

PHOTOCHEMICAL REACTIONS OF THE DIFLUORAMINO
RADICAL

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The behavior of the electronically excited difluoramino radical¹ with certain inorganic substrates² led us to investigate some photochemistry involving organic compounds.

Irradiation at 2537Å³ of alkanes with tetrafluorohydrazine⁴ gives alkyl difluoramines, reminiscent of photochlorination of hydrocarbons.⁵

¹C. L. Bumgardner and M. Lustig, *Inorg. Chem.*, **2**, 662 (1963).

²M. Lustig, C. L. Bumgardner and J. K. Ruff, *ibid.*, in press.

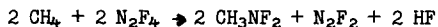
³A cold cathode mercury resonance lamp sealed into a Pyrex vessel was used. The difluoramino radical shows an absorption maximum at 2600Å with a 200Å half width. F. A. Johnson and C. B. Colburn, *J. Am. Chem. Soc.*, **83**, 3043 (1961).

⁴Tetrafluorohydrazine is a source of NF₂ radicals owing to the equilibrium N₂F₄ ⇌ NF₂. See ref. 3.

⁵C. Walling, "Free Radicals in Solution", John Wiley and Sons, New York, 1957, p. 352.

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For example, from irradiation of eight μ moles of methane and two μ moles of N_2F_4 for 30 minutes, difluoraminoethane,⁶ CH_3NF_2 , was obtained in 50% yield (40% conversion). Difluorodiazine,⁷ N_2F_2 , was also formed (50% yield) as indicated in the equation:



The products were characterized by mass and infrared spectrometry.

A similar reaction took place between *n*-butane and N_2F_4 , yielding 1- and 2-difluoraminoethanes in a ratio of 1.4:1, respectively, according to gas phase chromatography.^{8a} The major component was identified by comparing gas chromatography retention times, infrared and mass spectra with those of an authentic sample.⁹ The minor component was assigned on the basis of its retention time, infrared and mass spectrum which are similar to those of the 1-isomer. Interestingly, the ratio of products observed is about the same as the ratio of primary to secondary hydrogen atoms in *n*-butane.

Treatment of *trans*-butene-2 under the above conditions resulted in both substitution of an NF_2 group for hydrogen to give I^{10,11} and addition of the elements of NF_3 to the double bond to yield II¹⁰ in approximately equimolar amounts^{8b} (overall yield 74%).

⁶ J. W. Frazer, *J. Inorg. and Nuclear Chem.*, 16, 23 (1960).

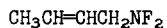
⁷ C. B. Colburn, F. A. Johnson, A. Kennedy, K. McCallum, L. C. Metzger
C. O. Parker, *J. Am. Chem. Soc.*, 81, 6397 (1959).

⁸ A 1/4" x 10' column packed with (a) Dow-Corning silicone oil 710 or
(b) dinonylphthalate supported on Chromosorb was employed. Helium acted
as the carrier gas and a thermal conductivity cell was used as the detector.

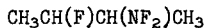
⁹ R. C. Petry, *J. Am. Chem. Soc.*, 82, 2400 (1960).

¹⁰ Satisfactory elemental analyses obtained.

¹¹ Another material believed to be 3-difluoraminoethene-1, an isomer of I,
was obtained in low yield.



I



II

The F^{19} n.m.r. spectrum of compound I showed a single resonance at -52.45δ .¹² The H^1 spectrum had signals at 4.60 τ (vinyl), 6.32 τ (a triplet, $J=28$ cps, due to coupling of the methylene hydrogens with fluorine); and at 8.42 τ (methyl) in the ratio expected for structure I. The infrared spectrum was also consistent, showing bands at 3100 cm^{-1} (vinyl H), 1680 cm^{-1} (double bond) and at 923, 898, 873 cm^{-1} (NF_2). Compound II appears to be a mixture of isomers, (incompletely resolved on gas chromatography), probably threo and erythro-II which would result from an indiscriminate radical reaction. The F^{19} n.m.r. spectrum of II had bands centered about -38.9δ ($\text{NF}'\text{s}$) and at 181.7 and 188.8 δ ($\text{CF}'\text{s}$) in the ratio of 2:1. The infrared spectrum indicated II was saturated (no absorption at 3100 cm^{-1} or at $1600\text{--}1700\text{ cm}^{-1}$) and contained C-F (band at 1120 cm^{-1}) and C- NF_2 (bands at 918 and 870 cm^{-1}) bonds. The complicated set of signals observed at 8.30-9.10 τ in the H^1 n.m.r. spectrum established the presence of the C-methyl groups.

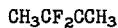
Ethylene underwent similar attack giving 1-fluoro-2-difluoraminoethane characterized by its n.m.r., infrared and mass spectra.

In analogy with butene-2, irradiation of N_2F_4 and butyne-2 gave products resulting from substitution (compound IV¹⁰) and addition to the unsaturated system (compound V¹⁰).

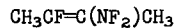
¹² Nuclear magnetic spectra were obtained on neat liquids with a Varian Associates, Model V-3000-B, high resolution spectrometer using a 40 mc. probe (30°). δ and τ values were calculated from measurements made relative to external trifluoroacetic acid and external benzene, respectively.



IV



V



VI

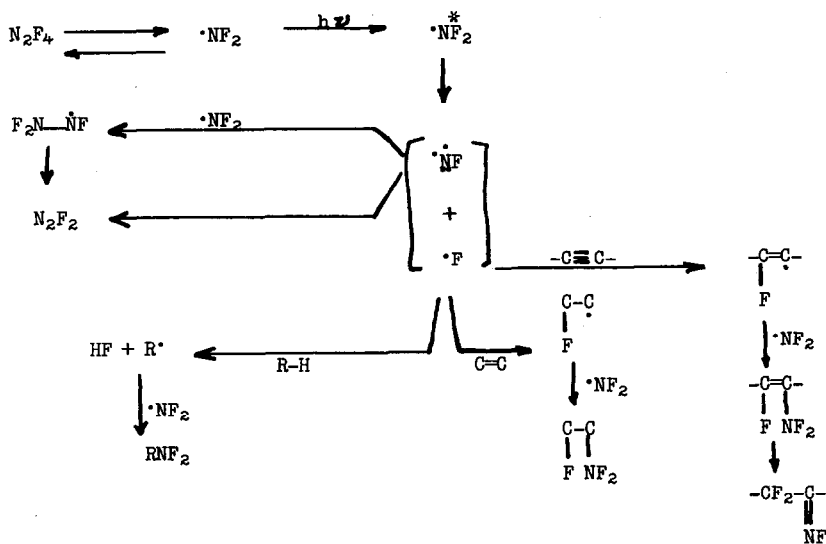
The F^{19} n.m.r. spectrum of IV displayed a single resonance at -52.8δ (NF). The proton spectrum consisted of a triplet ($J = 28$ c.p.s.) centered at 5.15τ (methylene), and a peak at 7.52τ (methyl). Signals from compound V were observed at -24.25δ (NF) and 93.8δ (CF) in the ratio of 1:2, and at 7.65 , 7.82 , 8.08 , 8.60τ (methyls). Bands in the infrared spectrum of IV were apparent at 820 , 890 , 910 cm^{-1} (NF) and 2260 cm^{-1} (acetylene); compound V showed bands at 876 and 933 cm^{-1} (NF), 1140 and 1210 cm^{-1} (CF) and 1660 cm^{-1} (C=N).

Compound V probably arises by rearrangement¹³ of the isomer VI, which is the initial product expected in view of the butene results described.

The above series of reactions, exemplifying direct difluoramination and fluorodifluoramination of hydrocarbons, may be rationalized by the following scheme.

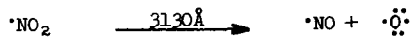
¹³ This allylic rearrangement may be compared with one reported by B. L. Dyatkin, L. S. German and I. L. Knunyants, Proc. Acad. Sci. USSR Sect. Chem., (English translation), 114, 489 (1957).





Reactions are believed to be initiated by $\text{F}\cdot$ (instead of $\cdot\overset{*}{\text{NF}}_2$) as no HNF_2 or bis-difluoramino compounds are observed.¹⁴ Since the N-F bond strength in NF_2 is estimated to be 71 kcal/mole¹⁵ and since 2537Å radiation corresponds

¹⁴Decomposition of NF_2 may be compared to photolytic decomposition of NO_2 which gives an oxygen atom and nitric oxide under certain conditions.



F. E. Blacet, T. C. Hall, and P. A. Leighton, *J. Am. Chem. Soc.*, **84**, 4011 (1962).

¹⁵A. Kennedy and C. B. Colburn, *J. Chem. Phys.*, **35**, 1892 (1961).

to 112 kcal/mole, there is sufficient energy to bring about rupture of NF_2 into F and NF.¹⁶

¹⁶Interestingly, D. E. Mann and J. J. Comeford at the Symposium on Covalent Inorganic Fluorine Compounds (148th meeting of American Chemical Society, Chicago, Sept., 1964) reported that they have obtained the infrared spectrum of a species they believe to be NF by irradiating NF_2 in a matrix at low temperature.

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