Chemistry of Tetrafluorohydrazine. IV. Addition Reactions with Halogenated Olefins, Norbornadiene, and 2,5-Dimethylfuran

G. N. SAUSEN AND A. L. LOGOTHETIS

Contribution No. 1098 from the Central Research Department, Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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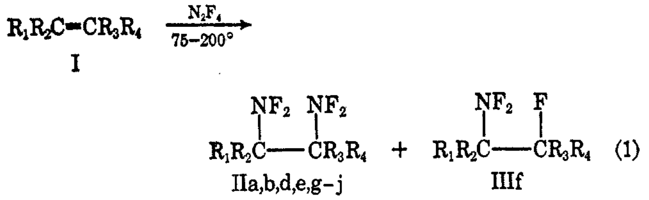
Reaction products of N_2F_4 with halogenated olefins, tetrafluorobutadiene, and norbornadiene are described. Most halogenated olefins give the normal adducts, 1,2-bis(difluoramino)alkanes, but tetrabromoethylene and dichlorohexafluorobutene give largely the products of NF_3 addition. The isomeric addition products from norbornadiene, 2,5-dimethylfuran, and tetrafluorobutadiene were isolated and characterized.

Tetrafluorohydrazine adds readily to olefins to give the corresponding 1,2-bis(difluoramino)ethanes.[1] A mixture of the 1,2- and 1,4-bis(difluoramino) adducts has been obtained from 1,3-cyclooctadiene as well as isomeric mixtures of 1,4 adducts from cyclooctatetraene and 6,6-diphenylfulvene.[2] Substituted anthracenes gave the corresponding 9,10-bis(difluoramino)-9,10-dihydroanthracenes.[1c,3a] Dehydrofluorination of these adducts to give the corresponding N-fluorimino compounds has also been studied.[1e,3,4] We wish to describe the products obtained from addition of N_2F_4 to the completely halogenated olefins Ia–g, the highly halogentated olefins Ih–j, norbornene, and the dienes IV, V, and VI.

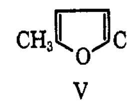


$$\underset{\text{I}}{R_1R_2C{=}CR_3R_4} \xrightarrow[75\text{–}200°]{N_2F_4} \underset{\text{IIa,b,d,e,g–j}}{R_1R_2\overset{NF_2}{C}\text{—}\overset{NF_2}{C}R_3R_4} + \underset{\text{IIIf}}{R_1R_2\overset{NF_2}{C}\text{—}\overset{F}{C}R_3R_4} \quad (1)$$

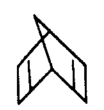
a, R_1, R_2, R_3, R_4 = F
b, R_1, R_2, R_3, R_4 = Cl
c, R_1, R_2, R_3, R_4 = Br
d, R_1, R_2 = F; R_3, R_4 = Cl
e, R_1, R_3 = F; R_2, R_4 = Cl
f, R_1, R_3 = CF_3; R_2, R_4 = Cl
g, R_1 = CF_3; R_2, R_3, R_4 = F
h, R_1, R_3 = F; R_2, R_4 = CN
i, R_1, R_3 = F; R_2 = C_6H_5; R_4 = C
j, R_1 = F; R_2 = C_6H_5; R_3, R_4 = Cl

$CF_2{=}CHCH{=}CF_2$

IV



V



VI

Tables I and II summarize the properties of the adducts obtained. With chloro and fluoro substituents (Ia,b,d,e,g–j) good yields of 1,2-bis(difluoramino)ethanes (IIa,b,d,e,g–j) are obtained at temperatures of 75–150°. Reaction temperatures as high as 200–225° may be utilized in these addition reactions, but above this temperature range thermal decomposition of N_2F_4 into NF_3 and nitrogen becomes extensive and interferes with the course of addition.

With a few of the olefins studied, so-called "abnormal" adducts were obtained. These adducts represent the addition of the elements of NF_3 to the olefinic linkage. For example, 2,3-dichlorohexafluoro-2-butene underwent reaction with N_2F_4 at 200° to give this "abnormal" adduct IIIf in 13% yield. Cesium fluoride catalysis[5,6] improved the yield in this reaction to 37%. None of the adduct II was observed. The remainder was starting olefin. Tetrabromoethylene (Ic), on the other hand, yielded the N-fluorimino compound VII in 67% yield, together with 14% of a second N-fluorimino compound, VIII. Compound

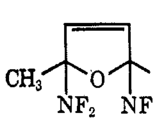
$$\underset{\text{Ic}}{CBr_2{=}CBr_2} + N_2F_4 \xrightarrow{155°}$$

$$\underset{\text{VII}}{CBr_2FC(Br){=}NF} + \underset{\text{VIII}}{F_2NCF(Br)C(Br){=}NF} \quad (2)$$

VII may arise from "abnormal" addition of NF_3 to tetrabromoethylene followed by elimination of BrF while compound VIII could arise by normal addition of N_2F_4 followed by elimination of a bromine molecule and internal rearrangement (see Mechanism). All of the eliminated bromine could be titrated with ethylene or 1-hexene.

Dienes react with N_2F_4 to give a mixture of 1,2 and 1,4 adducts as shown by Cantrell[2] in the 1,3-cyclooctadiene case. This was also the case with fluorinated dienes. For example, with 1,1,4,4-tetrafluorobutadiene (IV) the reaction proceeds nearly quantitatively at 38° to give a mixture consisting of 61% 1,4 and 35% 1,2 adducts.[7]

However, with 2,5-dimethylfuran the addition reaction took place at 78°, to give only one simple adduct in 43% yield, the remainder of the reaction mixture being a high-boiling residue. The product appears to be a single stereoisomer, 2,5-dimethyl-2,5-bis(difluoramino)dihydrofuran (IX), as judged by a



IX

broad singlet F^{19} nmr peak for the NF_2 group, a singlet for the vinyl protons at τ 3.74, and a triplet at τ 8.3 for the CH_3 (J_{F-H} = 2.5 cps). Addition of N_2F_4

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(1) (a) R. C. Petry and J. P. Freeman, Abstracts of the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p 46S; *J. Org. Chem.*, **32**, 4034 (1967); (b) A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc. Sect. A*, 582 (1966), 105 (1967), 864 (1967); (c) H. Cerfontain, *ibid.*, 6602 (1965); (d) T. E. Stevens and W. H. Graham, *J. Amer. Chem. Soc.*, **89**, 182 (1967); (e) F. A. Johnson, C. Haney, and T. E. Stevens, *J. Org. Chem.*, **32**, 466 (1967).

(2) T. S. Cantrell, *ibid.*, **32**, 911 (1967).

(3) (a) A. L. Logothetis, *ibid.*, **31**, 3686 (1966); (b) A. L. Logothetis and G. N. Sausen, *ibid.*, **31**, 3689 (1966); (c) T. E. Stevens, *ibid.*, **32**, 670 (1967); (d) S. K. Brauman and M. E. Hill, *J. Amer. Chem. Soc.*, **89**, 2127, 2131 (1967).

(4) See also G. N. Sausen and A. L. Logothetis, *J. Org. Chem.*, **32**, 2261 (1967), and R. C. Petry, C. O. Parker, F. A. Johnson, T. E. Stevens, and J. P. Freeman, *ibid.*, **32**, 1534 (1967), for reaction products obtained from N_2F_4 with acetylenes and allene.

(5) R. D. Dresdner, F. N. Tlumac, and J. A. Young, *J. Amer. Chem. Soc.*, **82**, 5831 (1960), showed that cesium fluoride is a catalyst for addition of NF_3 to hexafluoropropylene in a flow system at 320°.

(6) R. J. Shozda of this laboratory obtained a 68% yield of 2-difluoraminoheptafluoropropane by reaction of NF_3 with hexafluoropropylene at 250° in a closed system using cesium fluoride as a catalyst.

(7) The authors are indebted to Dr. R. J. Shozda for this experiment.

TABLE I

PROPERTIES OF 1,2-BIS(DIFLUORAMINO)ETHANES, $R_1R_2C(NF_2)C(NF_2)R_3R_4$

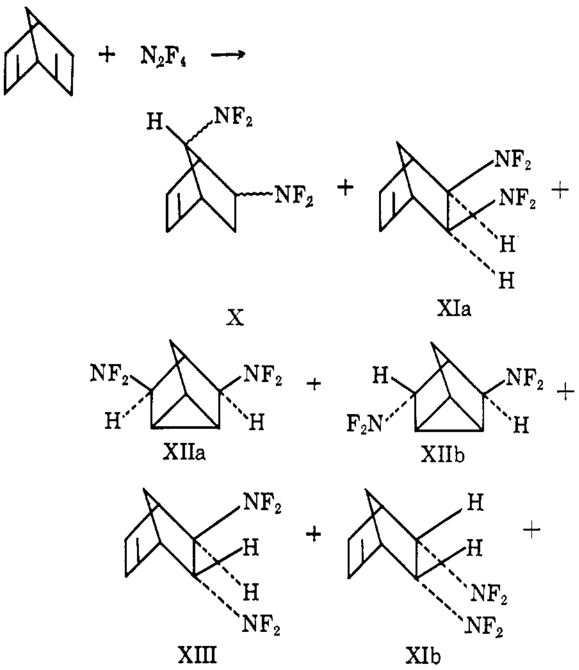
Olefin	Solvent	Temp, °C	Yield, %	Bp, °C (mm)	nD	Formula	Calcd, % C	Calcd, % H	Calcd, % F	Calcd, % N	Found, % C	Found, % H	Found, % F	Found, % N	Mol wt Calcd	Mol wt Found	Infrared absorption, 10.5–12 μ
$CF_2{=}CF_2$	None	75	93	0[a]		$C_2F_8N_2$			74.50				74.33		204	209	10.4, *10.7*, 11.45
$CF_2{=}CCl_2$	None	90	65	79	1.3478 (26°)	$C_2Cl_2F_6N_2$			48.11	11.83			48.03	11.41			*10.6*, 11.1, 11.5
$CCl_2{=}CCl_2$[b]	None	150	86	Mp 85.5–87.5		$C_2Cl_4F_4N_2$			28.16	10.38			28.19	10.17			11.0, *11.5*, 11.65
$CFCl{=}CFCl$	None	116	74	76	1.3477 (24°)	$C_2Cl_2F_6N_2$			48.11	11.83			47.89	11.87			*10.6*, 11.05, 11.35, 11.55–11.70 (d)
$CF_3CF{=}CF_2$	None	134	51[c]	35	<1.3000	$C_3F_{10}N_2$				11.03				10.99	254	255	
$CF(CN){=}CF(CN)$[i]	None	157	87	64		$C_4F_6N_4$[d]			52.28				50.84				*10.55*, 10.95, 11.2, 11.7
$C_6H_5CF{=}CFCl$	None	70	98	70 (5.0)	1.4462 (27°)	$C_8H_5N_2F_6Cl$[e]	34.49	1.80	40.92	10.06	35.00	1.96	40.90	10.27			10.6, 11.0, 11.2, 12.0
$C_6H_5CF{=}CCl_2$	None	120	59[f]	62 (0.5)	1.4814 (25°)	$C_8H_5N_2F_5Cl_2$[g]	32.57	1.71	32.20	9.50	33.87	1.87	31.93	9.51			10.36, 10.75, 10.98, 11.40, 11.68
Norbornene	$CHCl_3$	50	52[h]	89–94 (22)	1.4292 (25°)	$C_7H_{10}N_2F_4$	42.42	5.09	38.35	14.14	43.64	5.44	38.21	14.08			10.6, 11.3, 11.5, 11.95

[a] 1,2-Bis(difluoramino)tetrafluoroethane, bp 0°, was obtained by Bigelow and coworkers, *J. Amer. Chem. Soc.*, **83**, 5010 (1961), by the jet fluorination of $(CN)_2$. [b] Excess N_2F_4 (8 mol %) was used to obtain complete conversion of the olefin to adduct. The white solid, obtained directly from the bomb, was analytically pure. [c] Minimum yield, product was lost during work-up. [d] Mass spectrometric analysis showed *m/e* 166 (parent with loss of one NF_2 group) and smaller fragments in support of the 1:1 adduct structure. [e] Calcd for Cl, 12.73; found, 12.78. [f] About 8% $C_6H_5CF(NF_2)C(Cl){=}NF$ was also obtained and separated by gc. Ir bands in 10.5–12–4-μ region were present at 10.75, 11.25, 11.8 μ. [g] Calcd. for Cl, 24.04; found, 23.39. [h] F^{19} nmr showed three sets of quadruplets indicating the presence of *cis-exo*, *cis-endo*, and *trans* adduct. [i] S. Proskow (to Du Pont), U. S. Patent 3,121,734 (Feb 18, 1964).

to dienes like anthracene gave both *cis* and *trans* stereoisomers[3a] and one would expect that 2,5-dimethylfuran should also give two addition products. The isolation of one stereoisomer in only 43% yield suggests that the other stereoisomer is probably also formed, but that it is unstable under the reaction conditions and is decomposed. Models indicate that in the *cis* isomer the two NF_2 groups are very crowded, while in the *trans* isomer they are not. It is tentatively proposed, therefore, that the isomer isolated is the more stable *trans*-2,5-dimethyl-2,5-bis(difluoramino)-dihydrofuran (IX).

The N_2F_4 addition reaction with norbornadiene (VI) occurs readily at 50°, and a mixture of 1:1 adducts is obtained. Gas chromatographic analysis indicated the presence of four components in a ratio of 1:1:9:1 in order of elution. These isomeric components were separated, and their structures were tentatively established by means of infrared and nmr spectroscopy.

The first eluent was assigned the structure of 2,7-bis(difluoramino)bicyclo[2.2.1]hept-5-ene (X) of unknown stereochemistry. It showed unsaturation in the infrared at 6.1 μ, proton nmr indicated two different vinyl hydrogens, τ 3.45 and 3.70, and a single hydrogen in the bridge methylene position (τ 8.0),[8] and F^{19} nmr analysis showed the presence of two different $-NF_2$ groups. The next isomer is a symmetrical molecule and could be assigned the structure of di-*exo*-(XIa) or the di-*endo*-2,3-bis(difluoramino)bicyclo-[2.2.1]hept-5-ene (XIb). The structure is supported



(3)

by the presence of unsaturation in the infrared, 6.1 μ, two equivalent vinyl protons, τ 3.70, in the proton nmr spectrum, and two equivalent $-NF_2$ groups in the F^{19} nmr spectrum. The di-*exo* structure XIa is favored because radical attack is more likely to take place predominantly from the *exo* di-

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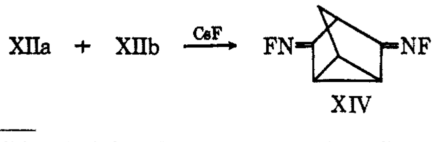
[8] The hydrogens at the highest magnetic field (τ 8.0–9.0) in the substituted norbornenes are assigned to the bridge methylene group: H. E. Simmons, Jr., *J. Amer. Chem. Soc.*, **83**, 1657 (1961).

TABLE II
F^{19} NMR SPECTRA OF DIFLUOROAMINO COMPOUNDS

1,2-Bis(difluoroamino)ethanes	Group	Chemical shift, cps[a]	Observed spin–spin coupling, cps
$F_2NCF_2CF_2NF_2$[b]	NF_2	−5057	None
	CF_2	+3332	None
$F_2NCF_2CCl_2NF_2$[b]	NF_2	−6060	None
	NF_2	−4880	None
	CF_2	+2330	Complex multiplet
$F_2NCCl_2CCl_2NF_2$	NF_2	−6608	None
$F_2NCFClCFClNF_2$[c]	NF_2	−6310, −5650, −5540, −5065	AB type
	CF	+2060, +2235	Badly split
$CF_3CF(NF_2)CF_2NF_2$[c]	NF_2	−5182	
	NF_2	−4865	
	CF_3	+268	
	CF_2	+2475	
	CF	+5626	
$NF_2CF(CN)CF(CN)NF_2$	NF_2	−5650	None
	CF	+4370	Complex multiplet
	CF	+4405	Complex multiplet
$C_6H_5CF(NF_2)CFCl(NF_2)$	NF_2	−3966, −3903	None[d]
	NF_2	−3707, −3662	None
	CF	+3627, +3792	Multiplets
	CF(Cl)	+1736, +1842	Multiplets
$C_6H_5CF(NF_2)CCl_2(NF_2)$	NF_2(C–F)	ν_A −6615, ν_B −6093,	AB, $J_a = J_b = 585$—each peak is a doublet
	NF_2(C–Cl_2)	ν_A −5464, ν_B −5154, $J = 580$	$J_{F\text{-}NF_2} = 12$)
	CF	+4726	Multiplet
$C_6H_5CF(NF_2)C(Cl){=}NF$	NF	−6220	
	NF_2	ν_A −5235, ν_B −4975	AB type, $J = 514$
Norbornene adducts	NF_2	−7750 to −5800	Three sets of quadruplets, hence three stereoisomers present, *cis-exo*, *cis-endo*, *trans*

[a] Fluorine nmr spectra were obtained from a Varian Associates high-resolution nmr spectrometer and associated electromagnet. Unless otherwise indicated spectra were obtained at 56.4 Mc/sec and approximately 14,000 gauss. Spectra were calibrated in terms of displacements in cycles per second (cps) from the F^{19} resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane. Negative frequency displacements are for resonances occurring at lower field than the reference. [b] The spectrum was obtained at 40 Mc/sec with reference to CF_3CO_2H = 0. The chemical shift recorded in the table has been recalculated to give the value at 56.4 Mc/sec with reference to 1,2-difluoro-1,1,2-2-tetrachloroethane = 0. A value of +625 cps for CF_3CO_2H at 56.4 Mc/sec was used. [c] Spectrum was determined at 40 Mc/sec with reference to 1,2-difluoro-1,1,2,2-tetrachloroethane = 0. The values given for chemical shifts are recalculated to 56.4 Mc/sec. [d] The four NF_2 peaks represent a mixture of *threo* and *erythro* isomers. The AB spectrum expected apparently approaches the A_2 system because of the large values (∼600 cps) of the coupling constants and chemical shifts.

rection.[9–12] The third and most abundant component was assigned as a mixture of di-*exo*- and *endo-exo*-3,5-bis(difluoramino)tricyclo[2.2.1.$0^{2,6}$]heptane (XIIa and b, respectively) in about 3:2 ratio. This assignment is supported by the absence of unsaturation in the infrared and absence of vinyl protons in the proton nmr, and the presence of one kind of $-NF_2$ group for XIIa and two kinds for XIIb. Elimination of 2 mol of hydrogen fluoride from this mixture of tricyclenes, by means of cesium fluoride, gave 3,5-bis(fluorimino)-tricyclo[2.2.1.$0^{2,6}$]heptane (XIV). It appears to be a mixture of *syn* and *anti* isomers as indicated by the



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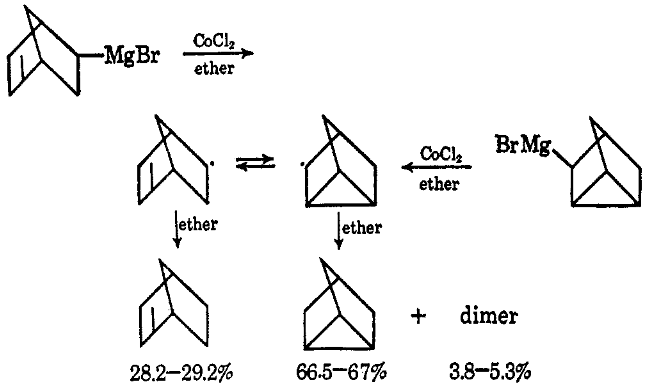
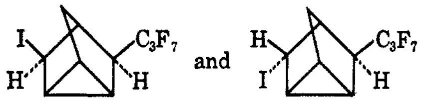
(9) D. I. Davies, J. N. Done, and D. H. Hey, *Chem. Commun.*, 725 (1966), report the following reaction.



It is concluded by the authors that the equilibrium lies toward the tricyclyl radical by about 2.3:1.

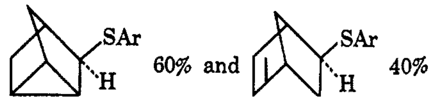
(10) The free-radical addition of arylsulfonyl halides to norbornadiene is described; S. J. Cristol and J. A. Reeder, *J. Org. Chem.*, **26**, 2182 (1961); S. J. Cristol and D. I. Davies, *ibid.*, **29**, 1282 (1964). The amount of tricyclene product was the largest when the halide was chlorine and smallest when it was iodine. This indicates that as the chain-transfer ability of the reagent increases (I > Br > Cl) the intermediate radical corresponding to XVII has a smaller chance to equilibrate ($k_3 \approx k_2 < k_4$) and more and more 2,3-disubstituted products are obtained. The N_2F_4 species has a chain-transfer ability close to chlorine if one compares the product distribution of the norbornadiene reaction with N_2F_4 and arylsulfonyl halides, excluding any differences in steric requirements (see ref 11).

(11) Addition of 1-iodoperfluoropropane to norbornadiene gave a mixture of the nortricyclyl adducts.



The absence of any 2,3-perfluoropropyliodonorbornene is explained by the fact that both iodo and perfluoropropyl groups are bulky and will be very crowded adjacent to each other: N. Brace, *ibid.*, **27**, 3027 (1962).

(12) Thiophenols react with norbornadiene under free-radical conditions to give the following mixture.

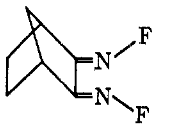


S. J. Cristol and G. D. Brindell, *J. Amer. Chem. Soc.*, **76**, 5699 (1954); S. J. Cristol, G. D. Brindell, and J. A. Reeder, *ibid.*, **80**, 635 (1958).

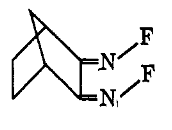
presence of two N–F resonances in the F^{19} nmr spectrum.

The last component to elute contained two isomers. The larger isomer (>90%) was assigned the *endo,exo*-2,3-bis(difluoramino)bicyclo[2.2.1]hept-5-ene (XIII) structure. It showed unsaturation in the infrared, 6.13 μ, and two nonequivalent vinyl protons in the nmr spectrum, τ 3.50. The F^{19} nmr spectrum showed two different kinds of $-NF_2$ groups. The minor component contained a single $-NF_2$ group belonging to a symmetrical structure, presumably the di-*endo*-2,3-bis(difluoramino)bicyclo[2.2.1]hept-5-ene (XIb).

Norbornene gave a normal adduct, 2,3-bis(difluoramino)norbornane (see Tables I and II), as a mixture of three isomers, *cis-exo* (largest), *trans-endo-exo*, and *cis-endo* (smallest). Dehydrofluorination by means of cesium fluoride in acetonitrile gave 2,3-bis(fluorimino)norbornane (XV) as a mixture of two stereoisomers, *anti-anti* (XVa) and *syn-anti* (XVb). The

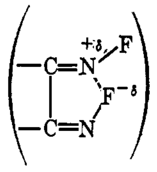


XVa



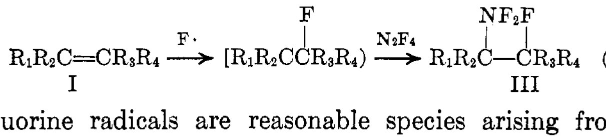
XVb

F^{19} nmr spectrum showed two peaks, one as a quadruplet of AB type, ν_A −6735, ν_B −6570 cps (J_{F-F} = 80 cps), and the other as a singlet at −5720 cps in a 2:1 ratio. The spectrum does not change by raising or lowering the temperature between −30 and 175°, or by changing solvent (neat, benzene, acetone, trifluoroacetic acid). The single nmr peak is assigned to the symmetrical isomer XVa and the quadruplet to the unsymmetrical isomer XVb. The large F–F coupling constant (80 cps) is very surprising since the two atoms are so far apart and coupling through space is usually ~1–10 cps.[3b,3d,13] It is possible that partial bonding between nitrogen and fluorine takes



place which brings the two fluorines in close proximity and accounts for the large coupling constant. For comparison, $-NF_2$ groups attached on unsymmetrical carbon atoms give coupling constants around 600 cps (see Table II).[1e,3b,3c,4]

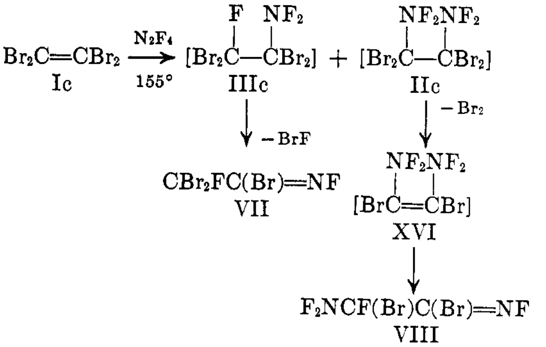
Mechanism.—Normal addition of N_2F_4 to olefins to give 1,2-bis(difluoramino)alkanes proceeds by a free-radical process involving difluoramino radicals ($\cdot NF_2$).[1a,b,e] The "abnormal addition" which occurs at temperatures of 150° or higher with certain olefins may proceed as shown in eq 5. Transient



$$\underset{I}{R_1R_2C{=}CR_3R_4} \xrightarrow{F\cdot} [R_1R_2\overset{F}{\overset{|}{C}}\dot{C}R_3R_4] \xrightarrow{N_2F_4} \underset{III}{R_1R_2\overset{NF_2}{\overset{|}{C}}-\overset{F}{\overset{|}{C}}R_3R_4} \quad (5)$$

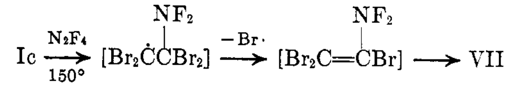
fluorine radicals are reasonable species arising from decomposition of difluoramino radicals at these elevated temperatures.[4] Bumgardner[14] obtained the "abnormal adducts" and substitution products when he irradiated mixtures of N_2F_4 and olefins. He postulated photochemical decomposition of an activated $\cdot NF_2{}^*$ to give a fluorine atom followed by addition to the olefin (eq 5).

The case of tetrabromoethylene combines both types of addition, "normal" and "abnormal," and may proceed as shown in eq 6. The intermediate



$$\begin{array}{ccccc} \underset{Ic}{Br_2C{=}CBr_2} & \xrightarrow[155^\circ]{N_2F_4} & \underset{IIIc}{[Br_2\overset{F}{\overset{|}{C}}-\overset{NF_2}{\overset{|}{C}}Br_2]} & + & \underset{IIc}{[Br_2\overset{NF_2}{\overset{|}{C}}-\overset{NF_2}{\overset{|}{C}}Br_2]} \\ & & \downarrow{\scriptstyle -BrF} & & \downarrow{\scriptstyle -Br_2} \\ & & \underset{VII}{CBr_2FC(Br){=}NF} & & \underset{XVI}{[Br\overset{NF_2}{\overset{|}{C}}{=}\overset{NF_2}{\overset{|}{C}}Br]} \\ & & & & \downarrow \\ & & & & \underset{VIII}{F_2NCF(Br)C(Br){=}NF} \end{array} \quad (6)$$

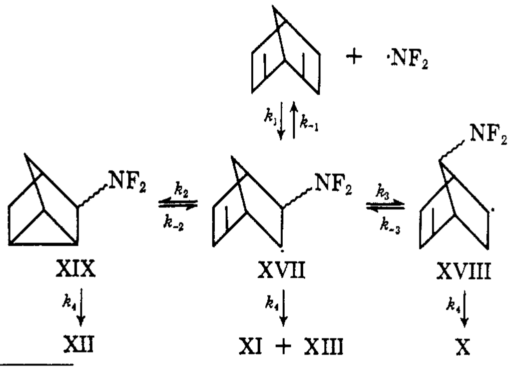
addition products, however, are not stable and in the case of IIIc the elements of BrF are lost to give VII. In the case of IIc, bromine is lost to give the vinyl-NF_2 compound XVI which rearranges to the more stable VIII.[4] Products obtained from 9,10-dibromoanthracene corresponded to the loss of bromine from the intermediate addition product.[3a] One cannot exclude, however, an alternate route in explaining the formation of VII, namely the addition of an NF_2 radical to Ic followed by expulsion of a bromine radical to give a vinyl-NF_2 compound which rearranges to VII (eq 7). A similar pathway was used by Petry,



$$Ic \xrightarrow[150^\circ]{N_2F_4} [Br_2\dot{C}\overset{NF_2}{\overset{|}{C}}Br_2] \xrightarrow{-Br\cdot} [Br_2C{=}\overset{NF_2}{\overset{|}{C}}Br] \longrightarrow VII \quad (7)$$

et al.,[4] to explain the product obtained from β-bromostyrene and N_2F_4. Presumably VIII could also arise from VII *via* free-radical replacement of bromine by $\cdot NF_2$.[15]

The addition of N_2F_4 to norbornadiene gives results typical of a radical process. The initially formed intermediate XVII can react by chain-transfer reaction to give products XI and XIII or can equilibrate to the isomeric radical intermediates XVIII and XIX which in turn react with N_2F_4 or $\cdot NF_2$ to give products X and XII (eq 8). It appears that the isomerization of



(8)

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[13] Long-range coupling constants, J ~ 7 cps, have been reported for bicyclo[2.2.1]hexane and bicyclo[2.2.1]heptane derivatives between an *endo* proton and bridge methylene protons: J. Meinwald and A. Lewis, *J. Amer. Chem. Soc.*, **83**, 2769 (1961); J. Meinwald and Y. C. Meinwald, *ibid.*, **85**, 2514 (1963).

[14] For photochemical decomposition of N_2F_4 to give a fluorine atom, see C. L. Bumgardner, *Tetrahedron Lett.*, 3683 (1964).

[15] J. W. Frazer, *J. Inorg. Nucl. Chem.*, **16**, 63 (1960), describes the ultraviolet light catalyzed reaction of alkyl iodides with N_2F_4 to give difluoraminoalkanes. W. H. Graham and C. O. Parker, *J. Org. Chem.*, **28**, 850 (1963), describe the reaction of trityl bromide with N_2F_4 to give trityldifluoramine.

XVII and the establishment of an equilibrium takes place at a faster rate than the chain-termination process. However, the relative rates of isomerization (k_2, k_{-2}, k_3, k_{-3}) compared with the rates of chain transfer (k_4) are not known. One can speculate, however, that, since the tricyclene XII is the predominant product, the most stable free-radical intermediate is XIX.[10] Similar results to those above were obtained when norbornadiene was treated under free-radical conditions with arylsulfonyl halides,[10] thiophenols,[12] and 1-iodoperfluoropropane.[11] It is difficult to correlate the chain-transfer ability of various species as judged by the ratio of products formed, since steric crowding in the final product is probably also important.[11,12]

Experimental Section[16]

General Procedure.—In Table I the results of the additions of N_2F_4 to olefins are summarized. These reactions were carried out in 80-ml or 240-ml Hastelloy-C-lined shaker tubes behind a barricade. *Caution is essential in handling N_2F_4.* Reactions should be carried out on as small a scale as possible to minimize laboratory handling hazards of the products. Adequate shielding is essential during work-up of the products as explosions may occur.[3a]

The procedure for carrying out the addition reactions was as follows: The olefin and solvent were charged into the shaker tube, and the tube was cooled (−80°) and placed in position behind the barricade. The N_2F_4 was charged into the cold tube by pressure drop from a barricaded cylinder, and the tube was heated with shaking for the required time. The reactions were followed by the pressure drop observed. The tube was cooled to 25°, and volatile products were collected in a cooled, evacuated cylinder, and any residual liquid or solid products were separated and characterized in the usual way. In a typical reaction a mixture of 16 g of 1,1-dichloro-2,2-difluoroethylene (0.12 mol) and 10.8 g of N_2F_4 (0.10 mol) was heated in an 80-ml shaker tube at 90° for 2 hr. A pressure drop from 150 to 0 psi was observed. The liquid product obtained (26 g, ~100% yield) was combined with another run and distilled to give a 65% yield of product, $F_2NCF_2CCl_2NF_2$, bp 79°, $n^{25}D$ 1.3478 (see Table I for further characterization).

1,2,2-Tribromo-1-fluorimino-2-fluoroethane (VII).—A mixture of 34.4 g (0.1 mol) of tetrabromoethylene and 9.4 g (0.09 mol) of N_2F_4 was heated at 155° for 4.5 hr with shaking. The crude product, 36 g, was "titrated" with 1-hexene to remove the bromine formed during the reaction. Gas chromatographic analysis of this product was carried out on a 2-m column of 20% tetrafluoroethylene–propylene telomer oil on firebrick at 102° with a helium carrier gas flow of 40 ml/min and showed the presence of 49% $CFBr_2C(Br){=}NF$ (VII) (retention time, 24 min), 9% $CFBr(NF_2)C(Br){=}NF$ (VIII) (retention time, 10 min), and 35% 1,2-dibromohexane. Fractionation of the crude product through a 10-in. Podbielniak column gave as a first fraction **1,2-dibromo-1-fluorimino-2-difluoramino-2-fluoroethane (VIII)**, a colorless liquid, bp 78° (175 mm). The infrared spectrum (liquid) showed absorption at 6.30 (C=NF) and 10.40, 10.95, 11.45, and 11.90 μ (N-F). F^{19} nmr showed peaks at −7770 cps (singlet, =NF), an AB type quartet (NF_2, ν_A −5939, ν_B −5661 cps, J_{F-F} = 446 cps), and a peak at +2080 cps (multiple, C–F) in a ratio of 1:2:1.

Anal. Calcd for $C_2Br_2F_4N_2$: N, 9.73. Found: N, 9.71.

The major product of the reaction, 1,2,2-tribromo-1-fluorimino-2-fluoroethane (VII) distilled later as a yellow liquid, bp 87° (71 mm), $n^{25}D$ 1.5167. The infrared spectrum showed bands at 6.35 (C=NF) and at 10.45 and 10.65 μ (N-F), and the F^{19} nmr analysis showed a single broad peak at −7445 cps (C=NF) and a multiple split peak at −564 cps (C–F) in approximate area ratios of 1:1.

Anal. Calcd for $C_2Br_3F_2N$: F, 12.03; N, 4.44; mol wt, 316. Found: F, 11.34; N, 4.28; mol wt, 313 (mass spectrum, Br^{79}).

2,3-Dichloro-2-difluoramino-1,1,1,3,4,4,4-heptafluorobutane (IIIf).—A mixture of 12.0 g (0.05 mol) of 2,3-dichlorohexafluoro-2-butene (Hooker Chemical Co.), 5.1 g (0.05 mol) of N_2F_4, and 1.0 g of cesium fluoride was heated with shaking at 200° for 6 hr to give a total of 10 g of liquid product. Gas chromatographic analysis of this product on a 2-m firebrick column packed with 20% of the ethyl ester of Kel-F acid 8114 (3M Co. trademark) at 50° with a helium carrier gas flow of 60 ml/min showed it to consist of 37% $CF_3C(Cl)NF_2CFClCF_3$ (retention time, 10 min) with the remainder largely starting olefin. In the absence of cesium fluoride the yield dropped to 13%. The adduct was purified by gas chromatography to give a colorless liquid, bp 95° (DTA).

The infrared spectrum showed bands at 11.25 (strong), 11.0, and 11.50 μ (NF), and F^{19} nmr showed a broad NF_2 peak at −5970 cps, two CF_3 peaks at 0 and +550 cps, and a C–F peak at +3200 cps in the correct area ratios.

Anal. Calcd for $C_4Cl_2F_9N$: C, 15.80; N, 4.61; F, 56.26; mol wt, 304. Found: C, 15.76; N, 4.81; F, 55.92; mol wt, 302 (vapor density).

The Reaction of N_2F_4 with 1,1,4,4-Tetrafluorobutadiene.[7]—A mixture of 8 g (0.06 mol) of 1,1,4,4-tetrafluorobutadiene[17] and 5.5 g (0.05 mol) of N_2F_4 was heated with shaking at 38° for 4 hr. The crude liquid product, after removal of unchanged N_2F_4, amounted to 10.9 g. Gas chromatographic separation on a 6-ft. column packed with 20% of the ethyl ester of Kel-F Acid 8114 on firebrick gave **1,2-bis(difluoramino)-1,1,4,4-tetrafluoro-3-butene** (35%) and **1,4-bis(difluoramino-1,1,4,4-tetrafluoro-2-butene** (61%).

Mass spectrometric analyses of the two isomers were quite similar, the largest *m/e* peak was 178 ($C_4F_6H_2N^+$). Infrared analysis of the 1,2 isomer showed major absorption bands at 3.2 (=CH), 3.32 (saturated CH), 5.7 ($F_2C{=}CH$), 7.5–8.5 region (C–F), 10.55, 10.7 (doublet, N–F), and 11.75 μ. Infrared analysis of the 1,4 isomer showed absorption at 3.2 (=CH), no band for C=C as predicted for the *trans* isomer, 7.5–9.0 (C–F), and 10.1, 10.7 μ (N–F). F^{19} nmr analysis of the isomeric mixture showed two major peaks of approximately the same area ratio, at −4828 (NF_2) and +2052 cps (CF_2).

The Reaction of N_2F_4 with Norbornadiene.—In a 240-ml tube containing 11 g (0.12 mol) of freshly distilled norbornadiene and 20 g of Halocarbon oil (Halocarbon Products Corp., Series 12-21), 13 g (0.125 mol) of N_2F_4 was condensed. The tube was sealed and heated at 50° for 1 hr. The products of three such reactions were combined and distilled to give 30 g (43%) of a mixture of 1:1 adducts as a colorless liquid, bp 60–62° (6.0 mm).

Anal. Calcd for $C_7H_8F_4N_2$: C, 42.86; H, 4.11; F, 38.75; N, 14.28. Found: C, 43.16; H, 4.34; F, 37.91; N, 15.57.

Gas chromatographic analysis on a 1-m column packed with 20% silicone 703 on firebrick at 101° with helium flow of 170 ml/min showed four peaks in approximate area ratio in order of elution of 8:7:76:9. The individual peaks were separated by preparative gas chromatography.

The first eluent (retention time, 6.2 min) was assigned as the 2,7-bis(difluoramino)bicyclo[2.2.1]hept-5-ene (X). The F^{19} nmr spectrum (neat) showed the presence of two different NF_2 groups in 1:1 ratio, one as an AB type quadruplet, ν_A −7257, ν_B −6757 cps, (J_{F-F} = 580 cps), each peak split into doublets (J_{F-H} ~ 30 cps), and the other into a quadruplet centered at −6595 cps (J_{F-H} ~ 30 cps).[13]

Anal. Calcd for $C_7H_8F_4N_2$: F, 38.75; N, 14.28. Found: F, 38.64; N, 14.23.

The second eluent (retention time, 7.7 min) was assigned as the di-*exo*-2,3-bis(difluoramino)bicyclo[2.2.1]hept-5-ene (XIa). The F^{19} nmr spectrum (neat) showed two relatively broad peaks in a 1:1 ratio at −6860 and −6730 cps. These peaks are the "strong" peaks of an AB-type pattern where the weak components were too broad and weak to record their position accurately, indicating that the two $-NF_2$ groups are equivalent.

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(16) All melting points were taken on a Fisher-Johns block and are not corrected. Boiling points are not corrected. Infrared spectra were measured on a Perkin-Elmer recording spectrophotometer, Model 21; the listings of infrared bands include those which are relevant to the structural arguments. Fluorine nmr spectra were obtained with a high-resolution spectrometer and associated electromagnet, both manufactured by Varian Associates, operating at 56.4 Mc/sec, approximately 14,000 G. Spectra were calibrated in terms of displacements in cycles per second (cps) from the F^{19} resonance of 1,2-difluoro-1,1,2,2-tetrachloroethane (Freon-112) as an external standard. One should add +3826 cps in order to get frequencies with respect to $CFCl_3$ (Freon-11). Negative frequency displacements are for resonances at lower field than the reference. Proton nmr spectra were determined with a Varian Associates A-60 spectrometer and are calibrated in τ values. Carbon–hydrogen analyses were repeatedly found to be higher (~1%) not because of impurities but because of the combustion difficulties caused by the presence of the difluoramino groups.

(17) J. L. Anderson, R. E. Putnam, and W. H. Sharkey, *J. Amer. Chem. Soc.*, **83**, 382 (1961).

Anal. Calcd for $C_7H_8F_4N_2$: F, 38.75; N, 14.28. Found: F, 38.60; N, 13.93.

The third and most abundant eluent (retention time, 11.5 min) showed in the F^{19} nmr spectrum (neat) three sets of quadruplets (AB type) in a ratio of about 3:1:1 indicating a mixture of two isomers. The large quadruplet, ν_A -7100, ν_B -6395 cps ($J_{F-F} = 585$ cps), split into doublets, $J_{H-F} \sim 30$ cps, belongs to a symmetrical isomer, assigned as the di-*exo*-3,5-bis(difluoramino)tricyclo[2.2.1.$0^{2,6}$]heptane (XIIa). The other two quadruplets, ν_A -7150, ν_B -6710 cps ($J_{F-F} = 585$ cps) and ν_A -7130, ν_B -6645 cps ($J_{F-F} = 590$ cps), both split into doublets $J_{H-F} \sim 30$ cps, belong to an isomer with two different $-NF_2$ groups assigned as the *endo-exo*-3,5-bis(difluoramino)tricyclo-[2.2.1.$0^{2,6}$]heptane (XIIb).

Anal. Calcd for $C_7H_8F_4N_2$: C, 42.86; H, 4.11; F, 38.75; N, 14.28. Found: C, 43.40; H, 4.12; F, 38.44; N, 14.56.

The fourth eluent (retention time, 14.0 min) showed in the F^{19} nmr spectrum (neat) two different NF_2 groups in 1:1 ratio, one as an AB-type quadruplet, ν_A -6935, ν_B -6530 cps ($J_{F-F} = 595$ cps), split in doublets ($J_{F-H} = 30$ cps) assigned as *endo-exo*-2,3-bis(difluoramino)bicyclo[2.2.1]hept-5-ene (XIII). In a very small amount (<10%) there appeared another quadruplet, ν_A -7465, ν_B -6715 cps ($J_{F-F} = 590$ cps), split into doublets ($J_{F-H} = 30$ cps) belonging to a symmetrical isomer with two identical NF_2 groups, presumably the di-*endo*-2,3-bis(difluoramino)bicyclo[2.2.1]hept-5-ene (XIb).

Anal. Calcd for $C_7H_8F_4N_2$: C, 42.86; H, 4.11; F, 38.75; N, 14.28. Found: C, 43.61; H, 4.13; F, 38.32; N, 14.06.

3,5-Bis(fluorimino)tricyclo[2.2.1.$0^{2,6}$]heptane (XIV).—A mixture of 7.0 g of cesium fluoride, 20 ml of acetonitrile, and 2.0 g of 3,5-bis(difluoramino)tricyclo[2.2.1.$0^{2,6}$]heptane (mixture of XIIa and b) was heated under reflux for 2 hr. The solid was removed by filtration, the excess acetonitrile was evaporated *in vacuo*, and the residue was dissolved in carbon tetrachloride. The carbon tetrachloride solution was filtered to remove insoluble impurities, evaporated to dryness to give a semisolid residue which slowly crystallized, and after two recrystallizations from ethanol had mp 50–53°; infrared maxima (Nujol) 5.94 (C=N), 11.8–12.5 μ (=N—F, and tricyclene); only end absorption in the ultraviolet; and F^{19} nmr (CCl_4) two single peaks at -5110 (large) and -5585 cps (small peak).

Anal. Calcd for $C_7H_6F_2N_2$: N, 17.95; F, 24.34. Found: N, 17.51; F, 24.54.

2,5-Dimethyl-2,5-bis(difluoramino)dihydrofuran (IX).—In an 80-ml tube containing 6.9 g (0.07 mol) of 2,5-dimethylfuran and 11.3 g of benzene was condensed 7.5 g (0.07 mol) of N_2F_4; the tube was sealed, and the mixture heated to 78° for 1 hr. The product was distilled to give 6.0 g (43%) of 2,5-dimethyl-2,5-bis(difluoramino)dihydrofuran as a colorless liquid: bp 43–45° (4 mm); $n^{25}D$ 1.3955; infrared maxima (neat), 3.20 (=CH), 3.32 and 3.4 (CH), 6.20 (C=C), 10.25, 11.00, 11.25, 11.50, and 11.73 μ (NF_2); proton nmr spectrum (neat) in τ values at 3.74 (singlet, =CH) and at 8.3 (triplet, $J_{H-F} = 2.5$ cps, CH_3); and F^{19} nmr, (neat) a single broad peak at -5234 cps (NF_2).

Anal. Calcd for $C_6H_8F_4N_2O$: C, 36.00; H, 4.03; N, 14.00. Found: C, 36.02; H, 4.48; N, 14.27.

2,3-Bis(fluorimino)norbornane (XV).—A mixture of 10 g of 2,3-bis(difluoramino)norbornane (mixture of isomers), 50 g of powdered cesium fluoride, and 100 ml of acetonitrile were refluxed for 5 hr. The solids were removed by filtration, the solvent was removed *in vacuo*, and the residue was dissolved in ethanol. The solution was treated with decolorizing carbon and filtered, on cooling 6.1 g (77.5% yield) of XV was obtained as white, fluffy crystals, mp 89–90°. The infrared spectrum (KBr) showed peaks at 3.39, 3.47 (C-H), 5.97, 6.05 (C=N), 11.25, 11.55, 12.00, 12.35 μ (=NF), and no absorption was observed in the ultraviolet.

Anal. Calcd for $C_7H_8F_2N_2$: C, 53.16; H, 5.10; F, 24.03; N, 17.71. Found: C, 53.32; H, 5.03; F, 23.81; N, 17.61.

Registry No.—IIa, 1426-41-1; IIb, 16159-09-4; IId, 16159-10-7; IIe, 16159-11-8; IIg, 16063-38-0; IIh, 16203-51-3; IIi (*threo*), 16159-13-0; IIi (*erythro*), 16159-30-1; IIj,16159-14-1; $C_6H_5CF(NF_2)C(Cl)=NF$, 16203-52-4; IIIf, 16159-15-2; VII, 16159-16-3; VIII, 16159-17-4; IX, 16159-18-5; X, 16159-19-6; XIa, 16159-24-3; XIb, 16159-20-9; XIIa, 16203-53-5; XIIb, 16203-54-6; XIII, 16159-21-0; XIV, 16203-55-7; XVa, 16159-22-1; tetrafluorohydrazine, 10036-47-2; XVb, 16159-23-2; norbonene adduct, *cis-exo*, 16159-31-2; norbonene adduct, *cis-endo*, 16159-32-3; norbornene adduct, *trans-endo-exo*, 16159-33-4.

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