

pling constants were taken from the experimental spectrum by approximation and used in the simulation of a spectrum.<sup>36</sup> The best agreement was obtained with hexaphenylene atropisomer 38a.

With this, I come to the end of my tour, which has led us from diyls, *via* ylides and ate complexes, to my idyll. As in any process coupled with life, it is ir-

(36) I wish to thank Dr. G. Schilling, Institut für Organische Chemie, Heidelberg, for his preparation and interpretation of the spectra.

reversible and can be retracted only in thought. Along the way, we came upon various points of interest which invited us to linger for a while. Ours, like all such rambling tours, possesses that special attraction that comes from knowing that the landscape spread out before us will be opened to view, not by intention, but by chance and surprise. I hope that this story will stimulate new interest in the field of carbanion chemistry as a place to linger and possibly further develop.

## Photodifluoramination and Atomic Fluorine Reactions

Carl L. Bumgardner\* and Ernest L. Lawton

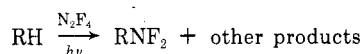
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### An Impurity Launches a Research Program

By 1958 four binary compounds of nitrogen and fluorine were known:  $\text{NF}_3$ ,  $\text{FN}_3$ , and *cis*- and *trans*- $\text{N}_2\text{F}_2$ .<sup>1</sup> In contrast to  $\text{NF}_3$ , which is particularly stable to both heat and a variety of chemical reagents, the other three on the list are highly reactive and frequently explosive. Colburn and Kennedy<sup>2</sup> in 1958 added another member to the series, tetrafluorohydrazine,  $\text{N}_2\text{F}_4$ , a reagent which promised to be stable enough to manipulate, yet reactive enough to be chemically interesting.

It was our good fortune to have available for study a sample of this new NF compound soon after its initial synthesis. Desiring to ascertain the gas-phase compatibility of  $\text{N}_2\text{F}_4$ , a potential fluorinating agent, with hydrocarbons, we made up various mixtures of low molecular weight alkanes and  $\text{N}_2\text{F}_4$ . At room temperature no chemical change was observed. However, when the mixtures were irradiated with a mercury resonance lamp (253.7 nm), a smooth reaction occurred, which resulted in replacement of a hydrogen atom with an  $\text{NF}_2$  group. Because of the formal



resemblance of this process to photochlorination, we dubbed it photodifluoramination.

But are the two photoreactions mechanistically analogous? In order to answer this question we turned to the problem of purifying the  $\text{N}_2\text{F}_4$  available at the time. The ultraviolet spectrum of the  $\text{N}_2\text{F}_4$  used in these exploratory experiments contained several absorption bands which were attrib-

uted to impurities, as well as the continuum expected for a saturated species like  $\text{N}_2\text{F}_4$ . After distillation and chromatography over a variety of columns, a sample of  $\text{N}_2\text{F}_4$  was obtained which gave a much simpler spectrum. However, besides the continuum, which had its low energy cut off at about 200 nm, there persisted a discrete absorption which had a maximum at 260 nm with a half-band width of 20 nm. The contaminant responsible for this band obviously was playing a role in photodifluoramination since the reaction was initiated by radiation near 260 nm.

While we were pondering the nature of this tenacious impurity, Colburn and Johnson were accumulating some curious observations regarding the physical behavior of  $\text{N}_2\text{F}_4$ . Out of a meeting with these investigators at which all of our puzzles were pooled, there emerged the idea that  $\text{N}_2\text{F}_4$  dissociates into  $\text{NF}_2$  radicals, establishing an equilibrium reminis-



cent of the  $\text{N}_2\text{O}_4$ - $\text{NO}_2$  system but unprecedented in hydrazine chemistry. This hypothesis was verified through an elegant series of experiments conducted by Colburn, Johnson, and coworkers.<sup>3</sup>

The steadfast "impurity" in  $\text{N}_2\text{F}_4$  could now be identified as  $\text{NF}_2$ . This radical is the species that gives rise to the 260 nm band and initiates photodifluoramination.

What happens to  $\text{NF}_2$  after it absorbs light and its reactions with various substrates is the subject of this Account.

### Atomic Fluorine from $\text{NF}_2$

The preliminary experiments on photodifluoramination of alkanes indicated that initially  $\text{NF}_2$  was

(1) H. J. Emelĕus, "The Chemistry of Fluorine and Its Compounds," Academic Press, New York, N. Y., 1969, p 77.

(2) C. B. Colburn and A. Kennedy, *J. Amer. Chem. Soc.*, **80**, 5004 (1958).

(3) F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, **83**, 3043 (1961); L. H. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *J. Chem. Phys.*, **35**, 1481 (1961); C. B. Colburn and F. A. Johnson, *J. Chem. Phys.*, **33**, 1869 (1960).

Near the end of World War II, Carl Bumgardner graduated from the Naval Oriental Language School, specializing in Japanese. He received his B.A.Sc. in Chemical Engineering from the University of Toronto in 1952, and in 1956 his Ph.D. in Chemistry from MIT. After a year's post-doctoral work with A. C. Cope, he took a research position with the Redstone Division of Rohm & Haas, Huntsville, Ala. In 1964, he joined the faculty of North Carolina State University at Raleigh. There he has been pursuing his research in the chemistry of nitrogen-fluorine compounds.

Ernest Lawton received his Ph.D. from North Carolina State University in 1969, working with Professor Bumgardner. Since then, he has been a Senior Research Chemist at Monsanto Company, in Durham, N. C.

Table I  
Selectivity Ratios per Hydrogen Atom for Various Radical Substitution Reactions

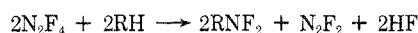
Entry	Radical source	Temp, °C	Substrate selectivity ratios				Molecular formula of products
			CH <sub>3</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>				
1 <sup>a</sup>	F <sub>2</sub> $\rightleftharpoons$ 2F	20	1	1.3	1.3	1	C <sub>4</sub> H <sub>9</sub> F
2	NF <sub>2</sub> + hν	25	1	1.2	1.2	1	C <sub>4</sub> H <sub>9</sub> NF <sub>2</sub>
3 <sup>a</sup>	Cl <sub>2</sub> $\xrightarrow{h\nu}$ 2Cl	35	1	3.9	3.9	1	C <sub>4</sub> H <sub>9</sub> Cl
		146	1	3.3	3.3	1	
4 <sup>b</sup>	N <sub>2</sub> F <sub>4</sub> $\rightleftharpoons$ 2NF <sub>2</sub>	250	1	5.1	5.1	1	C <sub>4</sub> H <sub>9</sub> NF <sub>2</sub>
5 <sup>a</sup>	Br <sub>2</sub> $\xrightarrow{h\nu}$ 2Br	146	1	82	82	1	C <sub>4</sub> H <sub>9</sub> Br
			FCH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>3</sub>				
6 <sup>a</sup>	F <sub>2</sub> $\rightleftharpoons$ 2F	20	<0.3	0.8	1.0	1	C <sub>4</sub> H <sub>9</sub> F <sub>2</sub>
7	NF <sub>2</sub> + hν	25	0.7	0.9	1.0	1	C <sub>4</sub> H <sub>9</sub> NF <sub>3</sub>
8 <sup>a</sup>	Cl <sub>2</sub> $\xrightarrow{h\nu}$ 2Cl	35	0.8	1.6	3.7	1	C <sub>4</sub> H <sub>9</sub> FCI
9 <sup>a</sup>	Br <sub>2</sub> $\xrightarrow{h\nu}$ 2Br	146	10	9	82	1	C <sub>4</sub> H <sub>9</sub> FBr

<sup>a</sup> P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960).  
*Tetrahedron*, **24**, 5089 (1968).

<sup>b</sup> Calculated from data of S. F. Reed, Jr., and R. C. Petry,

excited and that ultimately RNF<sub>2</sub> was produced. To fill in the intermediate stages, we examined the reaction stoichiometrically and kinetically.

Irradiation of N<sub>2</sub>F<sub>4</sub>-alkane mixtures in glass at 253.7 nm formed N<sub>2</sub>F<sub>2</sub>, SiF<sub>4</sub>, N<sub>2</sub>, and oxides of nitrogen in addition to RNF<sub>2</sub>. The small amounts of NO, N<sub>2</sub>O, SiF<sub>4</sub>, and N<sub>2</sub> arose from interaction of reactive intermediates (see below) and HF with the glass apparatus. Since the molar ratio of RNF<sub>2</sub> to N<sub>2</sub>F<sub>2</sub> produced was approximately 2:1 and the ratio of RNF<sub>2</sub> to N<sub>2</sub>F<sub>4</sub> consumed approached unity, the photodifluoroamination of alkanes can be represented by the equation



Kinetic runs using methane as the alkane showed photodifluoroamination to be zero order in alkane and one-half order in N<sub>2</sub>F<sub>4</sub>. The selectivity of the substitution process was then probed by determining selectivity ratios for the photodifluoroamination of *n*-butane and 1-fluorobutane.<sup>4</sup> The basic assumption of a radical selectivity study is that the relative rates of hydrogen abstraction at any position in the molecule are equal to the relative amounts of isomeric products formed from a given hydrocarbon, taking into account the number of hydrogens. The selectivity ratios relative to the methyl group of the hydrocarbon molecule therefore may be calculated as

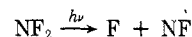
$$\text{selectivity ratio} = \frac{(\% \text{ isomer at position } x) / (\text{no. of H's at position } x)}{(\% \text{ primary isomer}) / (\text{no. of primary H's})}$$

The isomeric alkyldifluoramines, obtained in high yield, were isolated by a combination of vacuum line distillation and gas phase chromatography and identified by <sup>1</sup>H and <sup>19</sup>F nmr spectroscopy.<sup>4</sup> Table I summarizes results and presents pertinent data from the literature on other radical substitution reactions.

The comparisons in Table I clearly show that photodifluoroamination exhibits a very low degree of discrimination, indicative of a highly reactive hydrogen-abstracting species. In particular, the correlations between entries 1 and 2 and between 6 and 7 point to the fluorine atom as the intermediate re-

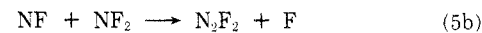
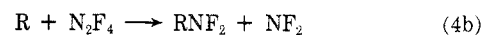
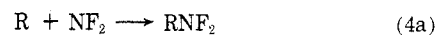
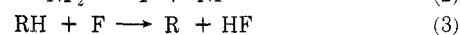
(4) C. L. Bumgardner, E. L. Lawton, K. G. McDaniel, and H. Carmichael, *J. Amer. Chem. Soc.*, **92**, 1311 (1970).

sponsible for removing hydrogen atoms from alkanes in the photodifluoroamination reaction. Consequently, we suggest that NF<sub>2</sub> undergoes photolysis to furnish atomic fluorine.<sup>4</sup> Since the N-F bond strength



in NF<sub>2</sub> is estimated to be 71 kcal/mol<sup>5</sup> and since 253.7-nm radiation corresponds to 112 kcal/mol, there is sufficient energy to realize this step.<sup>6</sup>

The data on alkane photodifluoroamination may be satisfactorily explained by the sequence



The observed stoichiometry can be obtained by multiplying steps 1-4a by 2 and adding step 5a. Alternatively, multiplying steps 3 and 4b by 2 and adding steps 1, 2, and 5b give the required result.

The equilibrium shown in step 1 is well documented,<sup>3,7</sup> and 253.7-nm radiation should be absorbed by NF<sub>2</sub> but not by N<sub>2</sub>F<sub>4</sub> or the hydrocarbon. If the equilibrium in step 1 is rapidly established,<sup>8</sup> the rate of step 2, R<sub>2</sub>, can be written

$$R_2 = k_2[\text{NF}_2] = k_2K^{1/2}[\text{N}_2\text{F}_4]^{1/2}$$

where K is the equilibrium constant for step 1 and k<sub>2</sub> is an intensity-dependent function relating the rate of step 2 to the NF<sub>2</sub> concentration. If step 2 is rate determining, then photodifluoroamination should exhibit half-order dependence on N<sub>2</sub>F<sub>4</sub> concentration and zero-order dependence on RH concentration, as found.<sup>4</sup>

(5) A. Kennedy and C. B. Colburn, *J. Chem. Phys.*, **35**, 1892 (1961).

(6) Consistent with the proposed photolysis is the work of P. L. Goodfriend and H. P. Wood, *J. Mol. Spectrosc.*, **13**, 63 (1964), who interpreted the details of the ultraviolet spectrum of NF<sub>2</sub> in terms of predissociation.

(7) H. E. Doorenbos and B. R. Loy, *J. Chem. Phys.*, **39**, 2393 (1963).

(8) We have calculated that the initial rate of photolysis of NF<sub>2</sub> for an initial concentration of N<sub>2</sub>F<sub>4</sub> = 2.3 × 10<sup>-3</sup> mol/l. is of the order of 10<sup>-7</sup> mol/l. sec at 25°. This value is orders of magnitude slower than the initial rate of dissociation of N<sub>2</sub>F<sub>4</sub> (at the same concentration) reported to be 0.45 mol/l. sec at 75° based on shock tube experiments: A. P. Modica and D. F. Hornig, *J. Chem. Phys.*, **49**, 629 (1968).

Confirmatory evidence for one of the products of step 2, NF, has been reported by Comeford and Mann,<sup>9</sup> who obtained the infrared spectrum of this species by irradiating NF<sub>2</sub> in a low-temperature matrix. Step 3 accounts nicely for the selectivity ratios calculated for butane and fluorobutane (Table I). The HF produced in this step was not isolated in our experiments but was largely removed by absorption towers to simplify work-up procedures. SiF<sub>4</sub>, the expected product of reaction of HF with glass, was present in all cases.

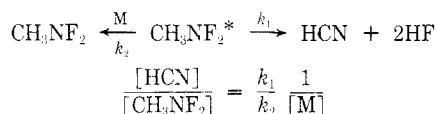
Both radical coupling (eq 4a) and abstraction (eq 4b) reactions are shown contributing to the formation of RNF<sub>2</sub>. The relative importance of these two reactions remains to be established.

Steps 5a and 5b represent possible pathways for generating N<sub>2</sub>F<sub>2</sub>. The latter seems to be a more likely route to N<sub>2</sub>F<sub>2</sub> than does eq 5a, which involves dimerization of a reactive intermediate. Hopefully, quantum yields will allow us to distinguish between these alternatives.

### Unimolecular Elimination of HF

In the photodifluoramination of methane,<sup>4,10</sup> HCN is formed in addition to CH<sub>3</sub>NF<sub>2</sub>. According to carbon mass balances, CH<sub>3</sub>NF<sub>2</sub> and HCN account for all of the methane consumed. At first the HCN was believed to arise from initially formed CH<sub>3</sub>NF<sub>2</sub> by bimolecular elimination reactions. However, the ratio CH<sub>3</sub>NF<sub>2</sub> to HCN was found to be time independent and pressure dependent, suggesting the incursion of an excited intermediate.

If an energetic CH<sub>3</sub>NF<sub>2</sub> molecule is the common precursor of stable CH<sub>3</sub>NF<sub>2</sub> and HCN, then the pressure dependence of the product ratio can be expressed quantitatively in the form



Consistent with this analysis, we find that the ratio [CH<sub>3</sub>NF<sub>2</sub>]/[HCN] is linearly related to the third body concentration, [M], and that the efficiency of the gases used to remove excess energy follows the order C<sub>2</sub>F<sub>6</sub> > CF<sub>4</sub> > CH<sub>4</sub> > N<sub>2</sub>. The conclusion that "hot" CH<sub>3</sub>NF<sub>2</sub> plays an important role in the reaction of CH<sub>4</sub> is corroborated by the work of Ross and Shaw,<sup>11</sup> who estimate the activation energy for unimolecular elimination of HF from CH<sub>3</sub>NF<sub>2</sub> to be 42 kcal/mol.

Interestingly the dehydrofluorination of vibrationally excited CH<sub>3</sub>NF<sub>2</sub> leads to HF laser emission. Padrick and Pimentel<sup>12</sup> estimate that the products, HCN + 2HF, of this reaction lie approximately 80 kcal below the ground state of CH<sub>3</sub>NF<sub>2</sub> formed by the reaction CH<sub>3</sub> + N<sub>2</sub>F<sub>4</sub> → CH<sub>3</sub>NF<sub>2</sub> + NF<sub>2</sub>. From their investigation of the laser emission, they estimate that 3% of this available energy is placed in HF vibrational modes. Collisional deactivation of the excited CH<sub>3</sub>NF<sub>2</sub> was also observed in their study.

In contrast to the methane case, photodifluoramination of FCH<sub>3</sub>, over the pressure range 100 to 200

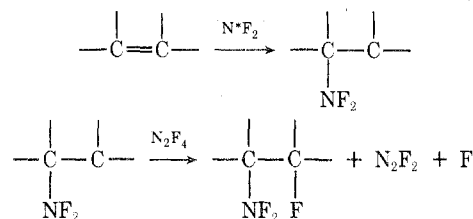
Torr, yields FCH<sub>2</sub>NF<sub>2</sub> which undergoes no detectable dehydrofluorination.<sup>13</sup> This finding is consistent with the idea that the C-F bond is a more efficient storer of vibrational energy than a C-H bond.<sup>14</sup>

### Photodifluoramination and Fluorination

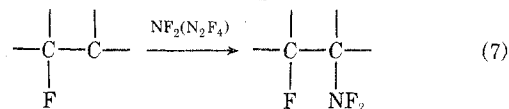
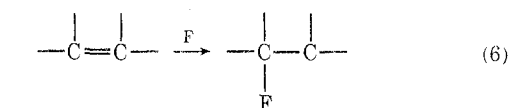
If, as proposed, atomic fluorine is an intermediate in the photodifluoramination of alkanes, then photolysis of NF<sub>2</sub> in the presence of alkenes ought to lead to products resulting from F capture; i.e., partial fluorination of the hydrocarbon should be observed. To test this prediction, we irradiated mixtures of N<sub>2</sub>F<sub>4</sub> and olefins.

From propylene, three carbon-containing products were isolated,<sup>4</sup> CH<sub>2</sub>=CHCH<sub>2</sub>NF<sub>2</sub>, CH<sub>2</sub>(F)CH(NF<sub>2</sub>)CH<sub>3</sub>, and CH<sub>2</sub>(NF<sub>2</sub>)CH(F)CH<sub>3</sub>. The first compound obviously arises by the substitution process shown to be characteristic of alkanes. Formation of CH<sub>2</sub>(F)CH(NF<sub>2</sub>)CH<sub>3</sub> and CH<sub>2</sub>(NF<sub>2</sub>)CH(F)CH<sub>3</sub>, however, entails addition of both F and NF<sub>2</sub>. Moreover, these adducts differ from the 1,2-bis(difluoramino) derivatives produced when olefins and N<sub>2</sub>F<sub>4</sub> are heated.<sup>15</sup> The simple thermal addition of N<sub>2</sub>F<sub>4</sub> does not play a role in the photochemical reaction, for no change is observed if the reactants are mixed at room temperature in the absence of light.

Two processes might be considered to account for the observed fluorination and difluoramination: (i) attack on the olefin by excited NF<sub>2</sub>, followed by abstraction of F from N<sub>2</sub>F<sub>4</sub> or some other F donor;



or (ii) addition of F to the double bond followed by introduction of the NF<sub>2</sub> moiety.



If NF<sub>2</sub> is added first to the olefin, some bis(difluoramino) adducts would be expected since ·NF<sub>2</sub> is an efficient radical trap.<sup>15</sup> The absence of such adducts, which are stable under the experimental conditions, constitutes evidence against a route involving difluoraminoalkyl intermediates. Thus, the scheme presented above to account for the photodifluoramination of alkanes can be modified to encompass the olefin results by introducing the addition reactions 6 and 7. The overall fluorination-difluoramination is described by

(13) C. L. Bumgardner, E. L. Lawton, and H. Carmichael, *J. Org. Chem.*, **36**, 3819 (1971).

(14) J. T. Bryant and G. O. Pritchard, *J. Phys. Chem.*, **71**, 3439 (1967); D. Sianesi, G. Nelli, and R. Fontanelli, *Chim. Ind. (Milan)*, **50**, 619 (1968); J. A. Kerr, D. C. Phillips, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1806 (1968).

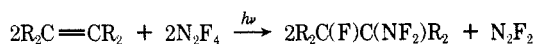
(15) A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 105 (1967).

(9) J. J. Comeford and D. E. Mann, *Spectrochim. Acta*, **21**, 197 (1965).

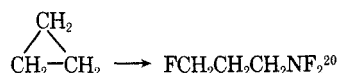
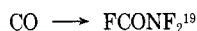
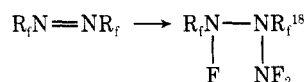
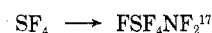
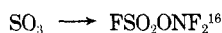
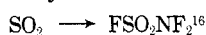
(10) C. L. Bumgardner, E. L. Lawton, and H. Carmichael, *Chem. Commun.*, 1079 (1968).

(11) D. S. Ross and R. Shaw, *J. Phys. Chem.*, **75**, 1170 (1971).

(12) T. D. Padrick and G. C. Pimentel, *J. Chem. Phys.*, **54**, 720 (1971).



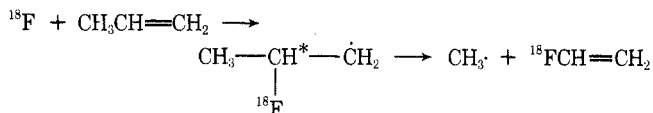
Analogous photoadditions of F and NF<sub>2</sub> have been observed with a variety of other substrates.



When atomic F adds to an olefinic linkage, chemical activation of the resulting intermediate can induce unimolecular decomposition which may compete with adduct formation. This interesting complication and its relation to orientation of F and NF<sub>2</sub> in unsymmetrical olefins will be examined in the next two sections.

### Unimolecular CH<sub>3</sub> Elimination

The exploratory propylene-N<sub>2</sub>F<sub>4</sub> experiments were carried out at an initial pressure of 150 Torr, which afforded a ratio of CH<sub>2</sub>(F)CH(NF<sub>2</sub>)CH<sub>3</sub> to CH<sub>2</sub>(NF<sub>2</sub>)CH(F)CH<sub>3</sub> equal to 3.0. From the work of Williams, Iyer, and Rowland,<sup>21</sup> however, it is clear that this value does not represent the true ratio of terminal to central addition of F to the double bond of propylene. These workers, utilizing trace amounts of <sup>18</sup>F in SF<sub>6</sub> as an inert gas and HI as radical scavenger, studied the addition of atomic F to propylene and noted the formation of FCHCH<sub>2</sub> in addition to the expected adducts, CH<sub>2</sub>FCH<sub>2</sub>CH<sub>3</sub> and CH<sub>3</sub>CHFCH<sub>3</sub>. Since the yield of FCHCH<sub>2</sub> increased with decreasing pressure, they interpreted their finding in terms of an elimination of CH<sub>3</sub> from a hot intermediate. Consistent with this view is our observa-



tion that CH<sub>3</sub>NF<sub>2</sub> and FCHCH<sub>2</sub> are obtained as by-products in the photodifluoroamination of propylene, the amount of CH<sub>3</sub>NF<sub>2</sub> and FCHCH<sub>2</sub> increasing with decreasing pressure.<sup>22</sup> Thus for the ratio of CH<sub>2</sub>(F)CH(NF<sub>2</sub>)CH<sub>3</sub> to CH<sub>2</sub>(NF<sub>2</sub>)CH(F)CH<sub>3</sub> to be a true reflection of the ratio of initial F attack at the terminal and internal carbon atom of the propylene double bond, the CH<sub>3</sub> elimination must be taken into account. The value of the ratio of terminal to central F attack, corrected for elimination,<sup>22</sup> is 1.45, in agreement with the number 1.35 obtained by Rowland, *et al.*,<sup>21</sup> using <sup>18</sup>F.

(16) M. Lustig, C. L. Bumgardner, and J. K. Ruff, *Inorg. Chem.*, **3**, 917 (1964).

(17) A. L. Logothetis, G. N. Sausen, and R. J. Shozda, *Inorg. Chem.*, **2**, 173 (1963).

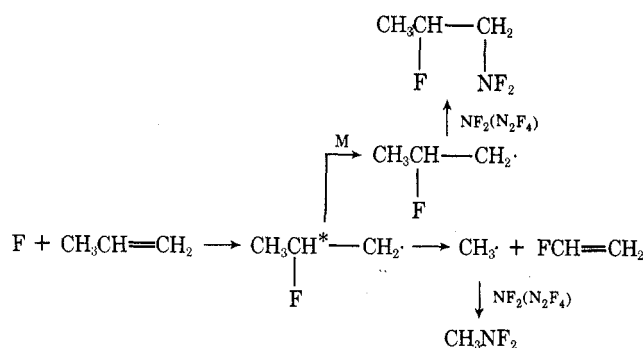
(18) G. N. Sausen, *J. Org. Chem.*, **33**, 2336 (1968).

(19) G. W. Fraser and J. M. Shreeve, *Inorg. Chem.*, **4**, 1497 (1965).

(20) C. L. Bumgardner and E. L. Lawton, *J. Org. Chem.*, **37**, 410 (1972).

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(22) J. G. Carver, unpublished observations. Butene-2 behaves similarly.



The isomeric radical with F on the terminal carbon atom, CH<sub>3</sub>CHCH<sub>2</sub>F, shows no tendency to undergo unimolecular elimination under the same conditions.

The parallel between the propylene-<sup>18</sup>F reaction and the photochemical propylene-N<sub>2</sub>F<sub>4</sub> reaction serves to undergird the thesis that atomic F is an intermediate in photodifluoroamination.

### Another Orientation Problem

A different type of orientation problem was encountered during the photodifluoroamination of 1,1-difluoroethylene, CF<sub>2</sub>CH<sub>2</sub>. Irradiation of N<sub>2</sub>F<sub>4</sub> (44 Torr) and CF<sub>2</sub>CH<sub>2</sub> (88 Torr) led to a 2.3:1.0 mixture, respectively, of CF<sub>3</sub>CH<sub>2</sub>NF<sub>2</sub> and CF<sub>2</sub>(NF<sub>2</sub>)CH<sub>2</sub>F. Although obtaining both isomers was not surprising, comparison of our results with those obtained from other radical addition reactions (Table II) reveals that the photodifluoroamination case is anomalous. It alone gives rise to a product distribution in which the major component is derived from a primary radical (XCF<sub>2</sub>CH<sub>2</sub>·) intermediate. To resolve this inconsistency we investigated the photodifluoroamination under a variety of conditions and found that the ratio of adducts is pressure dependent.<sup>23</sup> As the pressure increases, the ratio of CF<sub>3</sub>CH<sub>2</sub>NF<sub>2</sub> to CF<sub>2</sub>(NF<sub>2</sub>)CH<sub>2</sub>F decreases. When the reaction was carried out at a total initial pressure of about 400 Torr, CF<sub>2</sub>(NF<sub>2</sub>)CH<sub>2</sub>F became the predominant isomer, the "correct" one according to the data in Table II.

Table II  
Comparison of Radical Additions to CF<sub>2</sub>CH<sub>2</sub>

Radical, X	Orientation, ·CF <sub>2</sub> CH <sub>2</sub> X vs. XCF <sub>2</sub> CH <sub>2</sub> ·		Ref
Cl	3.5	1.0	a
CF <sub>3</sub> S	1.0	0	b
CF <sub>3</sub>	1.0	0	c
<sup>18</sup> F	4.0	1.0	d
F	1.0	2.3	This work

<sup>a</sup> J. F. Harris, Jr., *J. Amer. Chem. Soc.*, **84**, 3148 (1962).

<sup>b</sup> J. F. Harris, Jr., and F. W. Stacey, *ibid.*, **83**, 840 (1961).

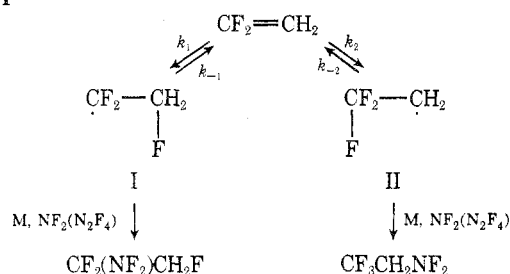
<sup>c</sup> R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 1199 (1953). <sup>d</sup> T. Smal, R. S. Iyer, and F. S. Rowland, *J. Amer. Chem. Soc.*, **94**, 1041 (1972).

One possible rationale described in Chart I involves reversible F addition to the olefin to generate hot intermediates I and II. If these revert to F and olefin in competition with deactivation and ultimate conversion to stable adducts, the observed pressure effect could be explained; *i.e.*, if  $k_1 > k_2$ ,  $k_{-1} > k_{-2}$ .

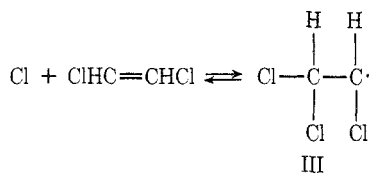
(23) R. J. Leonard, Jr., unpublished observations.

The condition of  $k_1 > k_2$  is in agreement with data in Table II on reactions under kinetic control.

Chart I

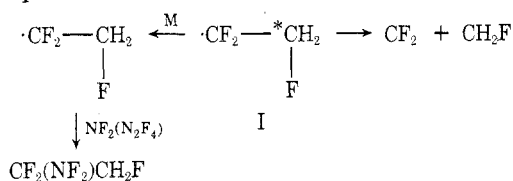


Ayscough, Cocker, and Dainton<sup>24</sup> observed that chlorine atoms add reversibly to *cis*- and *trans*-1,2-dichloroethylene in the gas phase to give hot intermediate III. Since decomposition of III into reactants



was found to result in partial isomerization of the starting olefin, we examined the photodifluoramination of *cis*- and *trans*-butene-2 to probe for reversible F addition. No isomerization of the butenes was observed over the pressure range used in the  $\text{CF}_2\text{CH}_2$  experiments. We conclude, therefore, that since reversible F addition is not important in the butene-2 case, it is probably not important when  $\text{CF}_2\text{CH}_2$  is the substrate.

A second explanation for the pressure trend involves carbon-carbon cleavage of hot intermediate I at low pressure.



Recent data indicate that the conversion  $\text{F} + \text{CF}_2\text{CH}_2 \rightarrow \text{CF}_2 + \text{CH}_2\text{F}$  may be nearly thermoneutral.<sup>25</sup> In contrast, the cleavage  $\text{F} + \text{CF}_2\text{CH}_2 \rightarrow \text{CF}_3 + \text{CH}_2$  is highly endothermic and would not be expected to be important even at low pressures. Thus, the decomposition pictured for hot  $\cdot\text{CF}_2\text{CH}_2\text{F}$  could account for the unusually high ratio of  $\text{CF}_3\text{CH}_2\text{NF}_2$  to  $\text{CF}_2(\text{NF}_2)\text{CH}_2\text{F}$  observed at low pressures. If this explanation is correct, mass balances should show that the combined yield of the two adducts drops as the pressure is decreased, a prediction that is being tested.

Still another possibility, F migration between hot intermediates I and II, cannot be ruled out at this stage.

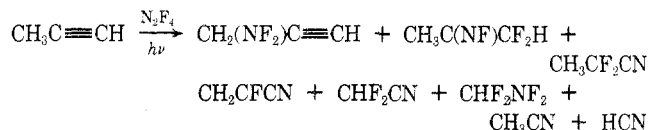


(24) P. B. Ayscough, A. J. Cocker, and F. S. Dainton, *Trans. Faraday Soc.*, 58, 284 (1962).

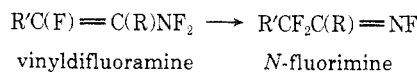
(25) F. S. Rowland, private communication.

## Photodifluoramination and Rearrangement

Having observed addition of F and  $\text{NF}_2$  to olefins, we investigated the photodifluoramination of methylacetylene and allene to extend the scope of the reaction. Irradiation of methylacetylene and  $\text{N}_2\text{F}_4$  gave a host of products, some of which contained fewer than three carbon atoms.<sup>26</sup>

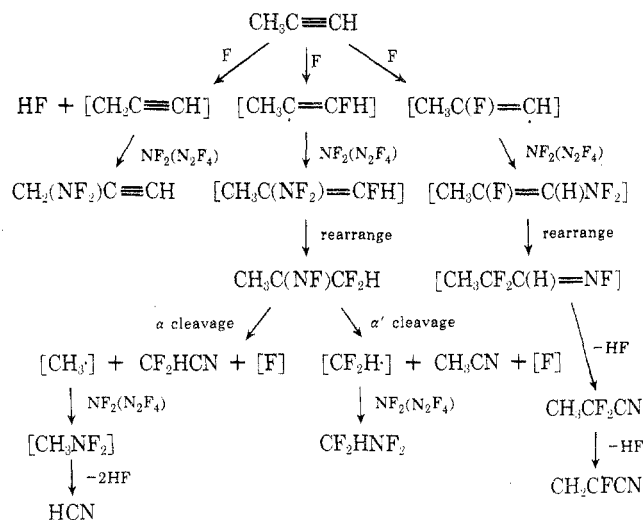


Formation of this array may be rationalized, nevertheless, by the scheme in Chart II which commences with abstraction by, and addition of, atomic F. Propargyldifluoramine,  $\text{CH}_2(\text{NF}_2)\text{C}\equiv\text{CH}$ , is a substitution product analogous to those observed from alkanes. Addition of F to the unsymmetrical triple bond can give rise to isomeric vinyl radicals and subsequently to two vinyl difluoramines. These unstable intermediates then rearrange<sup>26,27</sup> to produce the corresponding *N*-fluorimine isomer, which has two carbon-fluorine bonds and only one nitrogen-fluorine bond. If  $\text{R} = \text{H}$  in the *N*-fluorimine formulation, fac-



ile loss of HF would be expected, resulting in nitrile formation. This route explains the formation of  $\text{CH}_3\text{CF}_2\text{CN}$  (Chart II). Even when R is not equal to H nitriles are produced, but by a more fascinating pathway involving C-C rupture. Since *N*-fluorimines may be viewed as NF analogs of ketones, the  $\alpha$  and  $\alpha'$  cleavage reactions shown in Chart II may represent Norrish type I photolysis<sup>28</sup> of the imine  $\text{CH}_3\text{C}(\text{NF})\text{CF}_2\text{H}$ . The fragments from such a decomposition, as shown in Chart II, could account for the products containing only one or two carbon atoms. A study of the photochemistry of *N*-fluorimines is under way.

Chart II



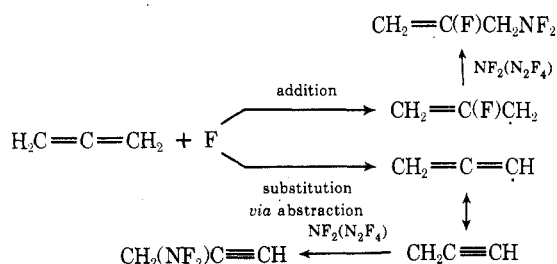
(26) G. Crowther, unpublished observations.

(27) C. L. Bumgardner, *Tetrahedron Lett.*, 3683 (1964).

(28) J. C. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 379.

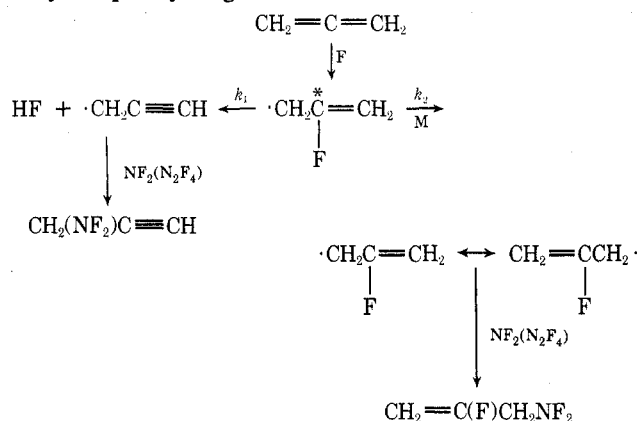
### A Missing Isomer

Photodifluoroamination of allene proved to be less complex than the methylacetylene case, at least with respect to number of products.<sup>29</sup> Two types of carbon-containing compounds were isolated, one resulting from addition of F and NF<sub>2</sub>, and the other from substitution of an NF<sub>2</sub> moiety for hydrogen. Propargyldifluoroamine, CH<sub>2</sub>(NF<sub>2</sub>)C≡CH, appeared to come about *via* allenic hydrogen abstraction followed by combination of NF<sub>2</sub> with the intermediate delocalized propargyl radical. The adduct, CH<sub>2</sub>C(F)CH<sub>2</sub>NF<sub>2</sub>, evidently was produced by attack of F at the central carbon atom of allene.



The ratio of CH<sub>2</sub>C(F)CH<sub>2</sub>NF<sub>2</sub> to CH<sub>2</sub>(NF<sub>2</sub>)C≡CH, however, was found to be linearly dependent on the total pressure of the system, a finding not accommodated by the above reaction scheme.

The data indicate that the two products have a common precursor, possibly a vibrationally excited 2-fluoropropene radical. This species may undergo collisional deactivation with inert body M to yield ultimately CH<sub>2</sub>C(F)CH<sub>2</sub>NF<sub>2</sub> or lose HF unimolecularly to give a propargyl radical which then furnishes CH<sub>2</sub>(NF<sub>2</sub>)C≡CH. This scheme does correctly predict the linear relation and is novel in that overall substitution occurs *via* addition-elimination instead of by simple hydrogen abstraction.

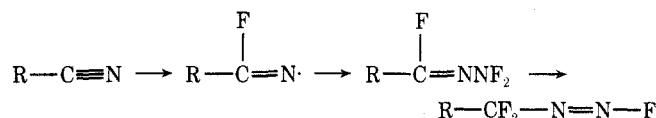


Also surprising is the fact that only one addition product was isolated from the allene reaction.<sup>30</sup> The missing adduct, with F on the terminal carbon atom, CH<sub>2</sub>C(NF<sub>2</sub>)CH<sub>2</sub>F, would be expected, on the basis of the previous observations, to rearrange to the imine CH<sub>2</sub>(F)C(NF)CH<sub>2</sub>F. This isomer, though, may disappear by  $\alpha$  cleavage reactions similar to those postulated in the methylacetylene case. Efforts to iso-

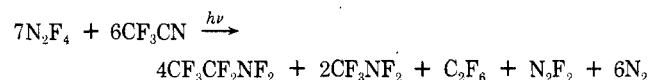
late products attributable to decomposition of this N-fluoroimine are in progress.

### An Analogy Pays Off

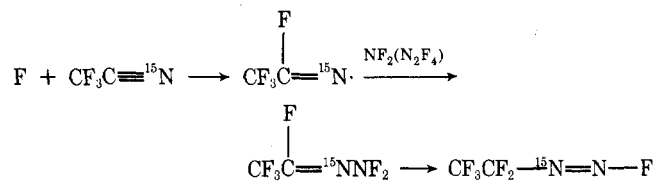
If a nitrile is used instead of an alkyne in the photodifluoroamination reaction, then the following sequence of steps leading to an alkylfluorodiazene might be anticipated.



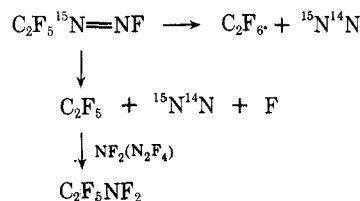
This prediction was tested by irradiating mixtures of N<sub>2</sub>F<sub>4</sub> and CF<sub>3</sub>CN. Results are summarized in the following equation.<sup>31</sup>



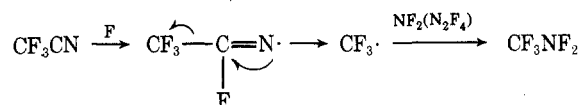
When <sup>15</sup>N-labeled trifluoroacetonitrile was used as the starting material, the label was found by mass spectroscopy to be exclusively in molecular nitrogen as <sup>14</sup>N<sup>15</sup>N. Consistent with the prediction, these results can be rationalized by a scheme analogous to that described for photodifluoroamination of substrates containing a carbon-carbon triple bond. De-



composition of C<sub>2</sub>F<sub>5</sub><sup>15</sup>NNF, the fluorine analog of alkyldiazene,<sup>32</sup> provides a simple route to CF<sub>3</sub>CF<sub>2</sub>NF<sub>2</sub>, C<sub>2</sub>F<sub>6</sub>, and N<sub>2</sub> correctly labeled.



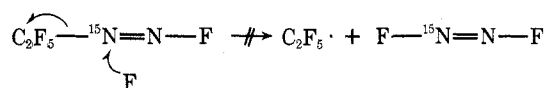
The CF<sub>3</sub>NF<sub>2</sub> observed may arise by the addition-elimination



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



no <sup>15</sup>N-labeled N<sub>2</sub>F<sub>2</sub> was observed, generation of R<sub>f</sub>· *via* the addition-elimination also may be dismissed.



Hydrocarbon nitriles are presently under investigation.

(29) C. L. Bumgardner and K. G. McDaniel, *J. Amer. Chem. Soc.*, **91**, 1032 (1969).

(30) R. L. Williams and F. S. Rowland, 7th Fluorine Conference, have observed both terminal and central addition to allene by atomic F from the <sup>18</sup>F(n,2n)<sup>18</sup>F nuclear reaction.

(31) J. C. Wozny and C. L. Bumgardner, *Tetrahedron Lett.*, in press.

(32) For discussion of alkyldiazenes, RN<sub>2</sub>H, see E. M. Kosower, *Accounts Chem. Res.*, **4**, 193 (1971).

## Summation and Outlook

Irradiation of  $N_2F_4(NF_2)$  provides a convenient source of atomic fluorine which can be used to introduce F into substrates and/or to form radicals which readily yield products containing the  $NF_2$  moiety. Vibrationally excited intermediates may be generated by this procedure at low pressures and a number of interesting unimolecular decomposition pathways studied. Fluoronitrene, NF, the fragment formed concomitantly with F in the photolysis of  $NF_2$ , is isoelectronic with  $O_2$ . How closely the chemistry of NF parallels that of  $O_2$  remains an intriguing chal-

lenge.<sup>33</sup> The photochemistry of *N*-fluorimines, analogs of ketones, promises to be a fruitful area of study. Uncovering evidence for alkylfluorodiazenes,  $RN_2F$ , suggests that other routes to these species should be sought, for they may well play a key role in the development of new fluorination methods.

*We are grateful to the National Science Foundation and the North Carolina State University Engineering Foundation for generous financial support.*

(33) The esr spectrum of NF has been obtained: A. H. Curran, R. G. McDonald, A. J. Stone, and B. A. Thrush, *Chem. Phys. Lett.*, **8**, 451 (1971).

# The Geometry of Intersecting Potential Surfaces

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The notion of a potential function for the motion of the nuclei in a molecular system takes different forms from different points of view.

For the classical idealist, the potential function is simply the work which must be done to bring the constituent atoms from infinite separation to some specified conformation. This definition gives no assurance that a potential function exists, or is unique, and it is sadly lacking in operational significance.

For the experimentalist, a potential function is that function which, when inserted into the appropriate quantum mechanical description of the nuclear motion, reproduces his data within their scatter. It is to be hoped that the same function is consistent with the results of more than one kind of experiment.

For the theoretician, a molecular potential function is a creature of the Born-Oppenheimer separation, and attention tends to focus on the limitations of this remarkably useful approximation.

A potential energy function is the basic premise, or the object of the game, in many different endeavors with small molecules. Many phenomena are thought of as being controlled by a single potential function and provide data for determining that function. Examples are vibrational energy levels of diatomic<sup>1,2</sup> and polyatomic<sup>3</sup> molecules, elastic scattering of atoms,<sup>4</sup> transport phenomena and gas imperfections,<sup>5,6</sup> and product energy distributions in atom-transfer reactions.<sup>7-9</sup> There are, however, other processes of a fundamentally different sort, which cannot be explained in terms of a single potential function. Examples are perturbations in bound states,<sup>10,11</sup> predissociation in small molecules,<sup>12,13</sup> collisional transfer of electronic energy,<sup>14,15</sup> and

electronic chemiluminescence.<sup>8,16</sup> These phenomena must be described in terms of the interaction of two (or more) electronic states or potential functions.

Comparing problems tractable in terms of a single electronic state with those which must involve two states is, quite literally, like comparing a line to a plane. In view of this great increase in complexity, I have chosen to isolate a small, but well-defined and fundamental, part of the problem. This Account is devoted to a discussion of the geometrical properties of triatomic potential functions in the neighborhood of an intersection. The intersection of electronic states raises fundamental questions about the precise definition of potential functions, their validity, and above all their usefulness.

## Definitions of Potential Functions

To begin with, there are the coordinates of the electrons, lumped together in the set  $q$ . The coordinates specifying the shape of the system or conformation<sup>17</sup> of the nuclei are  $(Q_1, Q_2, Q_3) \equiv Q$ . They

- (1) R. T. Pack, *J. Chem. Phys.*, **57**, 4612 (1972).
- (2) W. I. Newman and W. R. Thorson, *Can. J. Phys.*, **50**, 2997 (1972).
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- (6) G. C. Maitland and E. B. Smith, *Mol. Phys.*, **24**, 1185 (1972).
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- (12) C. E. Caplan and M. S. Child, *Mol. Phys.*, **23**, 249 (1972).
- (13) D. S. Ramsay and M. S. Child, *Mol. Phys.*, **22**, 263 (1971).
- (14) E. R. Fisher and E. Bauer, *J. Chem. Phys.*, **57**, 1966 (1972).
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- (16) T. Carrington in "Chemiluminescence and Bioluminescence," J. Lee, D. M. Hercules, and M. J. Cormier, Ed., Plenum Press, New York, N. Y., 1973.

Tucker Carrington was born in Cincinnati, Ohio, in 1927. Before accepting his present position as Professor of Chemistry at York University, he was at Yale University and the National Bureau of Standards. His work concerns spectroscopic studies of inelastic and reactive collisions of small molecules in known quantum states.