4,[12] except that the preparation of 5 was completed by work-up with deuterium oxide containing a small amount of deuterium chloride.

The samples of 2, 3, 4, and 5 were purified by preparative vapor phase chromatography on a 2-ft Apiezon column at 80°. Their percentage isotopic purity was calculated from low-voltage spectra. The low-voltage spectra of the corresponding cyclohexanones were much more amenable to analysis than the low-voltage spectra of the cyclohexanols themselves, owing to the low appearance potential of the $M^+ - 1$ ion of cyclohexanol. Consequently, small amounts of 4 and 5 were oxidized to the corresponding ketones,[12] 3,3,5,5-d_4-cyclohexanone (89% d_4, 11% d_3) and 4,4-d_2-cyclohexanone (86% d_2, 13% d_1, and 1% d_0), respectively.

The mass spectrum of O-d_1-cyclohexanol (1, 86% d_1, 14% d_0) was obtained as follows. Cyclohexanol was heated in deuterium oxide to 100° for 1 hr; the resulting cyclohexanol was isolated by ether extraction and introduced into the mass spectrometer after previous exchange of the inlet system with several samples of deuterium oxide.

The isotopic purities of 1–5 are summarized in Table V.

TABLE V
ISOTOPIC PURITIES OF DEUTERATED CYCLOHEXANOLS

	%				
Compd	d_0	d_1	d_2	d_3	d_4
1	14	86	...	...	...
2	2	98	...	...	...
3	...	...	...	3	97
4	...	...	...	11	89
5	1	13	86	...	...

Registry No.—Cyclohexanol, 108-93-0; water, 7732-18-5; 1, 14848-87-4; 2, 21273-02-9; 3, 21273-03-0; 4, 21273-04-1; 5, 21273-05-2.

Acknowledgment.—One of us (R. S. W.) would like to acknowledge a Morrell Fund Studentship.

(12) D. H. Williams, H. Budzikiewicz, Z. Pelah, and C. Djerassi, *Monatsh.*, **95**, 166 (1964).

Some Reactions of Difluoramino Compounds with Bases and Reducing Agents[1]

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Lithium borohydride reacted with ethyl 5,5-bis(difluoramino)hexanoate to give 5,5-bis(difluoramino)hexanol, and with 1,3,3-tris(difluoramino)butane to give 3,3-bis(difluoramino)butylamine, isolated as the trifluoroacetate. Hydrolysis of ethyl 5,5-bis(difluoramino)hexanoate with hot alkali gave 5,5-bis(difluoramino)hexanoic acid. This ester reacted with methanolic hydrazine to give the hydrazide, which was nitrosated to form the azide, which, in turn, was converted into the isocyanate and to 4,4-bis(difluoramino)pentylurea. Reduction of 2,2-bis(difluoramino)-5,5,5-trinitropentane with alkaline peroxide gave 2,2-bis(difluoramino)-5,5-dinitropentane, which was hydrolyzed to 4,4-bis(difluoramino)pentanoic acid. Reduction of cycloalkyl difluoramines with lithium aluminum hydride gave primary and rearranged secondary amines. Dimethyl N-phenyliminocarbonate was obtained from reactions of methoxide with α,α-dichloro-α-difluoraminotoluene, α-bromo-α,α-bis(difluoramino)-toluene, and α,α-dibromo-α-difluoraminotoluene. The latter was converted into α-bromo-α-fluoriminotoluene with ammonia or sodium 2-propanenitronate.

The synthesis of *gem*-bis(difluoramino) compounds by the reaction of carbonyl compounds with difluoramine has recently been reported.[2] 1,1-Bis(difluoramino)-1-halo compounds and 1-difluoramino-1,1-dihalo compounds were prepared by replacement reactions of halo, nitro, and nitroso compounds with difluoramine.[3,4] The present paper deals with some chemical properties of these compounds and their ability to withstand reaction conditions encountered in some common chemical transformations of other functional groups.

The effect of reducing agents on difluoramino groups has been studied by several groups. The reduction of tertiary difluoramino compounds by titanous ion gave fragmentation products indicative of nitrene intermediates, *e.g.*, acetone and methylamine from *t*-butyldifluoramine.[5] The formation of fluorimines from α-halodifluoramines has been reported using pyridine,[5] iodide ion,[6] ferrocene,[7] and iron carbonyl.[8] Simple primary and secondary alkyldifluoramines are readily dehydrofluorinated to give nitriles and fluorimines, respectively, although teritary alkyldifluoramines are relatively stable toward base.[5,9]

The reactivity of internal *gem*-bis(difluoramino)alkanes was screened in test-tube experiments using 2,2-bis(difluoramino)octane as a model compound. The starting material was recovered after 20 hr at ambient temperature from methanol solutions of hydrazine, sodium nitrite, and sodium azide, from a slurry with aqueous sodium borohydride, and from an ether solution of the more powerful reducing agent,[10] lithium borohydride. The compound did not react with aqueous potassium iodide, but when acetonitrile containing 10% water was used as the solvent, iodine was liberated slowly (several days for completion). The compound was reduced by lithium aluminum hydride but the products were not determined.

Using conditions under which the difluoramino

(1) This work was supported by the Office of Naval Research and the Advanced Research Projects Agency.

(2) K. Baum, *J. Amer. Chem. Soc.*, **90**, 7083 (1968).

(3) K. Baum, *J. Org. Chem.*, **34**, 2046 (1969).

(4) K. Baum, *ibid.*, **34**, 2049 (1969).

(5) R. C. Petry and J. P. Freeman, *ibid.*, **32**, 4034 (1967).

(6) R. L. Rebertus, J. J. McBrady, and J. G. Gagnon, *ibid.*, **32**, 1944 (1967).

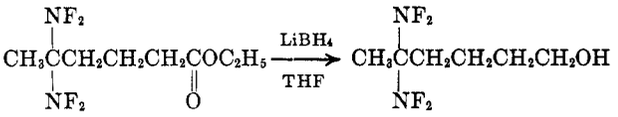
(7) R. A. Mitsch, *J. Amer. Chem. Soc.*, **87**, 328 (1965).

(8) V. A. Ginsburg and K. N. Sirnov, *Zh. Obshch. Khim.*, **37**, 1413 (1967).

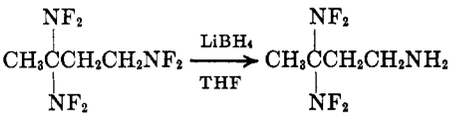
(9) F. A. Johnson, C. Haney, and T. E. Stevens, *J. Org. Chem.*, **32**, 466 (1967); G. N. Sausen and A. L. Logothetis, *ibid.*, **33**, 2330 (1968); A. L. Logothetis and G. N. Sausen, *ibid.*, **31**, 3689 (1966); S. K. Brauman and M. E. Hill, *J. Amer. Chem. Soc.*, **89**, 2127 (1967); A. S. Filatov and M. A. Englin, *Zh. Obshch. Khim.*, **38**, 1408 (1968).

(10) R. F. Nystrom, S. W. Chaikin, and W. G. Brown, *J. Amer. Chem. Soc.*, **71**, 3245 (1949).

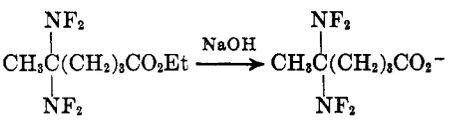
groups of 2,2-bis(difluoramino)octane were unreactive, it was possible to carry out selective reductions of other functional groups. Thus, ethyl 5,5-bis(difluoramino)-hexanoate was reduced to 5,5-bis(difluoramino)hexanol with lithium borohydride in tetrahydrofuran.



The possibility of selectively reducing primary difluoramino groups in the presence of *gem*-bisdifluoramino groups was examined using 1,3,3-tris(difluoramino)butane. The trifluoroacetate of 3,3-bis(difluoramino)butylamine was isolated in 22% yield after the reaction mixture was quenched with water, extracted with ether, and acidified with trifluoracetic acid. This reduction may proceed by dehydrofluorination followed rapidly by reduction of the nitrile. Attempts to prepare 3,3-bis(difluoramino)butyronitrile by reactions of 1,3,3-tris(difluoramino)butane with base resulted in complete decomposition, probably because of the acidic hydrogen adjacent to the difluoramino groups in the nitrile.

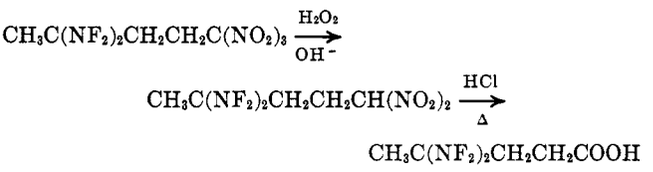


The inertness of isolated internal *gem*-bis(difluoramino) groups toward base, however, was found to be sufficient to allow hydrolysis of an ester group with hot alkali. Ethyl 5,5-bis(difluoramino)hexanoate was hydrolyzed in refluxing 10% aqueous sodium hydroxide, and 5,5-bis(difluoramino)hexanoic acid was isolated in 79% yield.

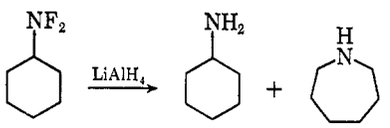


The inertness of *gem*-bis(difluoramino)alkanes toward nitrogen bases was utilized in applying the standard Curtius reaction sequence[11] to ethyl 5,5-bis(difluoramino)hexanoate. The ester reacted with methanolic hydrazine to give the hydrazide, an oil, which could not be separated from unreacted ester. Nitrosation gave the acyl azide, which evolved nitrogen on heating to give 4,4-bis(difluoramino)pentyl isocyanate. The isocyanate codistilled with ethyl 5,5-bis(difluoramino)hexanoate, which was carried through the reaction sequence, but was characterized by nmr spectra. The elemental analysis of the mixture of the two compounds agreed with quantitative nmr analysis. Addition of anhydrous ammonia to the mixture gave 4,4-bis(difluoramino)pentylurea, a solid which was fully characterized.

Selective reduction of a trinitromethyl group was carried out with 2,2-bis(difluoramino)-5,5,5-trinitropentane.[2] Although electronegatively substituted trinitromethyl compounds can be hydrolyzed to carboxylic acids with refluxing aqueous hydrochloric acid,[12] this compound was found to be unreactive under these conditions. Trinitromethyl compounds are generally reduced to dinitro compounds with alkaline hydrogen peroxide.[13] The reaction of 2,2-bis(difluoramino)-5,5,-5-trinitropentane with this reagent gave 2,2-bis(difluoramino)-5,5-dinitropentane, a high-boiling oil which could not be isolated in analytical purity. Nmr and infrared spectra were consistent with this structure. Hydrolysis of the dinitro compound with refluxing hydrochloric acid gave 4,4-bis(difluoramino)pentanoic acid. The latter reaction has been reported to be general for terminal dinitromethyl derivatives.[12]



Difluoraminocyclohexane and 1-difluoramino-1-methylcyclohexane were treated with lithium aluminum hydride with the objective of obtaining less complex products than those from 2,2-bis(difluoramino)-octane. Difluoraminocyclohexane was found to give a 70:30 mixture of cyclohexylamine and hexamethyleneimine. 1-Difluoramino-1-methylcyclohexane gave N-methylcyclohexylamine and two other amines, tentatively assigned the structures α-methylcyclohexylamine and α-methylhexamethyleneimine on the basis of nmr spectra of the mixture. Nitrocycloalkanes have



been treated with lithium aluminum hydride under the same conditions, and both simple reduction to primary amines and ring expansion to cyclic secondary amines were reported.[14] Presumably, nitrene intermediates are involved.

The reactions of some basic reagents with α,α-dibromo-α-difluoraminotoluene, α,α-dichloro-α-difluoraminotoluene, and α-bromo-α,α-bis(difluoramino)toluene were studied. Methanolic sodium methoxide reacted with each of these compounds to give dimethyl N-phenyliminocarbonate in high yield. These reactions can be rationalized on the basis of attack of methoxide on halogen, with loss of fluoride ion to give fluorimines. Addition of methoxide to the fluorimine would give an NF anion, which might undergo phenyl migration directly or through a nitrene intermediate resulting from loss of fluoride. Subsequent displacement of the remaining halogen or difluoramino groups by

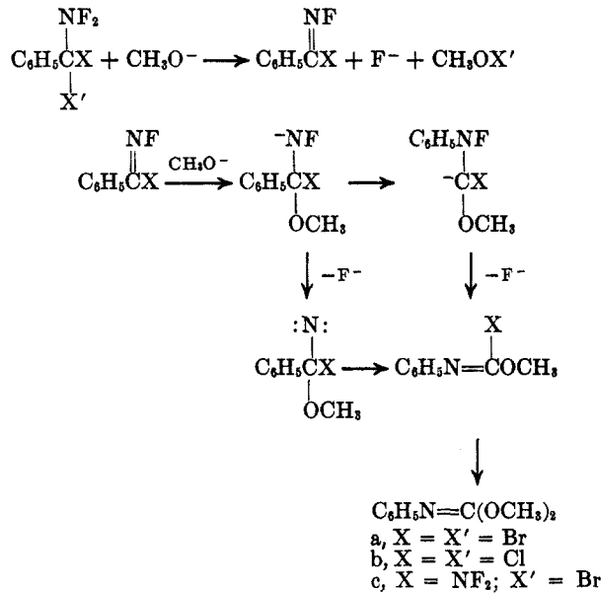
(11) P. A. S. Smith, *Org. Reactions*, **3**, 337 (1946).

(12) M. J. Kamlet, L. A. Kaplan, and J. C. Dacons, *J. Org. Chem.*, **26**, 4371 (1961).

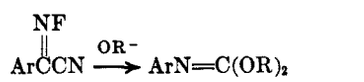
(13) D. J. Glover, *Tetrahedron, Suppl. 1*, **19**, 219 (1963).

(14) G. E. Lee, E. Lunt, W. R. Wragg, and H. J. Barber, *Chem. Ind.* (London), 417 (1958).

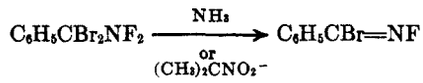
methoxide would give the iminocarbonate. This iminocarbonate was prepared previously by the reaction of phenyliminophosgene with methoxide.[15]



Stevens[16] has recently reported a similar rearrangement in the reaction of α-fluoriminoarylacetonitriles with alkoxides.



Fluorimines could not be isolated from the reactions of the above difluoraminotoluene derivatives with methoxide, even when the reactions were not carried to completion. However, the addition of α,α-dibromo-α-difluoraminotoluene to refluxing liquid ammonia gave α-bromo-α-fluoriminotoluene in 30% yield. The fluorine nmr spectrum of the fluorimine showed a single signal, suggesting that only one of the two possible *syn–anti* isomers was formed. This reduction was also accomplished using sodium 2-propanenitronate in methanol, but the product contained impurities that could not be prepared by distillation. Mechanistic details of



the reduction are unknown. Initial nucleophilic attack may take place on either bromine or fluorine. Also, free radical pathways such as have been observed for some displacement reactions of α-halonitro compounds[17] cannot be ruled out.

Experimental Section

Safety Precautions.—Because of the explosive properties of many difluoramino compounds, the safety precautions described previously[2] were followed.

(15) W. E. Smith, *Am. Chem. J.*, **16**, 372 (1892).
(16) T. E. Stevens, *J. Org. Chem.*, **32**, 670 (1967).
(17) G. A. Russel and W. C. Danen, *J. Amer. Chem. Soc.*, **88**, 5663 (1966).

5,5-Bis(difluoramino)hexanol.—Ethyl 5,5-bis(difluoramino)-hexanoate[2] (2.46 g, 0.010 mol) was added to 25 ml of tetrahydrofuran and 1 g of 80% lithium borohydride (0.04 mol) and the mixture was allowed to stand overnight. Water (25 ml) was added and the product was extracted with three 20-ml portions of ether, dried, and distilled to give 1.00 g (49% yield) of 5,5-bis-(difluoramino)hexanol, bp 53° (0.1 mm).

Anal. Calcd for $C_6H_{12}N_2F_4O$: C, 35.30; H, 5.88; N, 13.7. Found: C, 35.80; H, 6.01; N, 13.0.

The infrared spectrum consisted of bands at 3.0 (s), 3.40 (m), 3.45 (sh), 6.83 (m), 7.2 (m), 8.1 (w), 8.3 (w), 8.8 (w), 9.3–9.6 (s), 10.05 (s), 10.2 (s), 10.63 (w), and 11.1 μ (s).

The proton nmr spectrum (CCl_4) solution) showed a quintet (J = 2 cps) at δ 1.58 for the methyl, a broadened triplet (J = 3.5 cps) at δ 3.56 for $-CH_2OH$, a singlet at δ 3.75 for the hydroxyl, and broad multiplets at δ 1.95 and 1.58 for the methylenes. The fluorine spectrum consisted of a broadened band at ϕ^* −26.72.

3,3-Bis(difluoramino)butylammonium Trifluoroacetate.—A solution of 3.0 g (0.0142 mol) of 1,3,3-tris(difluoramino)butane[2] in 15 ml of ether was added with stirring to 1.25 g (0.057 mol) of lithium borohydride in 25 ml of tetrahydrofuran. After 2 hr, 20 ml of water was added slowly. The aqueous layer was extracted with two 20-ml portions of ether, and the combined organic solutions were dried over sodium sulfate. Trifluoroacetic acid (10 ml) was added and the solvent and excess acid were removed *in vacuo*. The addition of 10 ml of ether to the liquid residue gave 0.45 g (22% yield) of 3,3-bis(difluoramino)butylammonium trifluoroacetate, white needle crystals, mp 128–130° after vacuum drying. Recrystallization from ethanol and methylene chloride did not change the melting point.

Anal. Calcd for $C_6H_{10}N_3F_7O_2$: C, 24.92; H, 3.46; N, 14.54; F, 46.2. Found: C, 24.45; H, 3.24; N, 14.33; F, 46.2.

The proton nmr spectrum (D_2O solution) consisted of a quintet (J = 2.0 cps) at δ 1.72 for the methyl and multiplets at δ 2.5 and 3.2 for the methylenes. The fluorine spectrum showed a broadened signal at −103 ppm (from external trifluoroacetic acid).

5,5-Bis(difluoramino)hexanoic Acid.—A suspension of 3.0 g (0.0122 mol) of ethyl 5,5-bis(difluoramino)hexanoate[2] in 25 ml of 10% aqueous sodium hydroxide was refluxed with stirring for 1.5 hr. The resulting clear solution was cooled and acidified with 25% sulfuric acid. The product was extracted with three 30-ml portions of ether, dried over sodium sulfate, and distilled to give 2.06 g (79% yield) of 5,5-bis(difluoramino)hexanoic acid, bp 90° (0.1 mm).

Anal. Calcd for $C_6H_{10}N_2F_4O_2$: C, 33.03; H, 4.59; N, 12.85; F, 34.9. Found: C, 32.71, H, 5.01; N, 12.7; F, 35.3.

The infrared spectrum showed broad OH–CH absorption at 3.1–3.9 μ and bands at 5.86 (s), 6.87 (m), 7.10 (m), 7.22 (m), 7.80 (m), 8.90 (w), 9.70 (w), 10.26 (s), and 11.2 μ (s).

The proton nmr spectrum (CCl_4 solution) consisted of a quintet (J = 2 cps) at δ 1.65 for the methyl, a triplet (J = 6 cps) at δ 2.45 for the methylene adjacent to the carboxy group, a multiplet with maximum intensity at δ 2.03 for the other methylenes, and a singlet at δ 12.29 for –COOH. The fluorine spectrum showed a broadened signal at ϕ^* −26.8.

4,4-Bis(difluoramino)pentyl Isocyanate and 4,4-Bis(difluoramino)pentylurea.—A solution of 5.0 g (0.0203 mol) of ethyl 5,5-bis(difluoramino)hexanoate[2] and 0.84 g (0.025 mol) of 97% hydrazine in 10 ml of methanol was refluxed for 3 hr. The solvent was removed and the viscous residue was dried for 3 hr at 0.1 mm. Attempts to induce crystallization were unsuccessful. The residue was dissolved in 20 ml of chloroform, and 0.022 equiv of hydrochloric acid in 60 ml of water was added. This mixture was stirred at 0–3° while a solution of 0.022 equiv of potassium nitrite in 5 ml of water was added over a 15-min period. The chloroform layer was separated and the aqueous layer was extracted with 10 ml of cold chloroform. The chloroform solutions were combined, washed with two 10-ml portions of ice-water, and dried at 0° for 2 hr over sodium sulfate. The solution was then refluxed for 3 hr; nitrogen evolution was essentially complete after 1 hr. Distillation gave 2.0 g of colorless liquid, bp 61° (0.25 mm). The infrared spectrum of the product showed a strong isocyanate band at 4.4 μ, as well as all of the absorption bands of ethyl 5,5-bis(difluoramino)hexanoate. The proton nmr spectrum gave the signals reported for this ester and signals assignable to 4,4-bis(difluoramino)pentyl isocyanate (molar ratio 58:42 by integration). The methyl of the isocyanate gave

a quintet (J = 2.0 cps) at δ 1.56; the methylene adjacent to –NCO gave a triplet (J = 6.0 cps) at δ 3.35, and the other methylenes gave a multiplet at δ 1.93. The fluorine signal of the isocyanate was a broadened peak at ϕ^* −26.9.

Anal. Calcd for 58 mol % $CH_3C(NF_2)_2(CH_2)_3CO_2C_2H_5$, 42 mol % $CH_3C(NF_2)_2(CH_2)_3NCO$: C, 36.0; H, 4.98; N, 14.2; F, 31.8. Found: C, 35.5; H, 5.14; N, 14.5; F, 31.9.

Anhydrous ammonia was bubbled for 20 min into a solution of 0.50 g of the above mixture (0.193 g, 0.00090 mol of the isocyanate) in 25 ml of pentane. The product was filtered and recrystallized from pentane and methylene chloride to give 0.17 g (82% yield) of 4,4-bis(difluoramino)pentylurea, mp 85.5–86°.

Anal. Calcd for $C_6H_{12}N_4F_4O$: C, 31.03; H, 5.18; N, 24.14; Found: C, 30.88; H, 5.24; N, 24.32.

The infrared spectrum (KBr) showed the following peaks: 2.93 (s), 3.12 (m), 3.5 (w), 6.08 (s), 6.22 (s), 6.51 (s), 7.50 (m), 8.60 (w), 10.1 (m), 10.3 (m), 11.0 (m), 11.2 (m), and 11.55 μ (w).

The proton nmr spectrum in acetone-d_6 showed a broad multiplet at δ 6.11 for NH, a broad symmetrical band at δ 5.42 for NH_2, a distorted quartet (J = 6 cps) at δ 3.20 for CH_2–CH_2–NH, multiplets at δ 2.1 for the other methylenes, and a quintet (J = 2.2 cps) at δ 1.64 for $CH_3C(NF_2)_2$. The addition of D_2O removed the NH and NH_2 bands and collapsed the quartet to a triplet. The quartet thus arose because of nearly equal coupling to the adjacent CH_2 and NH. The fluorine spectrum consisted of a broadened band at ϕ^* −27.2.

From the pentane filtrate, 0.30 g of ethyl 5,5-bis(difluoroamino)hexanoate was recovered; its infrared spectrum was identical with that of an authentic sample.

5,5-Dinitro-2,2-bis(difluoramino)pentane (Impure).—A solution of 1.88 g (0.0285 mol) of 85% potassium hydroxide in 15 ml of methanol was added with stirring over a 30-min period at 0 to 10° to a solution of 3.0 g (0.0097 mol) of 5,5,5-trinitro-2,2-bis(difluoramino)pentane[2] and 1.7 ml (0.0146 mol) of 30% hydrogen peroxide in 12 ml of methanol. After an additional 15 min, 15 ml of water was added and the solution was acidified with 25% sulfuric acid. The product was extracted with three 25-ml portions of methylene chloride and dried over sodium sulfate. Removal of the solvent gave 1.83 g (71% crude yield) of 5,5-dinitro-2,2-bis(difluoramino)pentane, which had a carbonyl-containing impurity not removable by molecular distillation.

Anal. Calcd for $C_5H_8N_4F_4O_4$: C, 22.73; H, 3.03; N, 21.2; F, 28.8. Found: C, 23.2; H, 3.37; N, 18.0; F, 26.7.

The proton nmr spectrum showed a quintet (J = 2 cps) at δ 1.69 for the methyl, multiplets at δ 2.8 and 2.3 for the methylenes, and a triplet (J = 8 cps) at δ 6.18 for the methine. The fluorine spectrum showed a singlet at ϕ^* −27.16.

4,4-Bis(difluoramino)pentanoic Acid.—A mixture of 1.5 g (0.0057 mol) of the crude 5,5,-dinitro-2,2-bis(difluoramino)pentane and 40 ml of constant-boiling hydrochloric acid was refluxed for 4 hr. The resulting solution was cooled to room temperature and extracted with three 30-ml portions of methylene chloride. The methylene chloride solution was dried over sodium sulfate and distilled through a 25-cm Holzmann column to give a colorless liquid, bp 90° (0.05 mm), which was found by its ir spectrum to contain some starting material.

The mixture was dissolved in a minimum amount of 10% sodium hydroxide, and 1 ml of 3% sodium hypochlorite was added. After 15 min, the solution was extracted with methylene chloride and the organic phase was discarded. The aqueous phase was acidified with 10% sulfuric acid and the product was extracted with methylene chloride. The methylene chloride solution was dried over sodium sulfate and stripped of solvent. Molecular distillation of the residue gave 0.23 g (20% yield) of 4,4-bis(difluoramino)pentanoic acid.

Anal. Calcd for $C_5H_8N_2F_4O_2$: C, 29.41; H, 3.92; N, 13.7; F, 37.2. Found: C, 29.78; H, 4.13; N, 13.4, F; 36.0.

The infrared spectrum showed the following bands: 3.3 (m, br), 3.8 (sh), 5.80 (s), 7.0 (m), 7.19 (m), 7.64 (m), 8.10 (m), 8.7–8.9 (w), 9.4 (w), 9.9 (m), 10.2 (s), 10.4 (sh), 10.8 (sh), 11.03 (s), 11.3 (s), and 11.85 μ (w).

The proton nmr spectrum (CCl_4 solution) consisted of a quintet (J = 2 cps) at δ 1.68 for the methyl, overlapping multiplets for the methylenes with major components at δ 2.53 and 2.62, and a broadened singlet at δ 11.83 for the hydroxyl proton. The fluorine spectrum consisted of a broadened singlet at ϕ^* −26.86.

Reaction of Difluoraminocyclohexane with Lithium Aluminum Hydride.—A solution of 2.40 g (0.0179 mol) of difluoraminocyclohexane[18] in 5 ml of ether was added dropwise to a solution of 2.85 g (0.07 mol) of 95% lithium aluminum hydride in 75 ml of ether. After 20 hr, 20 ml of water was added slowly and the layers were separated. The aqueous layer was extracted with two 20-ml portions of ether. The combined ether solution was dried over sodium sulfate and distilled to give 1.3 g (73% total yield) of colorless liquid, bp 37° (7 mm). Gas chromatography [26% tris(cyanomethoxy)propane on Chromosorb W, 78°] and nmr showed that the product was a 70:30 mixture of cyclohexylamine (singlet at δ 0.91, NH_2; multiplet at δ 2.5, CH; multiplets at δ 1.07, 1.2, and 1.63, CH_2) and hexamethyleneimine (singlet at δ 1.17, NH; triplet at δ 2.76, CH_2–N; broadened band at δ 1.56, CH_2) by comparison with authentic samples.

Reaction of 1-Difluoramino-1-methylcyclohexane with Lithium Aluminum Hydride.—The above procedure with 3.0 g (0.0201 mol) of 1-difluoramino-1-methylcyclohexane[18] gave 1.62 g (71% yield) of colorless liquid, bp 40° (7 mm).

The nmr spectrum showed the presence of N-methylcyclohexylamine (singlet at δ 0.63, removed with D_2O, NH; singlet at δ 2.33, CH_3; multiplets with peaks at δ 1.68 and 1.23 for ring hydrogens) by comparison with an authentic sample. Other peaks in the spectrum are tentatively assignable to α-methylcyclohexylamine (singlet at δ 1.02, CH_3) and α-methylhexamethyleneimine (double at δ 1.01, $CHCH_3$). The relative amounts of the three components was approximately 2:1:2. Attempts to separate the mixture by gas chromatography were unsuccessful.

Dimethyl N-Phenyliminocarbonate.—A solution of 3.42 g (0.0114 mol) of α,α-dibromo-α-difluoraminotoluene[4] and 0.06 equiv of sodium methoxide in 80 mol of methanol was allowed to stand at ambient temperature for 18 hr. The solvent was removed *in vacuo* and 50 ml of methylene chloride was added. The mixture was filtered and distilled to give 1.11 g (59% yield) of dimethyl N-phenyliminocarbonate, bp 54–55° (0.15 mm).

Anal. Calcd for $C_9H_{11}NO_2$: C, 65.45; H, 6.66; N, 8.5. Found: C, 65.31; H, 6.73; N, 8.5.

The infrared spectrum showed peaks at 3.30 (m), 3.36 (m), 3.50 (m), 5.97 (vs), 6.26 (s), 6.70 (m), 6.82 (s), 7.0 (s), 7.73 (s), 7.80 (s), 8.40 (s), 9.30 (s), 9.70 (s), 11.1, 12.6 (m), 13.3 (s), 13.9 (s), 14.35 (s), and 15.3 μ (s). The proton nmr spectrum ($CDCl_3$ solvent) consisted of a methoxy signal at δ 3.78 and an aromatic multiplet.

The reaction of 1.47 g (0.005 mol) of α-bromo-α,α-bis(difluoramino)toluene[4] with 0.025 equiv of sodium methoxide in 40 ml of methanol at ambient temperature for 1 hr gave 0.58 g (70% yield) of the same product.

α,α-Dichloro-α-difluoraminotoluene[4] gave this compound in only 25% conversion in 1.5 hr at the reflux temperature of the solution. Starting material was recovered.

α-Bromo-α-fluoriminotoluene.—α,α-Dibromo-α-difluoraminotoluene[4] (2.45 g, 0.00815 mol) was added dropwise with stirring to 10 ml of anhydrous ammonia, refluxing under a −80° condenser with nitrogen sweep. After 1 hr, 15 ml of ether was added and the ammonia was allowed to escape. The ether solution was filtered and distilled to give 0.50 g (30.4% yield) of α-bromo-α-fluoriminotoluene, bp 29° (0.5 mm).

Anal. Calcd for C_7H_5NFBr: C, 41.58; H, 2.48; N, 6.93; F, 9.40. Found: C, 41.40; H, 2.56; N, 6.77; F, 9.54.

The infrared spectrum showed peaks at 3.27 (w), 6.30 (w), 6.45 (m), 6.72 (w), 6.92 (m), 8.0 (m), 10.50 (s), 10.82 (w), 11.20 (s), 13.15 (s), 14.55 (s), and 15.3 μ (s).

The proton nmr spectrum consisted of an aromatic multiplet with maximum intensity at δ 7.47, and the fluorine spectrum consisted of a broadened band at ϕ^* −64.1.

This product was also formed by reacting 2.45 g (0.00815 mol) of α,α-dibromo-α-difluoraminotoluene with 0.0163 mol of sodium 2-propanenitronate in 45 ml of methanol for 1 hr at ambient temperature. Distillation gave 0.98 g of material shown to be about 85% pure by gas chromatography, and containing six more volatile impurities.

Registry No.—5,5-Bis(difluoroamino)hexanol, 21272-94-6; 3,3-bis(difluoroamino)butylammonium trifluoroacetate, 21272-95-7; 5,5-bis(difluoroamino)hexanoic acid, 21272-96-8; 4,4-bis(difluoroamino)pentyl iso-

(18) K. Baum, *J. Org. Chem.*, **32**, 3648 (1967).

cyanate, 21272-97-9; 4,4-bis(difluoroamino)pentyl urea, 21272-98-0; 5,5-dinitro-2,2-bis(difluoroamino)-pentane, 21272-99-1; 4,4-bis(difluoroamino)pentanoic acid, 21273-00-7; dimethyl N-phenyliminocarbonate, 13997-51-8; α-bromo-α-fluoriminotoluene, 21273-07-4.

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Dehydrofluorination of Alkyldifluoramines[1]

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Kinetics of dehydrofluorination of several mono-, bis-, and tris(N,N-difluoramino)alkanes have been measured in diglyme–water (30:70) at 50 and 75°. The rates of these imine-forming reactions are relatively insensitive to the inductive and conjugative effects of substituents; the stereoselectivity of the dehydrofluorination seems to reflect the steric requirements of the alkyl group. The elimination appears to be a concerted process in which the degree of N–F bond breaking is not only quite extensive, but also nearly equal to the degree of C–H bond breaking in the transition state. All of the dehydrofluorination products have been fully characterized.

While the mechanisms of olefin-forming dehydrohalogenation reactions have been studied extensively,[2] the elimination of hydrogen halide across C–N bonds has received very little attention. Except for our earlier results,[3] the only reported kinetic data are for the base-catalyzed dehydrochlorination of benzalchlorimines.[4] With the recent availability of various alkyldifluoramines, we undertook an extensive investigation of the mechanism of elimination of hydrogen fluoride across C–N single bonds. The previous paper in this series[3] describes our early studies on one compound. We now wish to report our final results for several different mono-, bis-, and tris(N,N-difluoramino)alkanes, compounds **1–11** in Table I. The results from these compounds provide for the first time information regarding the nature of the transition state for dehydrofluorination reactions across C–N single bonds.

Results

The kinetics for dehydrofluorination of compounds **1–13** in Table I have been measured in diglyme (diethylene glycol dimethyl ether)–water (30:70, v/v) by means of an aliquot extraction–gas chromatographic technique. The data for **6**, **12**, and **13** have been reported previously.[3] In all cases the rate of disappearance of starting material was determined, and, where possible (**4–8**), the rate of appearance of product was also measured. All compounds were studied at 50°. Generally, kinetic experiments were performed at least in duplicate; lack of material prevented repeat measurements for **5** and **9**. The average observed rate constants for disappearance of starting material at 50° are given in Table I. The experimental error is ±3%; all rates followed pseudo-first-order kinetics to at least 80% reaction. Where both values could be determined, the rate of disappearance of starting material was within 8% of the rate of appearance of product. The latter rates for **6** and **7** showed induction periods. The case for **6** has already been discussed.[3] Although several different extraction solvents were tried, low concentrations may account for the failure to observe the various expected intermediates in the dehydrofluorination of **7**.

In general, product yields were greater than 80%, even for those products (**16**, **22**, and **23**, Table I) which were unstable in the reaction medium. The dehydrofluorinated materials were all identified by comparison with authentic material; the new N-fluorimines were independently prepared and characterized. Kinetic product isomer ratios were determined by vpc and nmr. Compounds **7** and **10** give 1:1 mixtures of *syn* and *anti* isomers (the *syn* and *anti* assignments refer to the fluorine and methyl group, or difluoramino group for **23**, on the C–N double bond). Compounds **8** and **9** give only one isomeric product each which is assigned the *syn* geometry from steric considerations alone. The complex stereochemistry for **6** has already been described;[3] the *syn* to *anti* isomer ratio of mono-N-fluorimines, **12** and **13**, formed from **6** is 3.2:1; the *syn,syn* to *syn,anti* ratio of bis-N-fluorimines, **19**, from **12** is 24.6:1; and the *syn,anti* to *anti,anti* ratio from **13** is 5.2:1.

Dehydrofluorination rates were also measured at 25° for **10** and at 75° for all other compounds. The activation parameters are included in Table I.

Discussion

Alkyldifluoramines undergo rapid general base catalyzed dehydrofluorination yielding N-fluoroketimines, aldimines, or nitriles.[5] Our results show that dehydrofluorination is quite fast, even when water acts as the base. Since the solvent, water, is the base, the kinetics in this aqueous system are pseudo first order. *sec-*

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