Photodifluoramination of Cycloalkanes

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Irradiation (253.7 nm) of cyclobutane, cyclopentane, and cyclohexane with tetrafluorohydrazine in the gas phase gives in high yield the corresponding difluoraminocycloalkanes. In contrast, similar treatment of cyclopropane results in a complex mixture including $F(CH_2)_3NF_2$, $F(CH_2)_2NF_2$, FCH_2NF_2, and $F(CH_2)_2CN$. Possible processes by which these products arise and the role of excited intermediates are examined.

Irradiation (253.7 nm) of tetrafluorohydrazine (N_2F_4) and acyclic saturated hydrocarbons in the gas phase leads to substitution of a hydrogen atom by an NF_2 moiety.[2] If the hydrocarbon reactant is unsaturated, addition of the elements of NF_3 across the multiple bond also becomes an important process.[2] To extend the scope of these reactions to cycloalkanes, we examined the photodifluoramination of cyclohexane, cyclopentane, cyclobutane, and cyclopropane. All of these compounds, with the notable exception of cyclopropane, smoothly undergo substitution. In contrast, addition and novel fragmentation occur in the case of the three-membered ring.

Results and Discussion

Results are summarized in Tables I, II, and III.

Table I shows that cyclobutane, cyclopentane, and cyclohexane all undergo substitution of hydrogen by NF_2, a reaction previously found[2] to be characteristic of acyclic alkanes. This substitution process is believed to involve the following steps (1–4).[2]

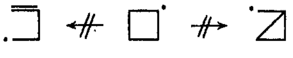
$$N_2F_4 \longrightarrow 2NF_2 \qquad (1)$$

$$NF_2 \xrightarrow{h\nu} NF + F \qquad (2)$$

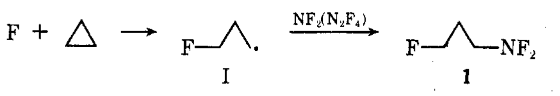
$$RH + F \longrightarrow HF + R \qquad (3)$$

$$R + NF_2(N_2F_4) \longrightarrow RNF_2 \qquad (4)$$

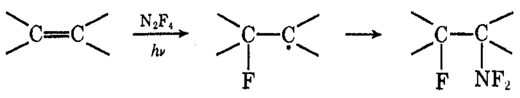
As shown by the first three entries in Table I, difluoraminocycloalkanes were isolated in high yield and no ring cleavage or isomerization of the intermediate cycloalkyl radical was detected. These observations in the case of cyclobutane provide additional evidence, this time from a gas-phase reaction at 25°,[3] that the cyclobutyl radical is stable with respect to isomerization to cyclopropylcarbinyl and allylcarbinyl forms.



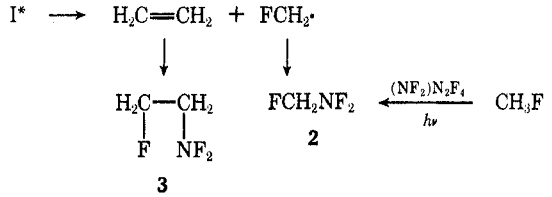
On the other hand, entry 4, Table I shows that the only C_3 products isolated from the cyclopropane reaction are acyclic, suggesting that F attacks at a C–C bond to give intermediate I.



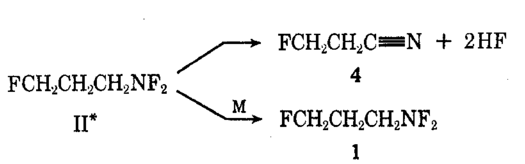
Capture of intermediate I by an NF_2 group would lead to 1-difluoramino-3-fluoropropane (1) in analogy with addition reactions of alkenes,[2] alkynes, and other unsaturated substrates.[4]



Formation of the unusual C_1 and C_2 fragments[5] given in Table I may be rationalized in terms of intermediate I also. If this radical is chemically activated, I*, it may undergo unimolecular decomposition to ethylene and the fluoromethyl radical. The latter intermediate



would be expected to be converted readily to difluoraminofluoromethane (2), which was independently synthesized by photolysis of NF_2 with methyl fluoride. Since ethylene is known to yield 1-difluoramino-2-fluoroethane (3) under the reaction conditions, finding this adduct in Table I is understandable once a source of ethylene is provided.[6] Generation of I in an excited state seems plausible, since rupture of the highly strained ring accompanies formation of the very strong C–F bond.[7] Also, if intermediate II is produced "hot," II*, dehydrofluorination to give 1-cyano-2-fluoroethane (4) can compete with deactivation steps



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[1] NASA Fellow.

[2] (a) C. L. Bumgardner, E. L. Lawton, K. G. McDaniel, and H. Carmichael, *J. Amer. Chem. Soc.*, **92**, 1311 (1970); (b) for a general review, see W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969, pp 206–228.

[3] In the liquid phase at 0°, chlorination of cyclobutane gives cyclobutyl chloride free of allylcarbinyl chloride and 1,4-dichlorobutane: C. Walling and P. S. Fredricks, *J. Amer. Chem. Soc.*, **84**, 3326 (1962).

[4] C. L. Bumgardner and M. Lustig, *Inorg. Chem.*, **2**, 662 (1963); M. Lustig, C. L. Bumgardner, and J. K. Ruff, *ibid.*, **3**, 917 (1964); C. L. Bumgardner and K. G. McDaniel, *J. Amer. Chem. Soc.*, **91**, 1032 (1969); C. L. Bumgardner and G. P. Crowther, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

[5] The general process $RCH_2CH_2\cdot \rightarrow R\cdot + H_2C{=}CH_2$, although common in hydrocarbon pyrolyses [C. Walling in "Molecular Rearrangements," Part 1, P. de Mayo, Ed., Interscience, New York, N. Y., 1963, p 440] would not be expected to be facile at room temperature. Furthermore, radicals of the type FCH_2CH_2CHR generated by hydrogen abstraction during photodifluoramination do not fragment (ref 2).

[6] C. L. Bumgardner, *Tetrahedron Lett.*, 3683 (1964).

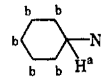
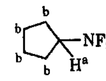
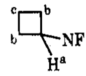
[7] The energy initially associated with I* is the sum of the translational energy of the reacting F and cyclopropane, the activation energy, and the enthalpy of the reaction. This last value should be substantial since the strain energy of the cyclopropane ring is estimated to be 46 kcal/mol [J. D. Roberts and M. C. Caserio, "Basic Principles of Organic Chemistry," W. A. Benjamin, New York, N. Y., 1965, p 113] and the C–F bond strength is in the neighborhood of 110 kcal/mol [J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 824.]

TABLE I
PHOTODIFLUORAMINATION OF CYCLOALKANES

Entry	Starting material	Product	Yield,[a] %	Type of process
1	Cyclohexane	Difluoraminocyclohexane	70	Substitution
2	Cyclopentane	Difluoraminocyclopentane	62	Substitution
3	Cyclobutane	Difluoraminocyclobutane	56	Substitution
4	Cyclopropane	1-Difluoramino-3-fluoropropane (**1**) 1-Difluoramino-2-fluoroethane (**3**) Difluoraminofluoromethane (**2**) 1-Cyano-2-fluoroethane (**4**)	b	Addition and fragmentation

[a] Based on the equation $2RH + 2N_2F_4 \rightarrow 2RNF_2 + N_2F_2 + 2HF$. [b] Depends on pressure; see Experimental Section and Table III.

TABLE II
CHARACTERIZATION OF PHOTOPRODUCTS[a]

Entry	Starting material	Products	Registry no.	Chemical shift[b] ϕ	Chemical shift[b] δ	Coupling constant, Hz	Ir, cm^{-1}
1	Cyclohexane		14182-78-6	−43.2 (NF_2)	3.29 (t in m, CH^a) 1.10–2.10 (m, $CH_2{}^b$)	$J_{FH^a} = 26$	2950 (CH) 2860 (CH) 965 (NF_2) 843 (NF_2)
2	Cyclopentane		14182-80-0	−53.2 (NF_2)	3.93 (t in m, CH^a) 1.60–2.30 (m, CH^b)	$J_{FH^a} = 23$	2950 (CH) 930 (NF_2) 840 (NF_2)
3	Cyclobutane		32979-58-1	−44.6 (NF_2)	4.20 (t in m, CH^a) 2.67 (m, CH^b) 2.28 (m, CH^b) 1.99 (m, $CH_2{}^c$)		2950 (CH) 950 (NF_2) 915 (NF_2) 850 (NF_2)
4	Cyclopropane	$^{a}FCH_2{}^{b}CH_2{}^{c}CH_2{}^{d}NF_2{}^{e}$	20575-36-4	+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, $CH_2{}^d$)	$J_{F^aH^b} = 48$ $J_{F^aH^c} = 25$ $J_{H^bH^c} = 6$ $J_{F^eH^d} = 28$ $J_{H^cH^d} = 6$	2960 (CH) 1129 (CF) 1070 (CF) 935 (NF_2) 845 (NF_2)
		$^{a}FCH_2{}^{b}CH_2{}^{c}NF_2{}^{d}$	3732-68-1	+224.3 (t in t, CF) −54.3 (NF_2)	4.64 (d in t, $CH_2{}^b$) 3.75 (t in d, in t, $CH_2{}^c$)	$J_{F^aH^b} = 48$ $J_{F^aH^c} = 23$ $J_{F^dH^c} = 25$ $J_{H^bH^c} = 5$	2950 (CH) 1060 (CF) 868 (NF_2) 860 (NF_2)
		$^{a}FCH_2NF_2{}^{b}$	3732-65-8	+202.8 (t, CF) −27.6 (NF_2)	5.15 (d in t, CH_2)	$J_{F^aH} = 48$ $J_{F^bH} = 22$	2950 (CH) 1130, 1125 (CF) 929, 860, 845, 940, 935 (NF_2)
		$FCH_2{}^{a}CH_2{}^{b}CN$	504-62-1	+216.8 (t in t, CF)	4.52 (d in t, $CH_2{}^a$) 2.65 (d in t, $CH_2{}^b$)	$J_{FH^a} = 45$ $J_{FH^b} = 22$ $J_{H^aH^b} = 5$	2990, 2920 (CH) 2260 (CN) 1080 1040 (CF) 1010

[a] Mass spectra and satisfactory combustion analyses (±0.4% for C, H, N) were obtained for new compounds in entries 2–4: Ed. The data recorded in entry 1 for difluoraminocyclohexane agree with those reported by K. Baum, *J. Org. Chem.*, **32**, 3648 (1967), and by C. M. Sharts, *ibid.*, **33**, 1008 (1968), who prepared this compound by different routes. [b] Spectra were run as approximately 5% by volume solutions in deuteriochloroform with the probe temperature at 25°. Fluorine (^{19}F) chemical shifts (ϕ) are in parts per million relative to fluorotrichloromethane as an external reference. Proton (^1H) chemical shifts (δ) are in parts per million downfield relative to tetramethylsilane as an internal reference. Ratios of signals agreed with assigned structures.

TABLE III
PRESSURE DEPENDENCE OF PRODUCTS FROM IRRADIATION OF CYCLOPROPANE AND N_2F_4

	Mmol of product			
		−86° trap		
Inert gas (CF_4)	−33° Trap FCH_2CH_2CN	FCH_2CH_2-CH_2NF_2	FCH_2-CH_2NF_2	−126° Trap FCH_2NF_2
None	0.25	Trace	0.08	0.60
310 Torr	0.15	0.06	0.07	0.63

which yield a ground state molecule. Photodifluoramination of methane is known to give mixture of CH_3NF_2 and HCN, the latter product arising from decomposition of excited CH_3NF_2.[8] Therefore, the partitioning of I* between **1** and the fragments (Table

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[8] C. L. Bumgardner, E. L. Lawton, and H. Carmichael, *Chem. Commun.*, 1079 (1968).

I) and the ratio of **4** to **1** should be pressure dependent.[9]

Table III indicates that increasing the pressure by addition of inert CF_4 does favor production of **1** at the expense of **4**. Interestingly, though, the amounts of **2** and **3** remain unchanged so that fragmentation of I* is unaffected. This difference in quenchability between I* and II* may be attributed to the higher energy of the former.[10]

The results in Table I contrast with those from photochlorination of cyclopropane, which yields mainly the substitution product, chlorocyclopropane, in the gas phase below 100° and the addition product, 1,3-dichloropropane, in the liquid phase at 0°.[11] Moreover, Fettis, Knox, and Trotman-Dickenson[12] observed that cyclopropane and fluorine, in the temperature range −60 to 20°, react to give fluorocyclopropane (substitution) and a fluoropropene, which presumably comes about *via* isomerization of the small ring fluoride. In our study the failure to observe any difluoraminocyclopropane, the simple substitution product, is puzzling. Since the yield of volatile products from the cyclopropane reaction was small, the possibility exists that difluoraminocyclopropane was produced, but was removed by secondary decompositions resulting in high-molecular-weight materials (see Experimental Section). In any event, formation of **1** from cyclopropane appears to be a clear case of radical addition to the small ring and **2** and **3** obviously arise from C–C cleavage unprecedented in the chemistry of cyclopropane.

Experimental Section[13]

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

Starting Materials.—Cyclohexane (Matheson Coleman and Bell, spectral grade), cyclopentane (Columbia Organic Chemicals, 99%), cyclopropane (Matheson, 99%), methyl fluoride (Matheson, 99%), and carbon tetrafluoride (Matheson, 99.7%), were used as received except for cyclopentane, which was redistilled prior to use. Cyclobutane was synthesized from cyclobutyl bromide (Ash Stevens, 99%) by the method described by Pomerantz, *et al.*[14] Tetrafluorohydrazine of the (mol %) composition 99.3% N_2F_4, 0.1% N_2O, 0.4% NO, 0.1% N_2, 0.1% NF_3, and 0.02% N_2F_2 was kindly supplied by the Gorgas Laboratory of the Redstone Research Division of the Rohm and Haas Co., Huntsville, Ala.

Photodifluoramination of the Cycloalkanes.—Results are summarized in Table I. The reaction of cyclopropane is described as an example. A high-vacuum system was used to transfer reactants to a 650-ml Pyrex glass reaction vessel. Kel-F90 fluorocarbon grease was used on all joints and stopcocks. The lamp employed in the photolyses was a low-pressure cold cathode mercury resonance lamp (Hanovia 2537) housed in a spiral Vycor 791 glass envelope of sufficient thickness to filter all radiation below 210 nm and to transmit approximately 60% of the 253.7-nm radiation. A 5000-V AC transformer (Nester-Faust NFUV-400) served as the power supply. The immersion lamp was sealed into the center of the reaction vessel. Photolyses were conducted at room temperature. The reaction mixture, consisting of a 1:1 molar ratio of hydrocarbon to tetrafluorohydrazine at 270 Torr total initial pressure, was irradiated for 90 min.

Difluoraminoalkanes were separated from the other products,[15] SiF_4, N_2F_2, oxides of nitrogen, and unchanged starting material, by trap-to-trap distillation on the vacuum line through −33, −86, −126, and −197° traps in series. The contents of each trap were purified further by chromatography on a Barber and Coleman Model 5000 gas chromatograph using a QF-1 column and a Bendix Model 12 Time-of-Flight mass spectrometer as a detector. In those cases where the vacuum line fractions consisted of mixtures, the composition was determined by analysis of the ^1H nmr spectrum. Pure compounds were isolated by collecting samples as they were eluted from the chromatographic column. In order to obtain sufficient material for characterization (Table II), fractions from four successive runs were combined.

To determine product variation with pressure, the reaction described above was repeated with the addition of 310 Torr of the inert gas, CF_4. Results are recorded in Table III.

Of the 15 mmol of carbon atoms introduced in the 5 mmol of cyclopropane charged, only 3 mmol of carbon atoms were accounted for as products or recovered starting material. The remainder appeared in the form of a brown residue coating the walls of the reaction vessel. Such residues were not obtained when cyclohexane, cyclopentane, or cyclobutane was the reactant.

Cyclopropane (135 Torr) was irradiated alone for 60 min in the apparatus described to determine the photolytic stability of the hydrocarbon. No decomposition was detected by infrared or mass spectroscopy.

Registry No.—N_2F_4, 10036-47-2; cyclohexane, 110-82-7; cyclopentane, 287-92-3; cyclobutane, 287-23-0; cyclopropane, 75-19-4.

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(9) Another possible route to cyanide **4** involves secondary decomposition of **1** *via* radical attack at the carbon atom bearing the NF_2 group. This

$$FCH_2CH_2CH_2NF_2 \xrightarrow[-HF]{F} FCH_2CH_2CHNF_2 \xrightarrow[-HF]{-F} \mathbf{4}$$

explanation is unattractive, however, for no bisdifluoramines such as $FCH_2CH(NF_2)CH_2NF_2$ were found. Photodifluoramination of difluoraminoethane, for example, not only yields acetonitrile but 1,2-bisdifluoraminoethane (ref 2).

(10) According to RRK theory [S. W. Benson and G. Haugen, *J. Phys. Chem.*, **69**, 3898 (1965)], the rate constant, k_e, for unimolecular decomposition of a "hot" molecule is given by

$$k_e = A[(E - E_1)/E]^{s-1}$$

A and E_1 are the Arrhenius parameters for decomposition of a thermalized molecule, *E* is the energy of the vibrationally excited species, and *s* is the number of effective oscillators.

(11) J. D. Roberts and P. H. Dirstine, *J. Amer. Chem. Soc.*, **67**, 1281 (1945). See also references cited in footnote 3.

(12) G. C. Fettis, J. H. Knox, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1064 (1960).

(13) Proton nuclear magnetic resonance, fluorine nuclear magnetic resonance, infrared, and mass spectra were obtained using the following instruments, respectively: Varian HA-100 high-resolution spectrometer, Varian DA 60 high-resolution spectrometer, Beckman IR-5A-spectrophotometer, and either a Consolidated Model 620, Bendix Model 12, or Associated Electronic Model MS 902 mass spectrometer.

(14) P. Pomerantz, A. Fookson, T. W. Mears, S. Rothberg, and F. L. Howard, *J. Res. Nat. Bur. Stand.*, **52**, 59 (1954).

(15) Identified by their infrared and mass spectra.