Chemistry of Tetrafluorohydrazine. III. Addition Reactions with Acetylenes and with Allene. Bis(difluoramino)ethylenes

G. N. Sausen and A. L. Logothetis

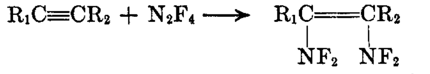
Contribution No. 1283 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware

Received January 17, 1967

The reaction of N_2F_4 with acetylenes, 2,4-hexadiyne, and allene under thermal conditions is described. Acetylenes give initially the *cis*- and *trans*-2,3-bis(difluoramino)ethylenes (I), which are not very stable and are easily isomerized thermally or photolytically to 1-difluoramino-2-(N-fluorimino)ethanes (II and III). With acetylenes with perfluoroalkyl substituents, it is possible to isolate compounds of structure I in good yield. Allene yielded a 1:1 mixture of *syn*- and *anti*-1-difluoramino-3-fluoro-2-(N-fluorimino)propane (X). The most likely pathway for this reaction is the addition of the NF_2 radical to the acetylenic bond to give an intermediate vinyl radical (VIII) which has time to equilibrate before being trapped by N_2F_4 or NF_2 species.

The addition reaction of N_2F_4 with olefins to give 1,2-bis(difluoramino)ethanes has been described by Petry and Freeman.[1] Dijkstra, Kerr, and Trotman-Dickenson[2] have studied the kinetics of this reaction in the gas phase, and Cerfontain[3] studied the kinetics of the liquid phase reaction of N_2F_4 with stilbene and anthracene. In previous papers in this series, the addition reaction of N_2F_4 with anthracene and halogenated anthracenes to give 9,10-bis(difluoramino)-9,10-dihydroanthracenes was described.[4a] Similarly, the addition of N_2F_4 to terminal olefins in the presence of alkali metal fluorides, initially gives the 1:1 adduct which then loses hydrogen fluoride to form in one step N-fluoriminonitriles.[4b] In these difluoramino-containing compounds, the NF_2 group is attached to saturated carbon. A number of other examples of compounds containing similarly bonded NF_2 groups is known[5] as well as examples of compounds with NF_2 groups attached to sulfur,[6,7] nitrogen,[8] and oxygen.[9-13] The present paper describes the reaction of N_2F_4 with acetylenes to obtain vinyl difluoramino compounds, as yet an unknown class of organic molecules.

It was found that the initial reaction products are 1,2-bis(difluoramino)ethylenes (I), but their stability depends upon the substituents on the acetylenic carbon. When the substituents are perfluoroalkyl groups, one can readily isolate the adducts Ia and Ib in good yield as a mixture of *cis* and *trans* isomers. Prolonged heating causes isomerization of I to a mixture of 1-difluoramino-2-(N-fluorimino)ethanes (II and III). When the substituents are CN, alkyl, or aryl, the 1-difluoramino-2-(N-fluorimino)ethanes (IIId–g) are the major products. With 2,4-hexadiyne, a similar addition reaction occurs. However, only 1 mole of N_2F_4 is consumed, and a mixture of fluorine-containing products is obtained. The infrared spectrum shows a band at 4.4 μ, assignable to an acetylenic linkage. Hence, the product mixture is probably derived from a 1,2 addition of N_2F_4 (eq 3) rather than a 1,4 addition (eq 4). Even with excess N_2F_4 and higher reaction temperatures, only monoadducts are isolated.



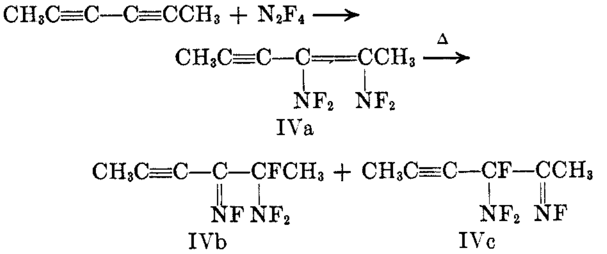
$$R_1C{\equiv}CR_2 + N_2F_4 \longrightarrow R_1\underset{NF_2}{C}{=}\underset{NF_2}{C}R_2 \quad (1)$$

I (*cis* and *trans*)

$$R_1\underset{NF_2}{C}{=}\underset{NF_2}{C}R_2 \xrightarrow{\Delta} R_1\underset{NF}{\overset{}{C}}{-}\underset{NF_2}{C}FR_2 + R_1\underset{NF_2}{C}F{-}\underset{NF}{C}R_2 \quad (2)$$

cis and *trans* II III

a, $R_1 = CF_3$; $R_2 = CF_3$
b, $R_1 = CF_3$; $R_2 = C_4F_9$
c, $R_1 = CF_3$; $R_2 = H$
d, $R_1 = CN$; $R_2 = CN$
e, $R_1 = C_6H_5$; $R_2 = C_6H_5$
f, $R_1 = C_6H_5$; $R_2 = C({=}O)F$
g, $R_1 = C_6H_5$; $R_2 = CH_3$

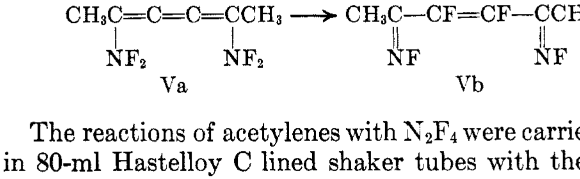


$$CH_3C{\equiv}C{-}C{\equiv}CCH_3 + N_2F_4 \longrightarrow CH_3C{\equiv}C{-}\underset{NF_2}{C}{=}\underset{NF_2}{C}CH_3 \xrightarrow{\Delta}$$

IVa

$$CH_3C{\equiv}C{-}\underset{NF}{C}{-}\underset{NF_2}{C}FCH_3 + CH_3C{\equiv}C{-}\underset{NF_2}{C}F{-}\underset{NF}{C}CH_3 \quad (3)$$

IVb IVc



$$CH_3C{\equiv}C{-}C{\equiv}CCH_3 + N_2F_4 \longrightarrow$$

$$CH_3\underset{NF_2}{C}{=}C{=}C{=}\underset{NF_2}{C}CH_3 \longrightarrow CH_3\underset{NF}{C}{-}CF{=}CF{-}\underset{NF}{C}CH_3 \quad (4)$$

Va Vb

The reactions of acetylenes with N_2F_4 were carried out in 80-ml Hastelloy C lined shaker tubes with the precautions described in the Experimental Section. Reaction of hexafluoro-2-butyne at 170° for 1 hr gave Ia in ~90% yield as a 42:58 mixture of *cis/trans* olefin isomers. A small amount (~1%) of product assigned the structure of the rearranged compound IIa was present in the reaction mixture. The two most abundant isomers were separated by gas chromatography as colorless liquids, bp 49 and 56°. The structural assignment of the lower boiling material as the

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[1] 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.

[2] A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc. A*, 582 (1966).

[3] H. Cerfontain, *ibid.*, 6602 (1965).

[4] For papers I and II in this series, see (a) A. L. Logothetis, *J. Org. Chem.*, **31**, 3686 (1966); (b) A. L. Logothetis and G. N. Sausen, *ibid.*, **31**, 3689 (1966).

[5] For leading references to the synthesis and chemistry of organic and inorganic N–F compounds and a review of the literature through 1960, see C. J. Hoffman and R. G. Neville, *Chem. Rev.*, **62**, 1 (1962). See also, A. V. Pankratov, *Uspekhi Khim.*, **32**, 336 (1963); C. B. Colburn, *Endeavour*, **24**, 138 (1965). For a more complete list of references, see paper I in this series.[4a]

[6] A. L. Logothetis, G. N. Sausen, and R. J. Shozda, *Inorg. Chem.*, **2**, 173 (1963); G. H. Cady, D. F. Eggers, and B. Tittle, *Proc. Chem. Soc.*, 65 (1963); E. C. Stump, Jr., C. D. Padgett, and W. S. Brey, Jr., *Inorg. Chem.*, **2**, 648 (1963); E. C. Stump, Jr., and C. D. Padgett, *ibid.*, **3**, 610 (1964).

[7] C. L. Bumgardner and M. Lustig, *ibid.*, **2**, 662 (1963).

[8] G. N. Sausen, U. S. Patent 3,149,165 (1964).

[9] M. Lustig and G. H. Cady, *Inorg. Chem.*, **2**, 388 (1963).

[10] G. N. Sausen, U. S. Patent 3,214,465 (1965).

[11] J. K. Ruff, *Inorg. Chem.*, **4**, 1788 (1965).

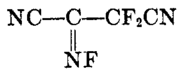
[12] J. M. Shreeve, L. C. Duncan, and G. H. Cady, *ibid.*, **4**, 1516 (1965).

[13] W. H. Hale, Jr., and S. M. Williamson, *ibid.*, **4**, 1342 (1965).

trans isomer (Ia) was tentatively made on the basis that it eluted first from the gas chromatography column,[14] its simpler infrared spectrum lacks the 6.15-μ (C═C) band which is present in the higher boiling isomer, and it is solid at −78° while the higher boiling isomer is still liquid at −78°, in agreement with a more symmetrical structure. The F^{19} nmr spectrum of each isomer has single bands for the NF_2 and CF_3 groups.

The rearranged fluorimino compound IIa was obtained as the major product when the reaction was carried out at 195° (5 hr) or when Ia was first isolated and then heated at 195° for 5 hr. Rearrangement can also take place *via* ultraviolet irradiation. However, the reaction is not clean and only 50% of II was recovered. The F^{19} nmr spectrum for this compound was particularly interesting. Five resonance signals were observed for IIa (see Table I) corresponding to the five types of fluorine present, but each signal consisted of two peaks. The presence of double peaks is attributed to the presence of *syn* and *anti* isomers around the C═N group.[4b] All the isomers Ia (*cis* and *trans*) and IIa have very similar mass spectra, the largest peak being *m/e* 247 (parent − 1F), a further proof of their isomeric nature. Similarly, reaction of N_2F_4 with perfluoro-2-heptyne gave a mixture of *cis*- and *trans* olefin isomers (Ib) in a ratio of ~1:5. The isomer that eluted first on the gas chromatographic column was again assigned the *trans* structure.

Reaction of dicyanoacetylene with N_2F_4 at 140° gave the rearranged adduct IId as the principal product. Two other minor components separated by gas chromatography were identified as VI (mixture of *syn* and *anti* isomers) and VII.



$NC{-}\underset{\overset{\|}{NF}}{C}{-}CF_2CN$

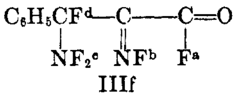
VI

$NC{-}\underset{\overset{\|}{NF}}{C}{-}\underset{\overset{\|}{NF}}{C}{-}CN$

VII

With the phenyl-substituted acetylenes the principal reaction products in each case were the rearrangement products II and III.[15] From the unsymmetrical acetylenes (f and g) mixtures of rearrangement products (II and III) are possible. Methylphenylacetylene gave both isomers IIg and IIIg as shown by gas chromatography and nmr spectra.

Phenylpropiolyl fluoride, however, appears to have given only one isomer (IIIf) as shown by the nmr spectrum and the quantitative formation of a pure anilide derivative (mp 166.5–167.5°). The spectrum of the distilled IIIf showed two doublets at −6896 and −6475 cps for ═NF^b and O═CF^a groups whose coupling through four bonds was quite large ($J_{F^aF^b}$ ~ 30 cps) when compared to the observed multibond spin couplings in other systems.[16] There was also observed



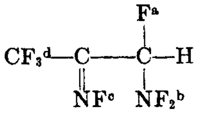
$C_6H_5\underset{NF_2^c}{CF^d}{-}\underset{\overset{\|}{NF^b}}{C}{-}\underset{F^a}{C}{=}O$

IIIf

a quartet centered at −5180 cps (J = 596 cps) for the NF_2^c group attached on an asymmetric carbon, as well as a peak at +4985 cps for the CF group. No other peaks were observed indicating that the other isomer IIf was not formed in any detectable amounts.

The F^{19} nmr spectra (see Table I) of these rearrangement products (II and III) generally showed an AB pattern for the NF_2 grouping with additional small splitting caused by the fluorine attached to the same carbon. The reason that a quadruplet of the AB type (J ~ 600 cps) appears is that the NF_2 group is attached on an asymmetric center and the two fluorines become nonequivalent. This is analogous to the already observed phenomenon of a *gem*-difluoro group next to an asymmetric center, *e.g.*, $R_4CF_2CR_1R_2R_3$, where the two fluorines are not equivalent (quartet of the AB type, J_{FF} ~ 100–150 cps). It seems, therefore, that the nitrogen inverts very slowly, keeping the free-electron pair essentially fixed in space resembling the configuration of an RCF_2 group.[16]

Reaction of N_2F_4 with trifluoromethylacetylene gave the rearrangement product IIc as the major reaction product. The nmr spectrum helped to assign the structure II (rather than III) to this compound. It is interesting to note that F^a was split primarily by H (J ~ 50 cps) and secondarily by F^b and F^c to give a signal at +6025 cps with a multiple-peak pattern. F^d was split primarily by F^c (J ~ 25 cps) and secondarily by F^a and F^b (J ~ 3 cps) to give the observed "doublet into quintuplet" peak (−100 cps). Apparently, long-range coupling by hydrogen was not observed. F^c was a broad singlet at 25°, but at −70° quadruplet splitting was observed (Table I). F^b appeared as a broadened singlet at 25°, but the typical AB pattern was observed at −70°. The proton pattern showed eight signals of equal intensity, caused by primary splitting by F^a (J ~ 50 cps) and separate secondary splitting by each fluorine of the NF_2 group. Again no splitting by F^d was observed.



$CF_3^d{-}\underset{\overset{\|}{NF^c}}{C}{-}\underset{NF_2^b}{\overset{F^a}{C}}{-}H$

IIc

Discussion

This addition reaction with acetylenes appears to proceed *via* a nonstereospecific mechanism similar to that proposed[1-4] for the reaction of N_2F_4 with olefins. Since N_2F_4 undergoes ready dissociation into NF_2 radicals even at low temperatures,[17] an initial NF_2 radical attack as shown in eq 5 to give intermediate VIII,

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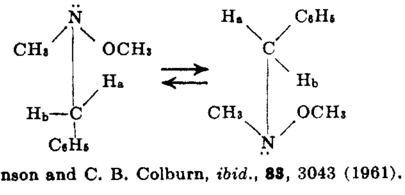
[14] R. A. Hively [*Anal. Chem.*, **35**, 1921 (1963)] discusses the assignment of *cis–trans* configuration to olefins. The *trans* isomer normally elutes first from the gc column.

[15] R. C. Petry, C. O. Parker, F. A. Johnson, T. E. Stevens, and J. P. Freeman (forthcoming publication) have also observed rearrangement products from the reactions of N_2F_4 with diphenylacetylene and with allene (private communication from Dr. Stevens).

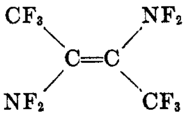
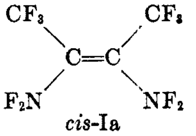
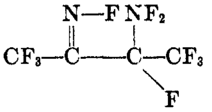
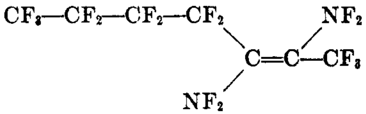
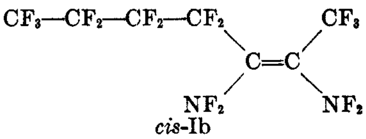
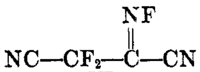
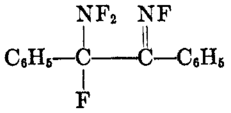
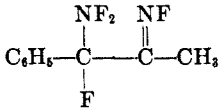
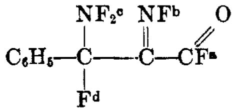
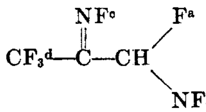
[16] D. R. Davis, R. P. Lutz, and J. D. Roberts, *J. Am. Chem. Soc.*, **83**, 246 (1961); M. Takahashi, D. R. Davis, and J. D. Roberts, *ibid.*, **84**, 2935 (1962); J. Meinwald and Y. C. Meinwald, *ibid.*, **85**, 2514 (1963); A. H. Lewin, *ibid.*, **86**, 2303 (1964). D. L. Griffith and J. D. Roberts [*ibid.*, **87**, 4089 (1965)] discuss the slow inversion of nitrogen, at −40° to give an AB quartet for H_a and H_b.



[17] F. A. Johnson and C. B. Colburn, *ibid.*, **83**, 3043 (1961).

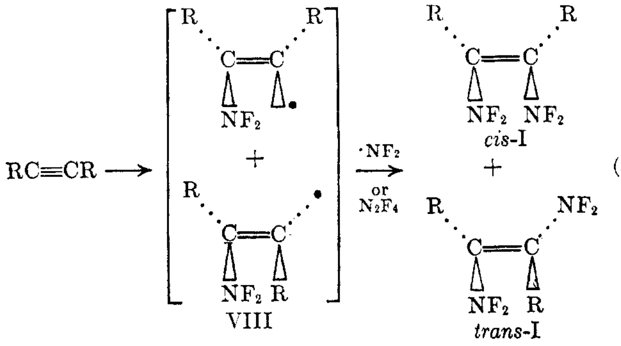
TABLE I

F^{19} NMR SPECTRA OF THE N_2F_4–ACETYLENE ADDUCTS

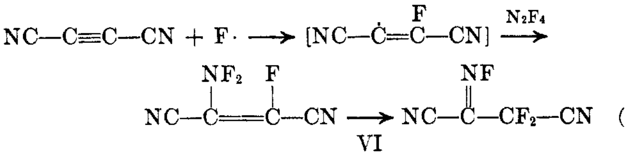
Compd	F^{19} chemical shift, cps[a–c]	Coupling constants
 *trans*-Ia	−6347 (s, NF_2) −527 (s, CF_3)	
 *cis*-Ia	−6510 (s, NF_2) −396 (s, CF_3)	
 IIa	−7100 (=NF)[d] −5090 (NF_2)[d] −78 (CF_3)[d] +502 (CF_3)[d] +5860 (—CF)[d]	
 *trans*-Ib	−6445 (s, NF_2) −6374 (s, NF_2) −573 (s, =CCF_3) +913 (CF_3) +2106 (CF_2) +3015 (CF_2) +3418 (CF_2)	
 *cis*-Ib	−6950 (NF_2) −6420 (NF_2) −500 (=CCF_3) +910 (CF_3) +2315 (CF_2) +2965 (CF_2) +3435 (CF_2)	
 VI	−8056 (s, =NF) +1277 (s, CF_2)	
 IId	−8680 (s, =NF) −5627 (d, NF_2) +3949 (t, CF)	J_{FNF_2} = 14 cps[e] J_{NF_2F} = 14 cps
 IIe	−5934 (s, =NF) −5150 (q, NF_2)[f] +5098 (m, CF)	$J_{N<^{F}_{F}}$ = 575 cps
 VII	−8412 (s, =NF)	
 IIIg	−5875 (=NF) −5300 (q, NF_2)[f] +4199 (t into m, CF)	$J_{N<^{F}_{F}}$ = 572 cps
 IIIf	−6896 (d, =NF) −6475 (d, $\overset{O}{\overset{\|}{C}}F$) −5180 (q, NF_2)[f] +4985 (m, CF)	$J_{F^aF^b}$ ~ 30 cps $J_{F^bF^a}$ ~ 30 cps $J_{N<^{F}_{F}}$ ~ 596 cps
 IIc	−7055 (q, =NF)[g] −5510 (q, NF_2)[f,g] −100 (d into quintuplet, CF_3)[g] +6025 (d into m, CF)[g]	$J_{F^cF^d}$ = 25 cps $J_{N<^{F}_{F}}$ ~ 600 cps $J_{F^dF^c}$ = 25 cps, $J_{F^dF^a}$ = 5 cps J_{FH} ~ 50 cps

[a] All spectra were run neat using an external reference of Freon-112 (1,2-difluoro-1,1,2,2-tetrachloroethane). [b] All the resonances of the fluorine attached on nitrogen are relatively broad peaks, owing to the quadripolar relaxation of the N^{14} nucleus, and fine spin–spin couplings with other fluorines and with protons is obscured. [c] Singlets, doublets, triplets, and quartets are denoted as s, d, t, and q, respectively. [d] Each peak appears as two signals indicating that it is a mixture of *syn* and *anti* isomers. [e] These coupling constants are obtained from an ABX pattern and are averages of J_{AX} and J_{BX}. The triplet CF would probably be further split on higher resolution since this is an ABMX system. The authors are indebted to a referee for calling this to their attention. [f] The quartets (q) are further split (J ~ 2–3 cps) by the CF. [g] The spectrum was run around −70° for better resolution.

which then reacts with excess N_2F_4 or $\cdot NF_2$ to give adduct I (*cis* and *trans*), seems to be the pathway of this reaction.[18] The isomerization of I to II and III is a competing process, as shown in the hexafluoro-2-butyne reaction where both *cis*- and *trans*-Ia were isolated and were in turn isomerized to 2-difluoramino-3-(N-fluorimino)heptafluorobutane (IIa or IIIa). This rearrangement either proceeds thermally or is catalyzed by ultraviolet light. A similar rearrangement of a vinyl-NF_2 intermediate is proposed by Bumgardner[19] in the photochemical reaction of N_2F_4 with 2-butyne and by Logothetis[4a] in the thermal reaction of N_2F_4 with 9,10-dibromoanthracene. It is not known whether inter- or intramolecular, or both, transfer of fluorine is involved. Reversal of the addition reaction to give VIII (CN rather than NF bond cleavage) as an intermediate seems unlikely in view of the relative strength of the CN bond *vs.* that of the NF bond. The isolation of VI as a minor product from the reaction of dicyanoacetylene with N_2F_4 probably occurred as shown in eq 6. At 140° there are many possible pathways to the formation of a transient fluorine radical.



VIII cis-I trans-I (5)

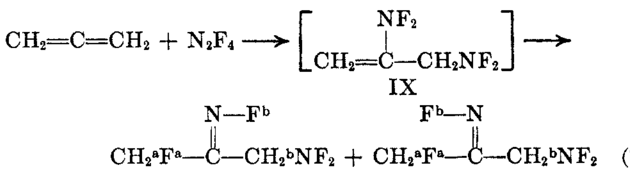


$$\mathrm{NC{-}C{\equiv}C{-}CN + F\cdot \longrightarrow [NC{-}\dot{C}(F){=}C{-}CN] \xrightarrow{N_2F_4} NC{-}C(NF_2){=}C(F){-}CN \longrightarrow NC{-}C({=}NF){-}CF_2{-}CN} \quad (6)$$

VI

Addition to Allene

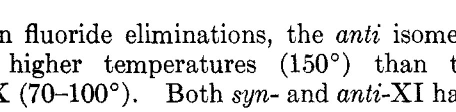
Allene and N_2F_4 reacted at 70° in *o*-dichlorobenzene solvent to give a 40% yield of liquid product and some dark, solid residue. Gas chromatographic analysis of the liquid products indicated the presence of mainly two 1:1 allene–N_2F_4 adducts in about equal amounts. The two isomers were separated by preparative gas chromatography and shown to have very similar infrared spectra (C=N absorption peaks at 6.02 and 6.05 μ, respectively) and mass spectra. They were assigned as *syn*- and *anti*-1-difluoramino-3-fluoro-2-(N-fluorimino)propane (X), respectively, on the basis of their nmr spectra. It is assumed that coupling constants between the anisotropic group F^b and CH_2^a, F^a, CH_2^b are larger when these groups are *cis* rather than *trans* to each other.[20] Thus, the isomer with $J_{H^aF^b} = 4.8$ cps, $J_{F^aF^b} = 10$ cps, and $J_{H^bF^b} = 0$ cps is assigned as *syn*-X and the isomer with $J_{H^aF^b} = 2.3$ cps, $J_{F^aF^b} = 2.4$ cps, and $J_{H^bF^b} = 2.4$ cps is assigned as *anti*-X. The chemical shifts of F^a, CH_2^a, CH_2^b in the two isomers are also different.[21-24] Thus in *anti*-X, F^a shifts to higher magnetic field (shielded), CH_2^a shifts to lower (deshielded), and CH_2^b to higher fields (shielded) in comparison to *syn*-X (see Table II).



$$\mathrm{CH_2{=}C{=}CH_2 + N_2F_4 \longrightarrow \left[CH_2{=}C(NF_2){-}CH_2NF_2\right] \longrightarrow CH_2^aF^a{-}C({=}N{-}F^b){-}CH_2^bNF_2 + CH_2^aF^a{-}C({=}N{-}F^b){-}CH_2^bNF_2} \quad (7)$$

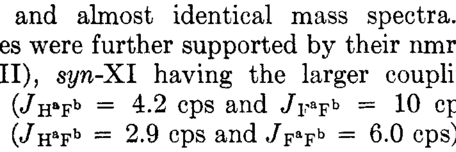
IX anti-X syn-X

Both isomers X eliminate 2 moles of hydrogen fluoride on treatment with sodium fluoride in *o*-dichlorobenzene[4] to give the corresponding *anti*- and *syn*-3-fluoro-2-(N-fluorimino)propionitrile (XI). The reaction is stereospecific and only one compound is obtained in almost quantitative yield from each isomer, indicating that no isomerization of *syn*- to *anti*-XI or *vice versa* took place under these conditions. Thus from *anti*-X one gets the *anti*-XI and from *syn*-X one gets the *syn*-XI. A difference was observed in the respective hydrogen fluoride eliminations, the *anti* isomer X requiring higher temperatures (150°) than the *syn* isomer X (70–100°). Both *syn*- and *anti*-XI have very similar infrared (C=N absorption peaks at 6.18 and 6.17 μ) and almost identical mass spectra. Their structures were further supported by their nmr spectra (Table II), *syn*-XI having the larger coupling constants,[20] ($J_{H^aF^b} = 4.2$ cps and $J_{F^aF^b} = 10$ cps) than *anti*-XI, ($J_{H^aF^b} = 2.9$ cps and $J_{F^aF^b} = 6.0$ cps), analogous to the two isomers of X. The chemical shift of F^a is to higher magnetic field (shielded) and that of



$$\mathrm{CH_2F{-}C({=}N{-}F){-}CH_2NF_2 \xrightarrow[150^\circ]{NaF} CH_2^aF^a{-}C({=}N{-}F^b){-}CN} \quad (8)$$

anti-X anti-XI



$$\mathrm{CH_2F{-}C({=}N{-}F){-}CH_2NF_2 \xrightarrow[100^\circ]{NaF} CH_2^aF^a{-}C({=}N{-}F^b)CN} \quad (9)$$

syn-X syn-XI

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[18] For a recent review of free radical additions to acetylenes, see F. W. Stacey and J. F. Harris, Jr., *Org. Reactions*, **13**, 150 (1963).

[19] C. L. Baumgardner, *Tetrahedron Letters*, 3683 (1964).

[20] The *cis* coupling constants, J_{FCF_3}, in the fluoro olefin cases $\mathrm{F}{>}\mathrm{C{=}C}{<}\mathrm{CF_3}$ are reported to be larger than the *trans* coupling constants; see J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, Book Co., Inc., New York, N. Y., 1959, p 335, and S. Andreades, *J. Am. Chem. Soc.*, **84**, 864 (1962). This observation is consistent with recent proposals involving direct through-space coupling when the interacting fluorine atoms are close to each other; see L. Petrakis and C. H. Sederholm, *J. Chem. Phys.*, **35**, 1243 (1961).

[21] Oximes of aldehydes and unsymmetrical ketones can exist in *syn* and *anti* forms. The nmr spectra of various aldoximes were investigated by W. D. Phillips [*Ann. N. Y. Acad. Sci.*, **70**, 817 (1958)] who found that the aldehydic proton was at lower magnetic fields in the *syn* than in the *anti* isomer. Similarly, E. Lustig [*J. Phys. Chem.*, **65**, 491 (1961)] found that the *α* hydrogens in a ketoxime were also found at lower magnetic fields in the *syn* than in the *anti* isomer.

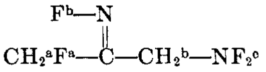
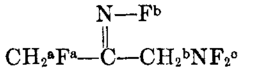
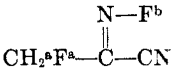
[22] In alkyl nitrites [W. D. Phillips, C. E. Looney, and C. R. Spaeth, *J. Mol. Spectry.*, **1**, 35 (1957)] and nitrosamines [C. E. Looney, W. D. Phillips, and E. L. Reilly, *J. Am. Chem. Soc.*, **79**, 6136 (1957)] the *α* hydrogens *syn* to the anisotropic groups are shifted to lower magnetic fields.

[23] In the 2,4-dinitrophenylhydrazones of aldehydes, the aldehydic proton *cis* to the anisotropic group is shifted to lower magnetic fields: G. J. Karabatsos, B. L. Shapiro, F. M. Vane, J. S. Fleming, and J. S. Ratka, *ibid.*, **85**, 2784 (1963).

[24] In dinitrophenylhydrazones, 2,4-dinitrophenylhydrazones, and semicarbazones of unsymmetrical ketones, the *α* protons *syn* to the anisotropic groups are shifted to higher magnetic fields because they are in the radius of the electronic current of the aromatic ring: G. J. Karabatsos, J. D. Graham, and F. M. Vane, *ibid.*, **84**, 753 (1962); G. J. Karabatsos and R. A. Taller, *ibid.*, **85**, 3624 (1963).

TABLE II

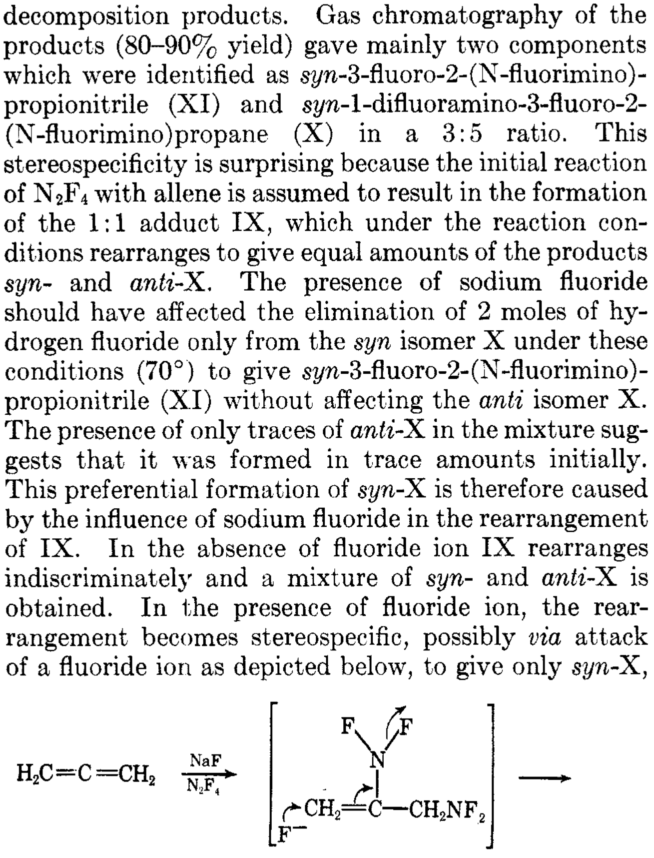
SPIN COUPLING CONSTANTS AND CHEMICAL SHIFTS OF *syn*- AND *anti*-N-FLUORIMINO COMPOUNDS

Compound[a]	F^{19} chemical shift, cps[b-d]	H^1 proton shift (τ), ppm[c,d]	Coupling constants, cps					
			$J_{H^aF^a}$	$J_{H^aF^b}$	$J_{H^bF^c}$	$J_{F^aF^b}$	$J_{H^bF^a}$	$J_{H^bF^b}$
 $CH_2{}^aF^a\text{—}\overset{\overset{F^b\text{—}N}{\Vert}}{C}\text{—}CH_2{}^b\text{—}NF_2{}^c$ *syn*-X	+9225 (t in d in t, CF) −7015 (t, NF_2) −5935 (s, =NF)[e]	4.90 (d in d, $CH_2{}^a$) 5.36 (t in d, $CH_2{}^b$)	46	4.8	29	10	2.8	0
 $CH_2{}^aF^a\text{—}\overset{\overset{F^b\text{—}N}{\Vert}}{C}\text{—}CN$ *syn*-XI	+9065 (t in d, CF) −7672 (s, =NF)[e]	4.74 (d in d, $CH_2{}^a$)	46	4.2		10		
 $CH_2{}^aF^a\text{—}\overset{\overset{N\text{—}F^b}{\Vert}}{C}\text{—}CH_2{}^bNF_2{}^c$ *anti*-X	+9705 (d in m, CF)[f] −6870 (t, NF_2)[e] −5920 (s, =NF)[e]	4.60 (d in d, $CH_2{}^a$) 5.50 (t in t, $CH_2{}^b$)	47	2.3	28	2.4	2.4	2.4
 $CH_2{}^aF^a\text{—}\overset{\overset{N\text{—}F^b}{\Vert}}{C}\text{—}CN$ *anti*-XI	+9480 (d in d, CF) −6856 (s, =NF)[e]	4.63 (d in d, $CH_2{}^a$)	46	2.9		~6.0		

[a] All spectra were run neat using an external reference. [b] From F-112 (1,2-difluoro-1,1,2,2-tetrachloroethane). [c] Singlets, doublets, and triplets are denoted by s, d, and t, respectively; thus t in d in t means a triplet, each peak split into doublets, each doublet split into triplets. [d] The chemical shift is referred to the center of the multiplets. [e] All the resonances of the fluorine attached on nitrogen are relatively broad peaks, owing to the quadripolar relaxation of the N^{14} nucleus, and fine spin-spin couplings with other fluorines and with protons is obscured. [f] The multiplet (m) is composed of 12 peaks.

$CH_2{}^a$ to lower magnetic fields (deshielded) in *anti*-XI in comparison with *syn*-XI.

When the N_2F_4 addition to allene was run in *o*-dichlorobenzene in the presence of sodium fluoride,[4] a cleaner reaction took place with little accompanying decomposition products. Gas chromatography of the products (80–90% yield) gave mainly two components which were identified as *syn*-3-fluoro-2-(N-fluorimino)-propionitrile (XI) and *syn*-1-difluoramino-3-fluoro-2-(N-fluorimino)propane (X) in a 3:5 ratio. This stereospecificity is surprising because the initial reaction of N_2F_4 with allene is assumed to result in the formation of the 1:1 adduct IX, which under the reaction conditions rearranges to give equal amounts of the products *syn*- and *anti*-X. The presence of sodium fluoride should have affected the elimination of 2 moles of hydrogen fluoride only from the *syn* isomer X under these conditions (70°) to give *syn*-3-fluoro-2-(N-fluorimino)-propionitrile (XI) without affecting the *anti* isomer X. The presence of only traces of *anti*-X in the mixture suggests that it was formed in trace amounts initially. This preferential formation of *syn*-X is therefore caused by the influence of sodium fluoride in the rearrangement of IX. In the absence of fluoride ion IX rearranges indiscriminately and a mixture of *syn*- and *anti*-X is obtained. In the presence of fluoride ion, the rearrangement becomes stereospecific, possibly *via* attack of a fluoride ion as depicted below, to give only *syn*-X,



(10)

which partially dehydrofluorinates in the presence of sodium fluoride to yield *syn*-XI.

Experimental Section[25]

General Procedure. (Caution Must Be Exercised in the Handling of N_2F_4![14])—These reactions were carried out in 80- or 240-ml Hastelloy C-lined shaker tubes unless otherwise specified, behind a barricade. **Remote operation during N_2F_4 reaction is imperative, and adequate shielding is essential** for work-up of the products![14] Quantities of reactants should be held to a minimum. All distillations were carried out behind shields, and a distillation chaser such as Halocarbon Oil (Halocarbon Products Corp., Series 12-21) was employed to prevent overheating of the pot residue.

2,3-Bis(difluoramino)-1,1,1,4,4,4-hexafluoro-2-butene (Ia).—An 80-ml shaker tube was charged with 10.0 g (0.062 mole) of hexafluoro-2-butyne[26] and 11.7 g (0.11 mole) of N_2F_4 and heated at 170° for 1 hr. The tube was cooled quickly to 60–70°, and the reaction mixture was distilled into an evacuated cylinder cooled at −196° to give a total of 22 g of crude product. Unreacted starting materials were removed by applying vacuum at −78° (1–2 mm), to leave behind as a liquid 15.9 g (96–97% yield) of crude adduct. Gas chromatographic analysis[27] of this liquid showed it to be principally (92%) a 42:58 mixture of the *cis-trans* isomers of Ia. A minor amount (1%) of the rearranged isomer IIa was also present, as well as minor amounts (5% total) of other by-products.

The *trans* and *cis* isomers were separated and purified by preparative-scale gas chromatography (1 in. × 12 ft column, 0°).[27] The *trans* isomer was eluted first (31 min) as a colorless liquid, bp 49° (DTA) (solid at −78°), with infrared absorption bands at 8.25 (CF), 11.2 (NF), and 11.4 μ (NF). Principal peaks in the mass spectrometric analysis are summarized in Table III. The *cis* isomer was eluted next (52 min) as a colorless liquid, bp 56° (DTA) (liquid at −78°). The infrared spectrum showed

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(25) Boiling points and melting points are uncorrected. Infrared spectra were measured on a Perkin-Elmer recording spectrophotometer, Model 21, and the listings of infrared bands include those which are relevant to the structural assignments. Fluorine nmr spectra are summarized for each compound in Tables I and II. They were obtained with a high-resolution spectrometer and associated electromagnet (Varian Associates), operating 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 (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.

(26) Columbia Organic Chemical Co., Inc., Columbia, S. C.

(27) Gc analyses were carried out on a 0.25-in. column, packed with 20% of the ethyl ester of perhalooctanoic acid (Kel-F Acid 8114, 3M Co. trademark) on firebrick. Helium carrier gas flow was 60 ml/min. The column length and separation temperature were varied depending upon the volatility of the components to be separated. Typical conditions include the use of a 12-ft column at 0 or 25° and a 6-ft column at 0, 25, and 50°.

TABLE III

MASS SPECTRUM

m/e	Ion	Rel intensity, %
31	CF^+	8.41
50	CF_2^+	5.97
69	CF_3^+	100.00
76	$C_2F_2N^+$	3.50
114	$C_2F_4N^+$	5.97
176	$C_4F_6N^+$	3.74
247	$C_4F_9N_2^+$	12.90
266	$C_4F_{10}N_2^+$(P)	None

absorption bands at 6.15 (weak, C=C), 8.0 (CF), 11.35 (NF), and 11.75 μ (NF).

Anal. Calcd: mol wt, 266. Found: mol wt, 271 (gas density).

Major amounts of the rearranged isomer IIa were obtained when the thermal reaction was carried out at a higher temperature for a longer time. For example, reaction of 17 g (0.10 mole) of hexafluoro-2-butyne with 11.9 g (0.11 mole) of N_2F_4 at 195° for 5 hr gave 27.2 g of crude product. The starting materials were removed by distillation, as described above, and the residue was distilled through a 10-in. spinning-band still to give 16.7 g (63%) of colorless liquid, bp 43–47°. Gas chromatographic[27] analysis of the liquid showed it to contain 56% **2-difluoramino-3-(N-fluorimino)-1,1,1,2,4,4,4-heptafluorobutane** (IIa) which eluted first from the column, (gc retention time, 21.5 min), 13% *trans* olefin Ia, and 11% other NF containing products. Among these was a compound assigned the structure, **2,3-bis(N-fluorimino)-1,1,1,4,4,4-hexafluorobutane:** gc elution time 13 min; infrared maxima for C=N at 6.1 and 6.15, for CF at 7.75 and 8.25, and for NF at 10.1 and 10.8 μ; mass spectrometric analysis peak at *m/e* 228 corresponding to $C_4F_8N_2$ (parent ion). The rearrangement product IIa was further purified by gas chromatography and was obtained as a colorless liquid, bp 47°. Infrared maxima were present at 6.15 (strong, C=N), 8.0–8.25 (CF), and NF bands at 10.5, 10.8, and 11.3 μ. Principal peaks in the mass spectrometric analysis are summarized in Table IV.

TABLE IV

MASS SPECTRUM

m/e	Ion	Rel intensity, %
31	CF^+	9.72
50	CF_2^+	4.55
69	CF_3^+	100.00
76	$C_2F_2N^+$	4.78
114	$C_2F_4N^+$	9.16
119	$C_2F_5^+$	23.92
247	$C_4F_9N_2^+$	0.15 (largest mass seen)
266	$C_4F_{10}N_2^+$(P)	None

Anal. Calcd for $C_4F_{10}N_2$: F, 71.41; mol wt, 266. Found: F, 71.30, 71.56; mol wt, 268 (gas density).

Ultraviolet Light Catalyzed Rearrangement of *cis*-Ia.—A 140-ml quartz tube was charged with 0.54 g of *cis*-Ia, and the evacuated tube was irradiated with a low-pressure mercury resonance lamp (mainly 2537 A) for 1.7 hr. The tube was cooled at −78°, and the volatiles were distilled off at 1 mm (0.05 g). The residue (0.49 g) was shown by gas chromatography to consist of 53% rearranged isomer IIa together with several minor components. None of the original *cis* isomer Ia remained.

2,3-Bis(difluoramino)perfluoro-2-heptene (Ib).—A mixture of 20 g (0.064 mole) of perfluoro-2-heptyne,[28] 15.6 g (0.15 mole) of N_2F_4, and 20 g of Halocarbon Oil[29] was heated in a 240-ml Hastelloy C lined shaker tube at 188° for 3 hr. The tube was cooled, and excess N_2F_4 was vented. The liquid reaction product was distilled from the Halocarbon Oil residue at reduced pressure to give 21.2 g (80%) of crude adduct. Gas chromatographic analysis[27] (2-m column, 59°) indicated a major component (45% over-all yield), presumably *trans*-Ib, which eluted first (10.5 min) and was isolated pure as colorless liquid, bp 114° (DTA). Infrared maxima were found at 6.19 (w, C=C), 8.0–8.5 (CF) and NF bands at 11.25, 11.7, and 12.17 μ.

Anal. Calcd for $C_7F_{16}N_2$: F, 73.06; N, 6.73. Found: F, F, 73.34; N, 7.78, 8.06.

The minor component, presumably *cis*-Ie, which eluted later (14.7 min) in 9% over-all yield was also isolated. The remainder of the material separated on the column was not collected, but was presumably a mixture of the rearrangement products IIb and IIIb.

Reaction of N_2F_4 with Dicycanoacetylene.—A mixture of 5.3 g (0.07 mole) of dicyanoacetylene[30] and 12.4 g (0.12 mole) of N_2F_4 was heated at 141° for 5 hr. The tube was cooled, the volatiles (7.1 g) which consisted largely of unchanged N_2F_4 were removed, and the yellow liquid residue (8 g) was analyzed by gas chromatography[27] at 70° on a 2-m column with a 25-ml/min helium flow rate. A minor component that eluted first (6.3 min) was isolated and identified as **2,2-difluoro-3-(N-fluorimino)succinonitrile** (VI), a colorless liquid, bp 65° (DTA) (12% over-all yield). Infrared maxima were present at 4.40 (C≡N), 6.19 (C=N), 8.37 (CF), 8.78 (CF), and 10.56 μ (NF). Principal mass spectrometric ions are summarized in Table V.

TABLE V

MASS SPECTRUM

m/e	Ion	Rel intensity, %
12	C^+	11.84
31	CF^+	29.06
50	CF_2^+	23.17
52	$C_2N_2^+$	11.80
76	$C_2F_2N^+$	100.00
78	$C_3N_3^+$	15.51
128	$C_4F_2N_3^+$	40.08
147	$C_4F_3N_3^+$(P)	None

The major component (33% over-all yield) that eluted next (11 min) was the rearranged adduct, **2-difluoramino-2-fluoro-3-(N-fluorimino)succinonitrile** (IId), which was isolated as a colorless liquid, bp 82° (DTA). Infrared maxima were found at 4.42 (C≡N), 6.22 (C=N), 8.4 (CF), and NF bands at 10.2, 10.7, and 11.1 μ. Principal mass spectrometric ions are summarized in Table VI.

TABLE VI

MASS SPECTRUM

m/e	Ion	Rel intensity, %
12	C^+	19.26
31	CF^+	73.35
38	C_2N^+	21.19
52	$C_2N_2^+NF_2^+$	38.72
57	C_2FN^+	35.59
71	$C_2FN_2^+$	17.29
76	$C_2F_2N^+$	100.00
109	$C_4FN_3^+$	20.66
128	$C_4F_2N_3^+$	99.52
161	$C_4F_3N_4^+$	0.96 (largest mass seen)
180	$C_4F_4N_4^+$(P)	None

Anal. Calcd for $C_4F_4N_4$: F, 42.21; N, 31.11. Found: F, 41.89; N, 30.80.

A second, minor component that eluted last (76 min) was isolated and identified as **2,3-bis(N-fluorimino)succinonitrile** (VII, 15% yield).[31] It was purified by sublimation and obtained as a colorless solid, mp 77–78°. Infrared maxima were found at 4.4 (C≡N), C=N bands at 6.31, 6.37, and 6.42 and NF bands at 10.10, 10.49, and 10.95 μ. No CF absorption bands were present.

Anal. Calcd for $C_4F_2N_4$: F, 26.75; N, 39.44; mol wt, 142. Found: F, 26.11; N, 39.42; mol wt, 142 (mass spectrum).

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(28) Perfluoro-2-heptyne was prepared by the thermal reaction of perfluoro-*n*-butyl iodide with trifluoropropyne (210° for 10 hr) followed by dehydrohalogenation with powdered potassium hydroxide at 85–115°. The crude product distilled from the reaction mixture as it was formed. Redistillation gave colorless perfluoro-2-heptyne, bp 54–56°. Fluorine nmr signals were present at −615 cps ($CF_3C{\equiv}C$), a triplet at +938 cps (CF_3), singlet at +2100 cps (${\equiv}CCF_2$), and singlets at +3285 cps (CF_2) and +3410 cps (CF_2) in agreement with the structure.

(29) Halocarbon Products Corp., Series 12-21. This inert diluent served to moderate the reaction.

(30) A. T. Blomquist and E. C. Winslow, *J. Org. Chem.*, **10**, 149 (1945).

(31) Compound VII may also be prepared by reaction of fumaronitrile with N_2F_4 at 145° in benzene solution in the presence of sodium fluoride.[b4]

In another N_2F_4–dicyanoacetylene reaction, the tube was heated at 135° for 1.5 hr and cooled quickly to 60–80°, and the reaction products were analyzed. Some unchanged dicyanoacetylene was recovered, but the major product was still the rearranged 1:1 adduct IId. Hence, thermal rearrangement of the initially formed olefin is very rapid in this case.

Reaction of N_2F_4 with Diphenylacetylene.—In an 80-ml shaker tube, a mixture of 8.5 g (0.048 mole) of diphenylacetylene, 5.2 g (0.05 mole) of N_2F_4, and 29 g of hexafluoropropylene dimer solvent was heated at 100° for 3 hr. The tube was cooled, and the liquid product was dissolved in petroleum ether (bp 60–90°) and decolorized by passage through a column of acid-washed alumina. The solvent was evaporated and the residue was distilled (Halocarbon Oil chaser) to give 4.6 g (34%) of **1-difluoramino-1-fluoro-2-(N-fluorimino)-1,2-diphenylethane** (IIe), as a yellow distillate, bp 98° (0.3 mm), $n^{25}D$ 1.5272. Infrared maxima were present at 3.25 (CH), C=N bands at 5.84, 6.15, 6.22, and 6.3, CF band at 8.1, and NF bands at 10.37, 10.75, 11.20, and 11.9 μ. Ultraviolet maxima were present at 220 mμ (ε 9500), 263 (1890), and 269 (1275).

Anal. Calcd for $C_{14}H_{10}F_4N_2$: C, 59.57; H, 3.57 F, 26.93; N, 9.93. Found: C, 60.69; H, 4.33; F, 26.91; N, 9.91.

Reaction of N_2F_4 with Methylphenylacetylene.—A 240-ml shaker tube was charged with 21.0 g (0.18 mole) of methylphenylacetylene[32] and 19.5 g (0.19 mole) of N_2F_4, and heated at 85° for 3 hr. The tube was cooled, and the brown liquid residue was distilled (Halocarbon Oil chaser) to give 13.3 g (32%) of a colorless liquid, bp 74–76° (3.0 mm). A gas chromatographic analysis on a 1-m column packed with 20% silicone-703 on Columnpak at 148° and a 120-ml/min helium flow showed two main components in 12% (7.75-min retention time) and 86% ratio (12.6-min retention time). Infrared maxima were present at 3.25 (CH), 3.40 (CH_3), 6.15 (C=N), 6.3 (C=N), 8.1 (CF), and NF bands at 10.75, 11.16, and 11.60 μ. Ultraviolet absorption maxima (EtOH) were present at 250 mμ (ε 844), 256 (750), 262 (700), and 269 (423).

Anal. Calcd for $C_9H_8F_4N_2$: C, 49.09; H, 3.66; F, 34.52; N, 12.73; mol wt, 220. Found: C, 49.71; H, 3.77; F, 34.46; N, 12.71; mol wt, 220 (mass spectrum).

Reaction of N_2F_4 with Phenylpropiolyl Fluoride.—A mixture of 11.7 g (0.079 mole) of phenylpropiolyl fluoride[33] and 9.2 g (0.088 mole) of N_2F_4 was heated at 70° for 2 hr. The tube was cooled and vented, and the brown, liquid residue was distilled under a nitrogen atmosphere to give 13 g (55%) of adduct as a colorless liquid, bp 35–36° (0.5 mm). Infrared maxima were found at 5.36 (C=O), 6.12 (C=N), and NF bands at 10.3, 10.67, 11.15, and 11.60 μ. Ultraviolet maxima were found at 270 mμ (ε 4050), 264 (1045), 257 (1060), and 225 (4050).

An **anilide** was prepared from IIIf by reaction with aniline in ether solution. It was obtained in quantitative yield after recrystallization from cyclohexane as a solid, mp 166.5–167.5°. Infrared absorptions (KBr) were found at 5.93 (C=O) and 6.00 μ (C=O). An ultraviolet maximum (EtOH) was found at 233 mμ (ε 11,600.)

Anal. Calcd for $C_{15}H_{11}F_4N_3O$: C, 55.39; H, 3.41; F, 23.37; N, 12.92. Found: C, 55.64; H, 3.72; F, 23.17; N, 12.56.

Reaction of N_2F_4 with 1,1,1-Trifluoropropyne.—In an 80-ml shaker tube, a mixture of 6 g (0.064 mole) of trifluoropropyne,[33] 10.4 g (0.10 mole) of N_2F_4, and 14 g of Halocarbon Oil[29] was heated at 155° for 1.5 hr. The tube was cooled and the products were distilled into a cylinder cooled at −196°. Unreacted starting material was distilled from the products at −95° (1–2 mm), and a liquid residue of 10 g remained. Gas chromatographic analysis[27] (12-ft column, 25°) showed the presence of a number of components and two were isolated. The one that eluted first (6.15 min) was tentatively identified as a mixture of *syn* and *anti* isomers of $CF_3C(=NF)CHF_2$ with infrared absorption at 6.02 (C=N), CF bands at 8.19, 8.29, and 9.05 and an NF band at 10.55 μ. Principal ions in the mass spectrometric analysis are summarized in Table VII.

The major product (16.25 min) was **1-difluoramino-2-(N-fluorimino)-1,3,3,3-tetrafluoropropane**, $CF_3C(=NF)CFNHF_2$ (IIc) isolated as a colorless liquid with infrared absorption at 6.04 (C=N), and NF bands at 10.2, 10.6, and 10.87 μ. The proton resonance spectrum showed eight bands of equal intensity at τ 5.23, 4.96, 4.94, 4.66, 4.45, 4.20, 4.13, and 3.86. Principal mass spectrometric ions are summarized in Table VIII.

TABLE VII

MASS SPECTRUM

m/e	Ion	Rel intensity, %
31	CF^+	14.07
50	CF_2^+	8.07
51	CF_2H^+	100.00
69	CF_3^+	53.10
76	$C_2F_2N^+$	4.78
77	$C_2F_2NH^+$	2.72
96	$C_2F_3NH^+$	4.32
146	$C_3F_5NH^+$	1.22
165	$C_3F_6NH^+$(P)	1.97

TABLE VIII

MASS SPECTRUM

m/e	Ion	Rel intensity, %
31	CF^+	14.21
51	CF_2H^+	48.65
58	C_2FNH^+	8.61
69	CF_3^+	100.00
114	$C_2F_4N^+$	10.63
146	$C_3F_5NH^+$	11.28
179	$C_3F_6N_2H^+$	0.14 (largest mass seen)
198	$C_3F_7N_2H^+$(P)	None

Reaction of N_2F_4 with 2,4-Hexadiyne.—A 240-ml shaker tube was charged with 12.5 g (0.16 mole) of 2,4-hexadiyne,[34] 19.0 g (0.18 mole) of N_2F_4, and 23 g of carbon tetrachloride, and the tube was heated at 70° for 3 hr. The tube was cooled and vented, and the solvent was removed from the product to leave a brown, residual liquid. Distillation of this liquid (Halocarbon Oil chaser) gave 12.3 g (42.5%) of colorless product, bp 72–73° (27 mm), $n^{25}D$ 1.4041.

Anal. Calcd for $C_6H_6F_4N_2$: C, 39.57; H, 3.32; F, 41.73; N, 15.38. Found: C, 40.11; H, 3.21; F, 41.32; N, 15.71.

Infrared maxima were present at 3.3, 3.4 (CH_3), 4.4 (C≡C), 6.15, 6.3 (C=N), and NF bands at 10.75, 11.08, and 11.55 μ. Only end absorption was present in the ultraviolet spectrum. The F^{19} nmr spectrum had a number of peaks of various intensity between −5000 and −6000 cps (NF peaks). The strongest peak was a singlet at −5310 cps whose intensity varied, (stronger in relation to the others, when the N_2F_4 + hexadiyne reaction was allowed to take place at 50° instead of 70°). Also, there were two single peaks at +3600 and +3820 cps (CF). It is assumed that a mixture of all three compounds, IVa (the −5310 cps is assigned to the two NF_2 groups), IVb, and IVc (the two peaks at +3600 and +3820 cps are assigned for the CF resonance, the NF peaks being unresolved between the −5000- and −6000-cps region) are present. A gas chromatographic analysis on a 1-m column packed with 20% silicone-703 on Columpak at 148° and 120 ml/min helium flow did not resolve the mixture.

The Reaction of N_2F_4 with Allene. A. In the Presence of Sodium Fluoride.—In a 240-ml tube containing 7.5 g (0.19 mole) of allene, 20 g of *o*-dichlorobenzene, and 10 g of sodium fluoride powder was condensed 15 g (0.145 mole) of N_2F_4, and the tube was sealed and heated at 70° for 6 hr. The products of two such runs were combined, and the volatiles were distilled into a Dry Ice trap, *in vacuo*, to give 18–20 g of product. A gas chromatographic analysis[27] on a 6-ft column at 50° gave three peaks in a ratio of about 30:50:1 in order of elution (retention times, respectively, 16, 22, and 30 min). Preparative gas chromatography on a 1-in. × 6 ft column[27] at 50° separated the two main components. The component that eluted first (retention time 16 min) had a boiling point of 100° and was identified as the *syn*-**3-fluoro-2-(N-fluorimino)propionitrile** (XI). Infrared maxima were found at 3.36 and 3.44 (CH), 4.44 (C—N), 6.17 (C=N), and NF bands at 9.41, 9.85, and 10.22 μ.

Anal. Calcd for $C_3H_2F_2N_2$: F, 36.52; N, 26.92; mol wt, 104. Found: F, 36.62; N, 26.02; mol wt, 104 (mass spectrum).

The next component (retention time 22 min) had a boiling point of 101° and was identified as the *syn*-**1-difluoramino-3-**

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[32] Methylphenylacetylene was prepared by reaction of phenylethynyllithium with methyl iodide: S. Dixon, *J. Org. Chem.*, **21**, 400 (1956).

[33] W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 543 (1960).

[34] 2,4-Hexadiyne was prepared according to the procedure of J. C. Kauer, U. S. Patent 2,952,718 (1960).

fluoro-2-(N-fluorimino)propane (X). Infrared maxima (neat) were found at 3.33, 3.37, and 3.44 (CH), and 6.05 μ (C=N).

Anal. Calcd for $C_3H_4F_4N_2$: C, 25.01; H, 2.80; F, 52.75; N, 19.45; mol wt, 144. Found: C, 26.18; H, 2.65; F, 52.74; N, 19.37; mol wt, 144 (mass spectrum).

The third and minor component (30-min retention time) was the *anti*-**1-difluoramino-3-fluoro-2-(N-fluorimino)propane** (X) which is characterized below.

B. In the Absence of Sodium Fluoride.—The reaction of N_2F_4 with allene was repeated as described above, with the exception that the sodium fluoride was omitted. There was obtained a dark reaction product from which only 14 g of volatile product was obtained. A gas chromatographic analysis[27] on a 6-ft column at 50° again gave three peaks but this time in a ratio of about 1:10:13, corresponding to *syn*-XI, *syn*-X, and *anti*-X (16-, 22-, and 30-min retention times, respectively). The 30-min retention-time peak was separated by preparative gas chromatography, bp 110°, and identified as *anti*-**1-difluoramino-3-fluoro-2-(N-fluorimino)propane** (X). Infrared maxima (neat) were found at 3.29 (CH), 3.37 (CH), and 6.02 μ (C=N).

Anal. Calcd for $C_3H_4F_4N_2$: F, 52.75; N, 19.45; mol wt, 144. Found: F, 51.45; N, 19.18; mol wt, 144 (mass spectrum).

syn-**3-Fluoro-2-(N-fluorimino)propionitrile (XI).**—A well-stirred mixture of 5.0 g of *syn*-1-difluoramino-3-fluoro-2-(N-fluorimino)propane, 10 ml of *o*-dichlorobenzene, and 5.0 g of powdered sodium fluoride was heated at 100° for 18 hr. The volatiles were distilled into a −78° trap, *in vacuo*, and this liquid was redistilled to give 3.0 g (82%) of *syn*-3-fluoro-2-(N-fluorimino)propionitrile as a colorless liquid, bp 98°, n^{25}_{D} 1.3730, homogeneous to gas chromatography and showing infrared, nmr, and mass spectra identical with those of the sample prepared above.

anti-**3-Fluoro-2-(N-fluorimino)propionitrile (XI).**—A well-stirred mixture of 3.2 g of *anti*-1-difluoramino-3-fluoro-2-(N-fluorimino)propane, 10 ml of *o*-dichlorobenzene, and 5.0 g of powdered sodium fluoride was heated at 150° for 18 hr. The product was distilled into a −78° trap, *in vacuo*, and this liquid was redistilled to give 2.2 g (90%) of *anti*-3-fluoro-2-(N-fluorimino)propionitrile as a colorlesss liquid, bp 97–98°, n^{25}_{D} 1.3810, homogeneous to gas chromatographic analysis[27] (retention time 23.5 min). The infrared spectrum (neat) showed peaks at 3.37 (CH_2), 4.44 (C≡N), 6.18 (C=N), 9.3 (NF), and 10.85 μ (NF).

Anal. Calcd for $C_3H_2F_2N_2$: C, 34.62; H, 1.94; F, 36.52; N, 26.92; mol wt, 104. Found: C, 35.27; H, 1.74; F, 36.48; N, 26.03; mol wt, 104 (mass spectrum).

Registry No.—*cis*-Ia, 13052-49-8; *trans*-Ia, 13052-50-1; *cis*-Ib, 13100-47-5; *trans*-Ib, 13015-97-9; *cis*-Ig, 13015-98-0; *trans*-Ig, 13015-99-1; IIa, 13016-00-7; IIc, 13016-01-8; IId, 13000-66-3; IIe, 10036-38-1; IIIf, 13016-03-0; IIIf anilide, 13016-04-1; IIIg, 13000-67-4; IVa, 13016-05-2; VI, 13016-06-3; VII, 13016-07-4; *syn*-X, 13016-08-5; *anti*-X, 13016-09-6; *syn*-XI, 13016-10-9; *anti*-XI, 13016-11-0; tetrafluorohydrazine, 3744-07-8; allene, 463-49-0; 2,3-bis(N-fluorimino)-1,1,1,4,4,4-hexafluorobutane, 13016-12-1; *syn*-$CF_3C(=NF)CHF_2$, 13016-13-2; *anti*-$CF_3C(=NF)CHF_2$, 13016-14-3; perfluoro-2-heptyne, 13016-15-4.

Acknowledgment.—The authors are indebted to the late Mr. Miller Nelson for assistance in carrying out the N_2F_4 reactions, to members of the Physical and Analytical Division for gas chromatography, infrared, mass spectral, and nmr analyses, and to Dr. E. M. Atadan of the Explosives Department for generous supplies of N_2F_4.

Chlorofluorocarbene and Dichlorocarbene. Comparative Reactivities in Addition to Olefins[1,2]

ROBERT A. MOSS AND ROBERT GERSTL

Wright Laboratory, School of Chemistry, Rutgers, The State University, New Brunswick, New Jersey

Received January 17, 1967

Relative rates of addition of chlorofluorocarbene to tetramethylethylene (31.0), trimethylethylene (6.5), isobutene (1.00), *cis*-butene (0.14), *trans*-butene (0.097), and 1-butene (0.0087) have been determined at −10°. The carbene was generated from *sym*-tetrachlorodifluoroacetone and potassium *t*-butoxide. An analogous set of data was obtained for dichlorocarbene (from chloroform and butoxide). The newly determined rates, relative to isobutene, were *cis*-butene (0.23), *trans*-butene (0.15), and 1-butene (0.011). A discussion of the factors influencing these rates is included. The importance of steric factors both in over-all addition rates and in chlorofluorocarbene stereoselectivity is stressed. Apparent reactions of chlorofluorocarbene aud potassium *t*-butoxide were observed.

Several investigators have tried to assess quantitatively electronic interactions between carbenic centers and various substituents. Perhaps the most basic attempt was that of Hine and Ehrenson, who, from extensive studies of haloform hydrolysis, derived parameters which reflected "the relative abilities of the four halogens to supply electrons to the deficient carbon atom."[3] Others attempted to study substituent carbene interactions by examining how carbene "electrophilicity"[4a,b] altered with substituent variation.[4c] Though many studies have been carried out to demonstrate the electrophilic character of carbene reactions,[5] these attempts to formally correlate electrophilicity and substituent variation have been fewer in number, and modest in success. Thus, Doering and Henderson compared the selectivity of dichlorocarbene over a set of olefinic substrates with the selectivity of dibromocarbene over the same set.[4c] Closs and Schwartz attempted a similar comparison of dichlorocarbene and chlorocarbene.[6] Closs and Moss studied the relative selectivities of substituted phenylcarbenes, over a constant set of olefins, as a function of substituent.[7]

For reasons appearing below, none of these attempts were particularly successful. We were therefore encouraged by our observation that, over a limited set of olefins, logarithms of relative addition rates of chlorofluorocarbene (CFC) and dichlorocarbene (DCC) ap-

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(1) Part IV in the series, "Stereoselectivity of Carbene Intermediates."

(2) Part III: R. A. Moss and R. Gerstl, *Tetrahedron*, **23**, 2549 (1967).

(3) J. Hine and S. J. Ehrenson, *J. Am. Chem. Soc.*, **80**, 824 (1958), and references therein.

(4) (a) J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954); (b) P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956); (c) W. v. E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958).

(5) See (a) W. Kirmse, "Carbene Chemistry," Academic Press Inc., New York, N. Y., 1964; (b) J. Hine, "Divalent Carbon," Ronald Press Co., New York, N. Y., 1964.

(6) G. L. Closs and G. M. Schwartz, *J. Am. Chem. Soc.*, **82**, 5729 (1960).

(7) G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964).