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: ν_{max}^{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 $\log P\ (\text{mm}) = -1728/T + 8.0208$; 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.

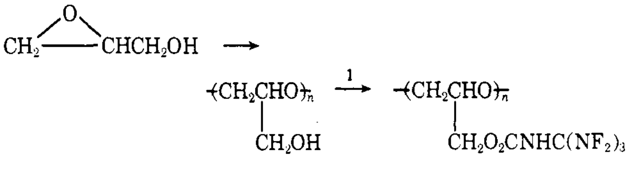
Reactions with Alcohols.—Alcohols reacted as expected with the isocyanate to form carbamates. No catalyst was necessary to obtain products from methanol, ethylene glycol, allyl alcohol, glycidol, polyglycidol, and poly(allyl alcohol). Di- and polycarbamates formed without difficulty from ethylene glycol 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

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[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).

$$(F_2N)_3CNCO + NH_3 \longrightarrow \underset{2}{(F_2N)_3CNHCONH_2} \xrightarrow{1} \underset{3}{[(F_2N)_3CNHCO]_2NH}$$

reacted slowly with additional isocyanate to form the biuret **3**. The urea and perchloric acid formed a perchlorate salt.

$$(F_2N)_3CNHCONH_2 + HClO_4 \longrightarrow (F_2N)_3CNHCONH_3{}^+ClO_4{}^-$$

Hydrazine reacted with 2 mol of isocyanate to form the biurea **4**. These products from ammonia and

$$2(F_2N)_3CNCO + N_2H_4 \longrightarrow \underset{4}{[(F_2N)_3CNHCONH]_2}$$

hydrazine are white solids, which explode violently upon mild impact. They decomposed, without melting, below 200° on a melting point block.

Nitramide and **1** formed an unstable adduct which decomposed into the carbamic acid **5** and nitrous oxide. The carbamic acid is also unstable and, in turn, forms the amine **6** and carbon dioxide.

$$(F_2N)_3CNCO \xrightarrow{NH_2NO_2} [(F_2N)_3CNHCONHNO_2] \xrightarrow{-N_2O} \underset{5}{(F_2N)_3CNHCO_2H}$$

$$(F_2N)_3CNHCO_2H \longrightarrow \underset{6}{(F_2N)_3CNH_2} + CO_2$$

Reaction with Water.—Usually water and isocyanates react to form ureas. However, isocyanates which bear strong electron-withdrawing substituents will give the amine instead.[5] As might be expected, therefore, **1** reacts with water to form the amine **6** rather

$$(F_2N)_3CNCO + H_2O \longrightarrow (F_2N)_3CNHCO_2H \longrightarrow \underset{6}{(F_2N)_3CNH_2} + CO_2$$

than the urea under ordinary conditions. A basic catalyst can be used, but is not necessary for reaction. The formation of the intermediate carbamic acid has been observed by nmr spectroscopy in an uncatalyzed reaction, and a small amount was isolated and characterized by its infrared spectrum.

Preparation of the urea **7** by reaction of the amine and

$$(F_2N)_3CNH_2 + (F_2N)_3CNCO \longrightarrow \underset{7}{(F_2N)_3CNHCONHC(NF_2)_3}$$

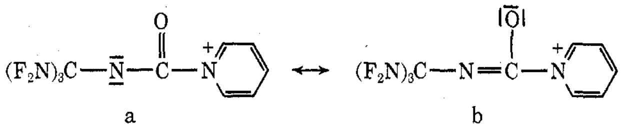
isocyanate was attempted. However, the amine was very unreactive. For example, there was no reaction after 19 days at room temperature in ethyl ether–trichlorofluoromethane solution. Even after 64 days only a small amount of reaction had occurred.

However, it was then discovered that triphenylphosphine oxide caused the amine and isocyanate to form a complex of the desired urea and triphenylphosphine oxide relatively rapidly.[6] The urea was displaced from the complex by trifluoroacetic acid and other acids. Complexes of tertiary phosphine oxides

$$(F_2N)_3CNH_2 + (F_2N)_3CNCO + (C_6H_5)_3PO \longrightarrow [(F_2N)_3CNH]_2C{=}O\cdot(C_6H_5)_3PO \xrightarrow{CF_3CO_2H} [(F_2N)_3CNH]_2C{=}O + (C_6H_5)_3PO\cdot CF_3CO_2H$$

and various acids are known, and the infrared spectra of some of the complexes have been described.[7] Comparison of the infrared spectra of the urea, triphenylphosphine oxide, and the crude complex indicated that the urea and phosphine oxide formed a complex in which the phosphine oxide is hydrogen bonded to the NH groups. This conclusion is based upon a shift to longer wavelength of the P=O absorption in the complex compared to the free phosphine oxide. The carbonyl group of the complexed urea is less hydrogen bonded than that of the free urea and absorbs at a shorter wavelength.

Adduct Formation with Pyridine.—When pyridine was treated with a 100% molar excess of the isocyanate in acetonitrile solution, or without a solvent, a high yield of a 1:1 adduct was obtained.[8] The isocyanate was liberated from the adduct by hydrogen chloride and boron trifluoride. The infrared spectrum of the adduct shows a strong carbonyl absorption at 1770 cm^{-1}. This wavelength is consistent with a structure in which there is little contribution from resonance hybrid b, probably because of enhanced stabilization of the negative charge on nitrogen by the tris(difluoramino)methyl group.



Several reaction products from the isocyanate and pyridine, in which the amount of pyridine was varied up to a maximum of 100 mol %, were examined by ^{19}F nmr. As the pyridine content of the mixture increased, the chemical shift of the tris(difluoramino)methyl peak became progressively more positive. However, only one peak was observed even though the amount of pyridine was insufficient to combine with all of the isocyanate. These data indicate that the pyridine–isocyanate complex rapidly exchanges with uncomplexed isocyanate.

The data seem more consistent with simple complex formation than with a dimerization induced by the pyridine. If pyridine does induce the formation of a dimer, the dimer must rapidly exchange with isocyanate and must also dissociate back to isocyanate when the pyridine is neutralized with acids.

Reaction with Dimethylformamide.—In harmony with the chemistry of other isocyanates,[9a,b] dimethylformamide and **1** condensed with the elimination of carbon dioxide to form the formamidine, a liquid of low volatility. The reaction took place easily at room temperature.

$$(F_2N)_3CNCO + HCON(CH_3)_2 \longrightarrow \underset{8}{(F_2N)_3CN{=}CHN(CH_3)_2} + CO_2$$

Attempted Reactions with Olefins.—Because **1** reacted easily with dimethylformamide at room temperature, as does *p*-toluenesulfonyl isocyanate,[9a] the

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[5] J. H. Saunders and K. C. Frisch, "Polyurethanes: Chemistry and Technology," Part I, Chemistry, Interscience, New York, N. Y., 1962, pp 76–78.

[6] Catalysis of isocyanate reactions by pyridine *N*-oxide has been reported: J. Burkus, *J. Org. Chem.*, **27**, 474 (1962). To our knowledge, phosphine oxides have not been used before.

[7] J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. I, Interscience, New York, N. Y., 1958, p 287; D. Hadzi, *J. Chem. Soc.*, 5128 (1962).

[8] H. Ulrich, *Chem. Rev.*, **65**, 369 (1965), has reviewed comparable adducts of sulfonyl isocyanates.

[9] (a) C. King, *J. Org. Chem.*, **25**, 353 (1960); (b) M. L. Weiner, *ibid.*, **25**, 2245 (1960).

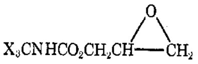
possibility that it would show reactivity with olefins comparable to chlorosulfonyl isocyanate[10] was investigated. While chlorosulfonyl isocyanate reacts readily with isobutylene and butadiene, **1** failed to react appreciably with isobutylene in the liquid phase at room temperature during 23 days. The mixture (96% recovery) was unchanged according to analysis by infrared spectroscopy. Similarly, 97% of a mixture of **1** and 1,3-butadiene was recovered after 8 days.

Attempted Reactions with Acids.—While a number of attempts were made to add acids to **1**, the usual result was little or no reaction. Formic acid and isocyanic acid failed to react in the absence of a catalyst. The isocyanic acid polymerized, but essentially all of **1** was recovered. Hydrogen chloride failed to react with **1** in trichlorofluoromethane solution with pyridine as the catalyst.

Nmr Spectra.—The ^{19}F nmr spectra for a number of compounds containing a tris(difluoramino)methyl group attached to a nitrogen substituent are listed in Table I in order of chemical shift. They occur within a relatively small range (−24.2 to −30.1 ppm). The chemical shifts of structurally similar compounds are further clustered within this range. Thus, the chemical shifts of compounds in which the tris(difluoramino)methyl group is attached to N_3, NF_2, or NCO are at the deshielded end, all of the compounds of the $(F_2N)_3CNHCON<$ type occur in approximately the middle of the range, and compounds in which tris(difluoraminomethyl) groups are attached to NH_2 and $N{=}CN(CH_3)_2$ groups are found at the shielded end of the range. It appears to be possible to use these empirical correlations to draw tentative conclusions about the possibility of a tris(difluoramino)methyl compound in an unknown mixture and even the type of compound present.

TABLE I

^{19}F NMR SPECTRA OF TRIS(DIFLUORAMINO)METHYL GROUPS ATTACHED TO VARIOUS NITROGEN SUBSTITUENTS

Compd ($X = NF_2$)	Solvent	δ_F[a]
$X_3CN{=}CHN(CH_3)_2$	$CFCl_3$	−24.2[b]
X_3CNH_2	$CFCl_3$	−24.5
X_3CNHCO_2H	$(C_2H_5)_2O$	−26.8
$X_3CNHCO_2CH_3$	$CFCl_3$	−26.8
	$CFCl_3$	−26.9[c]
$X_3CNHCO_2CH_2CH{=}CH_2$	$CFCl_3$	−27.2
$X_3CNHCONH_2$	$(C_2H_5)_2O$	−27.3
$(X_3CNHCONH)_2$	CH_3CN	−28.0
$(X_3CNHCONHCX_3)(Ph_3PO)$	CH_2Cl_2	−28.0
$(X_3CNHCO)_2NH$	$(C_2H_5)_2O$	−28.1[d]
$(X_3CNH)_2CO$	$(C_2H_5)_2O$	−28.2
X_3CN_3[e]	$CFCl_3$	−28.7
$X_3CNHCONH_3{}^+ClO_4{}^-$	CH_3NO_2	−28.9
X_4C[f]	$CFCl_3$	−29.5
X_3CNCO[f]	$CFCl_3$	−30.1

[a] Parts per million from trichlorofluoromethane (internal). [b] Weak additional peak at −27.6. [c] Weak additional peak at −25.9. [d] Very weak additional peak at −27.3. [e] M. D. Meyers, unpublished results. [f] Reference 2.

The adducts of tris(difluoramino)methyl isocyanate and active hydrogen compounds showed surprisingly sharp ^{19}F nmr peaks compared to tris(difluoramino)methyl isocyanate itself and many other NF compounds.

The proton nmr spectra of compounds with the $(F_2N)_3CNHCOY$ structure were observed as broad lines, a common shape for protons attached to nitrogen, in the range of τ 0.49–2.1. τ values of this magnitude indicate that the protons are more acidic than those of ordinary *N*-alkylamides,[11] an effect no doubt caused by the electron-withdrawing effect of the tris(difluoramino)methyl group. When the substituent Y also contained NH groups, the latter were observed as separate peaks, and so the proton environments of the NH groups are not rapidly averaged by exchange.

Experimental Section

Caution.—The compounds described 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.[12]

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

^{19}F nmr spectra (Table I) 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. ^{1}H nmr spectra were determined with either a Varian DP-60 or Varian A-60 spectrometer and calibrated with tetramethylsilane (internal). The results are reported in τ values.[13]

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

Methyl Tris(difluoramino)methylcarbamate.—Less than 1 mmol of isocyanate was condensed at −196° into a reactor containing anhydrous reagent-grade methanol in 30–50 mol % excess. The reaction was allowed to take place at room temperature. The excess methanol was removed by vacuum transfer, and the residual carbamate was purified by vacuum sublimation: mp 43–44°; $\nu_{\max}^{\text{mineral oil}}$ 3280 (NH), 1740 (C=O),[14] 1515 cm^{-1} (NH deformation)[14] and broad, strong NF absorptions.

Anal. Calcd for $C_3H_4F_6N_4O_2$: F, 47.09. Found: F, 47.70.

Ethylene *N*,*N'*-Bis[tris(difluoramino)methyl] dicarbamate.—Ethylene glycol (0.11 mmol) and the isocyanate (0.3 mmol) were allowed to react at room temperature for 25 hr. The volatile fraction was removed under vacuum to give a solid residue (49 mg, 96% yield of dicarbamate based on ethylene glycol): mp 136–137°; $\nu_{\max}^{\text{mineral oil}}$ 3236 (NH), 1748 (C=O), 1534 cm^{-1} (NH deformation), strong bands in the NF region.

Anal. Calcd for $C_6H_6F_{12}N_8O_4$: F, 47.29. Found: F, 46.70.

Allyl Tris(difluoramino)methylcarbamate.—Redistilled allyl alcohol (68 µl, 1.0 mmol) and the isocyanate (1.10 mmol) were allowed to react for 17 hr at room temperature. The reactor was then cooled to 0°, and the volatile fraction (0.11 mmol) was removed by vacuum transfer until the residue, a colorless liquid, showed no vapor pressure at room temperature. The yield was 269.8 mg (100% based on allyl alcohol).

The preparation was also carried out in trichlorofluoromethane and in ethyl ether. Center cuts of the carbamate were obtained by bulb-to-bulb distillation at room temperature: mp 11.6–12.6°; $\nu_{\max}^{\text{liquid}}$ 3436 (sh) and 3268 (NH), 2985 (CH), 1754 (C=O), 1520 (NH deformation), and 990–885 cm^{-1} (three broad bands,

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[10] R. Graf, *Justus Liebigs Ann. Chem.*, **661**, 111 (1963); H. Hoffmann and H. J. Diehr, *Tetrahedron Lett.*, **No. 27**, 1875 (1963).

[11] M. W. Dietrich and R. E. Keller, *Anal. Chem.*, **36**, 258 (1964).

[12] 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).

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

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

NF); proton nmr in carbon tetrachloride at τ 3.13 (broad, 1.0 H, NH), 5.31 (1.9 H, CH_2), *ca.* 4.67 (2.0 H, CH_2=), and *ca.* 4.10 (1.1 H, =CH-).[15]

Polymerization of the Allyl Tris(difluoramino)methylcarbamate.—The carbamate was converted to a viscous liquid by heat, either alone or with benzoyl peroxide as catalyst. A hard, amorphous, light amber solid could be isolated by removal of most of the volatile material under vacuum at 25–50° and then the extraction of the residue with carbon tetrachloride. The lack of absorption at 1420 cm^{-1} in Halocarbon oil indicated the absence of monomer.

2,3-Epoxypropyl Tris(difluoramino)methylcarbamate.—Eastman grade glycidol was freshly distilled bulb-to-bulb at *ca.* 60° under vacuum. The glycidol (0.99 mmol) and isocyanate (1.10 mmol) were combined at −196° and allowed to react at room temperature for 18 hr. The volatile fraction was removed at room temperature until the colorless, viscous liquid residue showed essentially no vapor pressure at room temperature. The yield was essentially quantitative: ν_{max}^{liquid} 3205 (NH), 1764 (C=O), 1522 cm^{-1} (NH deformation); ^{1}H nmr (in trichlorofluoromethane) τ 2.36 (1 H, broad, NH), *ca.* 5.4 and *ca.* 6.1 (2 H, $-OCH_2-$), *ca.* 6.75 (1 H, ring CH), *ca.* 7.2 (2 H, ring CH_2).

Anal. Calcd for $C_5H_6F_6N_4O_3$: F, 40.12. Found: F, 40.67.

Some infrared spectra of this carbamate showed weak bands which were characteristic of products obtained when this carbamate was treated with boron trifluoride (see below) or heated for several hours at 55–85°.

Reaction of 2,3-Epoxypropyl Tris(difluoramino)methylcarbamate Catalyzed by Boron Trifluoride.—A solution of the carbamate in trichlorofluoromethane was treated with a catalytic amount of boron trifluoride at −196° and then allowed to react at 0° overnight and at room temperature for *ca.* 27 hr. The product was washed with trichlorofluoromethane and dried under vacuum. Essentially the same product was formed when the carbamate was treated with boron trifluoride under comparable conditions, but without a solvent.

The product varied from an amorphous solid to a syrup and showed ν_{max}^{neat} 3425, 3226 (NH), 1764 (C=O), 1689, and 1522 cm^{-1} (NH deformation); ^{19}F nmr at −27.3 (strong, sharp), −26.4 (medium, sharp), and −24.5 ppm (very weak) in acetone-d_6.

Adduct of Polyglycidol and 1.—Polyglycidol was prepared as described in the literature[4] from 1 g of glycidol and 9 mg of pyridine. The polyglycidol (70 mg, 0.94 mmol) and 1 (1.1 mmol) were allowed to react for 21 hr at room temperature and for 24 hr at 59–60°. The volatile fraction was removed at room temperature and at 60–64° under vacuum. The yield of adduct was 228 mg, corresponding to the addition of 0.748 mmol of isocyanate and a fluorine content of 37.6% (found, 36.5%). The product was an amorphous white powder at 90 × magnification, $\nu_{max}^{mineral\ oil}$ 3425, 3268, 1767 (C=O), and 1531 cm^{-1} (NH deformation). The sample appeared to soften and melt from less than 60° to *ca.* 100° to give a clear viscous liquid. There was no sign of decomposition when heating was continued up to 150°.

Adduct of Poly(allyl alcohol) and 1.[16]—Poly(allyl alcohol) was prepared as described in the patent literature[17] by heating allyl alcohol at 100° for 144 hr with 2.1% of a 90% aqueous solution of hydrogen peroxide (1.9% hydrogen peroxide). The product was pumped on for 2 hr at 105°.

The poly(allyl alcohol) (0.88 mmol) and isocyanate (0.98 mmol) were allowed to react in acetonitrile for 18 hr at room temperature. The polymer dissolved as the reaction proceeded. A volatile fraction was removed by vacuum transfer at room temperature, and the residue was dissolved in anhydrous ethyl ether (0.5 ml). The ether solution was added dropwise to 12 ml of *n*-heptane, and the precipitated polymer was dried under vacuum, $\nu_{max}^{mineral\ oil}$ 3546, 3448, 3300, 1751 (C=O), and 1524 cm^{-1} (NH deformation). The polymer obtained was 86% of that calculated for complete reaction. The fluorine content indicated that some unchanged hydroxyl groups remained.

Anal. Calcd for $(C_5H_6F_6N_4O_2)_n$: F, 42.53. Found: F, 36.89.

Tris(difluoramino)methylurea.—The isocyanate (0.90 mmol) and anhydrous ethyl ether (7.8 mmol) were added by vacuum transfer to a reactor (*ca.* 4 ml) and stirred. The reactor was cooled to −196° and 0.86 mmol of anhydrous ammonia was added by vacuum transfer. The bath was then removed and, as soon as the reaction mixture liquefied, stirring was started. Stirring was continued for 1.25 hr. The volatile fraction was then removed under vacuum. The residue was dissolved in *ca.* 2 ml of dry ethyl ether, and the solution was transferred to two dry centrifuge tubes. Each solution was concentrated to *ca.* 0.4 ml using a stream of prepurified nitrogen. Anhydrous redistilled petroleum ether (bp 30–60°) was added to bring the total volume of solution in each tube to 3.5 ml. The white solid which precipitated was separated and dried at room temperature. The yield was 150 mg (0.66 mmol, 77% based on ammonia), $\nu_{max}^{mineral\ oil}$ 3559, 3390, 3205, 1733 (C=O), 1695 (C=O), and 1546 cm^{-1} (NH deformation). The ^{1}H nmr spectrum of an acetone-d_6 solution of the urea showed broad peaks at τ 1.52 (1 H, -NH-) and 3.62 (2 H, $-NH_2$); at −39 and −61° the two protons of the NH_2 group became nonequivalent.

Anal. Calcd for $C_2H_3F_6N_5O$: F, 50.20. Found: F, 50.33.

Tris(difluoramino)methylurea Perchlorate.[18]—Reaction of the urea (0.3 mmol) and perchloric acid (0.3 mmol) in chloroform at −60° for 1 hr followed by warming to room temperature produced a white, hygroscopic solid, which decomposed below 55°: $\nu_{max}^{mineral\ oil}$ in a polyethylene cell[19] 3356, 3226, 2505, 1689 (C=O), and 1105 cm^{-1} (ClO_4^-); ^{1}H nmr τ 0.05 (3 H, broad, $-NH_3^+$) and 1.12 (1 H, broad, -NH-).

Anal. Calcd for $C_2H_4ClF_6N_5O_5$: F, 34.80; N, 21.38. Found: F, 34.74; N, 20.91.

1,5-Bis[tris(difluoramino)methyl]biuret (3).—Approximately 1.0 ml of anhydrous ethyl ether and 1.54 mmol of 1 were vacuum transferred into a reactor (*ca.* 4 ml). The mixture was stirred at room temperature and recooled to −196°, and 0.54 mmol of ammonia was then added by vacuum transfer. The bath was removed. As soon as the reaction mixture liquefied, it was stirred for 15 min. After 1 week, the volatile fraction was removed by vacuum transfer. A solution of the solid residue in 2.2 ml of anhydrous ethyl ether was centrifuged to remove a trace amount of yellow solid and divided into two equal parts. The ether was removed under vacuum and the solid residues were dried for 1 hr at 59°. The yield of solid was 168 mg (0.384 mmol, 71% yield based on ammonia). The biuret appeared to decompose without melting below 200°.

Anal. Calcd for $C_4H_3F_{12}N_9O_2$: F, 52.16; N, 28.84. Found: F, 50.35; N, 28.59.

The ^{1}H nmr spectrum consisted of either two broad overlapping peaks at τ 0.49 and 0.72 (respective area ratio 2:1) or a single, very broad peak at τ 0.58 in which the overlapping peaks had merged (probably by NH exchange). The biuret is apparently capable of existing in two solid modifications with different infrared spectra. Thus, the modification initially obtained had $\nu_{max}^{mineral\ oil}$ 3344, 1770 (sh), 1754, 1724, 1709 (sh), 1538 cm^{-1}. Exposure of this material to atmospheric moisture did not affect its infrared spectrum. However, when samples of the biuret with this spectrum were allowed to stand at room temperature, the spectrum in the 3600–1700-cm^{-1} range slowly changed to $\nu_{max}^{mineral\ oil}$ 3597, 3521, 3226, 1754, and 1730 cm^{-1}. When this latter modification was recovered from ether solution or was heated at 80° it converted to the original form.[20]

1,6-Bis[tris(difluoramino)methyl]biurea (4).—A solution of 16.3 μl of technical anhydrous 98.5% hydrazine (0.50 mmol of hydrazine) in 1.5 ml of acetonitrile (reagent grade, dried over P_2O_5 and distilled) was prepared under a nitrogen atmosphere and transferred to a reactor (*ca.* 4 ml). The reactor was then cooled in a liquid nitrogen bath and evacuated, and 1.1 mmol of isocyanate was added by vacuum transfer. The liquid nitrogen bath was replaced with an ice bath. As soon as the reaction mixture liquefied, stirring was started. After 15 min the ice bath was removed. After a total reaction time of 1 hr, the clear yellow solution and 0.7 ml of an acetonitrile rinse were transferred under nitrogen to a centrifuge tube. The solution was treated with portions of decolorizing charcoal until the yellow

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[15] The spin-spin coupling patterns were indicative of the allyl group by comparison with Varian Associates, "NMR Spectra Catalog," 1962, Spectrum 34.

[16] We wish to thank Mr. E. J. Schriffert, of these laboratories, for this experiment.

[17] N. V. de Bataafsche Petroleum Maatschappij, Dutch Patent 66,784 (1950); *Chem. Abstr.*, **45**, 5451 (1951).

[18] We wish to thank Mr. E. J. Schriffert, of these laboratories, for this experiment.

[19] I. Cohen, *J. Chem. Educ.*, **39**, 262 (1962); T. Robinson, *Nature (London)*, **184**, 448 (1959).

[20] We wish to thank Dr. J. J. Keavney and J. Habermann, of these laboratories, for the latter experiment.

color had been removed. The supernatant liquid was decanted into two tared centrifuge tubes. Each tube was heated in an oil bath (55°) and the solvent was removed in a stream of nitrogen until the volume of solution was 0.3 ml. The warm solutions were then diluted to 1.0 ml with reagent grade methylene chloride. Crystals immediately separated. After approximately 0.75 hr at room temperature, the crystals, which were initially almost invisible in the solvent, had become white. The crystals were separated (centrifuge) and each portion was washed with 0.8 ml of methylene chloride and dried at room temperature. The yield of white solid was 125 mg (0.28 mmol of the biurea, 55% yield), $\nu_{\max}^{\text{mineral oil}}$ 3344, 3247, 3067, 1715, and 1555 cm^{-1}. ^{1}H nmr in acetonitrile showed two broad peaks with an area ratio of 1:1 at τ 2.09 and 2.44.

Anal. Calcd for $C_4H_4F_{12}N_{10}O_2$: F, 50.43; N, 30.98. Found: F, 50.71; N, 30.06, 31.41.

Reaction of Nitramide with 1.—Nitramide[21] (34.3 mg, 0.554 mmol) was dissolved in anhydrous ethyl ether (*ca.* 0.3 ml). The solution was added to a reactor which was made by sealing a 5-mm o.d. nmr tube to a Lab-Crest valve. Isocyanate (0.58 mmol) and tetramethylsilane (0.1 mmol) were added by vacuum transfer, and the reaction was allowed to proceed at room temperature. After *ca.* 2.5 hr, a ^{1}H nmr spectrum showed a broad, strong peak at τ 0.18 assigned to the adduct and broad, weak peaks at -1.4 and 1.2, which are assigned to the carbamic acid **5**.[22] After about 30 hr, peaks caused by the carbamic acid were present and, as well, a broad peak at τ 5.5, probably caused by tris(difluoramino)methylamine.

A gas, which amounted to 0.69 mmol, was separated after 2 additional days. Analysis by mass spectrometry found 75.2% nitrous oxide (0.52 mmol), 22.8% carbon dioxide (0.16 mmol), and 1.7% tetramethylsilane.

Hydrolysis of Tris(difluoramino)methyl Isocyanate.—A reactor was made by sealing a 5-mm o.d. nmr tube to a Lab-Crest valve and charged with 8.0 μl (0.44 mmol) of water. Ethyl ether (*ca.* 0.2 ml), isocyanate (0.46 mmol), and trichlorofluoromethane (0.3 mmol) were added to the reactor by vacuum transfer. The reaction was allowed to proceed at room temperature. A ^{19}F nmr spectrum of the reaction mixture after *ca.* 7 hr showed strong peaks at -24.3, -26.8, and -29.9 ppm assigned to the amine **6**, carbamic acid **5**, and isocyanate, respectively. After 4 days a ^{1}H nmr spectrum showed a broad peak assigned to the amine at τ 5.50 and two broad peaks assigned to the carbamic acid at *ca.* 1.2 and *ca.* -1.2.

A small amount of a white solid, which appears to be the carbamic acid, was isolated from a reaction of **1** with water: $\nu_{\max}$ 3344 (NH), 3125–2500 (CO_2H), 1715 (C=O), and 1536 cm^{-1} (NH deformation).

Tris(difluoramino)methylamine (6).—A reactor (*ca.* 1.3 ml) was charged with 13 μl (0.72 mmol) of water and 0.71 mmol of the isocyanate, containing small amounts of **6** and silicon tetrafluoride. After 19 hr of reaction at room temperature the product was fractionated using a $-78°$ trap to retain the amine (0.5 mmol) and pass carbon dioxide. Samples of the amine were purified by fractional codistillation[23] or dried by passage of the vapors through magnesium perchlorate ("Dehydrite") or phosphorus pentoxide. Extended contact results in decomposition. Properties of the amine were determined: $\nu_{\max}^{\text{gas}}$ NH_2 at 3571, 3472, and 1613 cm^{-1}; ^{1}H nmr τ 6.80 (weak unassigned peak at 8.50), in trichlorofluoromethane; estimated (by extrapolation of vapor pressure data) bp 95°;[24] mol wt, 184 (gas density) (calcd 184).[24]

Attempted Reactions of Tris(difluoramino)methylamine and Tris(difluoramino)methyl Isocyanate in the Absence of Triphenylphosphine Oxide.—The amine (0.3 mmol) and isocyanate (0.3 mmol) were heated in a small reactor (volume *ca.* 1.3 ml) at 62° (1 hr), 64–92° (1 hr), and 92° (4$^1/_3$ hr). A liquid phase was present throughout the treatment. Most of the mixture of starting materials was recovered unchanged.

Reaction of Tris(difluoramino)methylamine and Tris(difluoramino)methyl Isocyanate in the Presence of Triphenylphosphine Oxide.—Two reaction mixtures were prepared which were comparable with the exception that only one contained triphenylphosphine oxide. The compositions of the reaction mixtures were as in Table II. After 8 days at room temperature, the ^{19}F nmr spectra were determined. Reaction A, which contained triphenylphosphine oxide, showed a strong signal at -28.0 ppm due to the complex of **7** and triphenylphosphine oxide, as well as the two signals of the isocyanate and amine. Reaction B showed only the two signals of the starting materials.

TABLE II

Component	Reaction A, mmol	Reaction B, mmol
$(F_2N)_3CNCO$	0.33	0.33
$(F_2N)_3CNH_2$	0.31	0.31
$(C_6H_5)_3PO$	0.09	None
Benzene	1.0	1.0
$CFCl_3$ (internal nmr standard)	0.54	0.54

1,3-Bis[tris(difluoramino)methyl]urea (7).—An approximately 4-ml Pyrex glass reactor, made from a Lab-Crest quick-opening needle valve with a Teflon stem, was equipped with a stirring bar, flamed under vacuum, and filled with nitrogen. The reactor was then charged with 139 mg (0.50 mmol) of triphenylphosphine oxide (Aldrich Chemical Co., mp 156–157°), 9.0 μl (0.50 mmol) of water, and 1.0 ml of benzene (reagent grade, further dried over "Baker Analyzed" sodium–lead alloy, 9.7% active sodium). The reactor was cooled to $-196°$, evacuated, thawed, again cooled to $-196°$, and briefly pumped on. The isocyanate (1.0 mmol) was condensed into the reactor at $-196°$. The $-196°$ bath was removed, and (after 10 min) the reaction mixture was stirred for 2 hr. Bubbles, probably of carbon dioxide, were observed. After 7 days at room temperature, the volatile fraction was removed and fractionated in the vacuum line using a trap at $-132°$. The fraction which passed through the trap amounted to 0.57 mmol. An infrared spectrum showed characteristic carbon dioxide absorptions and only weak NF absorptions. Analysis by mass spectrometry indicated >90% carbon dioxide. The solid residue was pumped on through a $-196°$ trap until no more volatiles were retained by the trap.

The solid residue[25] was washed out of the reactor with trifluoroacetic acid. The resulting 3.0 ml of solution was divided into three parts. Each part was concentrated to 0.5 ml. The small amount of solid present was dissolved by warming the mixture in a water bath. Then each solution was diluted to 4.0 ml with reagent grade carbon tetrachloride, mixed, and placed in an ice–water bath for 45 min. The solid **7** was separated from the cold solution (centrifuge), washed twice with 0.5-ml portions of carbon tetrachloride, and dried. The yield of **7** was 38% based on the isocyanate charged. ^{1}H nmr indicated 2.4% by weight of triphenylphosphine oxide, although an infrared spectrum of a mull in mineral oil did not detect any of this impurity. Triphenylphosphine oxide, when present in **7** in sufficient amounts, was detected through peaks at 1149, 1120, and 746 cm^{-1}.

In a preferred alternative procedure, the crude complex was dissolved in methylene chloride to give 3.0 ml of solution. Any insoluble material was removed (centrifuge). Aliquots (1 ml) of the solution were diluted to 3.5 ml with methylene chloride and treated with 0.5 ml of trifluoroacetic acid.[26] As previously described, the mixture was cooled, and **7** was separated, washed with methylene chloride, and dried.

The analytical sample was washed twice with methylene chloride and a third time with hot methylene chloride.

Anal. Calcd for $C_3H_2F_{12}N_8O$: F, 57.85; N, 28.43. Found: F, 58.04; N, 28.63.

The sample showed $\nu_{\max}^{\text{mineral oil}}$ 3311 (NH) and 1704 cm^{-1} (C=O), ^{1}H nmr τ 1.39 (broad); the material sublimed when a melting point determination with a Fisher-Johns apparatus was attempted and turned somewhat yellow and partially sublimed when heated up to 200° in a sealed tube under nitrogen.

Microscopy[27] has shown the presence of liquid inclusions in

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(21) C. A. Marlies, V. K. LaMer, and J. Greenspan, *Inorg. Syn.*, **1**, 68 (1939). Prepared by R. F. Phillips of these laboratories.

(22) The ^{1}H nmr spectrum of nitramide has been reported by J. D. Ray and R. A. Ogg, Jr., *J. Chem. Phys.*, **26**, 1452 (1957).

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

(24) We wish to thank J. J. Keavney, R. S. Kolat, and J. P. Habermann for the boiling point, and M. D. Meyers and E. J. Schriffert for the molecular weight.

(25) The solid residue from a similar reaction mixture showed $\nu_{\max}^{\text{mineral oil}}$ 1779 (C=O) and 1149 cm^{-1} ($\equiv$P=O$\cdots$NH=).

(26) The solid which precipitates is very difficult to see in the mixture of methylene chloride and trifluoroacetic acid.

(27) Microscopical work by F. Farwell of these laboratories.

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, $\nu_{\max}^{\text{mineral oil}}$ 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, $\nu_{\max}$ 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.

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[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

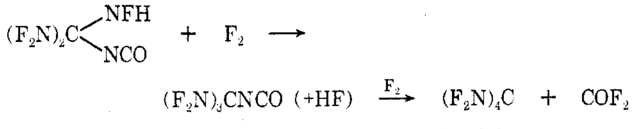
WILLIAM C. FIRTH, JR.,* SIMON FRANK, AND M. D. MEYERS

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]



$$(F_2N)_2C{=}NF + HNCO \longrightarrow (F_2N)_2C\begin{matrix}\diagup NFH\\ \diagdown NCO\end{matrix}$$

$$(F_2N)_2C\begin{matrix}\diagup NFH\\ \diagdown NCO\end{matrix} + F_2 \longrightarrow$$

$$(F_2N)_3CNCO\ (+HF) \xrightarrow{F_2} (F_2N)_4C + COF_2$$

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

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[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).