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PHOTODIFLUORAMINATION OF A SERIES OF HEXAFLUOROACETONE IMINES

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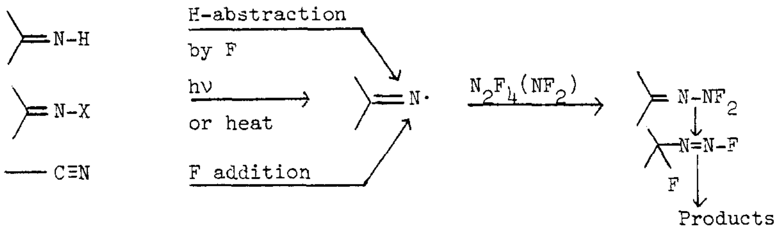
SUMMARY

Gas phase irradiation of N_2F_4 (NF_2) in the presence of hexafluoroacetone imine (I), N-chlorohexafluoroacetone imine (II), or N-bromohexafluoroacetone imine (III) resulted in the formation of products that correspond to either perhalogenation of the unsaturation or conversion of the substrate to a saturated halocarbon. The mechanism suggested involves the formation of an imino radical that reacts with $N_2F_4(NF_2)$ to produce N,N-difluorohydrazone, $(CF_3)_2C{=}N{-}NF_2$. A bimolecular homolytic displacement (S_H2') by Cl and F on the hydrazone forms an intermediate diazene which leads to the observed products. N-fluorohexafluoroacetone imine is inert to F atoms and NF_2 under the reaction conditions.

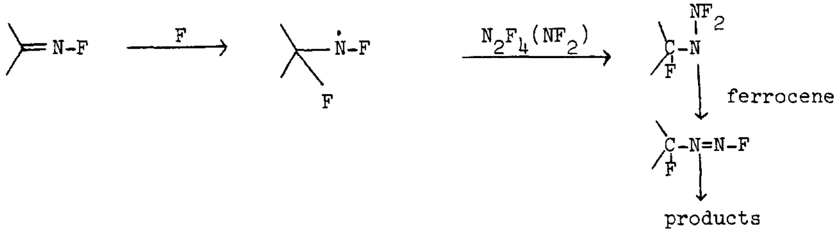
INTRODUCTION

Alkylfluorodiazenes, RN=NF, have been implicated as intermediates in the reaction of nitriles with N_2F_4. [1] This reaction is believed to involve addition of atomic fluorine (from photolysis of NF_2) to the carbon-nitrogen triple bond to produce imino radicals (RC(F)=N·). Capture of these intermediates by $N_2F_4(NF_2)$ leads to N,N-difluorhydrazones ($RC(F){=}NNF_2$) which tautomerize to fluoralkyldiazenes ($RCF_2N{=}NF$). Decomposition of the diazenes in the presence of $N_2F_4(NF_2)$ accounts for the final products, RCF_3, N_2, and RCF_2NF_2.

If this general hypothesis is correct then alternative methods of producing imino radicals in the presence of $N_2F_4(NF_2)$ should likewise give rise to alkylfluorodiazenes and products derived from diazene decomposition. To test this notion we studied the generation of imino radicals by H-abstraction from imines and by homolysis of the nitrogen-halogen bond in N-haloimines.



Since addition of atomic fluorine to the carbon-nitrogen triple bond occurs, we considered similar attack at the carbon-nitrogen double bond of imines a possibility In the case of a N-fluoroimine this path could lead to an alkyl trifluorohydrazine which might be converted to the diazene by defluorination with ferrocene.[2]



Consequently, we investigated the reactions of hexafluoroacetone imine (I), N-chlorohexafluoroacetone imine (II), N-bromohexafluoroacetone imine (III), and N-fluorohexafluoroacetone imine with N_2F_4.

RESULTS AND DISCUSSION

To ascertain the photolytic stability of the imine starting materials, we irradiated these reactants at 254 nm, the wavelength used for photolysis of NF_2·. Whereas $(CF_3)_2C{=}NF$ was found to be inert, $(CF_3)_2C{=}NCl$ decomposed to give principally CF_3Cl and CF_3CN along with several high molecular weight products. Previously, Middleton and Krespan reported that N-bromohexafluoroacetone imine underwent photolysis to give hexafluoroacetone azine, [3] presumably by way of an intermediate imino radical. Hexafluoroacetone imine was found by Toby and coworkers to yield mainly CF_3CN along with some CF_3H, but no C_2F_6; these observations were explained by invoking a vibrationally excited singlet imine.[4]

Photolysis of excess of N_2F_4 (NF_2) with N-fluorohexafluoroacetone imine at 254 nm for two hours resulted in no reaction involving the imine. This is the first unsaturated compound found to be stable to atomic fluorine generated by photolysis of NF_2. It is also interesting to note that although the N-F bond is cleaved in NF_2, the N-F bond of the imine and also of alkyl difluoroamines is unaffected. Neither the imine nor the amine absorbs radiation at 254 nm. Recent publications [5-8] deal with the solution phase chemistry of N-fluorohexafluoroacetone imine, but no free radical or photolytic reactions were reported. Photolysis of another perfluoroimine, $CF_3N{=}CF_2$, results in carbon-nitrogen cleavage, but no double bond addition products.[9]

In contrast to the N-F imine, irradiation of an equimolar mixture of N-chlorohexafluoroacetone imine (II) and N_2F_4 for one hour yielded two major products, 2-chloro-2-difluoraminohexafluoropropane (V) and 2-difluoraminoheptafluoropropane (VI). Minor products included 2-chloroheptafluoropropane (VII), 2,2-dichlorohexafluoropropane (VIII), and perfluoropropane (IX). At low pressures, chlorotrifluoromethane was also obtained. No CF_3CN was found in the product mixture, even at low pressure. However, CF_3CN is known to react with N_2F_4 under the reaction conditions.[1] In addition difluorodiazene, N_2F_2, generally formed when $N_2F_4(NF_2)$ is photolyzed at 254 nm [1], was isolated.

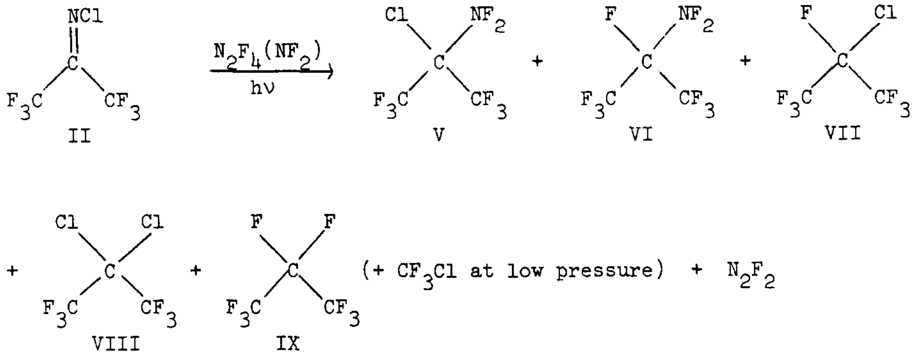


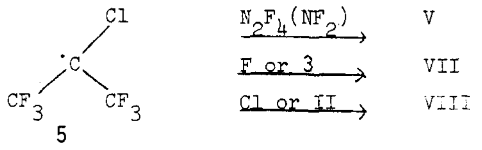
Table I summarizes the product distributions obtained at several different initial pressures. These results suggest that photolysis of the N-chloroimine results in homolytic cleavage of the nitrogen-chlorine bond. If the primary step was carbon-carbon bond cleavage, products containing less than three carbons would be expected, but such compounds were not observed except at low pressure when unimolecular decomposition of the imino radical 1 becomes important as shown in Scheme 1.

At high pressures bimolecular reactions dominate and radical 1 is converted largely to hydrazone 2 by N_2F_4 (NF_2). Although intramolecular rearrangement of 2 to diazene 3 followed by decomposition of the latter to give radical 4 can account for VI, VII, and IX, the presence of chlorine-containing compounds V and VIII suggests that another intermediate, 5, is also involved.

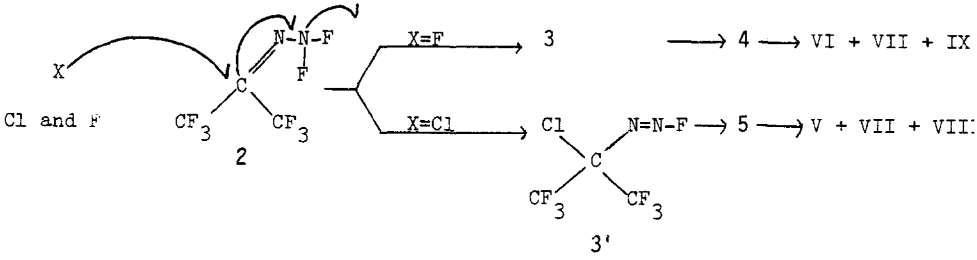
Table I

Relative Product Ratios from N_2F_4 + $(CF_3)_2CNCl$ Reactions

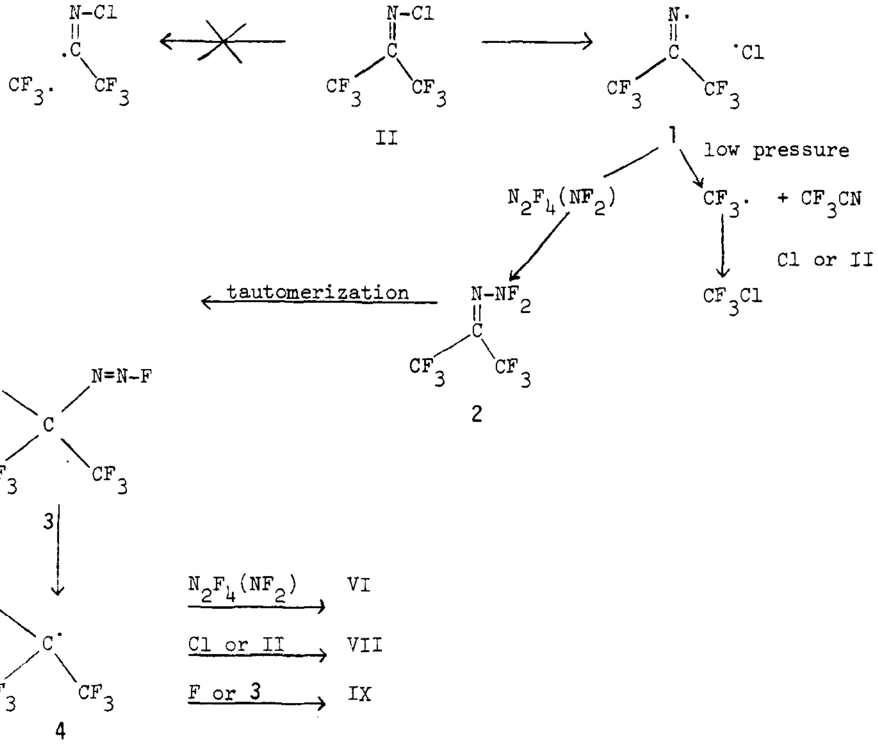
Reactants (torr)		Relative Ratios					
		$(CF_3)_2CFNF_2$	$(CF_3)_2CClNF_2$	$(CF_3)_2CFCl$	$(CF_3)_2CCl_2$	$(CF_3)_2CF_2$	CF_3Cl
$(CF_3)_2CNCl$ (50) N_2F_4 (50) CF_4 (300)	$\xrightarrow{h\nu}$	0.82	1.00	0.56	0.27	0.15	0.00
$(CF_3)_2CNCl$ (10) N_2F_4 (10)	$\xrightarrow{h\nu}$	1.18	1.00	0.63	0.11	0.32	0.83
$(CF_3)_2CNCl$ (17) N_2F_4 (17) Cl_2 (17)	$\xrightarrow{h\nu}$	0.42	1.00	0.55	0.28	0.25	0.61



If we assume intramolecular attack by both Cl (from photolysis of II) and F (from photolysis of NF_2) on 2 and concommitant loss of F from nitrogen, then both diazenes 3 and 3' can be formed, which respectively yield 4 and 5, the required precursors.



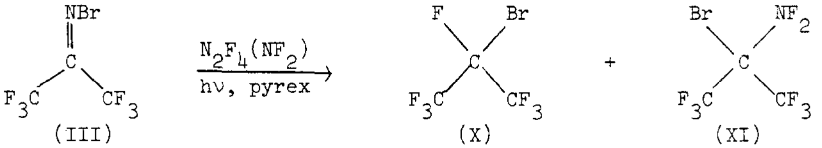
Scheme 1



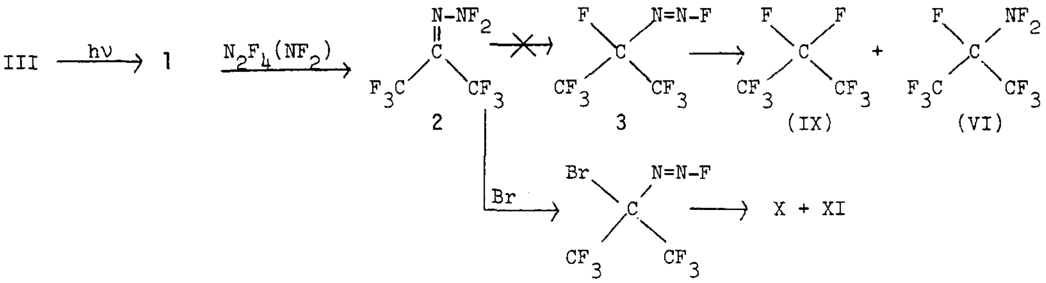
This transformation of 2 may be formulated as an S_H2' process. The driving force for such a reaction includes two factors. First, the energy changes are favorable: a strong C-X bond is formed and a weak N-F bond is broken. Second, the intermediate possesses excess vibrational energy that is most easily dissipated by loss of a F atom. Shobatake [10] observed a similar bond cleavage in the gas phase when 3-hexene was treated with atomic F.

Pyrolysis of N-chlorohexafluoroacetone imine (II) with N_2F_4 (3:1 molar ratio) gave trifluoroacetonitrile in addition to the compounds formed during photolysis. The imino radical 1 is able to undergo rapid unimolecular elimination under these conditions.[1] The close parallel between the photochemical and thermal reactions indicates that concerted 2 + 2 (photochemically allowed) collapse of 3 and 3' is not important.

Irradiation of five mmoles N_2F_4 and two mmoles of N-bromohexafluoroacetone imine (III) for three hours through a Pyrex filter resulted in the formation of mainly 2-bromoheptafluoropropane (X), along with 2-bromo-2-difluoraminohexafluoropropane (XI) but no perfluoropropane.

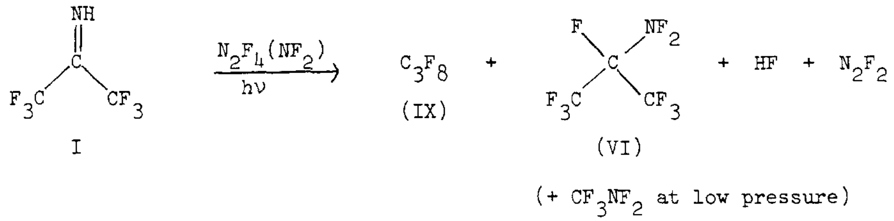


Under the reaction conditions, no free fluorine atoms are generated from NF_2 since NF_2 does not absorb above 380 nm.[11] The absence of perfluoropropane (IX) and 2-difluoraminoheptafluoropropane (VI) in the product mixture provides additional evidence that hydrazone 2 does not rearrange intramolecularly to diazene 3.



Therefore, as in the N-chloroimine case, an addition-elimination reaction (S_H2') is suggested.

Irradiation of N_2F_4 and hexafluoroacetone imine (I) at 254 nm led to the formation of mainly perfluoropropane (IX) and 2-difluoraminoheptafluoropropane (VI) along with HF and N_2F_2. Difluoraminotrifluoromethane, CF_3NF_2, was obtained at low pressure.



Fluorine atoms produced during the photolysis of NF_2 first abstract a hydrogen from I to form imino radical 1. Subsequent product formation occurs by the same pathway as described for the other imines which give rise to radical 1.

From these experiments, we conclude that despite its extreme reactivity, atomic fluorine does not add to a perfluoro imino linkage and that photolytic reactions between imines and N_2F_4 involve an imino radical intermediate. We suggest that capture of this species by $N_2F_4(NF_2)$ results in the formation of an N,N-difluorohydrazone and that reaction of the hydrazone by a bimolecular homolytic displacement (S_H2') yields diazenes that are the precursors of the final products.

EXPERIMENTAL SECTION

CAUTION: Nitrogen fluoride compounds, particularly N_2F_4 and N_2F_2 are potentially explosive.[5-7, 12-13] All reactions and manipulations were conducted in small quantities behind adequate shielding.

All reactant and product manipulations were conducted on a standard, medium-wall Pyrex high vacuum line equipped with high vacuum stopcocks. The N_2F_4 irradiation reactions were generally performed in a cylindrical Pyrex glass vessel fitted with a Hanovia water cooled quartz immersion well No. 19434, a mercury manometer, and a vacuum outlet. The light source was a 450 watt Hanovia high pressure mercury vapor lamp No. 679A-36 jacketed by a Hanovia 7910 Vycor filter (absolute cut-off 210 nm). Product separation procedures have already been described.[14]

Preparation of N-Fluorohexafluoroacetone Imine: Ten mmoles of 2-iodoheptafluoropropane and 20 mmoles of N_2F_4 were irradiated in a one liter Pyrex bomb for two hours. Iodine crystals formed on the vessel walls, and the gaseous products were distilled through several -126°C traps. The trapped products were condensed into a one liter flask containing 10 g ferrocene in 10 ml o-dichlorobenzene. The flask was sealed and heated with stirring to 90-100°C for 38 hours. The mixture was distilled through three traps: -86°C, -126°C, and -196°C. N-fluorohexafluorohexafluoroacetone imine was obtained in 70% yield from the -126°C trap. It was 90% pure as determined by ^{19}F NMR spectrometry; the impurity was 2-difluoraminoheptafluoropropane (VI).

Preparation of N-Bromohexafluoroacetone Imine: The method of Middleton and Krespan [2] was used with slight modification. Hexafluoroacetone imine (25 mmole) was slowly condensed onto methyl lithium (20 mmole) in an evacuated one liter flask. The solution was allowed to warm slowly to room temperature. The excess hexafluoroacetone imine and ether was pumped off. The flask was opened to a nitrogen atmosphere, and the salt was dissolved in 20 ml of benzonitrile. The

Preparation of N-Chlorohexafluoroacetone Imine: The method of Ruff [15] was modified by the use of a glass reaction vessel. Ten mmoles of hexafluoroacetone imine and 10 mmoles of dry chlorine were condensed onto 3.0 g CsF (transferred in a dry box) in an evacuated one liter flask. The mixture was allowed to stand at room temperature overnight. The mixture was then distilled through a -126°C trap and found to be composed of N-chlorohexafluoroacetone imine, hexafluoroacetone azine, and hexafluoroacetone in a ratio of 1:0.8:0.4.

Purification was accomplished by gas chromatography on a 10 ZFl column. N-chlorohexafluoroacetone imine was obtained in 40% yield (λ_{max} = 327.5 nm, ε = 35).

solution was cooled to 0°C, and bromine (20 mmole) in 10 ml of benzonitrile was added dropwise with stirring. The mixture was frozen with liquid nitrogen and degassed several times, and was finally distilled into a -196°C trap. N-bromohexafluoroacetone imine (7 mmole), approximately 75% pure, was obtained. The major impurities were hexafluoroacetone imine and hexafluoroacetone azine as determined by ^{19}F NMR.

Preparation of 2-Chloroheptafluoropropane: Two mmoles of 2-iodoheptafluoropropane and four mmoles of dry chlorine were condensed into an evacuated one liter Pyrex bomb and, after equilibration at room temperature, were irradiated for one hour. The mixture was distilled through -86°C and -196°C traps. The product was found in the second trap in 90% yield. ^{19}F NMR 81.4ϕ (d, J = 6.6 Hz), 144.6ϕ (septuplet, J = 6.6 Hz). Mass spectrum m/e (204, 206), (185, 187), 169, 150, (135, 137), 119, (116, 118), 100, (85, 87), 69, all signals display the proper isotope intensity. Infrared spectrum (μ) 7.38(M), 7.66(S), 7.96(S), 8.39(M), 8.80(S), 10.25(S), 13.15(W), 13.90(S).

Pyrolysis of II was done in a 350 ml monel bomb at 120°C for 19.5 hours. Product analysis was the same as for the photolysis.

All product spectra can be found in the literature [16] except for 2-chloro-2-difluoraminopropane (^{19}F NMR CF_3 71.4ϕ (t, J = 11 Hz), NF_2-37.3ϕ) and 2-bromo-2-difluoraminopropane (^{19}F NMR CF_3 78.4ϕ (t, J = 12 Hz), NF_2-44.6ϕ). The mass spectrum of each compound was consistent with its structure.

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