rich or Frinton Laboratories) except for 4-cyclopropylbenzoyl chloride. The preparation of which is described below. The acid chlorides were prepared in the usual manner from the respective carboxylic acids and thionyl chloride. Fluorosulfonic acid was obtained from Allied Chemical Co. and antimony pentafluoride was procured from Alfa Inorganic.

Nmr Spectra.—All spectra were recorded on a Varian A-60 nmr spectrometer equipped with a variable-temperature probe. Spectra were scanned within 15 min after sample preparation. The chemical shifts (δ) are reported in parts per million downfield from TMS using tetramethylammonium tetrafluoroborate (δ 3.10) as the secondary standard.

Infrared Spectra.—Spectra were recorded on a Perkin-Elmer Infracord Model 137-G using a AgCl cell. The cation samples in FSO_3H–SbF_5 caused substantial etching of the cell.

Ultraviolet Spectra.—Spectra were recorded on a Model 202 Perkin-Elmer recording spectrometer using 0.2-cm quartz absorption cells. Sample concentration were 10^{-2} to 10^{-3} M.

Sample Preparation.—Samples were prepared by adding ~0.1 g of the acid chloride in a dropwise manner to ~1.0 ml of FSO_3H–SbF_5 (1:1 M) at room temperature. A ratio of 1:1 by volume of sulfur dioxide was used for the low-temperature samples. The usual intense peak at −10.9 ppm and that of $H_3{}^+O$ at −10.5 ppm were observed in all cases.

4-Cyclopropylbenzoyl Chloride.—Cyclopropylbenzene[27] was brominated according to the method of Levina and coworkers.[28] 4-Bromocyclopropylbenzene was obtained as a colorless liquid boiling at 97–98° (10 mm) (63%).

4-Cyclopropylbenzoic acid was prepared *via* the Grignard reagent and was obtained as a white crystalline solid melting at 156–157° (45%). Hart and Levitt[29] report a melting point of 157–158°. 4-Cyclopropylbenzoyl chloride was prepared by refluxing the carboxylic acid with 1 M excess of thionyl chloride for 2 hr. The acid chloride distilled as a colorless liquid, bp 89–90° (0.5 mm). The product gave an nmr spectrum consisting of two doublets centered at −7.93 and −7.09 ppm and two complex multiplets centered at −1.96 and −0.95 ppm in a proton ratio of 2:2:1:4, respectively.

Registry No.—**1**, 1571-83-1; **2**, 20122-33-2; **3**, 20122-34-3; **4**, 20122-35-4; **5**, 20122-36-5; **6**, 20122-37-6; **7**, 20122-38-7; **8**, 20122-39-8; **9**, 20122-40-1; **10**, 20122-41-2; **11**, 20122-42-3; **12**, 20122-43-4; **13**, 20122-44-5; **14**, 20122-45-6.

Acknowledgment.—The author would like to acknowledge the assistance of Mr. J. W. Lalk for the preparation of some of the acid chlorides.

(27) T. F. Corbin, R. C. Hahn, and H. Schechter, *Org. Syn.*, **44**, 30 (1964).

(28) R. Y. Levina, P. A. Gembitskii, and E. G. Treshchova, *Zh. Obshch. Khim.*, **33**, 371 (1963); *J. Gen. Chem.*, **33**, 364 (1963).

(29) H. Hart and G. Levitt, *J. Org. Chem.*, **24**, 1261 (1959).

The Alkylation of Difluoramine with Carbonium Ions[1]

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The acid-catalyzed reactions of difluoramine with olefins, alcohols, alkyl halides, ketones, and acetals yield organic difluoramino derivatives. These reactions appear to take place by reaction of a carbonium ion with difluoramine. Interpretation of the results is discussed in terms of carbonium ion stability and reactivity.

Previous reports of the chemistry of difluoramine from these laboratories have focused on its reactions with basic reagents, such as amines[2,3] and imines,[4] in which the fluorine–nitrogen bonds were broken. Recently, the addition of difluoramine to aldehydes and ketones was reported.[5] This reaction may be viewed as a special example of an alkylation reaction whereby a difluoramino group is attached to carbon. A preliminary report of other alkylations has also appeared.[6]

Results

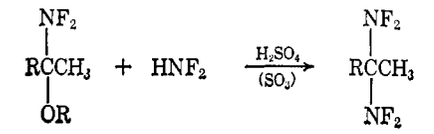
It has been found that a variety of compounds which react with acids to produce carbonium ions will alkylate difluoramine to produce new organic difluoramino compounds. The conditions required for alkylation depend on the ease of carbonium ion formation and the reactivity of the carbonium ion. Some comment will be made on the various factors involved during the discussion of these reactions. Some difluoramines prepared in this way are listed in Table I.

Olefins.—1,1-Dialkylethylenes, enol ethers and esters, and ketene acetals react with difluoramine in the presence of acid catalysts to produce the corresponding alkyl difluoramine. α,β-Unsaturated carbonyl compounds also add difluoramine readily.

The conditions of this addition reaction appeared to depend upon the nucleophilic character of the olefin. For example, ketene acetals and enol ethers reacted directly with difluoramine without added acid, enol esters required an added acid catalyst (a sulfonic acid ion-exchange resin, Amberlyst 15,[7] proved useful), and hydrocarbon olefins required concentrated sulfuric acid as catalyst.

Acrolein and methyl vinyl ketone reacted with difluoramine without catalyst to yield the conjugate addition products. Acrolein reacted further by addition to the carbonyl group. Acrolein diethyl acetal, on the other hand, reacted initially at the α-ether carbon atom, but with acid catalysis the bis product resulting from reaction at both carbonium ion centers was produced.

When the HNF_2–enol ether or enol ester products were treated with more difluoramine in the presence of 100% sulfuric acid or fuming sulfuric acid, the ether or ester function was replaced by a difluoramino group.



(1) This work was carried out under Army Ordnance Contract No. DA-01-021 ORD-5135.

(2) C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *J. Amer. Chem. Soc.*, **85**, 97 (1963).

(3) C. L. Bumgardner and J. P. Freeman, *ibid.*, **86**, 2233 (1964).

(4) W. H. Graham, *ibid.*, **88**, 4677 (1966).

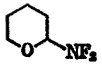
(5) J. P. Freeman, W. H. Graham, and C. O. Parker, *ibid.*, **90**, 120 (1968).

(6) W. H. Graham and J. P. Freeman, *ibid.*, **89**, 716 (1967).

(7) Trademark of Rohm and Haas Co., Philadelphia, Pa.

TABLE I

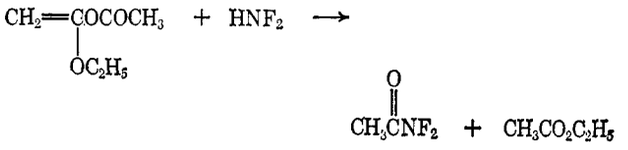
ALKYLATIONS OF DIFLUORAMINE

Alkylating agent	Catalyst	Product	Registry no.	Analysis: Calcd, % C	H	N	F	Found, % C	H	N	F	^{19}F nmr shift), ϕ
$(C_6H_5)_3CBr$	Liquid SO_2	$(C_6H_5)_3CNF_2$[a]										−32.4
$(C_6H_5)_2CHOH$	SO_2, Amberlyst 15	$(C_6H_5)_2CHNF_2$	14092-52-5	71.22	5.06	6.39	17.33	71.18	5.17	6.55	17.4	−48.6
$C_6H_5CCl_3$[c]	CF_3CO_2H	$(C_6H_5)CCl_2NF_2$	14092-53-6	39.65	2.38	6.61	17.92	39.51	2.84	6.78	18.7	−43.5
$(C_6H_5)_2C(Cl)_2$	Neat	$(C_6H_5)_2C(Cl)NF_2$	20122-15-0	61.5	3.95	5.52	15.0	61.57	4.02	5.41	16.38	−27.1
$(CH_3)_2C{=}CH_2$	H_2SO_4	$(CH_3)_2CNF_2$[a]	646-55-9									
$(CH_3)_2C{=}CHCH_3$	H_2SO_4	$(CH_3)_2C(C_2H_5)NF_2$	14092-55-8	48.76	9.00	11.38		48.96	9.01	11.54		−25.1
$CH_2{=}C(Cl)CH_3$	Amberlyst 15	$(CH_3)_2C(Cl)NF_2$	20122-18-3	28.8	4.5	10.9	29.3	28.9	5.1	11.2	27.7	−34.3
	Neat		14092-58-1	43.8	6.57	10.21	27.7	43.89	6.56	10.42	27.2	−28.1[b]
$CH_2{=}CHOCH_2CH(CH_3)_2$	Amberlyst 15	$CH_3CH(NF_2)OCH_2CH(CH_3)_2$	20122-20-7	47.06	8.50	9.15	24.84	49.95	8.91	9.80	21.04	−39.5[b]
$CH_2{=}CHCH(OC_2H_5)_2$	Neat	$CH_2{=}CH{-}CH(NF_2)OC_2H_5$	16452-22-5	43.79	6.62	10.22	27.72	43.86	6.79	10.32	27.1	−26.1[b]
$CH_2{=}CHCH(OC_2H_5)_2$	Amberlyst 15	$NF_2CH_2CH_2CH(NF_2)OC_2H_5$	20122-22-9	31.58	5.80	14.74	39.93	32.00	5.74	14.73	39.2	−53.6; −25.5[b]
$CH_2{=}CCH_3$ $\quad\quad\vert$ $\quad OCOCH_3$	Amberlyst 15	$(CH_3)_2C(NF_2)OCOCH_3$	20122-23-0	39.22	5.90	9.15	24.84	39.16	6.11	8.94	24.20	−20.6
$CH_2{=}CHOCOCH_3$	Amberlyst 15	$CH_3CH(NF_2)OCOCH_3$	20122-24-1	34.54	5.07	10.07	27.32	34.74	5.27	10.48	26.41	−26.6[b]
$CH_2{=}C(OC_2H_5)_2$	Neat	$CH_3C(NF_2)(OC_2H_5)_2$	20122-25-2									−18.7
$CH_3C(OCH_3)_3$	Neat	$CH_3C(NF_2)(OCH_3)_2$[d]	14092-57-0									−18.7
$CH_2{=}CHCOCH_3$	Neat	$NF_2CH_2CH_2COCH_3$	20122-27-4	39.02	5.73	11.38	30.87	39.33	6.13	11.28	29.3	−54.1
$CH_2{=}CHCHO$	Neat	$NF_2CH_2CH_2CH(OH)NF_2$	20122-28-5	22.37	3.13	17.38	47.18	23.06	4.35	17.33	47.04	c

[a] An example of the reverse of this reaction has been reported. Dissolution of triphenylmethyl difluoramine in sulfuric acid produces difluoramine. W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1963). [b] The ^{19}F nmr spectrum was interpreted as the AB portion of an ABX pattern. Typically J_{AB} = 590–600 cps. Details of such spectra will be reported in a separate publication. The values reported here represent the center of the overlapped center lines of the AB quartets. In some cases the outer lines were detectable, at other times not. [c] See Experimental Section. [d] These products were not easily purified for analysis. [e] Cl 32.6% (Calcd 33.44%).

This reaction is analogous to the recently reported conversion of ketones to *gem*-difluoramines[8] by difluoramine and sulfuric acid which probably proceeds through the ketone–HNF_2 adduct.[5]

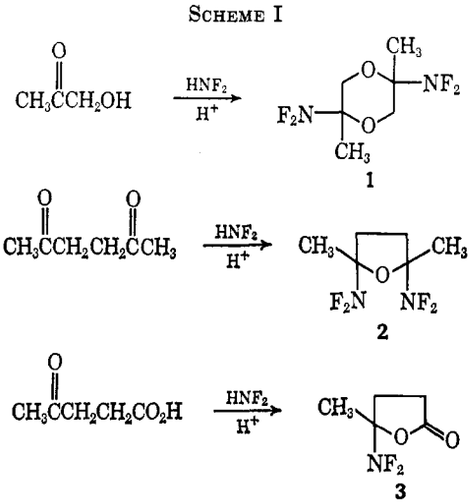
In a unique case the difluoramine adduct of a vinyl ester decomposed spontaneously. Addition of difluoramine to α-ethoxyvinyl acetate[9] produced a mixture of ethyl acetate and N,N-difluoracetamide.[10] This reaction is similar to that of hydrogen chloride and this ester which yields acetyl chloride.[9] Anhydrides react with difluoramine in the presence of Amberlyst 15 to produce difluoramides also.



Alcohols and Alkyl Halides.—Certain alcohols such as triphenylcarbinol, *t*-butyl alcohol, and benzhydrol react with difluoramine in the presence of acids to yield the corresponding difluoramines.[11] Similarly, certain halides such as triphenylmethyl bromide and benzotrichloride alkylate difluoramine. In concentrated sulfuric acid in the presence of difluoramine 2-chloro-2-difluoraminopropane is converted in low yields into 2,2,-bis(difluoramino)propane. In general, vinyl halides did not prove to be a useful source of *gem*-difluoramines.

Aldehydes, Ketones, and Their Derivatives.—It has been reported that simple ketones are converted into *gem*-difluoramines by reaction with difluoramine in sulfuric acid.[8] During that study it was noted that certain nucleophilic functional groups interfere with the reaction. For example, hydroxyacetone is converted into 2,5-bis(difluoramino)-2,5-dimethyl-1,5-dioxane (**1**), acetonylacetone into 2,5-bis(difluoramino)-2,5-dimethylfuran (**2**), and levulinic acid into γ-difluoramino-γ-valerolactone (**3**) (Scheme I). Use of stronger acids effects cleavage of ether **2** to the tetrakis(difluoramine).[8]

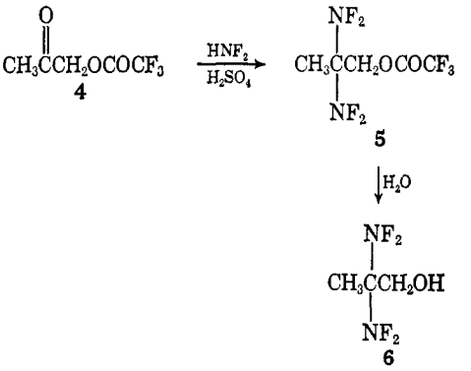
SCHEME I



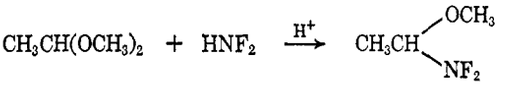
(8) K. Baum, *J. Amer. Chem. Soc.*, **90**, 7083 (1968).
(9) H. H. Wasserman and P. S. Wharton, *ibid.*, **82**, 661 (1960).
(10) R. C. Petry and J. P. Freeman, *ibid.*, **83**, 3912 (1961).
(11) See Table I, footnote *a*.

It has now been found that the carbonyl group of trifluoroacetoxyacetone (**4**) but not of acetoxyacetone is readily converted into a *gem*-difluoramino group (**5**) by HNF_2–H_2SO_4. The trifluoroacetate (**5**) may in turn be hydrolyzed to the alcohol **6** which could not be prepared directly from hydroxyacetone (Scheme II).

SCHEME II



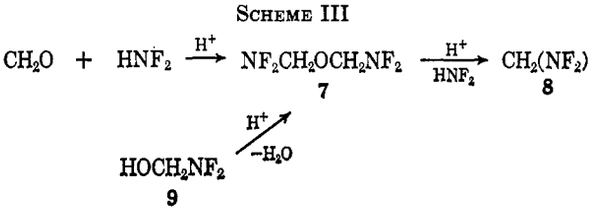
Acetals react smoothly with difluoramine in the presence of Amberlyst 15 to yield α-difluoramino ethers. These compounds, in turn, react as outlined above with difluoramine in the presence of sulfuric acid to yield the bis(difluoramine). *ortho* esters react with difluoramine itself to yield α-difluoramino ketals. However, efforts



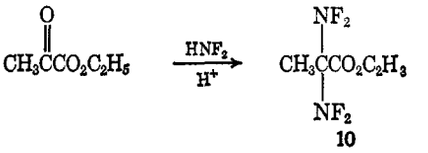
to replace the other alkoxy groups with difluoramine failed.

Formaldehyde reacts with difluoramine in concentrated sulfuric acid to yield α,α′-bis(difluoramino)-methyl ether (**7**),[12] but in 100% sulfuric acid it is converted into bis(difluoramino)methane (**8**). Treatment of difluoraminomethanol (**9**)[6] with difluoramine in concentrated sulfuric acid also produced the ether **7** (Scheme III).

SCHEME III



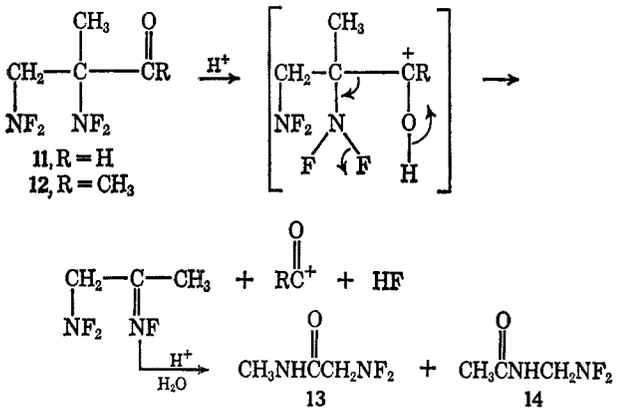
In general, negatively substituted carbonyl compounds were more resistant into conversion into the *gem*-difluoramine. Efforts to convert biacetyl or glyoxal into tetrakis(difluoramines) were completely unsuccessful. However, it was possible to convert ethyl pyruvate into ethyl α,α-bis(difluoramino)propionate (**10**).



(12) S. F. Reed, Jr., and R. C. Petry, *Tetrahedron*, **24**, 5089 (1968).

Part of the problem with α-dicarbonyl compounds appears to be related to the instability of α-difluoramino carbonyl compounds in acid. Thus, 2,3-bis(difluoramino)-2-methylpropionaldehyde (**11**) and 1,2-bis(difluoramino)-2-methyl-3-butanone (**12**) decomposed in a mixture of difluoramine and sulfuric acid to a mixture of amides **13** and **14**. Carbon monoxide was identified as another decomposition product of aldehyde **11**. It is believed that their products arise according to Scheme IV. Beckmann rearrangements

SCHEME IV

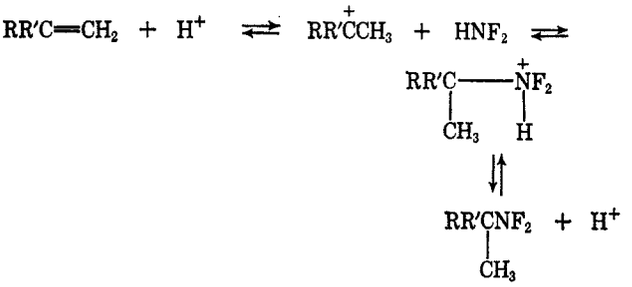


of fluorimines have been observed frequently in sulfuric acid.[13] This fragmentation appears to be chemically related to the instability of vinyl difluoramines[14,15] and of α-difluoraminosilanes.[16] In all these cases a difluoramino group is attached to a carbon atom adjacent to an atom with an available bonding orbital (sp^2 carbon and sp^3d^0 silicon).

Discussion

All of these alkylation reactions can be explained in terms of carbonium ion theory. The type of acid catalyst required directly reflected the stability of the carbonium ion intermediate. For example, among the olefins examined the order of reactivity found was vinyl ethers > vinyl esters > 1,1-dialkylethylenes. No added acid was necessary with the vinyl ethers, a sulfonic acid ion-exchange resin functioned for the esters, and concentrated sulfuric acid was required for the ethylenes. It appeared that some olefins yielded too stable carbonium ions while others were not stable enough. Thus, no difluoramines were obtained in this study from styrenes of *sym*-dialkylethylenes nor from simple olefins like propylene and cyclohexene under the same conditions that isobutylene reacted rapidly.

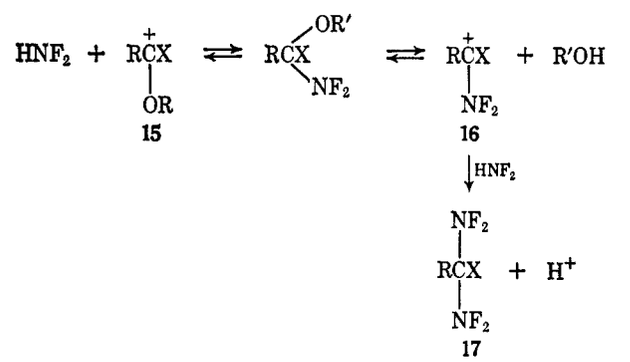
These reactions can be understood in terms of the equilibria involved. At high acid concentrations there will be a high concentration of carbonium ion. Since difluoramine must be a very weak nucleophile, the carbonium ion must be electrophilic enough to drive the reaction to product. If the ion is a stable one [*e.g.*, $(RO)_2CH^+$, $(C_6H_5)_2C^+CH_3$], very little difluoramino compound is produced, because in strong acid the reverse



reaction is favored; upon dilution of the reaction mixture with water difluoramine is recovered. If the carbonium ion is too reactive [*e.g.*, $(CH_3)_2CH^+$, $CH_3CH_2^+$], it will react with olefin or solvent and little if any difluoramino compound is found.

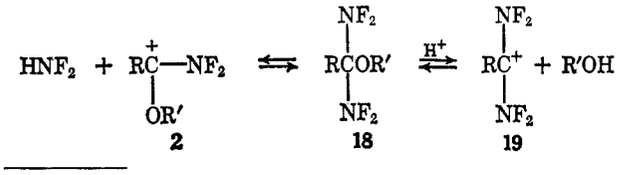
The behavior of α-alkoxydifluoramines is of particular interest. The monoalkoxy compounds react to produce *gem*-difluoramines, but dialkoxy derivatives liberate difluoramine in strong acid. These results may be understood as shown in Scheme V. Undoubtedly, when

SCHEME V



X = H or alkyl, ion **15** is more stable than ion **16** but no reaction occurs that removes ion **15** from the reaction scene. On the other hand, ion **16** is siphoned off to the *gem*-difluoramine by reaction with HNF_2. The *gem*-difluoramines are generally insoluble in sulfuric acid and separate as an insoluble layer which displaces the equilibrium. The position of equilibrium is also affected by the relatively greater basicity of the alcohol than of difluoramine. When the alcohol is tied up as an oxonium salt, reversal of the ionization of the α-alkoxydifluoramine is prevented.

However, when X = OR′, the chemistry of the whole system changes. The stability of ion **15** becomes extremely high and the equilibrium is displaced far to the left. In addition, the *gem*-difluoramine **17** is no longer acid insoluble because of the presence of the ether function and it is no longer removed from the reaction zone.[17,18] While, in principle, ionization of a compound such as **18** to ion **19** is possible, in fact, no



(13) T. E. Stevens, *Tetrahedron Lett.*, 3017 (1967).

(14) R. C. Petry, C. O. Parker, F. A. Johnson, T. E. Stevens, and J. P. Freeman, *J. Org. Chem.*, **32**, 1534 (1967).

(15) W. H. Graham, Abstracts of Papers, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(16) R. C. Petry and J. P. Freeman, *J. Org. Chem.*, **32**, 4026 (1967).

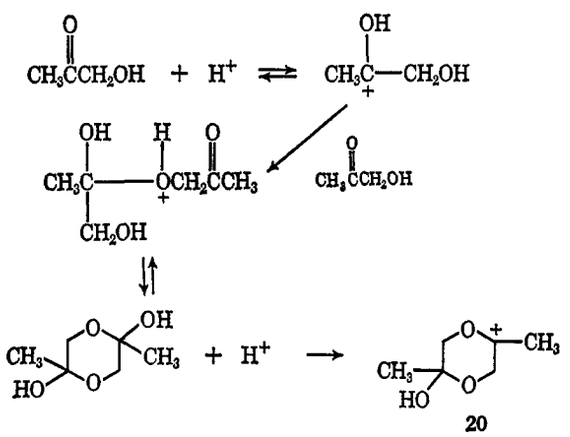
(17) Removal of the difluoramino product from the acid solution has important practical implications also since organic difluoramines are decomposed through nitrogen–fluorine bond cleavage in strong acids.

(18) K. Baum and H. M. Nelson, *J. Amer. Chem. Soc.*, **88**, 4459 (1966).

products derived from such an ion have ever been obtained, regardless of the acid strength or difluoramine concentration. The relatively greater stability of ion **2** over ion **19** favors the reverse reaction.

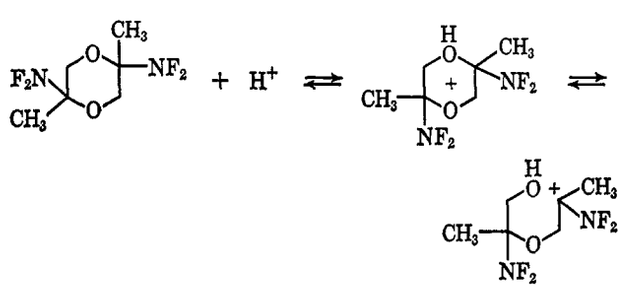
The other observations on reactivity appear to be consistent with these generalizations. The cyclizations of hydroxyacetone, acetonylacetone, and levulinic acid are due to the fact that groups like hydroxyl and carbonyl are more nucleophilic than difluoramine and react more rapidly with the carbonium ion. Probably more important is the fact that these cyclization reactions yield more stable carbonium ions. For example, the reaction of hydroxyacetone in acid may be viewed according to Scheme VI. Carbonium ion **20** is appar-

SCHEME VI



20

ently a more stable ion than the simple protonated carbonyl compound. It may in turn now react with difluoramine to give the final product **1**.[19] Probably



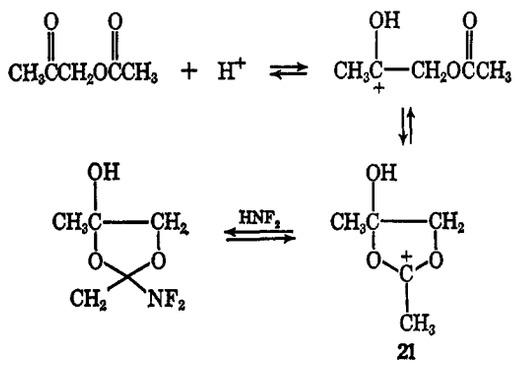
the reason that acetoxyacetone yields no product is due to the great stability of the cyclized carbonium ion, **21** (Scheme VII). There is little driving force for reaction of this ion with difluoramine. Again, the difluoramino product, being still highly oxygenated, cannot separate from the acid as an insoluble layer.

Consistent with this hypothesis is the fact that α-trifluoroacetoxyacetone can be converted into 2,2-bis-(difluoramino)propyl trifluoroacetate (**22**) by HNF_2–H_2SO_4. In this case the cyclized carbonium ion is destabilized by the trifluoromethyl group and the unfavorable equilibrium present in the acetate is displaced (Scheme VIII).

These reactions are very sensitive to acid strength. Many reactions that could not be accomplished in concentrated sulfuric acid proceed quite smoothly in

(19) Since α-difluoramino ethers can be cleaved by HNF_2–H_2SO_4, it might at first be surprising that further reaction does not occur with ether **1**. Apparently, the equilibrium is very unfavorable in this case because of ease of cyclization.

SCHEME VII



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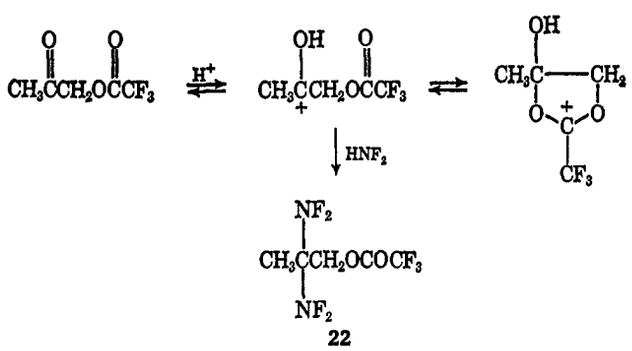
SCHEME VIII



22

15% fuming sulfuric acid or with sulfur trioxide itself. Fluorosulfonic acid also proved to be a very useful catalyst. The effectiveness of sulfur trioxide (Sulfan B) is in part due to its reaction with difluoramine to produce difluoraminosulfonic acid (**23**).[20] While this

$$HNF_2 + SO_3 \rightleftharpoons NF_2SO_3H$$

23

compound is not very stable, it serves as a very powerful acid catalyst in its own right and as a source of solubilized difluoramine.[21] The stronger acids also serve, of course, to produce carbonium ions from more highly electronegatively substituted substrates.

A typical example of the effect of acid strength may be seen in the formaldehyde–HNF_2 reaction. In concentrated sulfuric acid the ion $NF_2CH_2^+$ is probably not produced in any reasonable concentration or is immediately trapped by water or formaldehyde which are better nucleophiles than difluoramine. In stronger acid where the better nucleophiles are probable completely protonated this ion is produced and finds only difluoramine to react with.

Experimental Section

Safety Precautions.—It should be recalled that difluoramine is highly explosive in the condensed state and particularly during melting.[22] While a −130° bath (methylcyclohexane) has been used successfully as indicated in the experiments described, a −117° bath (80% Freon 11–20% CCl_2=CHCl) proved to be more reliable and is recommended.

(20) W. H. Graham, unpublished results.

(21) Difluoramine is not particularly soluble in concentrated sulfuric acid and there was no evidence for its extensive protonation in this solvent. Little remains in solution unless an atmosphere of difluoramine is maintained above the solvent.

(22) J. P. Freeman, A. Kennedy, and C. B. Colburn, *J. Amer. Chem. Soc.*, **82**, 5304 (1960).

Olefin Addition Reactions.—Three techniques were used: (1) a mixture of the olefin and difluoramine alone; (2) a mixture of difluoramine and olefin with a small amount of Amberlyst 15 resin added; and (3) a mixture of difluoramine and olefin in sulfuric acid as solvent. In some early experiments these reactions were carried out at subatmospheric pressures in U tubes on a vacuum line. Later it was found convenient to use pressure reactors equipped with a magnetic stirring bar and a Fischer–Porter Teflon pressure valve. These reactors have been described.[23] Typical examples of these techniques will be given.

Addition of Difluoramine to Dihydropyran.—Into a U tube containing a magnetic stirring bar and manometer (total volume 260 ml) attached to a vacuum line was placed 0.42 g (0.005 mol) of dihydropyran. The sample was degassed by alternate freeze–thaw cycles; 224 cc (STP) (0.010 mol) of difluoramine was condensed into the tube by means of a −130° slush bath. The mixture was warmed to ambient temperature and stirred overnight. The pressure had dropped from a maximum of 430 mm to 120 mm during this time. Fractionation of the mixture through traps at −80 and −130° gave 40 cc (STP) of recovered HNF_2 in the −130° trap. The −80° trap contained the liquid product. Vpc analysis showed essentially no starting material and only one major product peak. (See Table I for characterization.)

Addition of Difluoramine to Isopropenyl Acetate.—A heavy-walled 10-ml Pyrex tube[23] fitted with a Fischer–Porter Teflon needle valve, a ball joint for attachment to the vacuum line, and a magnetic stirring bar was charged with 0.40 g (0.004 mol) of isopropenyl acetate and approximately 0.05 g of Amberlyst 15 catalyst. The tube was degassed in the vacuum line by alternate freeze–thaw cycles and 132 cc (0.004 mol) of HNF_2 was condensed into the tube at −130°. The valve was closed and the contents were warmed to ambient temperature and stirred for 1 hr. The reaction mixture was fractionated through traps at −80 and −130°. Essentially no difluoramine was recovered in the −130° trap. The product, 2-difluoramino-2-propyl acetate, was obtained in quantitative yield in the −80° trap as a water-white liquid. (See Table I.)

Addition of Difluoramine to Isobutylene.—A 100-ml U tube containing 10 ml of concentrated sulfuric acid was degassed and 67 cc (0.003 mol) of difluoramine was condensed in at −130°. The mixture was allowed to warm to room temperature and stirred for 15 min. The contents of the U tube were distilled through traps at −80, −130, and −196°. The liquid in the −80° trap was identified as *t*-butyldifluoramine by its mass spectrum and by comparison of its infrared spectrum with that of an authentic sample.[11]

Acrolein and HNF_2.—A heavy-walled Pyrex tube equipped with a Teflon needle valve and a magnetic stirrer was loaded with 0.26 g (0.004 mol) of degassed acrolein and 264 cc (0.0118 mol) of difluoramine at −130°. The mixture was allowed to warm to room temperature and was stirred for 2.5 hr. The contents were then distilled on a vacuum line through traps at −24, −80, and −130°.

1,3-Bis(difluoramino)propanol had a vapor pressure of 10 mm at −24°.

Anal. Calcd for $C_3H_6F_4N_2O$: C, 22.37; H, 3.13; N, 17.38; F, 47.18. Found: C, 23.06; H, 4.35; N, 17.33; F, 47.04.

Its infrared spectrum showed a strong band in the OH region and no band attributable to a carbonyl group. Its ^{19}F nmr spectrum consisted of a triplet at ϕ −52.8, J_{HF} = 27 cps (CH_2NF_2); the secondary NF_2 group is the AB portion of an ABX pattern, F_A at ϕ −25.6, F_B at ϕ −21.2, J_{AB} = 602 cps, J_{AX} = 10 cps, J_{BX} = 30 cps [$CH(NF_2)OH$].

Preparation of 2,2-Bis(difluoramino)propane.—The procedure used for the isobutylene–HNF_2 reaction was followed using 1.0 ml of 100% sulfuric acid, 0.3 g (0.002 mol) of 2-difluoramino-2-propyl acetate (Table I), and 124 cc (0.0055 mol) of difluoramine. The mixture was stirred for 1.5 hr and then distilled on a vacuum line. The recovered difluoramine amounted to 0.0039 mol. The product, 2,2-bis(difluoramino)propane, was retained in a −80° bath and was identified by comparison of its infrared and nmr spectra with those of an authentic sample,[8] yield 0.001 mol (50%).

Preparation of 2,2-Bis(difluoramino)propanol.—Acetonyl trifluoroacetate was prepared by adding 37 g (0.5 mol) of hydroacetone to 125 g (0.6 mol) of trifluoroacetic anhydride at 10°. The mixture was stirred at room temperature for 30 min and then refluxed for 30 min. The excess trifluoroacetic anhydride was removed by distillation and the ester, bp 45° (170 mm), was obtained in 72% yield.

A mixture of 5 ml of concentrated sulfuric acid and 5 ml of 30% fuming sulfuric acid was placed on a 1-l. round-bottomed flask containing a magnetic stirrer and cooled to −80°. Acetonyl trifluoroacetate, 2.0 g (0.012 mol), was added and the resulting solution was degassed thoroughly. Difluoramine (500 cc) was condensed in at −80° and the mixture was stirred at room temperature for 3.5 hr. It was then distilled through a trap at −63° which retained the 2,2-tris(difluoramino)propyl trifluoroacetate, which was further purified by distillation, bp 52° (30 mm), yield 1.1 g (40%).

The trifluoroacetate was added to 3 ml of methanol and heated until all the methyl trifluoroacetate had distilled. The residue was distilled through traps at −25 and −80°. Several distillations of this type freed the product of methanol at which time it crystallized in the −25° trap. 2,2-Bis(difluoramino)propanol was obtained as a water-white liquid.

Anal. Calcd for $C_3H_6F_4N_2O$: C, 22.22; H, 2.73; N, 17.28; F, 46.89. Found: C, 22.61; H, 4.22; N, 16.60; F, 45.1.

Its ^{19}F nmr spectrum showed a singlet at ϕ −26.8. Its ^1H spectrum consisted of a pentuplet at τ 8.33 [$CH_3C(NF_2)_2$], a sharp singlet at τ 6.56 (OH), and a pentuplet at τ 5.9 [$(NF_2)_2$-CCH_2–].

Paraformaldehyde and Difluoramine. A. Sulfuric Acid Catalyst.—A solution of 0.12 g (0.004 mol) of concentrated sulfuric acid in a 100-ml U tube on a vacuum line was degassed and 224 cc (0.01 mol) of difluoramine was condensed in at −130°. The mixture was warmed to room temperature and stirred there overnight. The mixture was then distilled through traps at −80, −130, and −196°. The product in the −80° trap was identified as α,α'-bis(difluoraminomethyl) ether by comparison of its infrared spectrum with that of an authentic sample.[18,24]

B. 100% Sulfuric Acid Catalyst.—Into an evacuated U tube equipped with magnetic stirring bar and manometer (total volume of 250 ml) and containing 10 ml of 100% sulfuric acid and 0.3 g (0.01 mol) of paraformaldehyde was condensed 448 cc (0.02 mol) of HNF_2 by means of a −130° methylcyclohexane slush bath. The mixture was stirred for 3 hr at room temperature at which time the pressure was steady at 455 mm. A mass spectrum at this point indicated that about 90% of the vapor phase was bis(difluoramino)methane. This would indicate a yield of at least 60%. When the product was fractionated through −80, −130, and −196° traps, the bulk of the product was held up in the −80° trap but some reached the −130° methyl cyclohexane slush trap. A small amount of bis(difluoraminomethyl) ether was also retained in the −80° trap. The complete separation of bis(difluoramino)methane from the ether and difluoramine was accomplished by stirring the mixture over fuming sulfuric acid (to remove HNF_2), removing the volatile contents, and stirring them over water (to remove SO_3), and removing the water over concentrated sulfuric acid.

Bis(difluoramino)methane is a colorless liquid with a vapor pressure of 690 mm at 28°. Its ^{19}F nmr spectrum showed a broad singlet at ϕ −43.4; its proton spectrum consisted of a pentuplet centered at τ 4.7 (J = 22 cps). Its mass spectrum showed no parent molecular ion but major peaks at m/e of 66 ($CH_2NF_2^+$), 47 (CH_2NF^+), 47 ($CHNF^+$), 28 (CH_2N^+), and 27 (CHN^+). Because of its highly explosive and volatile nature no attempt to obtain an elemental analysis was made.

Preparation of Ethyl α,α-Bis(difluoramino)propionate.—Ethyl α-difluoramino-α-hydroxypropionate[5] (2.15 g, 12.7 mol) was placed in a 25-ml pressure bulb equipped with a magnetic stirring rod and a Fischer–Porter needle valve.[22] The bulb was cooled to −80° and 4.5 g of 27% fuming sulfuric acid (which contained 15.2 mmol of free SO_3) was pipetted through the valve opening. The bulb was attached to vacuum line and evacuated, and 20 mmol of HNF_2 condensed into it at −130°. The bulb was then allowed to warm to room temperature and the contents were stirred overnight. The bulb was cooled again to −80° and excess HNF_2 (90 cc, STP) was removed by distillation. The pressure bulb was opened and the residual liquid transferred to a round-bottomed flask and distilled through a −80° trap. The contents of this trap were distilled again under vacuum at room temperature giving ethyl α,α-bis(difluoramino)propionate retained at −40° with vapor pressure of 4.0 mm at 0°: yield 1.60 g (61.7%). The product was dissolved in Freon 11, extracted

(23) R. P. Rhodes, *J. Chem. Educ.*, **40**, 423 (1963).

(24) M. J. Csiesla, K. F. Mueller, and O. Jones, *Tetrahedron Lett.*, 3683 (1964).

with ice water until the washes were neutral, dried, and reisolated by retention at −40° during vacuum transfer, thereby removing acidic impurities.

Anal. Calcd for $C_5H_8F_4N_2O_2$: C, 29.41; H, 3.92; N, 13.73; F, 37.25. Found: C, 29.51; H, 4.75; N, 14.04; F. 36.92.

The ^{19}F nmr spectrum consisted of a very strong line at ϕ −13 flanked at ±630 cps by two weak lines. The spectrum was interpreted as an AA'BB'X_3 type with $J_{AB} = J_{A'B'}$ = 630 cps. Coupling of all fluorine with the methyl group is visible in the proton spectrum with $J_{AX} \sim 2.5$ cps.

Registry No.—Difluoramine, 10405-27-3; 2,2-bis(difluoramino)propanol, 20122-29-6; bis(difluoramino)methane, 18338-50-6; ethyl α,α-bis(difluoroamino)propionate, 20122-31-0.

General Base Catalyzed Hydrolysis of N,N'-Dimethyl-N,N'-diphenylamidinium Salts

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The hydrolyses of N,N'-dimethyl-N,N'-diphenylformamidinium, -acetamidinium, and -benzamidinium salts in aqueous solutions are general base catalyzed, with Brønsted catalysis law β values near 0.4. Hydroxide ion catalyzed hydrolysis of tetrasubstituted amidinium salts is characterized by large negative entropies of activation and by kinetic solvent isotope effects, k_{H_2O}/k_{D_2O}, less than unity. Base-catalyzed hydrolysis of amidinium cations is slowed by bulky acyl substituents, and hydrolysis of substituted benzamidinium cations is accelerated by electron-attracting aryl substituents (ρ = 1.6). Hydroxide ion catalyzed hydrolysis of the formamidinium and benzamidinium salts is approximately first order in hydroxide ion concentration. The rate of hydrolysis of the acetamidinium salt tends to become independent of hydroxide ion concentration at high hydroxide ion concentrations, possibly due to reversible formation of a ketene aminal. All of these observations are satisfactorily accounted for by a mechanism involving rate-limiting general base catalyzed conversion of a tetrahedral hydrate of the amidinium cation into N-methylaniline and an N-methylanilide.

Hydrolysis reactions of N,N'-diarylformamidines and N,N'-diarylacetamidines in acidic solutions are characterized by large positive Hammett ρ values, large negative entropies of activation, and rates which are directly proportional to the hydrogen ion concentration and water activity, and inversely proportional to the acidity (h_0) of the reaction solutions. The diarylformamidines are about a thousand times more reactive than the diarylacetamidines in aqueous 20% dioxane hydrochloric acid solutions.[2-4] Hydrolysis of N,N'-diarylformamidinium ions is general base catalyzed, with a Brønsted catalysis law β value of 0.3.[2,3] These observations are consistent with a mechanism involving rate-limiting general base catalyzed conversion of a protonated tetrahedral intermediate into products (eq 1).[3,5]

$$\mathrm{ArN{=}CR{-}NHAr + H_3O^+ \rightleftharpoons Ar\overset{+}{N}H_2{-}\underset{\displaystyle R}{\overset{\displaystyle OH}{\overset{|}{\underset{|}{C}}}}{-}NHAr \xrightarrow{B:}}$$
$$\mathrm{ArNH_2 + RCONHAr + BH^+} \quad (1)$$

The kinetics of hydrolysis of N,N'-diarylformamidines under alkaline conditions is complex.[6] The rate of hydrolysis of formamidines having electron-releasing N-aryl substituents is nearly independent of hydroxide ion concentration and the structure of the aryl groups. Amidines having electron-withdrawing aryl substituents undergo hydrolysis by two processes, one which is independent of hydroxide ion concentration, and another whose rate is a nonlinear function of hydroxide ion concentration. Hydroxide ion catalyzed hydrolysis of N,N'-diarylformamidines probably involves rate-limiting reaction of a tetrahedral hydrate of the amidine with hydroxide ion, complicated by a side equilibrium between the amidine and an unreactive conjugate base (eq 2).

$$\mathrm{ArN{=}CH{-}NHAr + OH^- \rightleftharpoons ArN{\cdots}\bar{C}H{\cdots}NAr + H_2O}$$
$$\mathrm{ArN{=}CH{-}NHAr + H_2O \rightleftharpoons ArNH{-}CH(OH){-}NHAr \xrightarrow{OH^-}}$$
$$\mathrm{ArNHCHO + ArNH^- + H_2O} \quad (2)$$
$$\mathrm{ArNH^- + H_2O \rightleftharpoons ArNH_2 + OH^-}$$

The hydroxide-independent reaction is best rationalized in terms of rate-limiting reaction of the hydrated conjugate acid of the amidine with hydroxide ion (eq 1).

Alkaline hydrolysis of N,N'-disubstituted amidines is complicated by the existence of pH-dependent equilibria between the free amidines, their conjugate acids, and their conjugate bases. The amidinium ions are the more interesting of these three species, since they are implicated as intermediates under both acid and alkaline conditions.

Accordingly, we selected a series of N,N'-dimethyl-N,N'-diphenylamidinium cations, $C_6H_5N(CH_3){\cdots}\overset{+}{C}R{\cdots}N(CH_3)C_6H_5$, as substrates for a study of solvent, salt, and substituent effects on amidinium ion hydrolysis. These tetrasubstituted amidinium ions are isoelectronic with the conjugate acids of N,N'-disubstituted amidines, but possess no acidic proton.

Experimental Section

Preparation of Amidinium Salts.—N,N'-Dimethyl-N,N'-diphenylformamidinium tetrafluoroborate was prepared by adding 10 g of N,N',N''-trimethyl-N,N',N''-triphenyl orthoformamide[7] to 90 ml of 12% fluoroboric acid, heating the mixture on a steam bath until the orthoamide dissolved, adding 200 ml of water, and

(1) Taken from the M.A. Thesis of M. W. C.
(2) R. H. DeWolfe and R. M. Roberts, *J. Amer. Chem. Soc.*, **75**, 2942 (1953).
(3) R. H. DeWolfe, *ibid.*, **82**, 1581 (1960).
(4) R. H. DeWolfe and J. R. Keefe, *J. Org. Chem.*, **27**, 493 (1962).
(5) J. F. Bunnett, *J. Amer. Chem. Soc.*, **83**, 4971 (1961).
(6) R. H. DeWolfe, *ibid.*, **86**, 864 (1964).
(7) D. H. Clemens, E. Y. Shropshire, and W. D. Emmons, *J. Org. Chem.*, **28**, 1108 (1963).