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PHOTOLYSIS OF TETRAFLUOROHYDRAZINE WITH CYCLOPROPANE

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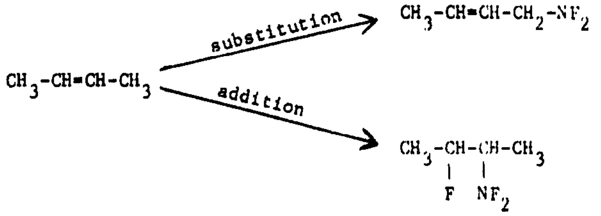
Irradiation of tetrafluorohydrazine, N_2F_4, at 2537 Å in the presence of alkanes results in substitution of a hydrogen atom by an NF_2 group.[1] When alkenes are exposed to N_2F_4 under the same conditions, addition of the elements of NF_3 to the double bond occurs in competition with hydrogen substitution.[1] Since cyclopropane displays characteristics of both a saturated and an unsaturated hydrocarbon,[2] we studied the photolytic decomposition of N_2F_4 in the presence of this strained compound.

$$\text{R-H} \longrightarrow \text{R-NF}_2$$

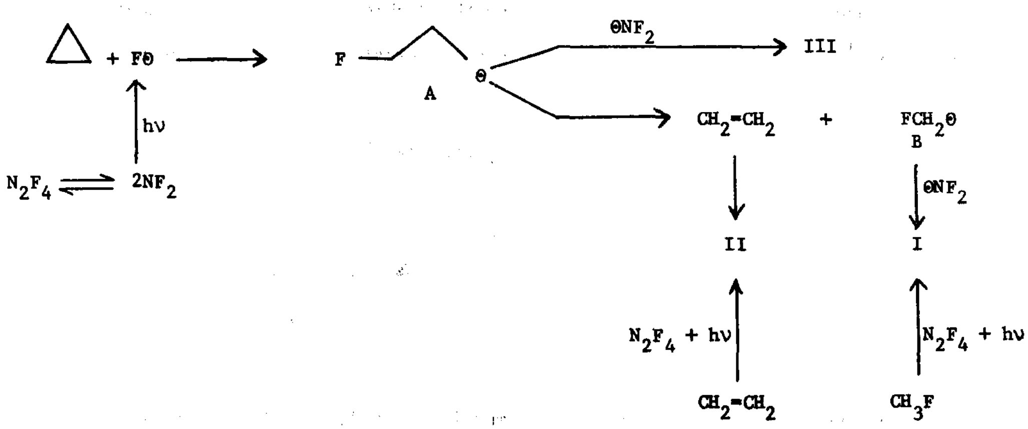


Irradiation (2537 Å) of a mixture containing 5 mmoles each of N_2F_4 and cyclopropane for 90 min. at room temperature resulted in a pressure-decreasing reaction and formation of a liquid. The reaction mixture was fractionated on a vacuum line and each fraction was analyzed by mass and infrared spectrometry. The more volatile fractions contained SiF_4, N_2F_2, HCN, unchanged cyclopropane and traces of NF_3 and recovered N_2F_4. The less volatile fractions contained partially fluorinated and difluoraminated products which were separated by gas phase chromatography over QF-1 (fluorosilicone). The components were isolated as they emerged from the chromatographic apparatus and were identified as fluorodifluoraminomethane (I), 1-difluoramino-2-fluoroethane (II), 1-difluoramino-3-fluoropropane (III), and 1-cyano-2-fluoroethane (IV).

FCH_2NF_2	$FCH_2CH_2NF_2$	$FCH_2CH_2CH_2NF_2$	FCH_2CH_2CN
I	II	III	IV

Table 1 summarizes the data upon which the structural assignments are based.

Although formation of compound III is formally analogous to the addition of the elements of NF_3 to the double bond of alkenes, no difluoraminocyclopropane, the substitution product, was found. This observation contrasts with the results of photochlorination of cyclopropane which yields mainly chlorocyclopropane (substitution) in the gas phase and 1,3-dichloropropane (addition) in the liquid phase.[3] More remarkable is the isolation from the N_2F_4 reaction of substantial amounts of compounds I and II. These C_1 and C_2-products, unprecedented in the chemistry of cyclopropane, *indicate that fragmentation is an important process and point to intervention of a common* intermediate, A.[4]



Combination of A with an NF_2 radical may yield III, whereas competitive unimolecular decomposition of A may lead to ethylene and radical B. This radical would be expected to be captured readily by NF_2 to give I, which was prepared independently (82% yield) by photolysis of N_2F_4 with methyl fluoride. Since ethylene is known to be converted to II under the same conditions,[1] finding II among the products of the cyclopropane reaction is not surprising once a source of ethylene is provided.

Formation of the extremely strong C-F bond[5] in A and concomitant rupture of the strained ring[2] may result in A being initially in a vibrationally excited state which, if not quenched, will furnish ethylene and B. Similarly, if III is formed in an excited state, dehydrofluorination to give IV can compete with deactivation steps which yield stable III.

TABLE 1

Characterization of Products

Compound	Chemical Shift^{A,B} ϕ*	δ	Coupling Constant^{C}	Relative Area^{D}	Infrared Band(cm^{-1})	Mass/ Charge
${}^{a}FCH_2NF_2^{b}$ I	+202.8(t,CF) - 27.6(NF_2)	5.15(d in t, CH_2)	$J_{F^aH} = 48$ $J_{F^bH} = 22$	$\frac{F^b}{F^a} = 2$	860(NF_2) 935(NF_2) 1130(CF)	85($F_3\overset{+}{C}H_2N$) 46($F\overset{+}{C}NH$) 33($F\overset{+}{C}H_2$)
${}^{a}FCH_2^{b}CH_2^{c}NF_2^{d}$ II	+224.3(t in t, (CF) - 54.3(NF_2)	4.64(d in t, CH_2^b) 3.75(t in d, into t, CH_2^c)	$J_{F^aH^b} = 48$ $J_{F^aH^c} = 23$ $J_{F^dH^c} = 25$ $J_{H^bH^c} = 5$	$\frac{F^d}{F^a} = 2$ $\frac{H^b}{H^c} = 1$	858(NF_2) 915(NF_2) 1100(CF) 1070(CF)	47($F\overset{+}{C}_2H_4$) 33($F\overset{+}{C}H_2$)
${}^{a}FCH_2^{b}CH_2^{c}CH_2^{d}NF_2^{e}$ III	+221.7(t in t, CF) - 54.4(NF_2)	4.50(d in t, CH_2^b) 2.05(d in m, CH_2^c) 3.70(t in t, CH_2^d)	$J_{F^aH^b} = 48$ $J_{F^aH^c} = 25$ $J_{H^bH^c} = 6$ $J_{F^eH^d} = 28$ $J_{H^cH^d} = 6$	$\frac{F^e}{F^a} = 1$ $\frac{H^b}{H^c} = 1$ $\frac{H^c}{H^a} = 1$	845(NF_2) 930(NF_2) 1129(CF) 1070(CF)	61($F\overset{+}{C}_3H_6$) 47($F\overset{+}{C}_2H_4$) 41($\overset{+}{C}_3H_5$) 33($F\overset{+}{C}H_2$)
$FCH_2^{a}CH_2^{b}CN$ IV	+216.8(t in t, CF)	4.52(d in t., CH_2^a) 2.65(d in t, CH_2^b)	$J_{FH^a} = 45$ $J_{FH^b} = 22$ $J_{H^aH^b} = 5$	$\frac{H^a}{H^b} = 1$	1040(CF) 2260(CN)	73($F\overset{+}{C}_3H_4N$) 52($\overset{+}{C}_3H_2N$) 45($F\overset{+}{C}_2H_2$) 33($F\overset{+}{C}H_2$)

A. Spectra were run approximately 5-percent by volume solutions in $CDCl_3$ at room temperature. F^{19} chemical shifts (ϕ*) are in parts per million relative to $CFCl_3$ as an external reference, and H^1 chemical shifts (δ) are in parts per million downfield relative to TMS as both an external and internal reference. Spectra of the neat liquids exhibited no significant differences from spectra of the solutions. Singlets, doublets, triplets, quartets, and multiplets are denoted as s, d, t, q, and m, respectively. Terminology "t in d in t" means a triplet with each peak split into doublet and each peak of doublet further split into triplet.

B. All resonances of fluorine bonded to nitrogen were broad signals (~300 cps), owing to the quadripolar relaxation of the N^{14} nucleus; therefore fine spin-spin coupling with other fluorines and protons was obscured.

C. Spin-spin coupling constants (J) are in cycles per second.

D. The ratios of the areas of the resonance signals are given.

$$\begin{tikzcd} & \mathrm{IV} + 2\mathrm{HF} \\ \mathrm{III}^{*} \arrow[ur] \arrow[dr, "M"'] & \\ & \mathrm{III} \end{tikzcd}$$

Therefore, the partitioning of A between III and the fragments and the ratio of III/IV should be pressure-dependent.[7]

Table 2 shows that increased pressure due to presence of inert CF_4 does favor production of III at the expense of IV. Interestingly, though, the amounts of I and II are essentially unchanged indicating that fragmentation of A is unaffected. These and other examples of chemical activation during difluoramination will be discussed more fully in a forthcoming paper.

TABLE 2

Product Distribution

Total Initial Pressure (Torr)	III (mmoles)	IV (mmoles)	II (mmoles)	I (mmoles)
270	trace	0.25	0.08	0.60
580 (270 Torr + 310 Torr of CF_4 added)	0.06	0.15	0.07	0.63

REFERENCES

1. C. L. Bumgardner, Tetrahedron Letters, 3683 (1964).
2. W. A. Bennett, J. Chem. Ed., 44, 17 (1967).
3. C. Walling and P. S. Fredricks, J. Am. Chem. Soc., 84, 3326 (1962). J. D. Roberts and P. H. Dirstine, ibid., 67, 1281 (1945).
4. The fluorine atom necessary for generating A from cyclopropane is believed to arise from photolysis of NF_2 into F and NF as previously suggested.[1] The presence of these moieties can also explain the SiF_4, N_2F_2 and NF_3 encountered in this and other work where N_2F_4 is photolyzed in glass.
5. $D(CH_3\text{-}F) \approx 108$ kcal, T. L. Cottrell, "The Strength of Chemical Bonds", second edition, Butterworths Scientific Publications, London, 1958, p. 202.
6. In a bimolecular association the energy (enthalpy + activation energy + thermal energy of reactants) is confined entirely to the product molecule.
7. Presence of more molecules in the reaction mixture will increase the frequency of collisions leading to more rapid deactivation of vibrationally excited intermediates.

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