaction in which no urea was added, only a trace amount of a solid product was produced.

The solid product was vacuum sublimed at 50°: mp 143–145° dec; $\nu_{\text{max}}^{\text{mineral oil}}$ 3230 (NH), 1780 and 1748 (C═O), and complex NF absorptions. The fluorine nmr spectrum in methanol solution showed broad peaks at −22.5 (NF_2) and 90.2 ppm (NF) from trichlorofluoromethane (internal). The compound was soluble in methanol, ethyl ether, and sulfur dioxide and insoluble in trichlorofluoromethane and benzene.

Anal. Calcd for $C_3H_2F_5N_5O_2$: F, 40.41; N, 29.79. Found: F, 39.69; N, 29.01.

Ethyl Bis(difluoramino)fluoraminomethylcarbamate.—Reagent grade ethanol (0.6 mmol), predried over Drierite, and **1** (0.6 mmol) were condensed into a 1.3-ml reactor at −196°. After 1 hr at room temperature, small amounts of difluoramine and ethanol were removed from the solid carbamate: mp 62–64°; $\nu_{\text{max}}^{\text{mineral oil}}$ 3410 (NH), 3220 (NH), 1740 (C═O),[8] and 1500 cm^{-1} (NH deformation),[8] and broad bands in the NF region; ^1H nmr (in trichlorofluoromethane) τ −0.45 (doublet, broad lines, NFH, J = 48.5 Hz), 3.67 (broad, NH), 5.76 (quadruplet, CH_2), 8.69 (triplet, CH_3); ^{19}F nmr (in trichlorofluoromethane) showed two broad peaks at −22.8 and −22.2 ppm caused by some nonequivalence in the NF_2 groups and a doublet (broad lines, $J = 45 \pm 5$ Hz) at 131.8 ppm (NFH).

The carbamate was stable at room temperature for at least 16 hr and in trichlorofluoromethane solution for at least 57 days.

Reaction of 1 with Water (Preparation of 1,1,2-Trifluoroguanidine).—A 1.3-ml reactor was charged with 0.5 mmol of water and anhydrous ethyl ether (solvent). Then **1** (0.38 mmol) and trichlorofluoromethane (0.5 mmol) were added by vacuum transfer to the reactor at −196°. The reaction mixture was allowed to stand for 1 hr at 0° and, finally, allowed to warm to room temperature. Effervescence occurred intermittently.

After 1 hr at room temperature, the ^{19}F nmr spectrum showed peaks for 1,1,2-trifluoroguanidine (−47.4, NF_2; 50.7, ═NF), aminobis(difluoramino)fluoraminomethane (−20.6, NF_2; 135.8 doublet, broad lines, NHF), and difluoramine (6.95). After 6 hr at room temperature, the sample showed strong signals due to the trifluoroguanidine and difluoramine, and much weaker signals at −36.9 and −35.2 ppm.

In another experiment, whose object was the preparation of the urea, **1** (0.48 mmol) and water (0.24 mmol) were combined at −196° and allowed to warm to room temperature. After 1 hr the volatile fraction at room temperature was removed, leaving a trace of unidentified yellow syrup. Infrared analysis of the volatiles showed difluoramine, silicon tetrafluoride, some recovered **1**, and the trifluoroguanidine. 1,1,2-Trifluoroguanidine was isolated by vacuum line fractionation using a −2° trap and identified by its major infrared absorptions: $\nu_{\text{max}}^{\text{gas}}$ 3584 and 3472 (NH_2), 1704 (C═N), 1570 (NH deformation), 870 cm^{-1} (broad, NF).

Reaction of 1 with 100% Sulfuric Acid.—The 100% sulfuric acid was prepared by adding 97% sulfuric acid to 20% fuming sulfuric acid until no fumes were observed when moist air was passed over the liquid (fair and foggy method).[17] The sulfuric acid was added to a 5-mm o.d. reactor to a height of 15 mm, and **1** (0.38 mmol) was added by vacuum transfer. After 0.5 hr of reaction infrared analysis of the volatile fraction showed recovered **1**, trifluoramidino isocyanate, and difluoramine. The reaction was allowed to resume. After 2 hr of reaction, infrared analysis showed only trifluoramidino isocyanate and difluoramine.

Tris(difluoramino)methyl Isocyanate (3).—The adduct **1** was fluorinated[10] and the resulting **3** was purified by fractional codistillation.[12] The fluorine nmr spectrum showed a broad, strong peak at −30.1 ppm in trichlorofluoromethane solution. This sample was stored for over 3 years without change in the nmr spectrum.

Anal. Calcd for $C_2F_6N_4O$: C, 11.4; N, 26.7; F, 54.3. Found: C, 11.7; N, 25.5; F, 52.7.

Additional samples were purified by treatment with 96% sulfuric acid. In a typical procedure, the crude isocyanate (1.4 mmol), which appeared to be contaminated with tris(difluoramino)methylamine and trifluoramidino isocyanate according to its infrared spectrum, was condensed at −196° into an evacuated reactor (volume *ca.* 4 ml) containing 1.0 ml of 96% sulfuric acid. The reaction mixture was allowed to thaw and was then stirred for 1 hr at room temperature. The product was fractionated in a vacuum line with traps at −45 and −78°. No gaseous material was retained by the −45° trap. The purified isocyanate (1.2 mmol) condensed at −78°. Analysis by fractional codistillation found 99.0% tris(difluoramino)methyl isocyanate, 0.6% (probably) tris(difluoramino)methylamine, and 0.4% (probably) carbon dioxide.

The following properties were determined on isocyanate which had been purified by treatment with sulfuric acid [mol wt 210 (calcd 210)]. The infrared spectrum was obtained by Mr. N. B.

---

[13] The various types of shielding to be used with such compounds have been described by C. L. Knapp, *Ind. Eng. Chem.*, **55**, No. 2, 25 (1963), and D. R. Smith, *J. Chem. Educ.*, **41**, A520 (1964).

[14] G. Brauer, "Handbuch der Praparativen Anorganischen Chemie," Vol. I, Ferdinand Enke, Stuttgart, Germany, 1960, p 592.

[15] We wish to thank Dr. Robert Church, formerly of these laboratories, for an initial gift of isocyanic acid.

[16] G. Herzberg and C. Reid, *Discuss. Faraday Soc.*, **9**, 92 (1950).

[17] W. J. Jolly, "Synthetic Inorganic Chemistry," Prentice-Hall, Englewood Cliffs, N. J., 1960, pp 122–123.

Colthup using a Perkin-Elmer Model 521 grating infrared spectrophotometer. Sample pressures of 11, 4, and 2 mm in a 100-mm cell were used: $\nu_{\max}^{\text{gas}}$ (w, m, s, v, sh = weak, medium, strong, very, shoulder) 3770 (vw), 3430 (vw), 3055 (vw), 2395 (w), 2292 (vs, NCO asymmetric stretching), 2247 (s), 2150 (vw, sh), 1587 (vw), 1488 (s, NCO symmetric stretching), 1400 (vw), 1180 (w), 1140 (m, N–C–N asymmetric stretching), 1080 (w), 1022 (w), 968 (s, sh, NF_2 stretching), 947 (s, NF_2 stretching), 907 (s, NF_2 stretching), 760 (vw), 700 (vw). The gas at pressures of 55 and 118 mm in a 5-cm quartz cell showed continuous absorption in the ultraviolet region beginning at *ca.* 270 mμ, with an extremely weak, anomalous peak at 253 mμ superimposed on the general absorption.

The vapor pressure curve was measured in a grease-free system constructed from Lab-Crest valves (Fisher and Porter Co.). Pressures were measured with a 10-mm o.d. mercury manometer and a meter stick. Temperatures were measured with a calibrated copper–constantan thermocouple, made from Leeds and Northrup No. 24-55-1-A wire, and a Leeds and Northrup temperature potentiometer, Cat. No. 8692. The sample was cooled to −78° and pumped on immediately before it was introduced into the vapor pressure apparatus. After the data were obtained the sample was analyzed by fractional codistillation [found: isocyanate, 99.4%, probably tris(difluoramino)methylamine, 0.6%]. The vapor pressure data were described by the equation log P (mm) = $-1728/T + 8.0208$; extrapolated bp 63 ± 1°; ΔH_v 7.91 kcal/mol; Trouton's constant 23.5.

Registry No.—**1**, 37950-68-8; **2**, 37950-69-9; **3**, 37950-70-2; pentafluoroguanidine, 10051-06-6; isocyanic acid, 75-13-8; ethyl bis(difluoramino)fluoraminomethylcarbamate, 37950-71-3; trichlorofluoromethane, 75-69-4; 1,1,2-trifluoroguanidine, 37950-72-4.

Acknowledgment.—We wish to thank Dr. J. E. Lancaster and Mrs. M. Neglia for obtaining the nmr spectra and Mr. J. H. Deonarine and staff of the Research Service Department of these laboratories for the elemental analyses. We also wish to thank Dr. V. P. Wystrach for encouragement and guidance.

The Chemistry of Tris(difluoramino)methyl Isocyanate

William C. Firth, Jr.,* and Simon Frank

American Cyanamid Company,[1] Stamford Research Laboratories, Stamford, Connecticut 06904

Received September 26, 1972

Tris(difluoramino)methyl isocyanate (**1**) reacted with a variety of reagents to form compounds containing a tris(difluoramino)methyl group attached to a nitrogen substituent. Carbamates were prepared from methanol, ethylene glycol, allyl alcohol, poly(allyl alcohol), glycidol, and polyglycidol. Ammonia gave the urea **2**, which was converted to the biuret **3** by additional isocyanate. The biurea **4** was formed with hydrazine. Results obtained when the isocyanate was treated with nitramide are also described. The isocyanate reacted with water to form the amine **6**, which reacted under special conditions with additional isocyanate to form the 1,3-disubstituted urea **7**. The isocyanate formed a 1:1 adduct with pyridine and a formamidine (**8**) with dimethylformamide. Isobutylene and butadiene did not react appreciably with the isocyanate, and acids did not give the expected reactions. Nmr spectra of the products are discussed.

The preparation of tris(difluoramino)methyl isocyanate (**1**)[2] made possible the relatively facile synthesis of a variety of interesting compounds containing a tris(difluoramino)methyl group attached to a nitrogen substituent, compounds containing the rare carbon tetranitrogen skeleton. The preparation and characterization of these derivatives are described in this paper.

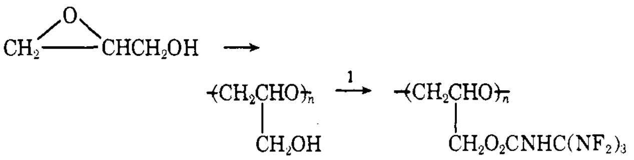
Reactions with Alcohols.—Alcohols reacted as expected with the isocyanate to form carbamates. No catalyst was necessary to obtain products from methanol, ethylene glycol, allyl alcohol, glycidol, polyglycidol, and poly(allyl alcohol). Di- and polycarbamates formed without difficulty from ethylene glycol and polyhydroxylic alcohols. However, satisfactory conditions for reaction with poly(vinyl alcohol) were not found, because of the lack of a suitable solvent. The carbamates were thermally quite stable. Thus, the methyl carbamate was recovered unchanged after 4 hr at 71-76° in a sealed tube, and the polyglycidol adduct was heated to 150° on a Koefler hot-stage microscope without sign of decomposition.

$$(F_2N)_3CNCO + ROH \longrightarrow (F_2N)_3CNHCO_2R$$

Attempted polymerization of allyl tris(difluoramino)methylcarbamate gave a viscous liquid from which an amorphous solid could be isolated.

The carbamate from glycidol and **1** gave a complex product when treated with boron trifluoride. Thus, two main peaks were observed in the fluorine nmr spectrum, and there was a strong unexpected infrared absorbtion at 1689 cm^{-1} in addition to the expected carbonyl absorption at 1764 cm^{-1}. A similar product was obtained when the glycidol adduct was heated in an attempt to effect the rearrangement reported[3] for N-substituted glycidyl carbamates. These materials were not characterized further.

The carbamate of polyglycidol was made by an alternate route involving polymerization of glycidol[4] followed by reaction with **1**. Similarly, an adduct of poly(allyl alcohol) and **1** was prepared. Both of these adducts contained some unchanged hydroxyl groups.



Reactions with NH Compounds.—Ammonia reacted rapidly with the isocyanate to form the urea **2**, which

---

[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, and by the Bureau of Naval Weapons under Contracts NOw 65-0277-c and NOw 66-0397-c.

[2] W. C. Firth, Jr., S. Frank, and E. J. Schriffert, *J. Org. Chem.*, **38**, 1080 (1973).

[3] Y. Inakura and Y. Taneda, *ibid.*, **24**, 1992 (1959).

[4] S. R. Sandler and F. R. Berg, *J. Polym. Sci., Part A-1*, **4**, 1253 (1966).