With minor variations the procedure of Cope was employed for the oxidation of this *trans*-2,3-diphenyl-2-butene.[20] To a solution of 46.5 g (0.22 mol) of *trans*-2,3-diphenyl-2-butene in 200 ml of chloroform which had been cooled to 20° was added 45 ml of a 40% peracetic acid solution containing 4 g of sodium acetate. The temperature was maintained below 35° during the course of the addition. The resulting reaction mixture was then stirred for 22 hr at room temperature after which it was poured into cold water. The oxirane was extracted with methylene chloride and the organic phase stirred with a 10% sodium carbonate solution, washed with water until neutral, dried, and the solvent removed. Recrystallization from methanol yielded *trans*-2,3-diphenyl-2,3-dimethyloxirane (60%), mp 107° (lit.[28] 107°).

**Preparation of 1,2-Diphenyl-1,2-epoxycyclohexane (2).** The procedure described by Cope[20] for the preparation of stilbene oxide was employed in this case. A solution containing 0.24 g (1.0 mmol) of 1,2-diphenylcyclohexene, prepared according to published procedures,[29,30] in 4.0 ml of methylene chloride was cooled to 10° and 1 ml of a 40% solution of peracetic acid containing 0.05 g of sodium acetate was added at such a rate that the temperature did not rise above 40°. The mixture was stirred at room temperature for 24 hr and then poured into water. The oxirane was extracted with methylene chloride, and the organic phase washed with a dilute sodium carbonate solution prior to being dried over anhydrous sodium sulfate. The solvent was then removed and the residue (0.2 g) was recrystallized from methanol to give the pure oxirane **2**, mp 77–78°.

*Anal.* Calcd for $C_{18}H_{18}O$: C, 86.30; H, 7.25. Found: C, 86.57; H, 7.36.

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[28] Ramart-Lucas and M. E. Salman-Legagneur, *Bull. Soc. Chim. Fr., Ser.*, **4**, **45**, 718 (1929).

[29] S. M. Parmertor, *J. Amer. Chem. Soc.*, **71**, 1127 (1949).

[30] P. Tomboulian, *J. Org. Chem.*, **26**, 2652 (1961).

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# Photodifluoramination of Alkanes and Alkenes

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*Received July 10, 1969*

**Abstract:** Selectivity ratios for photodifluoramination of *n*-butane, *n*-butyl fluoride, ethyl chloride, and ethyldifluoramine were determined by analyzing the isomeric mixture of alkyldifluoramines produced by irradiation of $N_2F_4$ with these substrates. Kinetic and stoichiometric information about the photodifluoramination process was obtained from a study of the photolysis of $N_2F_4$ with methane. Irradiation of $N_2F_4$ with propylene and isobutylene results not only in substitution of $NF_2$ for H but addition of F and $NF_2$ to the double bond. The F was found mainly on the terminal carbon atom. The experimental data are rationalized by reaction schemes which have as a common step photolysis of $NF_2$ into atomic fluorine and fluoronitrene, NF.

The observation[2] that $NF_2$ radicals (available from the equilibrium $N_2F_4 = 2NF_2$) absorb in the region of 2600 Å suggested that this system should show some interesting photochemistry. Exploratory experiments[3] in which $N_2F_4$ was irradiated at 2537 Å with alkanes indicated that the major process was substitution of a hydrogen atom by an $NF_2$ group, photodifluoramination, reminiscent of photochlorination. Similar treatment of alkenes and alkynes resulted in addition of the elements of $NF_3$ to the multiple bond.[3–5] Formation of these and analogous products from other substrates[6,7] was rationalized by postulating that $NF_2$ underwent photolysis to give fluoronitrene, NF, and atomic fluorine.

To test this hypothesis we have now (a) ascertained selectivity patterns for the substitution reaction by studying the photodifluoramination of *n*-butane, 1-fluorobutane, chloroethane, and difluoraminoethane; (b) obtained kinetic and stoichiometric information by examining the photodifluoramination of methane; and (c) determined orientational preferences in the addition reaction by investigating the photodifluoramination of propylene and isobutylene.

## Results

The experimental techniques employed in our selectivity study were similar to those used by Fredricks and Tedder[8] to study halogenations in the gas phase. However, photodifluoramination was carried out in a static system, whereas halogenations were conducted in a flow system. The basic assumption of radical selectivity studies is that the relative amounts of isomeric products formed from a given hydrocarbon are equal to the relative rates of hydrogen abstraction at any position in the molecule, corrected to a per-hydrogen basis. The selectivity ratios relative to the methyl

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[1] NASA Fellow.

[2] F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, **83**, 3043 (1961).

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

[4] C. L. Bumgardner and G. P. Crowther, Abstracts, 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 1969.

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

[6] C. L. Bumgardner and M. Lustig, *Inorg. Chem.*, **2**, 662 (1963).

[7] C. L. Bumgardner and E. L. Lawton, *Tetrahedron Lett.*, 3059 (1968).

[8] P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960).

**Table I.** Characterization of Photoproducts[a]

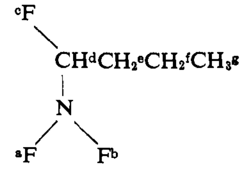
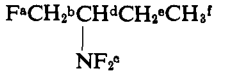
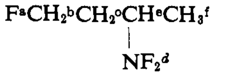
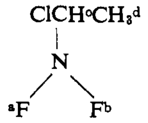
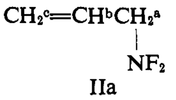
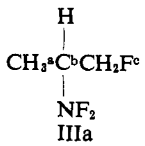
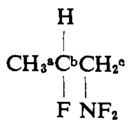
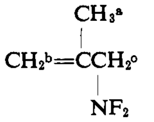
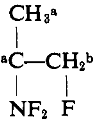
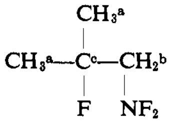
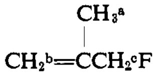
| Starting material | Product | Chemical shift[b] | | Coupling constant, Hz | Ir, $cm^{-1}$ |
|---|---|---|---|---|---|
| | | $\phi$ | $\delta$ | | |
| *n*-Butane | $CH_3^aCH_2^bCH_2^cCH_2^dNF_2$ | −56.7 ($NF_2$) | 3.43 (t in t, $CH_2^d$) | $J_{H^dF} = 29$ | 2970 (CH) |
| | | | 1.75–1.15 (m, $CH_2^bCH_2^c$) | $J_{H^cH} = 7$ | 920 ($NF_2$) |
| | | | 0.89, (t, $CH_3$) | $J_{H^aH^b} = 7$ | 845 ($NF_2$) |
| | $CH_3^aCH_2^bCH^c(NF_2)CH_3^d$ | −41.1 ($NF_2$) | 3.38 (t in m, $CH^c$) | $J_{H^cF} = 28$ | 2970 (CH) |
| | | | 1.60 (m, $CH_2^b$) | $J_{H^aH^b} = 7$ | 965 ($NF_2$) |
| | | | 1.21 (d, $CH_3^d$) | | 875 ($NF_2$) |
| | | | 0.94 (t, $CH_3^a$) | $J_{H^dH^c} = 6$ | 855 ($NF_2$) |
| 1-Fluorobutane |  | +171.4 (d in t, CF) | 4.85 (m, $CH^d$) | $J_{F^aF^b} = 540$ | 2960 (CH) |
| | | −25.3 (q of AB pattern, $NF_2$) | 1.20–1.90 (m, $CH_2^eCH_2^f$) | $J_{F^cH^d} = 48$ | 1145 (CF) |
| | | −19.5 (d, $F^a$) | 0.89 (t, $CH_3^g$) | $J_{F^cH^d} = 23$ | 918 ($NF_2$) |
| | | −30.4 (d, $F^b$) | | $J_{H^fH^g} = 6$ | 908 ($NF_2$) |
| | | | | | 878 ($NF_2$) |
| |  $F^aCH_2^b\underset{NF_2^c}{CH^d}CH_2^eCH_3^f$ | +230.9 (t in d, CF) | 4.57 (d in d, $CH_2^b$) | $J_{F^aH^b} = 48$ | 2960 (CH) |
| | | −40.9 ($NF_2$) | 3.46 (m, $CH^d$) | $J_{F^aH^d} = 23$ | 1050 (CF) |
| | | | 1.90 (m, $CH_2^e$) | $J_{H^bH^d} = 4$ | 980 ($NF_2$) |
| | | | 0.97 (t, $CH_3^f$) | $J_{H^eH^f} = 7$ | 875 ($NF_2$) |
| |  $F^aCH_2^bCH_2^c\underset{NF_2^d}{CH^e}CH_3^f$ | +220.5 (t in t, CF) | 4.46 (d in t, $CH_2^b$) | $J_{F^aH^b} = 47$ | 2960 (CH) |
| | | −39.3 ($NF_2$) | 3.62 (t in m, $CH^e$) | $J_{F^aH^c} = 23$ | 1060 (CF) |
| | | | 1.94 (m, $CH_2^c$) | $J_{F^dH^e} = 24$ | 975 ($NF_2$) |
| | | | 1.23 (d, $CH_3^f$) | $J_{H^bH^c} = 6$ | 880 ($NF_2$) |
| | | | | $J_{H^eH^f} = 6$ | 860 ($NF_2$) |
| | $F^aCH_2^bCH_2^cCH_2^dCH_2^eNF_2^f$ | +220.0 (t in t, CF) | 4.35 (d in t, $CH_2^b$) | $J_{F^aH^b} = 47$ | 2960 (CH) |
| | | −55.6 ($NF_2$) | 3.41 (t, in t, $CH_2^e$) | $J_{F^aH^c} = 23$ | 1065 (CF) |
| | | | 1.50–1.90 (m, $CH_2^cCH_2^d$) | $J_{F^fH^e} = 30$ | 935 ($NF_2$) |
| | | | | $J_{H^bH^c} = 4$ | 855 ($NF_2$) |
| | | | | $J_{H^dH^e} = 6$ | |
| Chloroethane | $ClCH_2^aCH_2^bNF_2$ | −54.0 ($NF_2$) | 3.82 (t in t, $CH_2^b$) | $J_{FH^b} = 27$ | 2990 (CH) |
| | | | 3.75 (t, $CH_2^a$) | $J_{H^bH^c} = 4$ | 955 ($NF_2$) |
| | | | | | 920 ($NF_2$) |
| | | | | | 845 ($NF_2$) |
| | | | | | 755 (CCl) |
| |  | −39.0 (q of AB pattern, ($NF_2$)) | 5.26 (m, $CH^c$) | $J_{F^aF^b} = 540$ | 2990 (CH) |
| | | −47.9 (d, $F^a$) | 1.80 (d, $CH_3^d$) | $J_{H^cH^d} = 7$ | 995 ($NF_2$) |
| | | | | | 890 ($NF_2$) |
| | | | | | 745 (CCl) |
| Difluoroaminoethane | $F_2NCH_2CH_2NF_2$ | −54.8 ($NF_2$) | 3.88 (t, $CH_2$) | $J_{FH} = 27$ | 2960 (CH) |
| | | | | | 975 ($NF_2$) |
| | $CH_3CN$[c] | | | | 880 ($NF_2$) |
| Ethane | $CH_3^aCH_2^bNF_2$ | −53.3 ($NF_2$) | 1.25 (t, $CH_3$) | $J_{FH^b} = 28$ | 2960 (CH) |
| | | | 3.48 (m, $CH_2$) | $J_{H^aH^b} = 7$ | 972 ($NF_2$) |
| | | | | | 860 ($NF_2$) |
| Propylene Ia |  $CH_2^c{=}CH^b\underset{NF_2}{CH_2^a}$ | −54 ($NF_2$) | 3.81 (t in d, $CH_2^a$) | $J_{H^aF} = 29$ | 3077 (CH) |
| | | | 5.58 (m, $CH^b$) | $J_{H^aH^b} = 7$ | 909 ($CH_2{=}$) |
| | IIa | | 5.21 and 5.06 (m, $CH_2^c$) | | 985 ($NF_2$) |
| | | | | | 826 ($NF_2$) |
| |  $CH_3^a\overset{H}{\underset{NF_2}{C^b}}CH_2F^c$ | −41 ($NF_2$) | 3.70 (m, $CH_3^a$) | $J_{H^cF^c} = 47$ | |
| | | | | | 2985 (CH)[d] |
| | | +230 (CF) | 3.75 (m, $CH^b$) | $J_{H^cH^b} = 5$ | |
| | | | 4.56 (d in d, $CH_2^c$) | | |
| | IIIa | | | | 1105 (CF) |
| | | | | | 1055 (CF) |
| |  $CH_3^a\overset{H}{\underset{F}{C^b}}\underset{NF_2}{CH_2^c}$ | | 1.49 (d in d, $CH_3^a$) | | 980 ($NF_2$) |
| | | −56 ($NF_2$) | 5.25 (m, $CH^b$) | | 877 ($NF_2$) |
| | | | 3.75 (m, $CH_2^c$) | | 862 ($NF_2$) |
| | | | | | 826 ($NF_2$) |
| | IVa | | | | |

**Table I** (*continued*)

| Starting material | Product | Chemical shift[b] $\phi$ | Chemical shift[b] $\delta$ | Coupling constant, Hz | Ir, cm$^{-1}$ |
|---|---|---|---|---|---|
| Isobutylene Ib |  $CH_2^b{=}C(CH_3^a)CH_2^cNF_2$<br>IIb | −56 ($NF_2$) | 1.83 (s, $CH_3^a$)<br>5.07 (s, $CH_2^b$)<br>3.97 (t, $CH_2^c$) | $J_{H^cF}$ = 29.9 | 3096 ($CH_2$=)<br>2950 (CH)<br>1661 ($CH_2$=)<br>971 ($NF_2$)<br>909 ($CH_2$=)<br>826 ($NF_2$) |
| |  $CH_3^aC(CH_3^a)(NF_2)$—$CH_2^bF$<br>IIIb | −29 ($NF_2$)<br>229 (t, CF) | 1.29 (d, $CH_3^a$)<br>4.39 (d, $CH_2^b$) | $J_{H^aF^c}$ ≈ 1<br>$J_{H^bF^b}$ = 48 | 2994 (CH)<br>1064 (CF)<br>971 ($NF_2$)<br>877 ($NF_2$) |
| |  $CH_3^a$—$C^c(CH_3^a)(F)$—$CH_2^bNF_2$<br>IVb | −61 ($NF_2$)<br>140 (m, CF) | 1.47 (d, $CH_3^a$)<br>3.64 (t in d, $CH_2^b$) | $J_{H^bF^b}$ = 29.6<br>$J_{H^bF^c}$ = 19 | 2994 (CH)<br>1059 (CF)<br>917 ($NF_2$)<br>901 ($NF_2$)<br>826 ($NF_2$) |
| |  $CH_2^b{=}C(CH_3^a)CH_2^cF$ | 216 (t, CF) | 1.76 (s, $CH_3^a$)<br>4.98 (s, $CH_2^b$)<br>4.73 (d, $CH_2^c$) | $J_{H^cF}$ = 46.2 | 3067 ($CH_2$=)<br>2941 (CH)<br>1656 ($CH_2$=)<br>1060 (CF)<br>909 ($CH_2$=) |
| | $(CH_3)_3C$–F | 151 (CF) | 1.38 ($CH_3$) | $J_{HF}$ = 21.5 | 2976 (CH)<br>1040 (CF) |

[a] Elemental analyses and mass spectra were consistent with assigned structures. [b] Spectra were run as approximately 5% by volume solutions in deuteriochloroform with the probe temperature at 25°. Fluorine ($^{19}F$) chemical shifts ($\phi$) are in parts per million relative to fluorotrichloromethane as an external reference. Proton ($^1H$) chemical shifts ($\delta$) are in parts per million downfield relative to tetramethylsilane as an internal reference. Ratios of signals agreed with assigned structures. [c] This product is believed to be the result of attack of F on the hydrogen atom $\alpha$ to the $NF_2$ group. The intermediate radical formed, $CH_3CHNF_2$, apparently undergoes rapid loss of F and HF to give the observed nitrile, C. L. Bumgardner and E. L. Lawton, to be published. [d] Ir for mixture of IIIa and IVa.

groups 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 the data collected in Table I. Table II summarizes the selectivity ratios.

In the reaction with methane, all of the $CH_4$ consumed was accounted for as $CH_3NF_2$ and HCN.[9] The molar ratio of the sum of these two to the $N_2F_2$ produced was approximately 2:1 whereas the ratio of $[CH_3NF_2 + HCN]/N_2F_4$ consumed approached unity. In addition to the products mentioned above small amounts of NO, $N_2O$, $SiF_4$ and $N_2$ were observed. Although carbon mass balances generally proved satisfactory (105 ± 5%), nitrogen and fluorine balances were variable. This is not surprising in view of the reactivity in glass of many fluorine compounds.[10] The data from the kinetic runs showed the reaction to be zero order in $CH_4$ and the rate of disappearance of $N_2F_4$ was tested for fit with equations for one-half,

**Table II.** Selectivity Ratios Per Hydrogen Atom

| Entry | Radical source | Temp, °C | Substrate | | | |
|---|---|---|---|---|---|---|
| | | | $CH_3$— | $CH_2$— | $CH_2$— | $CH_3$ |
| 1[a] | $F_2 \underset{h\nu}{\rightleftarrows} 2F$ | 20 | 1 | 1.3 | 1.3 | 1 |
| 2[b] | $NF_2 \underset{h\nu}{\longrightarrow} F + NF$ | 25 | 1 | 1.2 | 1.2 | 1 |
| 3[a] | $Cl_2 \longrightarrow 2Cl$ | 35 | 1 | 3.9 | 3.9 | 1 |
| | | 146 | 1 | 3.3 | 3.3 | 1 |
| 4[c] | $N_2F_4 \underset{h\nu}{\rightleftarrows} 2NF_2$ | 250 | 1 | 5.1 | 5.1 | 1 |
| 5[a] | $Br_2 \longrightarrow 2Br$ | 146 | 1 | 82 | 82 | 1 |
| | | | $FCH_2$— | $CH_2$— | $CH_2$— | $CH_3$ |
| 6[a] | $F_2 \underset{h\nu}{\leftrightarrows} 2F$ | 20 | <0.3 | 0.8 | 1.0 | 1 |
| 7[b] | $NF_2 \underset{h\nu}{\longrightarrow} F + NF$ | 25 | 0.7 | 0.9 | 1.0 | 1 |
| 8[a] | $Cl_2 \underset{h\nu}{\longrightarrow} 2Cl$ | 35 | 0.8 | 1.6 | 3.7 | 1 |
| 9[a] | $Br_2 \longrightarrow 2Br$ | 146 | 10 | 9 | 82 | 1 |
| | | | $ClCH_2$— | $CH_3$ | | |
| 10[b] | $NF_2 \xrightarrow{h\nu} F + NF$ | 25 | 0.9 | 1 | | |
| | | | $F_2NCH_2$ | $CH_3$ | | |
| 11 | $NF_2 \xrightarrow{h\nu} F + NF$ | 25 | ~1 | 1 | | |

[a] Reference 3. [b] This work; experiment repeated four to seven times. The standard deviation indicated selectivity ratios to be reproducible to ±5%. [c] Calculated from data of S. F. Reed and R. C. Petry, *Tetrahedron*, 5089 (1968).

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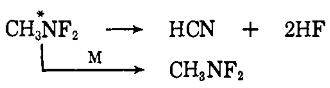
[9] The HCN is the product of unimolecular decomposition of

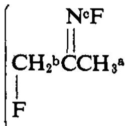
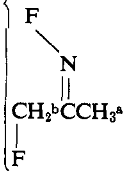
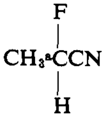
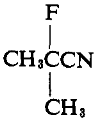


$$\overset{*}{CH_3NF_2} \longrightarrow HCN + 2HF \qquad \overset{*}{CH_3NF_2} \xrightarrow{M} CH_3NF_2$$

"hot" $CH_3NF_2$. For details, see C. L. Bumgardner, E. L. Lawton, and H. Carmichael, *Chem. Commun.*, 1079 (1968).

[10] A. M. Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958.

**Table III.** Characterization of Dehydrofluorinated Products

| Starting compd | Dehydrofluorinated products[b] | Chemical shift[a] $\phi$ | Chemical shift[a] $\delta$ | Coupling constant, Hz |
|---|---|---|---|---|
| IIIa |  $FCH_2^bC(=N^cF)CH_3^a$ | +28 (NF) | 1.99 ($CH_3^a$)<br>4.76 ($CH_2^b$) | $J_{H^bF^b} = 47$<br>$J_{H^bF^c} = 4$ |
| |  $FCH_2^bC(=NF)CH_3^a$ | +28 (NF) | 1.99 (d, $CH_3^a$)<br>4.85 (d in d, $CH_2^b$) | $J_{H^bF^b} = 45$ |
| IVa |  $CH_3^aCHFCN$ | | 1.59 ($CH_3$) | $J_{H^aF} = 23$<br>$J_{HH} = 6$ |
| IVb |  $(CH_3)_2CFCN$ | | 1.62 (d, $CH_3$) | $J_{HF} = 20.5$ |

[a] See Table I for explanation of symbols. [b] Products derived from IIIa were assigned the configurations shown on the basis of observation made on similar compounds by G. N. Sausen and A. L. Logothetis, *J. Org. Chem.*, **32**, 2661 (1967).

first, three-halves, and second-order dependence on $N_2F_4$ concentrations. The best fit (Figure 1) proved to be with the one-half order relationship.

Photolysis in the gas phase of $N_2F_4$ in the presence of propylene and isobutylene resulted in formation of $N_2F_2$, $SiF_4$, and a liquid. The reaction mixture was separated by bulb-to-bulb distillation followed by gas phase chromatography. Analysis of the $^1H$ and $^{19}F$ nmr spectra along with infrared and mass spectra served to establish the identity of the purified components (Table I). In the case of the carbon-containing products, structural assignments were verified by selective dehydrofluorination reactions using pyridine in chloroform. This base effected elimination of HF only from C–N atoms without disturbing F bound to carbon. Thus primary alkyldifluoramines were converted to nitriles, secondary difluoramines to N-fluorimines, but tertiary difluoramines did not react. These results are collected in Table III. Table IV summarizes the product distribution from the olefin reactions as determined by nmr and gas chromatographic analyses. As in the case of $CH_4$, approximately 0.5 mmole of $N_2F_2$ was obtained for every millimole of $N_2F_4$ decomposed.

**Table IV.** Product Distribution from Olefins

| Starting olefin | Products | Total yield,[a] % | Product ratios (*M*) III/IV | Product ratios (*M*) II/(III + IV) |
|---|---|---|---|---|
| Propylene Ia | IIa, IIIa, IVa | 50 | 3.0 | 1.0 |
| Isobutylene, Ib | IIb, IIIb, IVb | 75[b] | 3.1 | 1.2 |

[a] Based on the equations $2RH + 2N_2F_4 \rightarrow 2RNF_2 + 2HF + N_2F_2$ and $2R_2C{=}CH_2 + 2N_2F_4 \rightarrow 2R_2C_2H_2NF_3 + N_2F_2$. The yield of $N_2F_2$ was almost quantitative. [b] Also isolated from the isobutylene reaction were *t*-butyl fluoride and 3-fluoro-2-methylpropene.

## Discussion

The results may be discussed in terms of the following sequence of steps. The equilibrium shown in step 1

$$N_2F_4 = 2NF_2 \tag{1}$$

$$NF_2 \xrightarrow{h\nu} F + NF \tag{2}$$

$$R\text{-}H + F \longrightarrow HF + R \tag{3}$$

$$R + NF_2 \longrightarrow RNF_2 \tag{4a}$$

$$R + N_2F_4 \longrightarrow RNF_2 + NF_2 \tag{4b}$$

$$NF + NF_2 \longrightarrow N_2F_2 + F \tag{5}$$

is well documented[2,11] and 2537-Å radiation should be absorbed by $NF_2$ but not by $N_2F_4$ or the hydrocarbon. If the equilibrium in step 1 is rapidly established and (2) is rate determining then

$$\frac{d(\text{product})}{dt} = 2k_2(NF_2) = 2k_2K^{1/2}(N_2F_4)^{1/2} = \frac{-d(N_2F_4)}{dt}$$

where $K$ is the equilibrium constant for step 1 and $k_2$ is an intensity dependent function relating the rate of step 2 to the $NF_2$ concentration. Since reaction 3 represents the fate of F, the sequence predicts that the rate of photodifluoramination should exhibit one-half order dependence on $N_2F_4$ concentration and zero-order dependence on $CH_4$ concentration under the conditions of these experiments (Figure 1). The assumption that equilibrium 1 is rapid with respect to step 2 does not seem unreasonable in view of the work of Levy and Copeland,[12] who demonstrated that the rate of establishment of the equilibrium $N_2F_4 = 2NF_2$ is rapid compared with the reaction of fluorine gas with $NF_2$ at 75°. Calculations based on the data in Figure

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(11) (a) H. E. Doerenbus and B. R. Long, *J. Chem. Phys.*, **39**, 2393 (1963); (b) L. A. Piette, F. A. Johnson, K. A. Booman, and C. B. Colburn, *ibid.*, **35**, 1481 (1961); (c) F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, **83**, 3943 (1961).

(12) J. B. Levy and B. K. W. Copeland, *J. Phys. Chem.*, **69**, 3700 (1965).

1 and a value[11c] of $K = 6.34 \times 10^{-8}$ mole/l. (25°) indicate that the initial rate of photolysis of $NF_2$ ($-d(NF_2)/dt = -2d(N_2F_4)/dt$ for an initial concentration of $N_2F_4 = 2.3 \times 10^{-3}$ mole/l. is of the order of $10^{-7}$ mole/l. sec, a rate many orders of magnitude slower than the initial rate of dissociation of $N_2F_4$ at the same concentration which was calculated to be 0.45 mole/l. sec (at 75°) by Modica and Hornig from shock tube experiments.[13]

Since the N–F bond strength in $NF_2$ is estimated to be 71 kcal/mole[14] and since 2537 Å corresponds to 112 kcal/mole, there is sufficient energy to realize step 2.

Confirmatory evidence for one of the products of step 2, NF, was reported by Mann and Comeford,[15] who obtained the infrared spectrum of this species by irradiating $NF_2$ in a low-temperature matrix.

The HF produced by step 3 was not isolated in our experiments but was largely removed as indicated in the Experimental Section to simplify work-up procedures. $SiF_4$, the expected result of interaction of HF with glass, was present in all reactions.

Consistent with step 3 are the comparisons in Table II which clearly show that photodifluoramination exhibits a very low degree of discrimination indicative of a highly reactive hydrogen-abstracting species. In particular, the close parallel between entries 1 and 2 and between 6 and 7 point to the fluorine atom as the common reagent.

The slightly greater selectivity observed in entry 1 over entry 2 and in entry 6 over entry 7 may be due to the extra energy imparted to F produced by photolysis of $NF_2$. The total maximum excess kinetic energy of atomic fluorine, $E_F$, from photolysis may be estimated from the relation[16]

$$E_{(F)} = \left[\frac{hc}{\lambda} - D_{FN-F}\right]\left[\frac{M_{NF}}{M_F + M_{NF}}\right] = (112 - 71)\left(\frac{33}{52}\right) = 26 \text{ kcal/mole}$$

where $D_{FN-F}$ is the N–F bond dissociation energy[14] in $NF_2$ and $M$ is the mass of the fragments. The production of atomic fluorine having some extra energy could thus account for the differences between entries 1 and 2 and between 6 and 7 of Table II.

The results in Tables I and II and those contained in the paper on $CH_4$ present an interesting contrast with respect to chemical activation. Whereas decomposition of "hot" $CH_3NF_2$ plays an important role in the photodifluoramination of $CH_4$,[9] no evidence was obtained in the present investigation for analogous fragmentations. This is not unreasonable since the more complicated (relative to $CH_3NF_2$) alkyldifluoramines in Table I would decompose more slowly than $CH_3NF_2^*$, *i.e.*, the number of effective oscillators[17] will be greater for the products listed in Table I than for $CH_3NF_2$.

Since mercury manometers were used in these experiments, mercury photosensitized decomposition of $N_2F_4$ must be considered, *e.g.*

$$Hg^* + N_2F_4 \longrightarrow N_2F_2 + F_2 + Hg$$

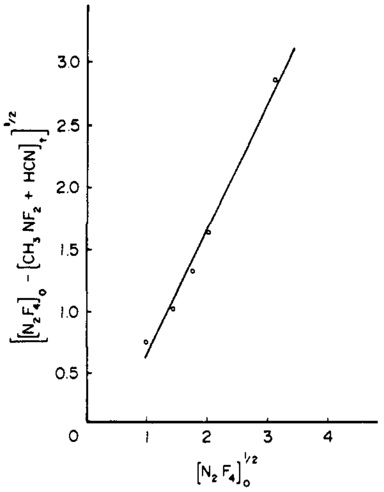


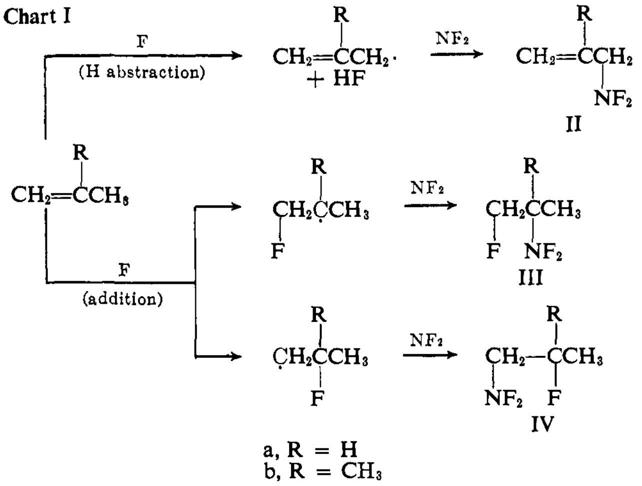
Figure 1. Half-order plot, $(N_2F_4)_0$ = millimoles of $N_2F_4$ at start, $[[N_2F_4]_0 - [CH_3NF_2 + HCN]_t]$ = millimoles of $N_2F_4$ remaining after 12 min of irradiation. Reactor volume, 650 ml; temperature, 25°.

The kinetic results, however, are not compatible with this possibility. The observation that a high-pressure quartz mercury lamp equipped with a Vycor filter gave the same products and product distributions as a low-pressure lamp fabricated in Vycor demonstrates that mercury photosensitization is unimportant.[18] An alternative to step 3 not ruled out kinetically is that excited $NF_2$, not F, abstracts H from R–H.[19] The

$$R\text{-}H + NF_2^* \longrightarrow HNF_2 + R$$

failure to observe any $HNF_2$ does not constitute evidence against this possibility since $HNF_2$ is not stable under these conditions.[20] An $NF_2$ with excess energy might conceivably display the indiscriminate behavior indicated in Table II. However, the olefin results point convincingly to the intermediacy of F in photodifluoramination reactions (Chart I).

**Chart I**



Isolation of the substitution products, IIa and IIb, was not surprising in view of the fate of alkanes under similar conditions. Formation of compounds IIIa, IIIb, and IVa, IVb, however, represents another process

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(13) A. P. Modica and D. F. Hornig, *J. Chem. Phys.*, **49**, 629 (1968).

(14) A. Kennedy and C. B. Colburn, *ibid.*, **35**, 1892 (1961).

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

(16) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley & Sons, Inc., New York, N. Y., 1966, p 647.

(17) J. A. Kerr, D. C. Phillips, and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 1806 (1968).

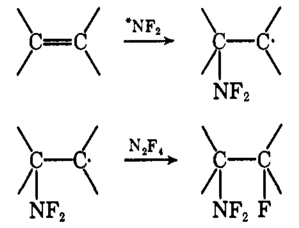
(18) Reference 16, p 689.

(19) For an analogous reaction involving $NO_2^*$, see F. E. Blacet, T. C. Hall, and P. A. Leighton, *J. Amer. Chem. Soc.*, **84**, 4011 (1962).

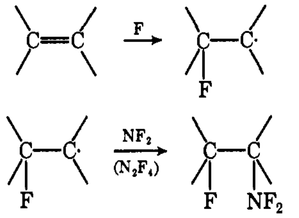
(20) Unpublished observations.

and shows that a fluorinating species is present in the reaction mixture. Moreover, these adducts (III and IV) differ from the 1,2-bisdifluoramino derivatives produced when olefins and $N_2F_4$ are heated.[21] The simple thermal addition of $N_2F_4$ does not play a role in the photochemical reactions, 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: (i) attack on the olefin by $^*NF_2$ followed by abstraction of F from $N_2F_4$ or some other F donor



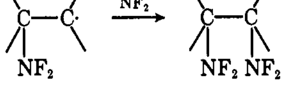
or (ii) addition to the olefin of F, followed by introduction of the $NF_2$ moiety



(6)

(7)

The III/IV ratios (Table IV) which measure orientational preferences, indicate that the latter sequence, involving initial F addition, is more consistent with the results. If $NF_2$ added first to the olefin, some bis-$NF_2$ adducts would be expected since $NF_2$ is an efficient radical trap.[21] The absence of such adducts which are stable



$E_a \simeq 0$

under these conditions constitutes additional evidence against formation of difluoraminoalkyl intermediates.[22] Formation of a substantial amount of adducts IVa and IVb (Table IV) with F on the internal carbon atom is not unreasonable considering the high reactivity of F. Atomic hydrogen, for example, shows approximately 6% nonterminal addition to propylene.[23] The relatively high II/(III + IV) ratios may also be ascribed to the low selectivity of F.

The scheme presented above to account for the photodifluoramination of alkanes can thus be easily modified (by introducing addition reactions 6 and 7) to encompass the olefin results.[24]

Step 4b, a bimolecular reaction between R and $N_2F_4$, represents another route to R–$NF_2$. The weak N–N bond in $N_2F_4$ ($\sim$20 kcal/mole)[14] and the high concentration[2] of $N_2F_4$ relative to $NF_2$ make step 4b an attractive possibility. The data available do not permit a choice between steps 4a and 4b at present.[25]

$$R + NF_2 \longrightarrow RNF_2$$

$$2R \longrightarrow R_2$$

$$R + N_2F_4 \longrightarrow RNF_2 + NF_2$$

Step 5 shows $N_2F_2$ arising *via* decomposition of the radical resulting from combination of NF with $NF_2$. This reaction, compatible with the stoichiometry observed, seems more probable than direct union of two NF fragments which would require a third body. The transformation in step 5 infers that NF behaves as a radical reagent, *i.e.*, that its spin state is $\cdot\underset{\cdot}{\overline{\text{N}}}\text{—F}$ rather than $|\overline{\text{N}}\text{—F} \leftrightarrow {}^{-}\overline{\text{N}}\text{=F}^{+}$. This is not unreasonable in view of the fact that NF is isolelectronic with $O_2$ and in terms of a Linnett structure,[26] would be constructed electronically with a seven- and five-electron spin set. Such a spin state for NF would also be consistent with the failure to observe any insertion or addition reactions which might be expected of a singlet NF species.[27] From a quantum-mechanical treatment of NF, Sahni has predicted the ground state of the species to be a triplet.[28] Experiments designed to establish this point are currently in progress.

We conclude that the photodifluoraminations of alkanes and alkenes described in this paper involve as the common primary step photolysis of $NF_2$ into NF and F.

## Experimental Section[29]

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

**Starting Materials.** Methane (Matheson, CP 99%), $CF_4$ (Matheson, 99.7%), $C_2F_6$ (Matheson, 99%), butane (Matheson, instrument grade), chloroethane (Matheson, CP), pyropylene (Matheson, 99.98%) and isobutylene (Matheson, 99%) were used as received after purity was checked by gas chromatography. 1-Fluorobutane, pure by nmr and gas chromatographic analyses, was synthesized from 1-bromobutane by the method of Hoffmann.[30] Irradiation of ethane and $N_2F_4$ by the procedure described below for preparation of $CH_3NF_2$ gave ethyldifluoramine, $C_2H_5NF_2$, in 60% yield. The product was purified by chromatography (QF-1) and was identified by its nmr spectrum (Table I). Tetrafluorohydrazine of the (mole per cent) 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 Redstone Research Laboratory, Rohm & Haas Co., Huntsville, Ala.

**Selectivity Ratios.** 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 2100 Å

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

[22] For similar results involving inorganic adducts, see M. Lustig, C. L. Bumgardner, and J. K. Ruff, *Inorg. Chem.*, 3, 917 (1964).

[23] R. J. Cvetanović in "Advances in Photochemistry," Vol. 1, W. A. Noyes, Jr., G. S. Hammond, and J. N. Pitts, Jr., Ed., Interscience Publishers, New York, N. Y., 1963, p 157.

[24] Also consistent with the proposed photolysis of $NF_2$ is the work of P. L. Goodfriend and H. P. Woods, *J Mol. Spectrosc.*, 13, 63 (1964), who interpreted the details of the ultraviolet spectrum of $NF_2$ in terms of predissociation.

[25] We are attempting to establish whether radical abstraction of $NF_2$ from $N_2F_4$ can be important through a kinetic study of competition reactions of the type.

[26] J. W. Linnett, *J. Amer. Chem. Soc.*, 83, 2643 (1961).

[27] The spin state of NF generated in solution from $HNF_2$ and base may be different from that of NF produced photochemically from $N_2F_4$ in the gas phase: C. L. Bumgardner, K. J. Martin, and J. P. Freeman, *J. Amer. Chem. Soc.*, 85, 97 (1963); W. J. le Noble and D. Skulnik, *Tetrahedron Lett.*, 5217 (1967).

[28] R. C. Sahni, *Trans. Faraday Soc.*, 63, 801 (1967).

[29] 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-IR5A spectrophotometer, and either a Consolidated Model 620, Bendix Model 12, or Associated Electronics Model MS902 mass spectrometer.

[30] F. W. Hoffmann, *J. Org. Chem.*, 15, 425 (1950).

and to transmit approximately 60% of the 2537-Å 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 consisted of a 10:1 molar ratio of hydrocarbon to tetrafluorohydrazine at 400 Torr total initial pressure.

Alkyldifluoramines were separated from the other products, $SiF_4$, $N_2F_2$, oxides of nitrogen and unchanged starting material by trap-to-trap distillation in the high-vacuum system through −80, −126, and −190° traps. The isomeric mixtures of alkyldifluoramines (retained in the −80° trap) were analyzed on a Varian Aerograph Model 90-P gas chromatograph using a 10 ft × $^3/_8$ in. column of 30% by weight QF-1 (fluorosilicone) supported on 60/80 mesh Chromosorb P. A thermal conductivity cell was employed as a detector; and helium was the carrier gas. Reaction products[31] were collected as they were eluted from the column and were identified by nuclear magnetic resonance, infrared and mass spectral analyses (Table I). The ratios of the areas of the chromatographic peaks were assumed to be directly proportional to the mole ratios of the isomeric products. This assumption is valid if the thermal conductivities of the isomers are equal. This assumption was previously made in selectivity studies of halogenations[8] and has been shown to be applicable to many isomeric compounds. The photolysis of tetrafluorohydrazine was carried out to 15, 50, and 100% completion. The ratios of isomeric products did not vary with the degree of decomposition of the tetrafluorohydrazine. Radical attack upon the initially formed alkyldifluoramine was not important under the reaction conditions due to the presence of excess hydrocarbon reactants and condensation of the liquid alkyldifluoramines. Results are collected in Table II.

**Photodifluoramination of Methane.** The apparatus and general procedure were the same as those described above. After mixtures of $CH_4$ and $N_2F_4$ were irradiated, the products were separated by passing the reaction mixture over sodium fluoride pellets to remove HF and distilling through a series of cold traps (−86, −126, −196). The HCN was collected in the −86° trap; the $CH_3NF_2$ was retained in the −126° trap. Identification was based on comparison of infrared and mass spectra with those of authentic samples.[32] In a number of cases the relative amounts of HCN and $CH_3NF_2$ determined by distillation were corroborated by quantitative mass spectral analysis of the crude reaction mixture. Recovered $CH_4$ and $N_2$ also were measured by this means. Difluorodiazine[33] ($N_2F_2$), recovered $N_2F_4$, $SiF_4$, NO, and $N_2O$, identified by infrared and mass spectra, were observed in the −196° trap. The amounts were determined by quantitative mass spectral analysis and, in the case of $N_2F_4$ and $N_2F_2$, by gas chromatography at 0° using a 5 ft 0.25 in. copper column packed with 30–60 mesh silica gel (F & M Scientific, A-40) and a helium flow rate of 30 $cm^3/min$. The response of the thermal conductivity cell to $N_2F_4$ and $N_2F_2$ was calibrated using pure samples.

Several photolyses were preformed with the high-pressure mercury vapor lamp (Hanovia 679A-36) and filter described below. For a given set of conditions, the conversion using the high-pressure lamp was higher than when using the low-pressure lamp, but the products and product ratio were unchanged.

**Photodifluoramination of Propylene and Isobutylene.** A high-vacuum system lubricated with Kel F90 fluorocarbon stopcock grease was used to transfer reactants to a cylindrical Pyrex glass reaction vessel fitted with a Hanovia quartz immersion well containing a water-cooled high-pressure mercury vapor lamp[34] (Hanovia 679A-36) and a 7910 Vycor filter (absolute cutoff at 2100 Å). Reactor volume was 750 ml. The starting reaction mixture consisted of 4 mmoles of olefin and 2 mmoles of $N_2F_4$ at a total pressure of 150 Torr. After 15 min radiation, the $N_2F_4$ was completely consumed. The reaction mixture was then passed over sodium fluoride pellets to remove HF and fractionated on the vacuum line. The less volatile fractions were further purified by gas phase chromatography at 45° using a 10 ft × $^3/_8$ in. column packed with 30% by weight of QF-1 (fluorosilicone) on 60/80 mesh Chromosorb P. Products were collected as they were eluted from the column and were identified by their nmr, ir, and mass spectra (Table I). The amounts recorded in Table IV were determined by chromatographic and nmr analyses. Infrared and mass spectral analyses showed the more volatile fractions to be mixtures of recovered olefin, *cis*- and *trans*-$N_2F_2$, $SiF_4$, and small amounts of nitrogen oxides and $NF_3$. During the reactions and work-up procedures formation of some polymeric material was noted.

**Dehydrofluorination Reactions.** Dehydrofluorinations were carried out on the samples of II, III, and IV used for nmr analysis. The samples containing 0.2–1.0 mmoles of the compound to be dehydrofluorinated were cooled to −40° (tetrachloroethane slush) or to −86° (Dry ice–methylene chloride). Pyridine (0.2 ml) was then added and the pressure caps were replaced on the nmr tubes. Progress of the reaction was followed by nmr (Table III). Elimination occurred readily at room temperature with primary and allyl difluoramines. The secondary compounds required heating at 60° for the reaction to go to completion. Tertiary compounds did not react.

**Acknowledgment.** We are grateful to the National Science Foundation for generous support of this work and to the National Aeronautics and Space Agency for a fellowship for E. L. L.

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(31) For product identification, runs were made using 6–8 mmoles each of hydrocarbon and $N_2F_4$ and irradiating for 60–90 min. Yields of alkylamines based on the equation $2RH + 2N_2F_4 = 2RNF_2 + N_2F_2 + 2HF$ ranged from 71 to 78%.

(32) J. W. Frazer, *J. Inorg. Nucl. Chem.*, **16**, 63 (1960).

(33) Both *cis* and *trans* forms obtained: R. Ettinger, F. A. Johnson, and C. B. Colburn, *J. Chem. Phys.*, **34**, 2187 (1961); R. H. Sanborn, *ibid.*, 33, 1855 (1969); S. King and J. Overend, *Spectrochim. Acta*, 22, 689 (1966).

(34) Similar results were obtained with a low-pressure (2537 Å) lamp housed in Vycor.