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.

Acknowledgment.—The author is grateful to Mr. K. Inouye for the elemental analysis, to Dr. H. M. Nelson and Mr. L. A. Maucieri for the nmr spectra, and to Mr. F. J. Gerhart and Mr. O. S. Schaeffler for assistance in the synthesis work.

Dehydrofluorination of Alkyldifluoramines[1]

SHARON K. BRAUMAN AND MARION E. HILL

Stanford Research Institute, Menlo Park, California 94025

Received March 20, 1969

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-*

(1) This work was supported by the Office of Naval Research, Contract Nonr 3760(00).

(2) (a) H. L. Goering and H. H. Espy, *J. Amer. Chem. Soc.*, **78**, 1454 (1956); (b) S. J. Cristol and R. S. Bly, Jr., *ibid.*, **82**, 142 (1960); (c) D. J. Cram, F. D. Greene, and C. H. DePuy, *ibid.*, **78**, 790 (1956); (d) W. H. Saunders, Jr., and R. A. Williams, *ibid.*, **79**, 3712 (1957); (e) C. H. DePuy and D. H. Froemsdorf, *ibid.*, **79**, 3710 (1957); (f) C. H. DePuy and C. A. Bishop, *ibid.*, **82**, 2532 (1960); (g) C. H. DePuy and C. A. Bishop, *ibid.*, **82**, 2535 (1960); (h) J. Šicher, J. Závada, and M. Pánková, *Chem. Commun.*, 1147 (1968); (i) N. B. Chapman and J. L. Levy, *J. Chem. Soc.*, 1673 (1952); (j) W. H. Saunders, Jr., S. R. Fahrenholtz, E. A. Caress, J. P. Lowe, and M. Schreiber, *J. Amer. Chem. Soc.*, **87**, 3401 (1965).

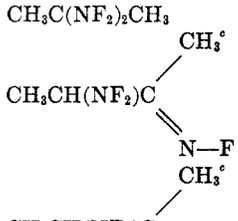
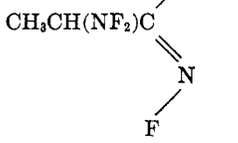
(3) S. K. Brauman and M. E. Hill, *ibid.*, **89**, 2131 (1967).

(4) C. R. Hauser, J. W. LeMaistre, and A. E. Rainsford, *ibid.*, **57**, 1056 (1935); W. E. Jordan, H. E. Dyas, and D. G. Hill, *ibid.*, **63**, 2383 (1941).

(5) (a) F. A. Johnson, C. Haney, and T. E. Stevens, *J. Org. Chem.*, **32**, 466 (1967); (b) R. C. Petry and J. P. Freeman, *ibid.*, **32**, 4034 (1967); (c) R. C. Petry and J. P. Freeman, Abstracts, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p S-46; (d) T. E. Stevens, *J. Org. Chem.*, **33**, 2660 (1968).

TABLE I

KINETIC DATA FOR OBSERVED DEHYDROFLUORINATION IN 30% AQUEOUS DIGLYME

Compound		Final product[a]		$k_{obsd}^{50°} \times 10^5$,[b]	$\Delta H^{\ddagger}$, kcal	
No.	Structure	No.	Structure	sec^{-1}	mol^{-1}	$\Delta S^{\ddagger}$, eu
1	$F_2NCH_2CH_2CH_2CH_3$	14	$NCCH_2CH_2CH_3$	2.88	17.3	−26.0
2	$F_2NCH_2CH(CH_3)_2$	15	$NCCH(CH_3)_2$	2.81	15.7	−30.9
3	$F_2NCH_2CH_2CH_2NF_2$	16	$NCCH_2CN$	4.58	17.9	−23.3
4	$F_2NCH_2C(NF_2)(CH_3)_2$	17	$NCC(NF_2)(CH_3)_2$	2.19	15.1	−33.2
5	$F_2NCH_2C(NF_2)_2CH_3$	18	$NCC(NF_2)_2CH_3$	15.9	14.0	−32.8
6	$CH_3CH(NF_2)CH(NF_2)CH_3$[c]	19	$CH_3C(=NF)C(=NF)CH_3$[c]	16.8	15.2	−29.2
7	$CH_3CH(NF_2)CH_2NF_2$	20	$CH_3C(=NF)CN$	7.05	17.3	−24.4
8	$CH_3CH(NF_2)C(NF_2)(CH_3)_2$	21	$CH_3C(=NF)C(NF_2)(CH_3)_2$	15.4	13.0	−35.9
9	$CH_3CH(NF_2)C(NF_2)_2CH_3$	22	$CH_3C(=NF)C(NF_2)_2CH_3$	25.8	15.4	−27.6
10	$(F_2N)_2CHCH_2CH_3$	23	$F_2NC(=NF)CH_2CH_3$	55.4	15.7	−25.0
11	$CH_3C(NF_2)_2CH_3$					
12		19	$CH_3C(=NF)C(=NF)CH_3$[c]	30.8		
13		19	$CH_3C(=NF)C(=NF)CH_3$[c]	31.0		

[a] See Results for product isomer ratios. [b] Average observed values for disappearance of starting material. [c] Reference 3.

Alkyldifluoramines react faster than the corresponding primary compounds.[6] The greater relief of steric strain and, more significantly, the increased stabilization of the C–N double bond by additional alkyl substitution[7] provide more of a driving force for reaction in the *sec*-alkyl series. *t*-Alkyldifluoramines, with no α hydrogens, are stable in the aqueous medium; 2,2-bis(N,N-difluoramino)propane (**11**) remained unchanged over a period of days at 50°.

In comparison with substituent effects on dehydrohalogenations across C–C bonds,[2] electronic effects of substituents appear to have considerably less influence on the rates of dehydrofluorination in alkyldifluoramines. While electronic and steric substituent effects cannot always be isolated, the kinetic data in Table I, when corrected statistically for the number of equivalent reaction sites, suggest that the inductive effect of an additional difluoramino group[8] is moderately small. As expected, the largest rate acceleration is found when the additional NF_2 group is in the α position (**10**). As shown by compounds **12** and **13**, intermediates in the dehydrofluorination of **6**, conjugative effects are comparatively small and unimportant in stabilizing the transition state. We have already shown[3] that the observed rate of appearance of the *syn,syn* isomer of **19** exhibits an induction period since the dehydrofluorination of intermediate **12** is not significantly faster than that of starting material, **6**. This behavior appears to be general for compounds which can lose hydrogen fluoride at adjacent sites. For example, the rate of appearance of final product, α-(N-fluorimino)propionitrile (**20**), from **7** also shows an induction period. However, intermediates could not be observed in this case.

When two eliminations occur at the same site to yield a nitrile, the second dehydrofluorination step is significantly faster than the first, N-fluorimine-forming step. The rates for appearance of product from **4** and **5** are linear to over 80% reaction, exhibiting no induction period, and they are equal to the rates of disappearance of starting material. No intermediates are observed for either compound. Computer fit of the kinetic data indicates that the second step of the sequential elimination must be at least 35 times as fast as the first step to observe this type of kinetic behavior. The related base-catalyzed dehydrochlorination of benzalchlorimines[4] in alcoholic solvents is a concerted elimination with a reasonable degree of carbanionic character in the transition state (ρ +2.24).

The product stereochemistry in the dehydrofluorination of alkyldifluoramines appears to reflect the steric requirements of the groups at the reaction site. The bulkier the R group in the *sec*-alkyl compounds, $CH_3CH(NF_2)R$, the more stereoselective is the dehydrofluorination. For primary R groups[6] (**7**), the ratio of isomeric products is 1:1; for secondary R groups (**6**), the *syn* to *anti* ratio is about 3:1; and for tertiary R groups (**8** and **9**), only the *syn* isomer is obtained. Since either fluorine in the NF_2 group can be lost, no distinction can be made between a *cis*- or *trans*-elimination mechanism because both could give the observed product stereochemistry. The similarity in activation parameters for all of the compounds studied (Table I) suggests a similarity in transition state and, therefore, in mechanism for dehydrofluorination. The stereoselectivity can be easily accounted for by the small differences in the activation energies.

(6) 2-(N,N-Difluoramino)butane loses hydrogen fluoride some eight times as fast as the primary butane (**1**) at 50°. Although vpc analysis indicates that the isomeric products are formed in equal amounts, lack of material has prevented complete characterization of the 2-(N-fluorimino)-butane.

(7) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, N. Y., 1961, pp 246–248; M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, **5**, 166 (1959); M. J. S. Dewar and H. N. Schmeising, *ibid.*, **11**, 96 (1960).

(8) The electronegativity of this group (3.3) is intermediate between that of an amino group and that of a fluorine atom: R. Ettinger, *J. Phys. Chem.*, **67**, 1558 (1963).

The kinetic data for the aqueous dehydrofluorination of alkyldifluoramines are consistent with a concerted elimination process. None of the difluoramines would be expected to be acidic enough to ionize to a discrete carbanion under such mild reaction conditions; this is supported by the lack of interconversion between diastereoisomers[3] of **6**. Although the N–F bond is quite weak, simple dissociation to give a fluoride ion and a full positive charge on nitrogen is equally unlikely. Loss of hydrogen fluoride, therefore, is a concerted elimination in which the C–H and N–F bonds are both breaking to some extent in the transition state. As evidenced by the large negative entropies of activation, the fluorine being lost is probably highly solvated in the transition state.[3,9] The degree of N–F bond rupture, therefore, must be extensive enough to produce a reasonable charge on the incipient fluoride ion. The modest influence of inductive and conjugative effects on the rates of dehydrofluorination, however, suggests a transition state in which little charge separation exists. The degree of N–F bond breaking then must be not only fairly extensive, but also nearly equal to the degree of C–H bond breaking in the transition state.

Because of a more highly charged transition state, concerted olefin-forming dehydrohalogenations[2] are considerably more sensitive to substituent electronic effects than is dehydrofluorination in alkyldifluoramines. For 2-phenylethyl halides with ethoxide in ethanol,[2g] the Hammett ρ increases in the order I < Br < Cl < F; ρ is +2.07 for the iodides while it is +3.1 for the fluorides. Since the ease of heterolytic cleavage for carbon–halogen bonds decreases in the order I > Br > Cl > F, carbanionic character would be expected to increase, and the extent of C–X bond breaking to decrease, along the series.[2c,j] While the inductive effect of the halogens (I < Br < Cl < F) is probably of less importance in determining the nature of the transition state, fluorine would be the most effective at stabilizing the negative charge. Although the highest degree of negative charge occurs in the transition state for dehydrofluorination, simple alkyl fluorides still do not exchange hydrogen faster than they eliminate hydrogen fluoride.[10] From kinetic deuterium isotope effects for several related 2-phenylethyl derivatives,[11] it is found that the C–X bond is breaking to some degree in the transition states for these eliminations. The extent of bond breaking, however, varies with the leaving group, solvent, and base.[2c,d] The concerted dehydrofluorination of simple alkyl fluorides would thus appear to involve considerable C–H bond cleavage and very little C–F bond cleavage in the transition state.

Compared with alkyl fluorides, dehydrofluorination of alkyldifluoramines is a more facile and more truly concerted process, with nearly equal degrees of C–H and N–F bond breaking in the transition state. In both the imine- and olefin-forming reactions, there is little or no apparent charge on the halogen-bearing atom in the transition state, and thus the extent of double-bond formation must nearly equal the extent of N–F or C–F bond breaking. For a given degree of C–H bond rupture, the heterolytic N–F bond cleavage is energetically more favorable than the C–F bond cleavage since in the former case simultaneous π-bond formation results in considerably more energy release, which more than compensates for the energy required to break the N–F bond.[12,13] Consequently, for a given degree of C–H bond rupture, relatively more N–F cleavage occurs, making this reaction more concerted. The transition state of the difluoramines is stabilized by hydration of the incipient fluoride ion, thus lowering the activation energy for elimination. Such stabilizing fluoride solvation is not so important in olefin-forming dehydrofluorinations since little C–F bond breaking has occurred in the transition state and the solvating power of the required medium is generally not so high.

Experimental Section[14]

Alkyldifluoramines.—These potentially hazardous compounds were prepared and fully characterized by several different contractors. Compounds **4**, **6**, **7**, and **8**, prepared by the method of Petry and Freeman,[5b] were supplied by Rohm and Haas Co., E. I. du Pont de Nemours and Co., and the Naval Ordnance Station at Indian Head, Md. The procedure of Baum[15] was used at Aerojet-General Corp. to prepare the geminate compounds, **10** and **11**; the same contractor also made **1**, **2**, and **3** by the method of Grakauskas.[16] The tris compounds, **5** and **9**, were prepared at Rohm and Haas Co. by the method of Freeman, Petry, and Stevens.[17] The alkyldifluoramines were characterized by elemental analysis, ir, and nmr. Because of the explosive nature of organic difluoramines, these compounds were normally handled and stored in high dilution in solvents such as methylene chloride, *sym*-tetrachloroethane, or Aroclor 1248 (a high-boiling tetrachlorobiphenyl produced by Monsanto). Small amounts of neat material were obtained by cautious distillation of the excess solvent, or distillation of the material from the high-boiling solvent; final purification was by preparative vpc on 20% dodecyl phthalate or 15% SE-30 columns. Sample purity was determined by vpc analysis. The tris(difluoramines) were only handled in solution; after careful purification, they were immediately dissolved in diglyme and used shortly thereafter in the kinetic studies.

Dehydrofluorination Products.—Under kinetic conditions, all dehydrofluorination products were identified by vpc peak retention time and/or peak enhancement upon addition of known material to the kinetic samples. Products **17**–**23** were independently prepared by dehydrofluorination of the corresponding alkyldifluoramine in an organic solvent, usually methylene chloride, using pyridine as the base. A typical procedure has already been described.[18] Dodecyl phthalate columns were used for the vpc isolations. The products were characterized by elemental analysis, ir, and ^{1}H and ^{19}F nmr. Internal tetramethylsilane (TMS) was used as standard for all ^{1}H nmr spectra; internal $CFCl_3$ was used as reference for the ^{19}F nmr spectra. The nmr data are for solutions (~15%, v/v), usually with $CFCl_3$ as solvent. The ^{19}F resonances of these compounds generally are broadened by nitrogen quadruple relaxation;[19] the broad singlets often are unresolved multiplets.

(9) K. J. Laidler and C. Pegis, *Proc. Roy. Soc., Ser. A*, **241**, 80 (1957).

(10) W. H. Saunders, Jr., and M. R. Schreiber, *Chem. Commun.*, 145 (1966).

(11) W. H. Saunders, Jr., and D. H. Edison, *J. Amer. Chem. Soc.*, **82**, 138 (1960).

(12) W. D. Good, D. R. Douslin, and J. P. McCullough, *J. Phys. Chem.*, **67**, 1312 (1963).

(13) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 88.

(14) Elemental analyses were performed by the Microanalytical Laboratory, Stanford University. Infrared spectra were recorded with a Perkin-Elmer 237-B grating spectrophotometer. ^{1}H and ^{19}F nmr spectra were obtained with a Varian HA-100 instrument.

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

(16) V. Grakauskas, Abstracts, 3rd International Symposium on Fluorine Chemistry, Munich, Germany, Sept 1965, p 220; see also C. M. Sharts, *J. Org. Chem.*, **33**, 1008 (1968).

(17) J. P. Freeman, R. C. Petry, and T. E. Stevens, *J. Amer. Chem. Soc.*, **91**, 4778 (1969).

(18) S. K. Brauman and M. E. Hill, *J. Amer. Chem. Soc.*, **89**, 2127 (1967).

(19) The ^{19}F nmr spectra of alkyldifluoramines, often characteristic of slow nitrogen inversion, will be discussed in detail in a separate publication by S. K. Brauman and M. E. Hill, *J. Chem. Soc.*, in press.

A. α-(N,N-Difluoramino)isobutyronitrile (17).[20]—No C≡N stretching frequency was observed in the neat ir spectrum of this compound. Its nmr data follow: ^{1}H nmr ($CFCl_3$) τ 8.39 (t, J = 1.3 Hz); ^{19}F nmr ($CFCl_3$) ϕ −41.0 (s).

Anal. Calcd for $C_4H_6F_2N_2$: C, 40.00; H, 5.04; N, 23.32. Found: C, 39.97; H, 4.74; N, 22.95.

B. α,α-Bis(N,N-difluoramino)propionitrile (18).—The original stock solution of **5** in *sym*-tetrachloroethane was diluted with toluene for this preparation: ir (neat) 2270 cm^{-1} (CN); ^{1}H nmr ($CFCl_3$) τ 8.04 (m); ^{19}F nmr ($CFCl_3$) ϕ −38.8 (AB quartet).

Anal. Calcd for $C_3H_3N_3F_4$: C, 22.94; H, 1.93; N, 26.74. Found: C, 23.18; H, 2.17; N, 26.79.

C. α-(N-Fluorimino)propionitrile (20).[21]—The *syn* and *anti* isomers could not be separated. The spectral data for an isomeric mixture follow: ir (neat) 2260 (CN), 1610 cm^{-1} (C=N); ^{1}H nmr ($CFCl_3$) τ 7.76 (s), 7.82 (d, J = 1.2 Hz); ^{19}F nmr ($CFCl_3$) ϕ −53.0 (s), −67.3 (s).

Anal. Calcd for $C_3H_3FN_2$: C, 41.87; H, 3.51; N, 32.54. Found: C, 42.14; H, 3.57; N, 32.35.

This compound was also isolated from a kinetic solution of twice the normal concentration. After reaction was complete, the entire aqueous mixture (250 ml) was extracted with 20 ml of toluene, the extract was dried ($CaCl_2$) briefly, and the product was isolated from the solvent by vpc. Only one peak was detectable by vpc. The isolated product was dissolved immediately in $CFCl_3$ for nmr analysis. The methyl protons of **20** in this solution integrated for a 1:1 mixture of *syn* and *anti* isomers.

D. 2-(N-Fluorimino)-3-(N,N-difluoramino)-3-methylbutane (21).—The neat material absorbed at 1640 cm^{-1} in the ir.

$$\underset{a}{CH_3}\underset{b}{C(=NF)}\underset{c}{C(NF_2)}\underset{d}{(CH_3)_2}$$

The ^{1}H nmr ($CFCl_3$) data follow: a, τ 7.96 (doublet of triplets, J_{ac} = 0.6 Hz, J_{ab} = 5.0 Hz); d, 8.51 (doublet of triplets, J_{cd} = 0.8 Hz, J_{bd} = 0.5 Hz). The ^{19}F nmr ($CFCl_3$) data follow: b, ϕ −28.5 (s); c, −26.0 (s).

Anal. Calcd for $C_5H_9F_3N_2$: C, 38.97; H, 5.89; N, 18.18. Found: C, 39.16; H, 6.00; N, 18.25.

This product was also isolated from a kinetic solution, as described for **20** above. Mixed pentanes were used for extraction; sodium sulfate was the drying agent. This material gave only one peak on the vpc. The ^{1}H nmr spectrum of the kinetic sample was found to be identical at both 60 (Varian A-60) and 100 MHz. It was also identical with the spectrum of the material prepared in pyridine–methylene chloride. This spectrum is interpretable only in terms of the presence of one isomer. From steric considerations alone, this isomer has been asssigned the *syn* configuration.

E. 2-(N-Fluorimino)-3,3-bis(N,N-difluoramino)butane (22).—The original stock solution of **9** in methylene chloride was diluted with additional methylene chloride for this preparation: ir (neat) 1630 cm^{-1} (C=N). The ^{1}H nmr ($CFCl_3$) follow: a, τ 7.83 (d, J_{ab} = 6.0 Hz); d, 8.12 (quintet, J_{cd} = 2.0 Hz). The ^{19}F nmr (*n*-heptane) data follow: b, ϕ −41.7 (s); c, −28.7 (AB quartet). Sample detonation on combustion precluded elemental analysis.

$$\underset{a}{CH_3}\underset{b}{C(=NF)}\underset{c}{C(NF_2)_2}\underset{d}{CH_3}$$

The compound, formed both in kinetic solution and in pyridine–methylene chloride, showed only one vpc peak. The ^{1}H nmr of the sample prepared in pyridine–methylene chloride analyzed for the presence of only one isomer. It is assumed that only this isomer is formed in the kinetic solutions and that it possesses the *syn* geometry.

F. N,N,N′-Trifluoropropionamidine (23).—The two geometric products were prepared in mixed pentanes and pyridine. The isomers were readily separated by vpc; the first isomer eluted was designated a, the second, b. Both isomers were characterized.

$$\underset{a}{F_2NC}\underset{b}{(=NF)}\underset{c}{CH_2}\underset{d}{CH_3}$$

Isomer a showed ir (gas) absorbance at 1660 cm^{-1} (C=N). The ^{1}H nmr (hexachlorobutadiene) data follow: c, τ 7.31 (doublet of overlapping quartets, J_{cb} = 6.2 Hz); d, 8.71 (t, J_{cd} = 7.7 Hz). The ^{19}F nmr ($CDCl_3$) data follow: a, ϕ −45.5 (s); b, −8.5 (s).

Isomer b showed ir (gas) absorbance at 1650 cm^{-1} (vw) (C=N). The ^{1}H nmr (hexachlorobutadiene) data follow: c, τ 7.38 (doublet of overlapping quartets, J_{cb} = 6.3 Hz); d, 8.73 (t, J_{cd} = 7.5 Hz). The ^{19}F nmr ($CDCl_3$) data follow: a, ϕ −42.4 (s); b, −13.6 (s). Sample detonation on combustion precluded elemental analysis.

The ratio of isomeric trifluoroamidines formed under kinetic conditions was determined by vpc. During the first 50% reaction in which no noticeable product decomposition occurred, the two isomers of **23** were formed in a 1:1 ratio.[22] Specific configurations cannot rigorously be assigned to these isomers from their spectral data.

Kinetic Studies.—The procedure used in measuring the dehydrofluorination kinetics has already been described.[3] Kinetic solutions were normally 8 × 10^{-3} M in the alkyldifluoramine. Either 20% dodecyl phthalate on 45/60 firebrick or 20% GE-SF-96 on 60/80 firebrick (5 ft × 0.25 in. SS) columns were used for vpc analyses. Aliquots of the diglyme stock solutions of the tris(difluoramines) were appropriately diluted with additional diglyme for each kinetic run. Because of low product solubility in the reaction medium, **5**, **8**, and **9** were studied at half the concentration normally used. The particular extraction solvent (mixed pentanes, mixed hexanes, mixed nonanes, benzene, toluene, nitrobenzene, or methylene chloride) employed was determined by the relative vpc retention time of the material being studied. Methylene chloride proved to be a poor choice for these studies; peak tailing on the vpc gave unreliable results for production of product.

To determine product yields, the vpc response characteristics and distribution coefficients for **16**, **17**, **19**, and **20** between 30% aqueous diglyme and the appropriate extraction solvent were measured. For all except **16** the yields were better than 80%. Malononitrile (**16**) was found to decompose in the presence of 2 equiv of hydrogen fluoride in 30% aqueous diglyme at 75° some 50 times as slowly as **3**. Products **22**, **23**, and **18** at 75° were relatively unstable under the kinetic reaction conditions and their rates of appearance could not be determined. The concentrations of these products reached a maximum value and then leveled off or slowly decreased after 50–85% reaction. Compound **23** slowly hydrolyzed to propionic acid.[22] Even for these unstable products, the yields appeared to be quite good.

In an attempt to trap and observe any possible reaction intermediates, aliquots were withdrawn from kinetic solutions of **4**–**7** at various reaction times and extracted with a number of different solvents. These organic extracts were analyzed by vpc on several types of columns. The complex behavior of **6** has already been described.[3] As would be expected from the kinetic results, no intermediates were detected for **4** and **5**. After an induction period of 60–100 min, the rate of appearance of **20** was linear to 80% reaction, and it was equal to the rate of disappearance of **7**. Such kinetic behavior would indicate the presence of mono and/or didehydrofluorination intermediates. Low concentrations could account for the failure to detect any such intermediates.

Registry No.—**1**, 10524-16-0; **2**, 18264-10-3; **3**, 21298-22-6; **4**, 16063-24-4; **5**, 21363-80-4; **6**, 16063-39-1; **7**, 15403-25-5; **8**, 21363-83-7; **9**, 21389-73-1; **10**, 19309-68-3; **11**, 19309-63-8; **12**, 16327-74-5; **13**, 16327-73-4; **17**, 16063-49-3; **18**, 21363-87-1; **20** (*syn*), 21372-56-5; **20** (*anti*), 21372-55-4; **21** (*syn*), 21372-57-6; **22** (*syn*), 21372-58-7; **23** (*syn*), 21372-60-1; **23** (*anti*), 21372-59-8.

Acknowledgment.—The authors are indebted to Mr. Derek Tegg for isolation of the alkyldifluoramines.

(20) This compound has been partially characterized.[5b]

(21) Although this compound has been characterized previously, the published nmr data were obtained under different conditions: A. L. Logothetis and G. N. Sausen, *J. Org. Chem.*, **31**, 3689 (1966).

(22) The *syn* and *anti* isomers of N,N,N′-trifluorohexanamidine hydrolyze at the same rate under these identical reaction conditions; k = 2.6 × 10^{-5} sec^{-1} for disappearance of starting material. Using this value for disappearance of **23**, the maximum concentration of **23** should be reached after five half-lives for k_{10} during the dehydrofluorination of **10**.