

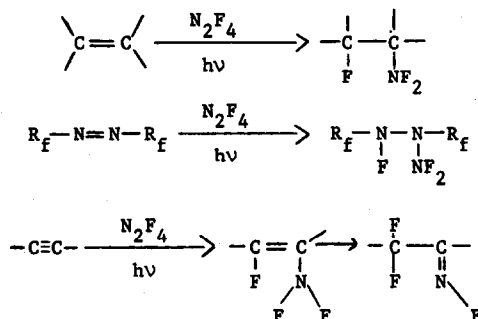
PHOTODIFLUORAMINATION OF  $\text{CF}_3\text{C}^{15}\text{N}$ : EVIDENCE FOR INTERMEDIATE  
FORMATION OF AN ALKYLFLUORODIAZENE

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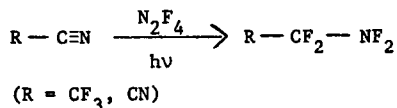
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Irradiation at 253.7 nm of alkenes,<sup>1</sup> azo compounds,<sup>2</sup> and alkynes<sup>3,4</sup> with tetrafluoro-  
hydrazine in the gas phase leads to the addition of the elements of  $\text{NF}_3$  across the unsaturated  
linkage.



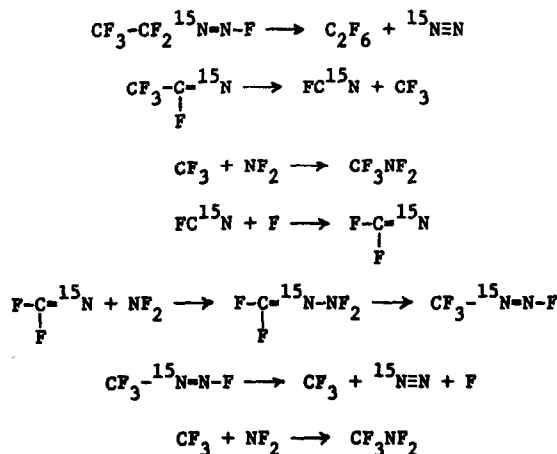
In the case of alkynes, the intermediate adduct rearranges to give the isomeric N-fluorimine.

However, when nitriles are irradiated with  $\text{N}_2\text{F}_4$ , apparent perfluorination of the nitrile  
group takes place.<sup>5,6,7</sup>



From the reaction of  $\text{CF}_3\text{CN}$  and  $\text{N}_2\text{F}_4$ , Glemser<sup>5</sup> reported the formation of  $\text{C}_2\text{F}_5\text{NF}_2$ . No other  
C-containing products were mentioned and several perfluorination mechanisms were suggested to  
account for this lone product. Dresdner<sup>6</sup> observed that irradiation of  $\text{N}_2\text{F}_4$  and  $(\text{CN})_2$  gave  
 $\text{F}_2\text{NCF}_2\text{CN}$ ,  $(\text{F}_2\text{NCF}_2)_2$ ,  $\text{C}_2\text{F}_5\text{NF}_2$ , and  $\text{CF}_4$ . The first two products represent perfluorination of  
nitrile groups. Although the results were contrasted to those obtained using other fluorinating

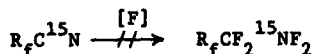
The significant amounts of  $\text{CF}_3\text{NF}_2$ ,  $\text{C}_2\text{F}_6$ , and excess  $\text{N}_2$  can be explained by the several terminating steps:



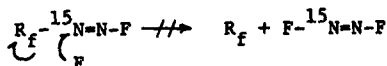
Decomposition of  $\text{R}_f\text{-}^{15}\text{N=N-F}$ , the fluorine analog of an alkyl diazene,<sup>10</sup> provides a simple route to  $\text{CF}_3\text{CF}_2\text{NF}_2$ ,  $\text{C}_2\text{F}_6$ , and  $\text{N}_2$  correctly labeled.

Although dimerization of perfluoromethyl radicals could furnish  $\text{C}_2\text{F}_6$ , the probability of  $\text{F}_3\text{C}$  collision with  $\text{NF}_2$  and  $\text{N}_2\text{F}_4$  is far greater than the probability of an encounter with another  $\text{F}_3\text{C}$ . Likewise, neither  $\text{C}_3\text{F}_8$  nor  $\text{C}_4\text{F}_{10}$  was observed from theoretically possible radical coupling combinations of the proposed perfluoroalkyl intermediates. The absence of  $\text{NF}_3(\text{F} + \text{NF}_2 \rightarrow \text{NF}_3)$  may be ascribed to the fact that  $\text{CF}_3\text{CN}$  is in much higher concentration than  $\text{NF}_2$ , and to the high reactivity of atomic F. On the other hand,  $\text{NF}$ , in analogy with  $\text{O}_2$ , is likely to be in its ground triplet state<sup>11</sup> and will tend to be scavenged by the most abundant radical species in the mixture; i.e., by  $\text{NF}_2$ .

Clearly ruled out by the results is any process requiring direct fluorination of the nitrile group.



Since no  $^{15}\text{N}$ -labeled  $\text{N}_2\text{F}_2$  was observed, generation of  $\text{R}_f\cdot$  via the addition-elimination also



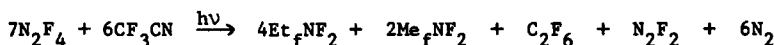
may be dismissed.

Hydrocarbon nitriles are presently under investigation.

agents ( $F_2$ ,  $CoF_3$ , and  $AgF_2$ ), the mechanism of perfluorination was not discussed.

We wish to report now a mass balance for the photo-initiated reaction of  $N_2F_4$  with  $CF_3CN$  and the fate of the nitrogen atom in  $CF_3C^{15}N$ .

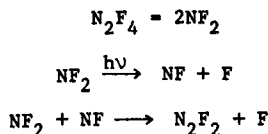
Irradiation with a high pressure mercury lamp equipped with a Vycor filter of  $CF_3CN$  (145 torr) and  $N_2F_4$  (223 torr) in a 990 ml-reactor for one hour resulted in 78% conversion of the  $CF_3CN$  (i.e., 22% of the  $CF_3CN$  recovered unchanged) and the formation of difluoramino-pentafluoroethane, difluoramino-trifluoromethane, hexafluoroethane, difluorodiazene, and molecular nitrogen in proportions approximated by the following equation.



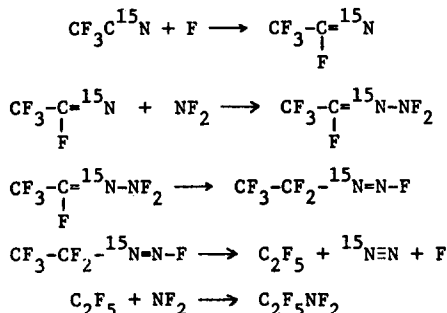
The products were identified by infrared, mass, and  $^{19}F$  NMR spectroscopy. Quantities were determined by gas chromatography at  $0^\circ$  using a Aerograph Autoprep model A-700 equipped with a 30' QF1 column<sup>8</sup> and by quantitative mass spectroscopy.

When nitrogen-15 labeled trifluoroacetonitrile<sup>9</sup> was used as the starting material the label was found by mass spectroscopy to be exclusively in molecular nitrogen as  $^{14}N^{15}N$ . There was no notable reaction between  $N_2F_4$  and  $CF_3CN$  either upon standing together for two hours at room temperature, or upon irradiation through a Pyrex filter for one hour. Furthermore,  $CF_3CN$  exhibited no change after irradiation through a Vycor filter for one hour.

These results can be accommodated readily by a mechanism analogous to that described for photodifluoramination of substrates containing a carbon-carbon triple bond.<sup>3,4</sup> The initiation steps:



are followed by a short chain reaction:



## REFERENCES AND FOOTNOTES

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7. In one case, however, L. M. Zaborowski and J. M. Shreeve, *Inorg. Chem.*, **10** (2), 407 (1971) reported that irradiation of  $N_2F_4$  with trichloroacetonitrile formed only  $CCl_3NF_2$  and  $NF_2CCl_2CN$ .
8. Presence of  $N_2F_2$  was confirmed by infrared and mass spectroscopy only.  $N_2F_2$  was not identified in the gas chromatogram.
9.  $CF_3C^{15}N$  was synthesized from ethyltrifluoroacetate (Pierce Chemical Co.) by adaptation of the H. Gilman and R. G. Jones, *J. Amer. Chem. Soc.*, **65**, 1458 (1943) procedure using  $^{15}N$ -ammonia (Stohler Isotope Chemicals, Inc. 95%).
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