Radical Reactions of Tetrafluorohydrazine. III.[1] Addition to Olefins

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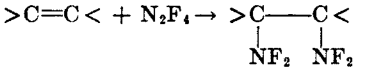
The addition of tetrafluorohydrazine to olefins to form 1,2-bis(difluoramino) compounds is a general reaction. Characterization of a variety of the adducts and some of their properties are reported.

Following the discovery of tetrafluorohydrazine in these laboratories,[3] a broad program to investigate the synthetic utility of this new reagent was undertaken in 1958. One of the early studies, the interaction of tetrafluorohydrazine and mercaptans,[4] suggested the radical nature of this reagent.[5] A brief report of the trapping of organic free radicals by difluoramino radicals has appeared[6] and the interaction of nitroso compounds and NF_2 radicals has been reported.[7]

In the intervening years a general and comprehensive study of the addition of tetrafluorohydrazine to olefins was made. Since there have recently been some reports of limited examinations of this reaction,[8,9] it seemed appropriate to report the results of our study of reaction 1.



$$>C{=}C< + N_2F_4 \rightarrow >\underset{NF_2}{\underset{|}{C}}-\underset{NF_2}{\underset{|}{C}}< \qquad (1)$$

Results

The addition of tetrafluorohydrazine to olefins is a rather general reaction yielding vicinal bis(difluoramines) in good yields. Some representative adducts are compiled in Table I. The only olefins that resist addition are the very weakly nucleophilic olefins such as maleic anhydride, tetracyanoethylene, 2,3-dinitro-2-butene, and the like.

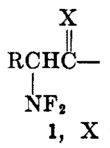
Reaction Conditions.—Many of the early studies of the olefin–N_2F_4 reaction were carried out in the gas phase at relatively low pressures (200–500 mm). Under these conditions aliphatic olefins react smoothly at 100°, but rather slowly below this temperature. Qualitatively, it was observed that electron-rich olefins reacted relatively more rapidly than electron-poor olefins. For example, perfluoropropylene reacts at a reasonable rate only above 140°, whereas α-methylstyrene absorbs N_2F_4 at room temperature. For preparative work and to extend the reaction to nonvolatile olefins, it is convenient to conduct this reaction under pressure in solvents such as methylene chloride, chloroform, Freon 113, and chlorobenzene. For this purpose the use of Fischer–Porter Aerosol pressure tubes was found to be safe and convenient. The small-scale, high-pressure apparatus recently described was also used.[10]

It should constantly be borne in mind that the mixture of a hydrocarbon and tetrafluorohydrazine is potentially highly explosive and all these reactions must be carried out with the requisite precautions. For comparison it should be noted that the heat of explosion of a hydrocarbon–N_2F_4 mixture is of the order of 1500 cal/g while that of a hydrocarbon–oxygen mixture is about 2300 cal/g.

Side Reactions.—In most cases this reaction was a very clean one and little contamination of the product was observed. The adducts do not attack glass under the conditions of the reaction. If the tetrafluorohydrazine contains any appreciable quantity of nitric oxide, a serious side reaction leading to β-difluoramino fluoroazoxy[1] compounds is noted.[11]

The addition reactions carried out in the gas phase at 100–120° and in solution were not complicated by hydrogen abstraction reactions. However, in later runs involving the use of a flow reactor operating at 200–250°, extensive allylic substitution was noted, particularly with the cyclic olefins, cyclopentene and cyclohexene.[11] In this respect, these reactions closely resemble free-radical chlorinations. It is recommended, therefore, that moderate temperatures be employed in these reactions to avoid these substitution reactions.

Adducts containing structural features of the type **1** were unstable under the reaction conditions and in few instances have pure adducts been isolated. It appears that these compounds lose hydrogen fluoride very readily, and that this elimination is followed by further acid-catalyzed decomposition reactions.[12]



$$R\underset{NF_2}{\underset{|}{C}}H\overset{X}{\overset{\|}{C}}-$$

1, X = N, O

No polymerization was noted during any of these reactions even with easily initiated monomers, indicating that the difluoramino radical is a very effective radical trap.

Characterization of Adducts. Physical Properties.—The bis(difluoramino) compounds as a class resemble the corresponding dichloro compounds in such physical properties as boiling point, solubility, and retention times on gas chromatography columns. These

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[3] C. B. Colburn and A. Kennedy, *J. Am. Chem. Soc.*, **80**, 5004 (1958).

[4] J. P. Freeman, A. Kennedy, and C. B. Colburn, *ibid*, **82**, 5304 (1960).

[5] C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

[6] R. C. Petry and J. P. Freeman, *J. Am. Chem. Soc.*, **83**, 3912 (1961).

[7] T. E. Stevens and J. P. Freeman, *J. Org. Chem.*, **29**, 2279 (1964).

[8] (a) A. L. Logothetis, *ibid.*, **31**, 3686 (1966); (b) A. L. Logothetis and G. N. Sausen, *ibid.*, **31**, 3689 (1966); (c) T. S. Cantrell, *ibid.*, **32**, 911 (1967); (d) H. Cerfontain, *J. Chem. Soc.*, 6602 (1965); (e) F. A. Johnson, C. Haney, and T. E. Stevens, *J. Org. Chem.*, **32**, 466 (1967).

[9] A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, *Sect. A*, 582 (1966); 105, 864 (1967).

[10] R. P. Rhodes, *J. Chem. Educ.*, **40**, 423 (1963).

[11] S. F. Reed, Jr., to be published.

[12] Direct preparation of the dehydrofluorinated adducts has been reported;[8b] in these reactions, the addition was carried out in the presence of sodium fluoride which effected the dehydrofluorination.

similarities may reflect the correspondence in electronegativity between the chloro and difluoramino groups.[13]

However, the dominant physical property of the difluoramino compounds is their potential explosive character. The relatively high heat of combustion of 1,2-bis(difluoramino)-4-methylpentane[14] reflects this property and the low molecular weight derivatives all show some sensitivity toward friction, impact, and heat. In view of this property these compounds should be handled as high explosives and all manipulations should involve small quantities and the use of safety shields.

The difluoramines may be stored in glass containers, but on prolonged standing in a warm humid atmosphere they will gradually attack glass. Polyethylene containers may also be used. These compounds may be distilled without decomposition. They are not unstable with respect to loss of hydrogen fluoride as are fluorocarbon amines as long as they are protected from alkaline reagents.[15]

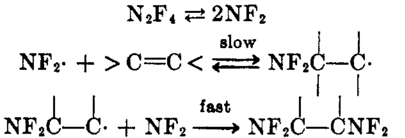
Elemental Analysis.—In general, the explosive character of the difluoramines did not cause problems in their analysis, although precautions were observed during their combustion. Occasionally a few of the compounds flashed or exploded in the combustion tube. It was found that insertion of a short length of tubing packed with magnesium oxide in the combustion train eliminated problems caused by the production of hydrogen fluoride.

It was found that fluorine analyses following combustion were generally low. Good results were obtained if the compounds were decomposed to fluoride ion by alkaline hydrolysis.[15]

Infrared Spectra.—Organic difluoramino compounds exhibit intense multiple absorption bands in the 9.5–15-μ region of their infrared spectra with the strongest bands generally occurring between 11 and 12 μ. No use has been made of these spectra for structural studies except for the qualitative purpose of determining that difluoramino groups were introduced.

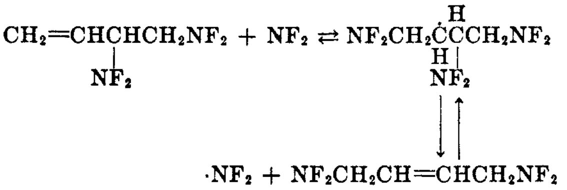
Nuclear Magnetic Resonance Spectra.—In most cases the characterization of these compounds has depended upon measurement of their F^{19} nuclear magnetic resonance spectra. The fluorine atoms of difluoramino groups absorb at relatively low fields (ϕ -25 to -50)[16] and are very sensitive to their chemical environment. For example, a difluoramino group attached to a primary carbon atom appears around ϕ -50 and that on a secondary carbon appears around -35. In addition, the coupling of the fluorine nuclei with adjacent hydrogens provided additional detailed information about the structure. Coupling (J_{HF}) between the fluorines on nitrogen and an α-hydrogen atom were of the order of 27–30 cps. When the difluoramino group was attached to an asymmetric carbon the fluorine atoms were magnetically nonequivalent and AB or ABX F^{19} spectra were observed.[16]

Mechanism.—The qualitative observations made in this investigation are in every way consistent with the suggestions about mechanism based on the kinetic study recently reported.[9] A free-radical mechanism in which the addition of the difluoramino radical to the olefin is the slow step is consistent with the effect of olefin structure on rate (eq 2). The olefin which produces the more stable free radical reacts faster. Thus, it is found that styrenes and butadiene are more reactive than simple aliphatic olefins, branched olefins are more reactive than straight chain, and halogen substitution reduces reactivity. The addition is nonstereospecific although there appears to be a slight conformational preference in the coupling step since the 2-butenes and the stilbenes yield slightly more of the *dl* adducts.[9,16] This preference is comparable to that observed in the addition of dinitrogen tetroxide to stilbene;[17] the two reactions share many other similarities.[17c]



$$N_2F_4 \rightleftarrows 2NF_2$$
$$NF_2\cdot + {>}C{=}C{<} \underset{}{\overset{\text{slow}}{\rightleftarrows}} NF_2\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot$$
$$NF_2\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}\cdot + NF_2 \xrightarrow{\text{fast}} NF_2\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}NF_2 \qquad (2)$$

The addition of the difluoramino radical (eq 2) appears to be reversible at higher temperatures (*vide infra*). 3,4-Bis(difluoramino)butene-1 was isomerized readily to 1,4-bis(difluoramino)butene-2 by N_2F_4, and efforts to saturate these olefins under conditions of the usual addition reactions were unsuccessful (eq 3).[18] Other groups that could be displaced as relatively stable radicals such as bromine and iodine also were lost during N_2F_4 additions. The reaction of β-bromostyrene with N_2F_4 in which such a reaction occurs has been described.[19]



$$CH_2{=}CH\underset{NF_2}{\underset{|}{C}}HCH_2NF_2 + NF_2 \rightleftarrows NF_2CH_2\overset{H}{\underset{H}{\dot{C}}}\underset{NF_2}{\underset{|}{C}}CH_2NF_2 \;\Big\downarrow\!\Big\uparrow\; \cdot NF_2 + NF_2CH_2CH{=}CHCH_2NF_2 \qquad (3)$$

Chemical Properties of Difluoramino Compounds. A. Dehydrofluorination.—The dominant chemical property of difluoramino compounds having α-hydrogen atoms is their propensity to undergo dehydrofluorination. This reaction is catalyzed by a variety of substances. For example, alcohols and water will slowly cause this reaction. In general, an external catalyst is required as these compounds may be stored for long periods of time without decomposition in dry glassware.

The products of the dehydrofluorination reaction

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[13] R. Ettinger, *J. Phys. Chem.*, **67**, 1558 (1963).

[14] W. D. Good, D. R. Douslin, and J. P. McCullough, *ibid.*, **67**, 1312 (1963).

[15] See Table I, footnote *a*.

[16] The F^{19} nmr spectra will be discussed in more detail in a separate publication by F. A. Johnson. For a limited discussion see ref 8e.

[17] (a) T. E. Stevens, *J. Am. Chem. Soc.*, **81**, 3593 (1959); (b) H. Shechter, J. J. Gardikes, and A. H. Pagano, *ibid.*, **81**, 5420 (1959); (c) H. Shechter, *Record Chem. Progr.*, **25**, 55 (1964).

[18] The predominant formation of the 1,4 adduct from butadiene may in part be due to isomerization of the 1,2 adduct. Interestingly, addition of N_2F_4 to 1,1,2-trifluorobutadiene gave exclusively the 1,4 adduct. No analysis of this product is available, but its proton and fluorine nmr spectra prove the structure conclusively; F^{19} spectrum shows: $\underline{NF_2}CH_2-$ (ϕ -45.8), $\underline{NF_2}CF_2-$ (15.0), $NF_2\underline{CF_2}-$ (+109.8), $-CH{=}\underline{CF}CF_2-$ (+124.3, broad doublet, $J_{HF} = 32$ cps). The H^1 spectrum shows: $NF_2\underline{CH_2}CH{=}CF-$ (τ 5.85, triplet of doublets, $J_{HNF} = 28$ cps, $J_{HNF} = 6$ cps), $-CH_2\underline{CH}{=}CF-$ (4.15, doublet of triplets, $J_{HF} = 32$ cps, $J_{HH} = 7$ cps).

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

TABLE I
OLEFIN–TETRAFLUOROHYDRAZINE ADDUCTS[a]

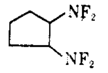
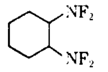
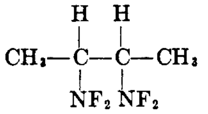
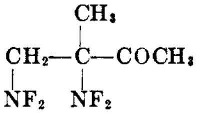
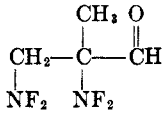
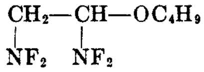
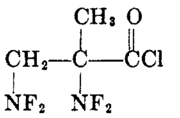
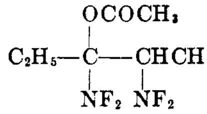
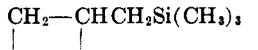
Compd	Bp, °C (mm)	Yield, %	Calcd, %			Found, %		
			C	H	N	C	H	N
$\underset{NF_2}{CH_2}-\underset{NF_2}{CH_2}$	70	60	18.19	3.05	21.21	18.60	3.29	20.55
$CH_3\underset{NF_2}{CH}-CH_2NF_2$	83	90	24.66	4.14	19.18	24.72	4.74	18.05
$C_4H_9\underset{NF_2}{CH}-CH_2NF_2$	47 (15)	82	38.30	6.38	14.89	38.14	6.82	15.15
$C_3H_7\underset{NF_2}{CH}-\underset{NF_2}{CH}CH_3$	45 (15)	80	38.30	6.38	14.89	38.08	6.76	14.95
$C_3H_7\overset{CH_3}{\underset{NF_2}{C}}-CH_2NF_2$	36 (18)	74	38.30	6.38	14.89	38.02	6.62	14.67
$NF_2CH_2CH{=}CHCH_2NF_2$	85 (108)	70	30.4	3.8	17.7	30.2	4.1	17.8
$NF_2CH_2-\underset{NF_2}{CH}CH{=}CH_2$	48 (108)	24	30.4	3.8	17.7	30.6	4.0	17.3
	54 (31)	82	34.82	4.65	16.28	35.50	4.80	16.80
	44 (4)		38.71	5.41	15.05	40.07	5.08	13.81
$(CH_3)_2\underset{NF_2}{C}-CH_2NF_2$	38 (69)	84	29.9	5.0	17.5	29.8	5.01	18.2
$(CH_3)_2CHCH_2\underset{NF_2}{CH}CH_2NF_2$	55 (35)	86	38.3	6.4	14.9	38.9	6.6	16.0
$C_6H_5\underset{NF_2}{CH}-CH_2NF_2$	60 (1)	84	46.16	3.87	13.46	46.43	3.95	13.73
$C_6H_5\overset{CH_3}{\underset{NF_2}{C}}-CH_2NF_2$	48 (0.1)	73	48.65	4.54	12.61	49.36	4.93	12.53
$C_6H_5\underset{NF_2}{CH}-\underset{NF_2}{CH}C_6H_5$	158°,[b] *meso*	37				59.60	4.48	9.88
	112°,[b] *dl*	50	59.15	4.26	9.86	59.03	4.63	10.82
$C_6H_5CH_2\underset{NF_2}{CH}CH_2NF_2$	55 (0.5)	63	48.65	4.54	12.61	48.92	5.02	12.94
$C_6H_5CH_2CH_2\underset{NF_2}{CH}CH_2NF_2$	80 (0.4)	62	50.85	5.12	11.86	51.52	5.39	12.01
p-$BrC_6H_4\underset{NF_2}{CH}-CH_2NF_2$	70 (0–0.01)	85	33.47	2.46	9.76	33.89	2.86	9.66
$ClCH_2\underset{NF_2}{CH}CH_2NF_2$	58 (60)	97	19.94	2.77	15.51	20.42	3.16	15.68
$Cl\underset{NF_2}{CH}-CH_2NF_2$	48 (200)	51	14.42	1.82	16.82	15.16	2.19	16.56
$Cl\underset{NF_2}{CH}-\underset{NF_2}{CH}Cl$	67 (200)	60	11.95	1.00	13.94	12.59	1.17	13.71
$Cl_2\underset{NF_2}{C}-\underset{NF_2}{CH}NF_2$	46 (25)		10.20	0.43	11.90	10.45	0.61	12.25
$C_6H_5\overset{Cl}{\underset{NF_2}{C}}-\overset{CH_3}{CH}NF_2$	60 (0.5)	78	42.12	3.53	10.92	42.01	4.05	11.17
$C_6H_5\overset{Br}{\underset{NF_2}{C}}-CH_2NF_2$	66 (0.5)	84	33.47	2.46	9.76	34.17	2.56	10.27
$CF_3\underset{NF_2}{CF}-CF_2NF_2$	35	95	14.20		11.0	14.7		11.2

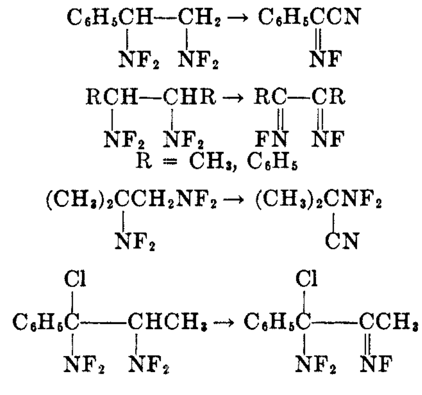
TABLE I (*Continued*)

Compd	Bp, °C (mm)	Yield, %	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
 $CH_3CH(NF_2)CH(NF_2)CH_3$	50 (94)	90	30.00	5.0	17.50	29.44	5.15	17.22
 $CH_2(NF_2)C(CH_3)(NF_2)COCH_3$	58 (20)		29.40	3.92	13.72	29.69	3.83	13.75
 $CH_2(NF_2)C(CH_3)(NF_2)CHO$	30 (15)	82	27.58	3.44	16.09	27.77	3.71	16.47
 $CH_2(NF_2)CH(NF_2)OC_4H_9$	38 (4)	83	35.47	5.45	13.79	35.25	5.30	14.46
 $CH_2(NF_2)C(CH_3)(NF_2)COCl$	47 (21)	60	23.02	2.39	13.42	24.16	3.68	13.79
 $C_2H_5C(OCOCH_3)(NF_2)CH(NF_2)CH_3$	60 (6)	60	36.21	5.21	12.07	36.15	5.43	12.10
 $CH_2(NF_2)CH(NF_2)CH_2CO_2H$[c]		68	25.26	3.16	14.74	25.78	3.44	15.42
 $CH_2(NF_2)CH(NF_2)CH_2Si(CH_3)_3$		80	33.03	6.42	12.84	33.39	6.13	13.62

[a] Fluorine analyses on these compounds were carried out by hydrolysis in aqueous alcoholic alkali and gave satisfactory results. [b] These temperatures are melting points. [c] This material was not distilled because it underwent dehydrofluorination upon heating.

depend upon the structure of the bis(difluoramine). Typical examples[20] are given in Scheme I. Several examples of these reactions will be found in the Experimental Section. The chemistry of the fluorimines produced in this reaction is quite interesting and will be the subject of a future communication. Suffice it to say that they undergo a number of reactions reminiscent of oxime esters such as the Beckmann and Neber rearrangements.[21] Vigorous alkaline treatment removed all the fluorine.[15]

SCHEME I



$$C_6H_5CH(NF_2)CH_2NF_2 \rightarrow C_6H_5C(=NF)CN$$

$$RCH(NF_2)CHR(NF_2) \rightarrow RC(=NF)C(=NF)R \quad R = CH_3,\ C_6H_5$$

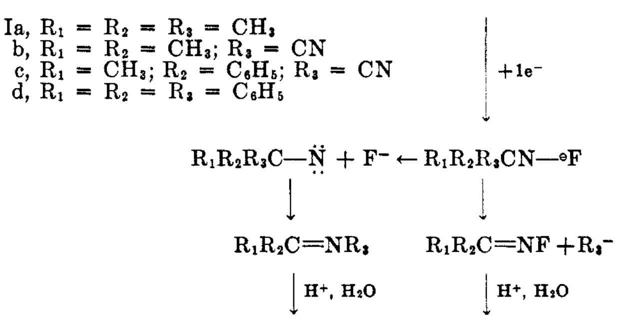
$$(CH_3)_2C(NF_2)CH_2NF_2 \rightarrow (CH_3)_2C(NF_2)CN$$

$$C_6H_5CCl(NF_2)CH(NF_2)CH_3 \rightarrow C_6H_5CCl(NF_2)C(=NF)CH_3$$

This dehydrofluorination reaction must always be kept in mind when attempting any chemical transformations of these compounds. However, it is possible to carry out acid-catalyzed esterifications of bis(difluoramino) alcohols and transesterification of their esters without dehydrofluorination interfering. Basic reagents, however, should be avoided.

B. Reduction.—While the bis(difluoramines) were readily reduced by a variety of reducing systems,[8c] these reactions have never achieved any synthetic utility. Apparently the reductions are accompanied by extensive rearrangements as the nitrogen–fluorine bonds are broken.

The reduction of four difluoramines by titanous ion was investigated briefly. 2-Difluoramino-2-methylpropane (Ia)[6] and α-difluoraminoisobutyronitrile (Ib)[6] were reduced by titanous chloride in acetic acid to acetone and methylamine. α-Difluoramino-α-phenylpropionitrile (Ic) yielded acetophenone and aniline, while triphenylmethyldifluoramine (Id) yielded benzophenone and aniline. These reactions may be interpreted in the following way.



$$R_1R_2R_3CNF_2 + 1e^- \rightarrow R_1R_2R_3CNF + F^{\ominus}$$

Ia, $R_1 = R_2 = R_3 = CH_3$
b, $R_1 = R_2 = CH_3$; $R_3 = CN$
c, $R_1 = CH_3$; $R_2 = C_6H_5$; $R_3 = CN$
d, $R_1 = R_2 = R_3 = C_6H_5$

$$R_1R_2R_3C\ddot{N} + F^- \leftarrow R_1R_2R_3CN{-}^{\ominus}F \quad (+1e^-)$$

$$R_1R_2R_3C\ddot{N} \rightarrow R_1R_2C{=}NR_3 \xrightarrow{H^+,\ H_2O} R_1R_2C{=}O + R_3NH_2$$

$$R_1R_2R_3CN{-}^{\ominus}F \rightarrow R_1R_2C{=}NF + R_3^- \xrightarrow{H^+,\ H_2O} R_1R_2C{=}O$$

It was noted that an excess of titanous ion suppressed the production of ketone from the nitriles. Since

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(20) Additional study of the kinetics and stereochemistry of one of these reactions was reported recently: S. K. Brauman and M. E. Hill, *J. Am. Chem. Soc.*, **89**, 2127, 2131 (1967).

(21) For specific examples, see T. E. Stevens and W. H. Graham, *ibid.*, **89**, 182 (1967); T. E. Stevens, *Tetrahedron Letters*, 3017 (1967).

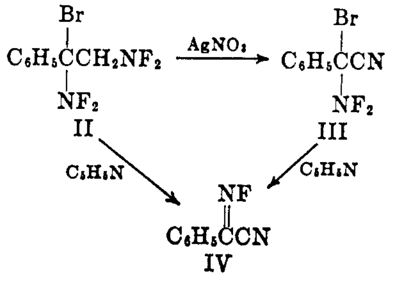
further reduction is not involved, the titanous ion may be functioning as an electrophilic catalyst to aid in the loss of fluoride ion from the reduction product. Attempts to place the titanous reductions on a quantitative basis failed even with these simple difluoramines, and reduction of the tetrafluorohydrazine–olefin adducts themselves led to very complex mixtures.

The difluoramino compounds could also be reduced electrochemically at a mercury electrode. Some correlations exist between the reduction potential and the structure of the difluoramino compound. This subject will be treated in a separate publication.

C. Attempted Substitution of Difluoramino Compounds.—It was of interest to know what reactivity the C–H bonds of difluoramino compounds exhibited in free-radical substitution reactions. Extensive efforts to effect free-radical halogenation failed completely. There was also no evidence for hydrogen atom abstraction when the difluoramines were heated with peroxides. This low reactivity toward radicals combined with the instability of these compounds in base precluded any substitution reactions and we have been unable to effect any chemical reaction (except dehydrofluorination) involving replacement of the hydrogen atom of difluoraminomethyl groups. In their resistance to free-radical reagents and their reactivity toward bases, the difluoramines resemble the corresponding nitro compounds.

Efforts to photochemically induce hydrogen atom abstraction from difluoramines by irradiating them in the presence of tetrafluorohydrazine[22a] led only to their decomposition.[22b] It appears from this and other work[23] that production of a radical adjacent to a difluoramino group results in loss of fluorine from that group and production of a fluorimine.

D. Effect of the Difluoramino Group on Other Functional Groups.[24–26]—The difluoramino group is a strongly electronegative group. In a general way it may be stated that its effect on neighboring functions is similar to that of the nitro group. For example, α-halogen atoms become quite positive in character. 1-Bromo-1-phenyl-1,2-bis(difluoramino)ethane (II) reacted with silver nitrate in refluxing acetonitrile to produce α-bromo-α-difluoraminophenylacetonitrile (III). Treatment of II or III with pyridine in refluxing benzene produced α-(fluorimino)phenylacetonitrile (IV).



Hydrolysis of α-difluoramino nitriles to the corresponding amides could be accomplished without degradation of the difluoramino group. However, because the α-difluoramino group had to be on a tertiary carbon to avoid concomitant dehydrofluorination, further hydrolysis to the acid was strongly resisted. Indeed, the study of the effect of the difluoramino group on the reactivity of other functional groups was complicated by the introduction of this steric factor.

In this study it has been established that tetrafluorohydrazine will add to olefins containing a wide variety of functional groups to produce the corresponding bis(difluoramino) compounds. These compounds may be purified by standard techniques and are readily characterized by their proton and fluorine nuclear magnetic resonance spectra. They undergo dehydrofluorination with a variety of reagents but otherwise the molecules behave in much the same way as compounds containing similar strongly electronegative groups.

Experimental Section

Olefin–Tetrafluorohydrazine Reactions.—Representative examples of the experimental procedures are provided. The bis(difluoroamino) compounds listed in Table I have been prepared by both these methods. Method B is probably the most convenient. A third method has been described in a recent publication.[8e]

In all instances, reactions of N_2F_4 under pressure were conducted in a high-pressure facility equipped with remote controls. Personnel must never be exposed to these reactions between the time when they are charged with N_2F_4 and when they are vented. Violent explosions have been observed on some occasions and exploratory reactions with new olefins should always be conducted on a small scale.

Gas Chromatography.—Three columns have been used successfully for the purification of these compounds. The most commonly used was a 10-ft ($^1/_8$ in. diameter) dinonyl phthalate–Chromosorb column. In addition GE—SF-96/Chromosorb and Carbowax columns were employed.

Nuclear Magnetic Resonance Spectra.—The nmr spectra recorded in this paper were measured over a span of 6 years under varying conditions. Most commonly carbon tetrachloride or deuteriochloroform were used as solvents. Prior to 1963 trifluoroacetic acid was used as an external standard and subsequently fluorotrichloromethane was used internally. All values have been converted to the ϕ scale, parts per million from CCl_3F. All measurements were made at 40 MHz.

Method A. 2,3-Bis(difluoroamino)propyl Chloride.—A 1-l. stainless steel bomb equipped with a pressure gauge, valve, and a ball joint for attachment to a vacuum line was charged *in vacuo* with 6.1 g (0.080 mole) of degassed allyl chloride and 0.147 mole of N_2F_4 (87% N_2F_4, impurities NF_3, C_2F_6). The bomb was heated in an oil bath at 120° for 4 hr. The pressure decreased from a maximum of 72 psig (104°) to a minimum of 28 psig (120°) during the heating period. After cooling to ambient temperature, the bomb was opened to the vacuum pump through traps maintained at −80 and −196°. The excess N_2F_4 fraction collected at −196° amounted to 0.073

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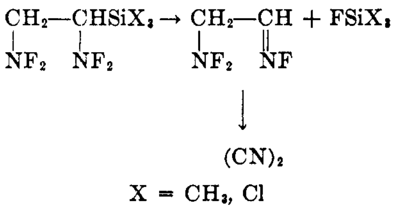
(22) (a) C. L. Bumgardner, *Tetrahedron Letters*, 3683 (1964). (b) We are indebted to Dr. C. L. Bumgardner for these experiments.

(23) D. Dybvig, *Inorg. Chem.*, **5**, 1795 (1966).

(24) Attempts to prepare α-difluoraminomethylsilanes were unsuccessful apparently because of their facile cleavage in the following manner.



$$\underset{NF_2}{CH_2}—\underset{NF_2}{CH}SiX_3 \rightarrow \underset{NF_2}{CH_2}—\underset{NF}{CH} + FSiX_3 \downarrow (CN)_2$$

X = CH_3, Cl

This decomposition reaction is similar to that reported for decomposition of chloro alkyl-[25]and fluoroalkylsilanes.[26] The instability of vinyldifluoramines[19] is probably a related reaction. In all of these reactions fluorine migrates from nitrogen to a more electropositive atom having an available bonding orbital. Such behavior is to be expected whenever such a situation arises. Other examples will be forthcoming in this series of papers.

(25) L. H. Sommer, L. J. Tyler, and F. C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2872 (1948).

(26) R. N. Haszeldine and J. C. Young, *Proc. Chem. Soc.*, 394 (1959).

mole (76% N_2F_4; remainder, NF_3, C_2F_6, trace allyl chloride). The product fraction collected at −80° weighed 13.0 g (0.072 mole; 90% yield). The product was distilled through a Holzman column at reduced pressure; bp 57° (60 mm). There was essentially no low-boiling cut or pot residue. The product was a clear, colorless liquid, $n^{20}{}_D$ 1.3868; $d^{20}{}_4$ 1.433, and showed F^{19} nmr resonance at ϕ −55.7 and −39.4 (see Table I for analysis).

Method B. Reaction of 1-Hexene and Tetrafluorohydrazine.—To a Fischer-Porter Aerosol tube of 100-ml capacity was introduced a mixture of 8.4 g (0.10 mole) of 1-hexene in 25 ml of Freon 113. The Aerosol tube was connected to a high-pressure manifold and the entire system was flushed three times with dry nitrogen. The system was then charged with tetrafluorohydrazine to 200 psi. The system was slowly heated with an external oil bath to a temperature of 100° and this temperature was maintained over a period of 3 hr. During this time the N_2F_4 pressure was maintained between 150 and 400 psi by recharging as necessary. After cooling, the mixture was degassed by venting the excess tetrafluorohydrazine and flushing several times with dry nitrogen. The reaction mixture was concentrated at reduced pressures and then distilled. Thus, **1,2-bis(difluoroamino)hexane,** 15.4 g (82%), bp 47–49° (15 mm), $n^{20}{}_D$ 1.3783, was obtained. The F^{19} nmr spectrum had a peak at ϕ −56.0, (triplet, $J_{HF} = 28$ cps) for the primary difluoramino group; the secondary NF_2 group was a quartet (−2226, −1542, −1438, −862 cps at 40 MHz, CCl_3F standard) split into doublets, $J_{HF} = 28$ cps.

Dehydrofluorinations. A. α-Cyanoisobutyronitrile.—A suspension of 3.24 g (0.0205 mole) of 1,2-bis(difluoramino)-2-methylpropane (Table I) in water was stirred virogously while 52.2 ml of 0.776 *N* sodium hydroxide solution (0.0405 mole) was added dropwise during about 10 min. The temperature of the mixture rose to 50° and then returned to room temperature as it was stirred for an hour following the addition. The organic product was extracted with methylene chloride, dried, and distilled. **α-Difluoraminoisobutyronitrile,** bp 71–72° (150 mm), was obtained in 32% yield. The F^{19} nmr spectrum had a peak at ϕ −41.2.

Anal. Calcd for $C_4H_6N_2F_2$: C, 40.00; H, 5.04; N, 23.33. Found: C, 39.79; H, 5.16; N, 23.44.

B. α-Difluoramino-α-methylphenylacetonitrile.—A solution of 5.6 g (0.1 mole) of potassium hydroxide in 100 ml of ethanol was added over a 1-hr period to a solution of 10.0 g (0.045 mole) of 1,2-bis(difluoramino)-2-phenylpropane (Table I) in 100 ml of ethanol while maintaining the temperature at 25°. The mixture was then passed into water and extracted with methylene chloride. Distillation yielded 6.7 g (81%) of **α-difluoramino-α-methylphenylacetonitrile,** bp 74° (2 mm). The F^{19} nmr spectrum gave an AB quartet centered at ϕ −43.9.

Anal. Calcd for $C_9H_8N_2F_2$: C, 59.33; H, 4.42; N, 15.38; F, 20.86. Found: C, 59.44; H, 4.63; N, 15.39; F, 21.1.

C. 1,2-Dichloro-1,2-bis(fluorimino)ethane.—1,2-Dichloro-1,2-bis(difluoramino)ethane (Table I) (2.8 g, 0.014 mole) was condensed into 5 ml of triethylene glycol at −80°. The mixture was warmed to room temperature and stirred for 20 min when gas evolution began. After stirring for 1.5 hr, the product was fractionated in a vacuum line and purified by gas chromatography, using a silicone column. The F^{19} nmr spectrum gave a peak at ϕ −53.6 (external CF_3CO_2H).

Anal. Calcd for $C_2Cl_2F_2N_2$: C, 14.92; Cl, 44.06; F, 23.61; N, 11.41. Found: C, 15.18; Cl, 44.07; F, 22.67; N, 17.99.

D. 1-Chloro-1-difluoramino-2-fluoriminocyclohexane.—The adduct from 5.0 g of 1-chlorocyclohexene and tetrafluorohydrazine in 30 ml of carbon tetrachloride (addition reaction solvent)[27] and 25 ml of ethanol was dehydrofluorinated with 29.4 ml of 1.46 *N* potassium hydroxide in 90% ethanol. The product, 5.6 g, was isolated by extraction and distillation, bp 68° (2.5 mm). The F^{19} nmr spectrum gave signals at ϕ −26 (=NF) and a quadruplet centered at −33.7 (—NF_2).

Anal. Calcd for $C_6H_8N_2F_3Cl$: C, 35.92; H, 4.02; N, 13.97; Cl, 17.7. Found: C, 36.18; H, 4.41; N, 14.31; Cl, 18.1.

E. 1-Chloro-1-difluoramino-1-phenyl-2-fluoriminopropane.—A solution of 10.0 g (0.039 mole) of 1-chloro-1-phenyl-1,2-bis-(difluoramino) propane (Table I) in 50 ml of ethanol and 100 ml of methylene chloride was treated with water and extracted with methylene chloride. The residue from the methylene chloride extract was chromatographed on a silica gel column packed in pentane–methylene chloride (10:1). Elution of the column with the same solvent and with pentane containing increasing amounts of methylene chloride gave 1-chloro-1-difluoramino-1-phenyl-2-fluoriminopropane, 7.2 g, as a colorless liquid.

Anal. Calcd for $C_9H_8ClN_2F_3$: C, 45.68; H, 3.41; N, 11.84; F, 24.1. Found: C, 45.28; H, 3.63; N, 13.06; F, 24.7.

The F^{19} nmr spectrum gave an AB quartet (NF_2): F_A at ϕ −43.3; F_B at −34.8; $J_{FF} = 552$ cps and a singlet at −34.8 (C=NF). The H^1 nmr spectrum gave a doublet at δ 1.97, $J_{HF} = \sim 5$ cps.

F. 2,3-Bis(fluorimino)butane.—2,3-Bis(difluoramino)butane (Table I) was treated in the same way described above. The product was isolated by distillation, bp 60° (700 mm), and then further purified by gas chromatography. The F^{19} nmr spectrum gave a peak at ϕ −33.2.

Anal. Calcd for $C_4H_6N_2F_2$: C, 40.00; H, 5.04; N, 23.33. Found: C, 39.88; H, 5.37; N, 23.26.

G. Preparation of 1-Bromo-1-difluoramino-1-phenyl-2-fluoriminopropane.—1-Bromo-1-phenyl-1-propane, bp 52° (0.5 mm), was prepared by dehydrobromination of 1-phenyl-1,2-dibromopropane.[28] Both of the isomers (*cis* and *trans*) were present since a mixture of *cis*- and *trans*-1-phenyl-1-propene was used to prepare the dibromide. A large chemical shift was noted in the nmr spectrum of the aliphatic protons. The methyl protons in one isomer were a doublet centered at τ 8.17. Vinyl proton resonance in the τ 3.9 region was complex in the isomer mixture.

The tetrafluorohydrazine adduct was prepared from 10 g of olefin, and the crude adduct was dehydrofluorinated as described. Purification was carried out by chromatography on silica gel; the product was a colorless liquid (8.95 g).

Anal. Calcd for $C_9H_8BrN_2F_3$: C, 38.45; H, 2.87; N, 9.97; F, 20.3; Br, 28.4. Found: C, 39.98; H, 2.71; N, 10.35; F, 20.2; Br, 28.4.

The F^{19} nmr spectrum showed an AB quartet (NF_2): F_A at ϕ −53.8; F_B at −47.7; $J_{FF} = 557$ cps and a singlet at −35.2 (—C=NF). The H^1 nmr spectrum showed a doublet at δ 1.98 (CH_3), $J_{HF} = 6$ cps.

A fraction eluted from the silica gel column by 3:1 pentane–methylene chloride (after the product described above) was **1-phenyl-1,2-bis(fluorimino)propane:** $\lambda_{max}^{cyclohexane}$ 248 mμ (ϵ_{max} 4370).

Anal. Calcd for $C_9H_8N_2F_2$: C, 59.33; H, 4.42; N, 15.38; F, 20.85. Found: C, 58.53; H, 4.93; N, 16.16; F, 20.4.

The F^{19} nmr spectrum gave (*syn*- and *anti*-isomer mixture) peaks at −1708, −1659, −1422, −1377 cps (CCl_4 solution, CCl_3F standard, 40 MHz).

Reactions of 1-Bromo-1-phenyl-1,2-bis(difluoramino)ethane. A. Reaction with Silver Nitrate.—A solution of 2.90 g (0.01 mole) of the bis(difluoramine) (Table I), 1.72 g (0.01 mole) of silver nitrate, and 4.0 ml of acetonitrile was protected from light and refluxed for 4 hr. The solution was cooled, filtered to remove a yellow precipitate, diluted with methylene chloride, and poured into water. The organic extracts were washed, dried, and flash distilled at 50° (0.1 mm). This distillate was fractionated to yield 0.25 g of **α-difluoramino-α-bromophenylacetonitrile,** bp 60° (0.5 mm). The F^{19} nmr spectrum showed an AB quartet (NF_2): F_A at ϕ −56.1; F_B at −52.3; $J_{FF} = 550$ cps.

Anal. Calcd for $C_8H_5BrN_2F_2$: N, 11.34; F, 15.38. Found: N, 11.45; F, 14.95.

B. Reaction with Pyridine.—A solution containing 5.0 g (0.0174 mole) of the bis(difluoramine), 2.3 ml (0.028 mole) of pyridine, and 50 ml of benzene was refluxed for 4 hr. The benzene was removed at reduced pressure and the residue was extracted with hexane. Evaporation of the hexane and distillation of the residue at 50° (0.5 mm) yielded 2.38 g of α-(fluorimino)phenylacetonitrile, identical with the sample produced from dehydrofluorination of 1,2-bis(difluoramino)phenylethane.

Preparation of α-Difluoramino-α-methylphenylacetamide.—A mixture of 0.5 g of α-difluoramino-α-methylphenylacetonitrile, 5 ml of 95% ethanol, 1.0 ml of 1 *N* ethanolic potassium hydroxide, and 1.0 ml of 30% hydrogen peroxide was stirred at 40–50° for 3 hr. The solution was diluted with water and

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[27] The bis(difluoramino) compound was not isolated and characterized.

[28] C. Hell and H. Baur, *Ber.*, **36**, 204 (1903). This reaction is reported to give 1-phenyl-2-bromo-1-propene.

extracted with warm pentane. The pentane-insoluble solid (0.15 g) was recrystallized from pentane–chloroform, mp 134–135°.

Anal. Calcd for $C_9H_{10}F_2N_2O$: C, 53.99; H, 5.04; N, 14.00; F, 18.98. Found: C, 53.27; H, 5.30; N, 13.75; F, 17.97.

Reductions with Titanous Chloride. 2-Methyl-2-difluoroaminopropane.[6]—To 0.61 g of the difluoramine in 10 ml of glacial acetic acid was added 1.5 ml of 20% titanous chloride reagent at 60°. The solution was heated 80° for an hour and then allowed to stir overnight. The clear solution was divided into two portions. One portion was treated with 2,4-dinitrophenylhydrazine reagent to yield a yellow solid, mp 125°, identical by mixture melting point and infrared spectrum with an authensample of acetone 2,4-dinitrophenylhydrazone.

The other portion was made alkaline and steam distilled. The distillate was treated with phenyl isothiocyanate to yield a white solid, mp 115°, identical with an authentic sample of N-methyl-N′-phenylthiourea.

α-Difluoramino-α-methylphenylacetonitrile.—To a solution 3.68 g (0.02 mole) of the difluoramine was added 60 ml of 20% titanous chloride reagent at 60°. The solution was heated at 75° for 2 hr at which point decolorization had been effected. The mixture was poured into water and extracted with methylene chloride. Concentration of these extracts yielded 0.36 g of unreacted difluoramine.

The aqueous solution was made basic and extracted with CH_2Cl_2. Concentration of these extracts yielded 2.4 g of a mixture of acetophenone (15%) and aniline (85%) identified by their infrared spectra and glpc retention times on a 5° silicone column at 148°.

Alkylations of Heterocyclic Ambident Anions. II. Alkylation of 2-Pyridone Salts[1a]

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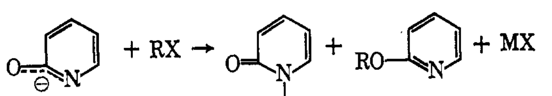
Alkali metal and silver salts of 2-pyridone were treated with simple alkyl halides and tosylates in a variety of solvents, and the ratios of nitrogen to oxygen alkylation were quantitatively assayed. By variation of the solvent and metal ion, virtually exclusive nitrogen or oxygen alkylation could be obtained in methylations, ethylations, and benzylations. Oxygen alkylation predominated in reactions with isopropyl compounds presumably owing to steric factors. A kinetic study in dimethylformamide demonstrated that reactions of ethyl and isopropyl iodides with the sodium salt were second order. Solvent had the largest effect on silver salt alkylations where alkoxypyridine formation was favored in poor ion-solvating media. Alkali metal salts were less solvent sensitive, but a moderate increase in oxygen alkylation was observed in dimethylformamide compared to protic and nonpolar solvents. The preference of the silver salt to alkylate on oxygen in nonpolar media is proposed to result from heterogeneous reaction.

The studies described in this paper are a continuation of our investigations of alkylation reactions of ambident anions derived from heterocyclic compounds.[2] A general method for alkylating 2-pyridones consists of reacting their metal salts, usually in a solvent, with alkyl halides.[3] It is well-known that this reaction can give both nitrogen and oxygen alkylation. Nitrogen *vs.* oxygen alkylation in the 2-pyridone system has been discussed by several authors,[3,4] but a reliable assessment of the factors which govern product distribution was limited by the absence of a sufficient body of comparable data. Thus, while it is commonly accepted that silver salts of 2-pyridones favor oxygen alkylation, and that the corresponding alkali metal salts favor nitrogen alkylation,[3] silver and alkali metal salts of 2-pyridone have not been alkylated in a common solvent under comparable reaction conditions. The solvent is currently recognized as an important consideration in ambident anion alkylations,[5] but its influence on alkylations of 2-pyridone salts has not been evaluated. It has been noted also that steric factors are significant in determining the alkylation site of 2-pyridones,[3] but only two examples of this influence were found in the literature. Both examples illustrated that oxygen alkylation was favored when a methyl group occupied the 6 position of 2-pyridone and bulky alkylating agents were employed.[6]



(1)

The present paper reports a systematic study of the sensitivity of the alkylation site of metal salts of 2-pyridone toward a number of factors known to have influence in other ambident anion systems.[4,5,7,8] Alkali metal and silver salts of 2-pyridone were treated with simple alkyl and benzyl halides or tosylates. Factors such as the cation, solvent, leaving group, and alkyl halide structure were systematically varied. Product ratios were quantitatively determined by vapor phase chromatography. Calibrations were made with characterized or known samples of the nitrogen and oxygen alkylated pyridines and 2-pyridone. Kinetic studies of alkali metal salt alkylations are described in the Experimental Section.

Results and Discussion

Table I summarizes data which show the influence of cation and alkylating agent in determining the reaction site in 2-pyridone. All reactions listed in this table were conducted in dimethylformamide under comparable reaction conditions. Influences due to variation of solvent are illustrated by Tables II and

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(1) (a) This investigation was supported by the U. S. Public Health Service Grant No. GM-12112 from the National Institute of General Medical Sciences; (b) Allied Chemical Corp. Fellow, 1964–1965.

(2) G. C. Hopkins, J. P. Jonak, H. Tieckelmann, and H. J. Minnemeyer, *J. Org. Chem.*, **31**, 3969 (1966).

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