

Received: October 16, 1977

PHOTODIFLUORAMINATION OF NITRILES

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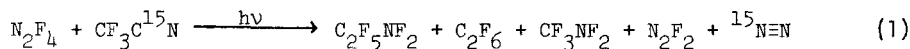
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SUMMARY

Gas phase irradiation of $N_2F_4(NF_2)$ in the presence of trifluoroacetonitrile, ^{15}N -trifluoroacetonitrile, or acetonitrile resulted in the formation of products that correspond to perfluorination of the unsaturation or to conversion of the substrate to a saturated fluorocarbon. The proposed mechanism involves atomic fluorine attack on the nitrile and subsequent rearrangement of the resulting N,N -difluorohydrazone, $R_2C(F)=NNF_2$, to an alkylfluorodiazene $R_2C(F)-N=N-F$. Decomposition of diazenes accounts for the observed products.

INTRODUCTION

In a brief earlier communication¹ we described the photodifluoramination of $CF_3C^{15}N$. The two principal organic products, $C_2F_5NF_2$ and C_2F_6 correspond, respectively, to perfluorination of the C-N triple bond and to conversion of the nitrile to a saturated fluorocarbon.

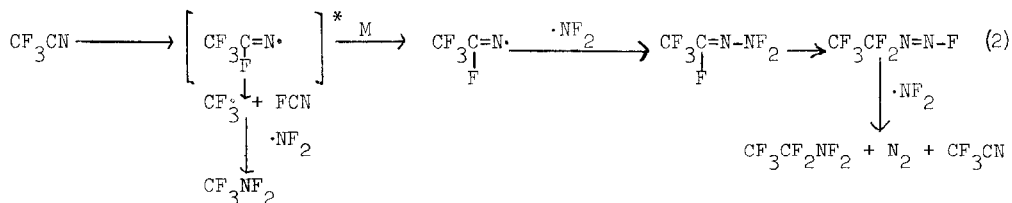


A mechanism to account for these observations was advanced that involves formation of $CF_3CF=^{15}NNF_2$, tautomerization of this intermediate to $CF_3CF_2^{15}N=NF$ which subsequently decomposes by several pathways. An explanation was also offered for the appearance of CF_3NF_2 which requires that C-C cleavage take place at some stage.

To extend the scope of the photodifluoramination of nitriles and to gain more information regarding the nature of the proposed intermediates, we studied the reaction of N_2F_4 with CF_3CN at various pressures and examined the photodifluoramination of CH_3CN , a substrate containing hydrogen atoms as well as the C-N triple bond.

RESULTS AND DISCUSSION

In the irradiation of CF_3CN and N_2F_4 at 254 nm, the ratio of $\text{C}_2\text{F}_5\text{NF}_2$ to CF_3NF_2 was found to increase with increasing total pressure as shown in Figure 1. The effect of increasing pressure is to stabilize the initially formed chemically activated (vibrationally excited) fluorine-nitrile adduct.^{2,3}



At low pressure the unimolecular radical elimination from $\text{CF}_3\text{C}(\text{F})=\text{N}\cdot$ predominates, giving $\text{CF}_3\cdot + \text{FCN}$. Such radical addition-eliminations have precedent in the literature. For example, Pritchard⁴ observed the conversion of acetonitrile to trifluoroacetonitrile when acetonitrile was exposed to a source of trifluoromethyl radicals

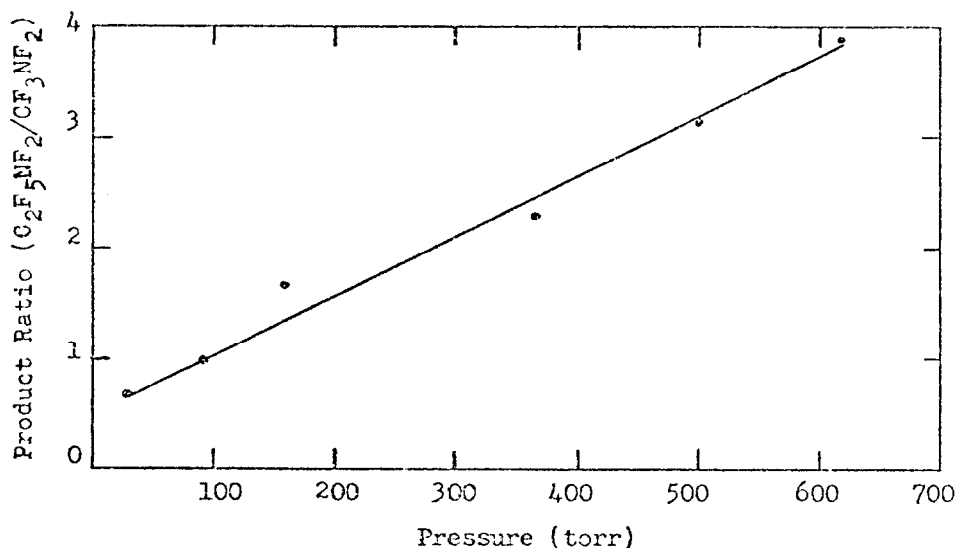
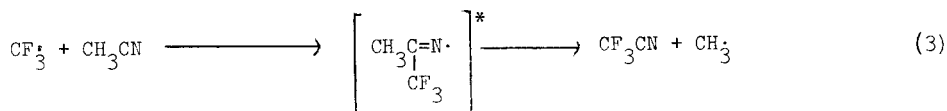
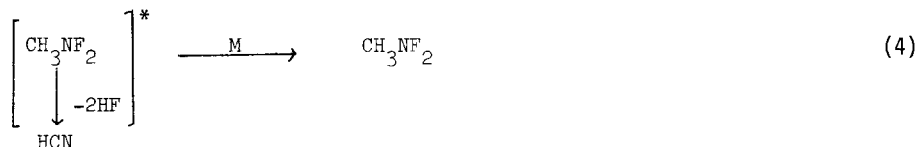


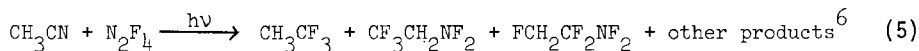
Figure 1. Difluoramine product ratio as a function of total initial reactor pressure.

A similar pressure effect was observed⁵ during the study of the irradiation of N_2F_4 with CH_4 . Whereas the total quantity of organic products (HCN and CH_3NF_2) remained constant, increasing pressure was found to increase the yield of CH_3NF_2 at the expense of HCN.

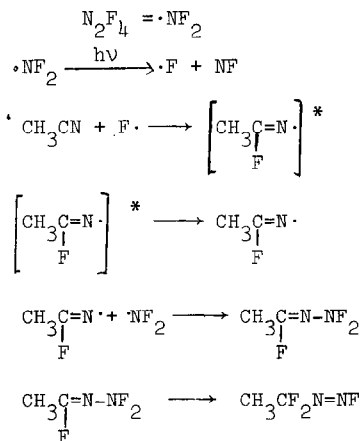


The observed pressure effect during photodifluoramination of CF_3CN (in reaction 1) thus supports the hypothesis that the imino radical $CF_3C(F)=N\cdot$ is an intermediate.

Irradiation of 2:1 molar mixtures of N_2F_4 and acetonitrile resulted in the formation of 1,1,1-trifluoroethane, 1,1,1-trifluoro-2-difluoraminoethane, and 1,1,2-trifluoro-1-difluoraminoethane.



Neither CH_3NF_2 nor $CH_3CF_2NF_2$, the expected products in light of the CF_3CN results, was found in the product mixture. A reasonable pathway for the acetonitrile reaction is shown in part in Scheme 1.



Scheme 1

However, irradiation of CH_3CF_3 and N_2F_4 under the conditions of reaction 5 yields only $\text{CF}_3\text{CH}_2\text{NF}_2$. Hence the $\text{CH}_2=\text{CF}_2$ produced in reaction 5 must arise via a thermally allowed $2\sigma + 2\sigma$ elimination of HF and N_2 from $\text{CH}_3\text{CF}_2\text{N}_2\text{F}$.

We conclude, therefore, that the structure of the intermediate diazene determines the mode of decomposition and consequently the nature of the final products.

EXPERIMENTAL SECTION

Caution: N_2F_4 and derivatives should be handled with care. The reactions and isolation operations were conducted routinely behind shields.

Starting Materials. Acetonitrile (Fisher), purified and dried by the method of Coetzee,⁷ ^{15}N -ammonia (Stohler, 95%), ethyl trifluoroacetate (PCR), and 1,1,1-trifluoroethane (PCR) were used after their purity was checked by gas chromatography. Tetrafluorohydrazine was obtained from two sources: (1) Redstone Research Laboratory, Rohm and Haas Co., Huntsville, Alabama, having the following analysis (mole %) 99.3% N_2F_4 , 0.1% N_2O , 0.4% NO , 0.1% N_2 , 0.1% N_2 , 0.1% NF_3 , and 0.02% N_2F_2 , and (2) PCR, 95%.

Description of Vacuum Apparatus and Method of Irradiation

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, a mercury manometer, and a vacuum outlet. The light source was a 450 watt Hanovia high pressure mercury vapor lamp jacketed by a vycor filter.

The reactor was isolated from the main vacuum line by a wooden explosion box. Materials were passed between the vacuum line and the reactor by way of a short piece of copper tubing and a glass vessel containing NaF pellets⁸ to absorb HF.

The organic substrates was transferred to the reactor by use of a liquid nitrogen bath. The nitrogen level was raised, and then N_2F_4 was admitted. The reactants were allowed to equilibrate at room temperature prior to irradiation. After irradiation, the products were distilled through a series of low temperature traps; dry ice-methylene chloride (-86°C), methylcyclohexane slush (-126°C), and liquid nitrogen (-196°C).

The liquid nitrogen fraction normally contained residual N_2F_4 as well as N_2F_2 , SiF_4 , and oxides of nitrogen. (N_2F_2 was found to decompose on prolonged

contact with glass to give SiF_4 , N_2 , and oxides of nitrogen.⁹ N_2F_4 also has been reported to react with glass slowly resulting in the formation of SiF_4 and NO .¹⁰ All fractions were analyzed by gas chromatography, ^{19}F and ^1H NMR, mass, and infrared spectrometry.

Gas chromatographic separations were achieved on a Varian Aerograph Model 90-P and an Aerograph Autoprep Model A-700 chromatographic instruments. Thermal conductivity detectors were employed. The carrier gas was helium. The gaseous mixture were injected via a glass loop, and the resolved components trapped as they left the instrument in a glass loop immersed in a liquid nitrogen bath. The mixtures were separated on 3/8" diameter columns of varying length packed with 30% QF1 (fluorosilicone) on a 60/80 mesh Chromosorb P in aluminum tubing or alternatively on a 30' column of 30% SE-30 on 45/60 Chromosorb W in aluminum tubing. The product were identified by infrared, mass, and ^{19}F NMR spectrometry. Gas chromatography was used to determine the amounts of N_2F_4 , CF_3CN , $\text{C}_2\text{F}_5\text{NF}_2$, C_2F_6 , and N_2 . Quantitative mass spectrometry was used to confirm the amount of N_2F_4 and CF_3CN , since column response to N_2F_4 decreased with repeated injections. N_2F_2 was identified by mass and infrared spectrometry only.

For the quantitative determination of mixtures resulting from irradiation of N_2F_4 and trifluoroacetonitrile, the thermal conductivity response was calibrated for N_2 , C_2F_6 , and CF_3CN with authentic samples. The product samples were taken directly from the reactor without prior distillation.

^{19}F nuclear magnetic resonance analysis was performed on samples condensed in thick walled NMR tubes with liquid nitrogen which was replaced with a -126°C bath before opening the tubes to the atmosphere. To each tube, 0.4 cc of 10% CFCl_3 (internal standard) in CCl_4 was added before sealing with a pressure cap.

The spectral properties of most of the products obtained in this study have been listed in the literature.¹¹ Hence, the observed product spectra have been checked against literature values and in many cases authentic samples.

Preparation of ^{15}N -Trifluoroacetonitrile

$\text{CF}_3\text{C}^{15}\text{N}$ was synthesized by modification of the procedure of Gilman and Jones¹²

Ten mmoles of ethyl trifluoroacetate was added to ten mmoles of $^{15}\text{NH}_3$ in an evacuated flask fitted with a Fisher-Porter needle valve. The flask was allowed to warm to room temperature with stirring. The volatile product (ethanol) was pulled off by vacuum. The residual white powder, ^{15}N -trifluoroacetamide, (mp $73 - 74^\circ\text{C}$) was mixed with 3.27 g P_2O_5 and heated to 150°C for three hours. The product, collected in a trap (-126°C) in 66% yield, was identified by mass spectral and ^{19}F NMR analysis.

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