

RADICAL REACTIONS OF TETRAFLUOROHYDRAZINE SATURATED HYDROCARBONS AND ETHERS¹

S. F. REED, JR. and R. C. PETRY²

Rohm and Haas Company, Redstone Research Laboratories, Huntsville, Alabama 35807

(Received in USA 5 October 1967; accepted for publication 11 March 1968)

Abstract—Difluoramino radicals attack aliphatic hydrocarbons and dialkyl ethers at 250–350° to produce alkyl difluoramines and difluoraminoalkyl ethers.

SEVERAL recent reports on the free radical chemistry of tetrafluorohydrazine describe its reaction via hydrogen abstraction from or coupling with organic substrates^{3–5} and its addition to olefins.^{6–9} The hydrogen abstraction reactions yield difluoramine and difluoramino-substituted compounds while the coupling and addition reactions yield only the latter. In the N₂F₄-olefin addition reaction it was noted that little hydrogen abstraction occurred with the simple aliphatic olefins;⁹ cyclic olefins¹⁰ such as cyclohexene gave substitution products in addition to the adducts under normal experimental conditions. Formation of the substitution products was considered to involve hydrogen abstraction by the difluoramino radical. The limited hydrogen abstraction from simple olefins by the ·NF₂ radical was attributed to a relative high activation energy for the process.* Continued interest in hydrogen abstraction from organic substrates by the difluoramino radical has led us to investigate the reaction of tetrafluorohydrazine with hydrocarbons and dialkyl ethers at elevated temperatures where hydrogen abstraction reactions would be most favorable. A kinetic study¹¹ of this reaction has been conducted, however, the investigators did not isolate or characterize any of the products. In addition the photolysis of hydrocarbons⁴ and dialkyl ethers⁵ with N₂F₄ has been shown to yield alkyl difluoramines and difluoraminoalkyl ethers, respectively, but, these reactions appear to involve fluorine atoms⁴ and photo-excited ketones⁵ as the hydrogen abstractor. In our work the objective was to determine the extent of hydrogen abstraction and the nature of the resulting products.

Hydrocarbons investigated included methane, ethane, propane, n-butane, isobutane, neopentane and n-hexane while the dialkyl ethers were dimethyl and diethyl ether. The reactions were conducted in the vapor phase at 150–500° in a flow reactor in the presence of an inert diluent. Reaction temperatures of 200–300° were preferred since at lower temperatures limited reaction took place and at higher temperatures extensive decomposition of reactants and products was observed. Product fractions were collected in cold traps, residual N₂F₄ removed, and examined by gas chromatography or mass spectroscopy. In all cases, except for methane and ethane, complicated product mixtures were obtained. The majority of these products were present

* The activation energy for hydrogen abstraction from hydrocarbons by ·NF₂ radical is high compared to bromine (ca. 20 kcal/mole vs 13 kcal/mole).¹¹

TABLE I. CHARACTERIZATION DATA ON PRODUCTS OF TETRAFLUOROHYDRAZINE-HYDROCARBON REACTIONS

Hydrocarbon	Products	NMR data		Elementary analyses			
		F ¹⁹	H ¹	Calculated		Found	
				%F	%N	%F	%N
Propane	CH ₃ CH(NF ₂)CH ₃	-40.8 ϕ	CH ₃ - τ 8.82 ($J = 7$ c/s)	40.00	14.75	40.94	14.24
			CH - τ 6.58 ($J_{HF} = 26$ c/s)				
n-Butane	CH ₃ CH ₂ CH ₂ NF ₂	-53.7 ϕ	($J_{HF} = 7$ c/s)	40.00	14.75	40.32	15.33
			CH ₂ NF ₂ - τ 6.58 ($J_{HF} = 28$ c/s)				
			($J_{HH} = 7$ c/s)				
n-Butane	CH ₃ CH(NF ₂)CH ₂ NF ₂ ^b CH ₃ CH ₂ CN ^b	-39 ϕ^a	CHNF ₂ - τ 6.82 ($J_{HF} = 27$ c/s)	34.15	12.83	34.32	13.81
		-53.9 ϕ	CH ₃ CH ₂ CH(NF ₂)CH ₃				
		-55.1 ϕ	CH ₃ CH ₂ CH ₂ CH ₂ NF ₂				
			CH ₃ NF ₂ - τ 6.58 ($J_{HF} = 27$ c/s)				
			CH ₃ CH ₂ CH(NF ₂)CH ₂ NF ₂				

Isobutane	$(\text{CH}_3)_2\text{C}-\text{NF}_2^c$							
	$(\text{CH}_3)_2\text{CHCH}_2\text{NF}_2$	-55.9 ϕ	$\text{CH}_2\text{NF}_2 - \tau 6.65 (J_{\text{HF}} = 30 \text{ c/s})$ $(J_{\text{HH}} = 7 \text{ c/s})$	34.15	12.83	34.92	12.76	
	$(\text{CH}_3)_2\text{C}(\text{NF}_2)\text{CH}_2\text{NF}_2^b$							
	$\text{CH}_3\text{CH}(\text{CH}_2\text{NF}_2)_2$	-54.4 ϕ	$\text{CH}_3 - \tau 8.92 (J_{\text{HH}} = 7 \text{ c/s})$ $\text{CH}_2\text{NF}_2 - \tau 6.92 (J_{\text{HF}} = 30 \text{ c/s})$ $(J_{\text{HH}} = 7 \text{ c/s})$	47.50	17.50	47.24	17.75	
Neopentane	$(\text{CH}_3)_3\text{CCH}_2\text{NF}_2$	-62.5 ϕ	$\text{CH}_3 - \tau 9.28 (J = 7 \text{ c/s})$ $\text{CH}_2\text{NF}_2 - \tau 7.02 (J = 30 \text{ c/s})$	30.90	11.38	29.63	11.05	
	$(\text{CH}_3)_3\text{C}(\text{NF}_2)\text{CH}_2\text{NF}_2^b$							
N-Hexane	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHCH}_3$	-36.7 ϕ^a	$\text{CHNF}_2 = \tau 5.98 (J \sim 30 \text{ c/s})$	27.94	10.30	28.21	10.15	
	$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{NF}_2$	-55.2 ϕ	$\text{CH}_2\text{NF}_2 - 7.08 (J = 30 \text{ c/s})$	27.94	10.30	27.47	10.65	
	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{NF}_2)\text{CH}_2\text{CH}_3$	-37.3 ϕ		27.94	10.30	27.61	10.31	

^a Center of complex multiplet; spectra taken at 40 Mc.

^b Ref. 9.

^c R. C. Fetty and J. P. Freeman, *J. Am. Chem. Soc.* **83**, 3912 (1961).

in minor quantities with the bulk of the mixture comprised of two to four major components representing 80–90% of the total mixture. Emphasis was placed on separating and identifying these major components. The products and their characterization data are shown in Table 1 (hydrocarbons) and Table 2 (dialkyl ethers). All compounds were isolated by preparative gas chromatography (>95% purity) since it was found impossible to effect their complete separation by distillation.

TABLE 2. CHARACTERIZATION DATA ON PRODUCTS OF TETRAFLUOROHYDRAZINE-ETHER REACTIONS

Product	F ¹⁹ NMR spectrum	Elemental analysis			
		Calc		Found	
		%F	%N	%F	%N
V	Broad peak centered at -32.6ϕ ($-\text{CH}_2\text{NF}_2$)	39.18	14.41	38.01	14.38
VI	Triplet centered at -32.0ϕ (CH_2NF_2); triplet ($J = 45$ c/s) centered at $+153.7 \phi$	49.63	12.19	49.19	12.76
VII	Triplet centered at -31.3ϕ ($-\text{CH}_2\text{NF}_2$)	51.32	18.94	49.0	19.02
VIII	Triplet centered at -28.6ϕ	45.75	16.85	44.1	17.61
IX	Doublet centered at -25.30ϕ $(>\text{CHNF}_2)$	30.20	11.20	30.10	12.61
X	Triplet centered at -55.7ϕ ($-\text{CH}_2\text{NF}_2$)	30.20	11.20	31.20	12.34
XI	Triplet centered at -55.7ϕ ($-\text{CH}_2\text{NF}_2$) singlet centered at -23.87ϕ (CHNF_2)	43.20	15.92	39.30	15.13

The structures of the products were confirmed by IR and NMR spectroscopy. Their IR spectra were distinguished by strong absorption bands in the range of $800\text{--}1100 \text{ cm}^{-1}$. Fluorine NMR spectra were consistent with that expected with fluorine resonance in the range of -65 to -25ϕ . In addition the proton NMR spectra were helpful in making structural assignments. Elemental analysis data were satisfactory in most instances, and gave support to the structural assignments based on spectral data.

Conversions of the substrates to products were low, being usually in the range of 5–25% with occasional higher conversions noted. To some extent the conversion to products was dependent upon the nature of the substrate. It is well known that the ease of abstraction of H atoms from aliphatic hydrocarbons follows the order $3^\circ > 2^\circ > 1^\circ$. For instance, in our studies conversion to products was higher for isobutane than neopentane other conditions being equal due probably to the greater ease of abstracting 3° relative to 1° H atoms. Higher conversions were generally obtained when using large N_2F_4 to hydrocarbon concentrations. In this study the N_2F_4 to hydrocarbon flow rates were varied from 2:1 to 10:1.

The relative selectivity of difluoramino radicals for 1°, 2° and 3° H atoms of the hydrocarbon substrates is shown in Table 3. These data were obtained on a qualitative basis from a comparison of peak areas of the various components on gas chromatography and indicate only the relative selectivity of the $\cdot\text{NF}_2$ radical for different types of H atoms in the substrates. In general the $\cdot\text{NF}_2$ radical is not highly

TABLE 3. CONVERSION AND PRODUCT RATIO DATA

Hydrocarbon	Conversion to products ^a (%)	Product ratio ^b			
		1°	2°	3°	Bis (difluoramines)
Propane	18	1.0	2.6	—	0.67
<i>n</i> -Butane	19	1.0	3.41	—	0.60
Isobutane	25	1.0	—	5.7	1.13 ^c
<i>n</i> -Hexane	21	1.0	4.41 ^d	—	—
Dimethyl ether	26	1.0	—	—	0.69
Diethyl ether	20	1.0	3.6	—	0.43

^a Conversions based on the weight of the product fraction assuming the products to represent mono(difluoramines). All reactions conducted at 250°.

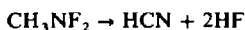
^b The selectivity ratios are all referred to the 1° difluoramine.

^c Combination of two bis(difluoramines).

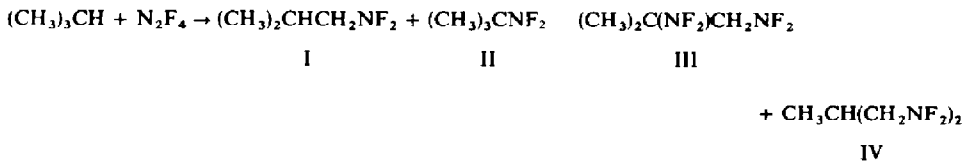
^d Combination of two 2° mono(difluoramines).

selective in its abstraction of H atoms, although there is a well defined preference for abstraction of hydrogen in the established order of 3° > 2° > 1°. In all cases 2° hydrogens were abstracted more easily than 1° as evidenced by the higher ratio of 2° to 1° difluoramines. These product ratios were changed by varying the relative concentrations of N_2F_4 and hydrocarbon only to the significant extent that the yield of the bis(difluoramines) were increased or decreased. These observations are based on the assumption that hydrogen abstraction occurs primarily by the difluoramino radical.

The product fractions obtained from the reactions of methane and ethane were found to contain difluoraminoethane and difluoraminoethane as the major products. These compounds were characterized by comparison of their mass and IR spectra with those previously reported.^{1,2} Some decomposition of these products were noted since hydrogen cyanide and acetonitrile were the impurities present in these two products fractions. Formation of the by-products is thought to occur by the thermal decomposition of the corresponding difluoramine as shown for difluoraminoethane.

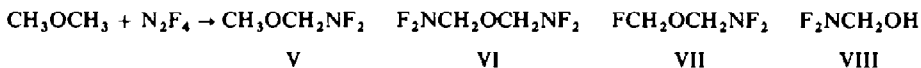


Propane and the higher members of the hydrocarbon series reacted with N_2F_4 to give more complex mixtures than methane or ethane. The spectrum of products obtained was similar to that found in free radical halogenation in the gas phase. In most instances the major components were represented by 1° and 2° mono(difluoramines) and vicinal bis(difluoramines). For example, the reaction with isobutane gave the following as major products.



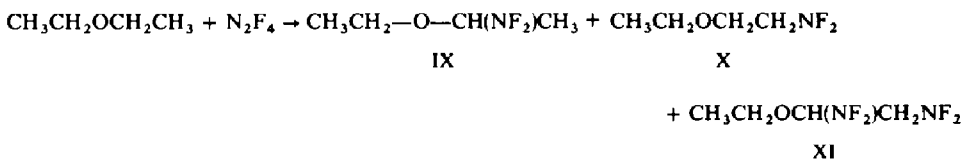
It is significant that no geminal bis(difluoramines) were among the major products. Previously it was pointed out that the difluoramino group deactivates an adjacent hydrogen to radical attack.⁹ Examination of the crude product mixtures by F¹⁹ NMR spectroscopy showed the presence of the NF₂ group, but only minor quantities of C—F bond formation in a few instances. In all cases when weak C—F absorption was evident, it apparently was restricted to the minor reaction products. Decomposition of the products was also minimal with these higher members of the hydrocarbon series, since propionitrile was the only decomposition product actually separated and characterized. In one other instance there was evidence of fragmentation of the hydrocarbon substrate. Neopentane apparently fragmented in an intermediate state resulting in the formation of 1,2-bis(difluoramino)-2-methylpropane (III).

The dialkyl ethers reacted in essentially the same manner to give 1° and 2° mono(difluoramines) as well as bis(difluoramines). Products obtained from dimethyl ether were methyl difluoraminomethyl ether (V), bis(difluoraminomethyl) ether (VI), fluoromethyl difluoraminomethyl ether (VII) and difluoraminomethyl alcohol (VIII).



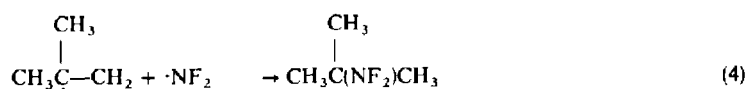
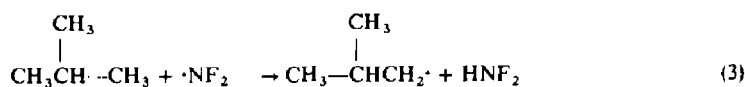
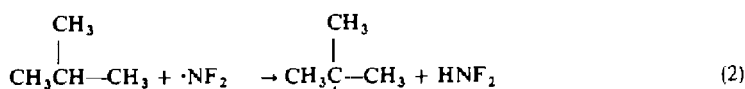
The presence of VII was the only instance where a fluorinated product was present in sufficient quantities for separation and identification. Difluoraminomethyl alcohol (VIII) could be formed through several possible means. One of the most plausible schemes involves the decomposition of the intermediate dimethyl ether radical to give formaldehyde which then reacts with difluoramine¹³ to give VIII.

Products obtained from diethyl ether were ethyl (1-difluoramino)ethyl ether (IX), ethyl (2-difluoraminoethyl) ether (X) and ethyl-1,2-bis(difluoramino)ethyl ether (XI). In this reaction the ratio of the 1- to 2-difluoraminoethyl ethers was 3.6 to 1

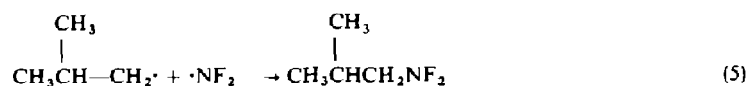


demonstrating the relative ease of hydrogen abstraction from the methylene group adjacent to the O atom. The only bis(difluoramino) compound present in significant quantities was XI, although other possible bis(difluoramines) were likely present as minor components.

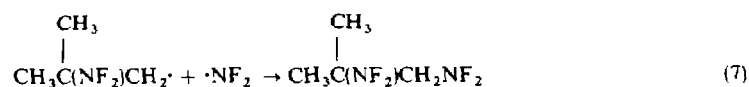
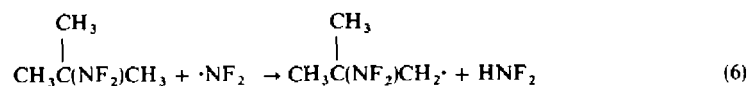
A simple free radical mechanism is proposed for the reaction of N₂F₄ with the hydrocarbons and dialkyl ethers involving the following sequence of reactions as depicted for isobutane.



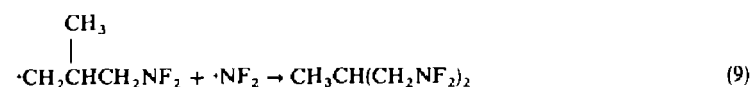
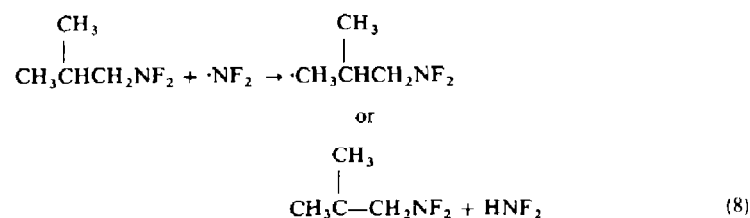
II



I



III



IV

After the dissociation of N_2F_4 the transformations involve a series of hydrogen abstraction and coupling reactions to give the observed products. As shown, the abstraction of hydrogen is accomplished by the difluoramino radical, however, fluorine radicals arising via decomposition may account for a limited portion of the hydrogen abstraction. Based on previous results^{11,14} where investigators were studying $\cdot \text{NF}_2$ radical reactions at similar temperatures, it is believed that hydrogen abstraction occurs primarily through the $\cdot \text{NF}_2$ radical. As a result, significant quantities of difluoramine (HNF_2) are formed which, under reaction conditions, decompose to give HF. Evidence for the formation of HF was apparent from the high degree of chemical attack (etching) on the glass cold traps used to collect the effluent gases from the reactor.

Undoubtedly a part of the HF was formed by decomposition of the alkyl difluor-

amines, however, the extent of this product decomposition is considered low due to (a) the short reaction times involved, (b) the fact that 3–4 components represented 80–90% of the products, and (c) the failure to isolate any decomposition products with the higher members of the series of compounds studied. Assuming decomposition occurred, it would likely affect the various alkyl difluoramines to essentially the same extent at these temperatures, and consequently, the ratio of products isolated would be near to their ratio of formation. These factors give support to the $\cdot\text{NF}_2$ radical selectivity data reported in Table 3.

Coupling of alkyl radicals was not observed and was not considered to be a major reaction due to the relative high concentration of the N_2F_4 to substrate employed. Both thermal decomposition of reactants and products occurring with loss of HF or fragmentation of intermediates was shown to contribute to the complexity of the reactions and possibly account for many of the minor, unidentified products resulting from alternate radical abstraction and coupling reactions of the various intermediate radicals.

This study has demonstrated that abstraction of hydrogen from organic substrates by the difluoramino radical occurs readily at temperatures of 200–300° resulting in the formation of mono- and bis(difluoramines). Our data show that the difluoramino radical is not particularly selective in its attack upon the organic substrate at reaction temperatures and would likely compare favorably with the chlorine radical in this respect. The general trend for hydrogen abstraction was in the order of $3^\circ > 2^\circ > 1^\circ$ as demonstrated by the ratio of difluoramines obtained.

Caution should be exercised in working with tetrafluorohydrazine. It is important to rigorously exclude oxygen (air) from mixtures of N_2F_4 and organic materials, otherwise, explosions are apt to result. In addition, extreme care should be taken in handling the NF_2 -containing products discussed in this paper due to their thermal and impact sensitivity.

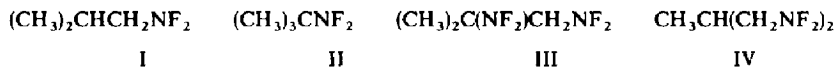
EXPERIMENTAL

All hydrocarbons and ethers were purchased from commercial sources and used as received. The tetrafluorohydrazine employed was of 95% purity containing CF compounds as impurities. IR spectra were obtained with a Perkin-Elmer Infracord spectrophotometer using a NaCl prism while NMR spectra were obtained with a Varian Associates, Model V-3000-B, high resolution spectrometer using a 40-Mc probe (F^{19}) and a Varian Associates, Model A-60, spectrometer (H^1). An Aerograph Instrument, Model A-100-C, with a dinonyl phthalate on chromosorb column was used for all gas chromatography work. Typical experimental conditions are described for the tetrafluorohydrazine-isobutane reaction.

This reaction was conveniently carried out in a flow reactor composed of feed lines for N_2F_4 , isobutane and He connected through separate calibrated flow meters into a single line to the reactor, a copper coil $\frac{1}{4}$ in. in diam and 25 ft in length. The reactor was completely enclosed in an electrical furnace and the temp measured by means of thermocouples placed within the furnace immediately adjacent to the reactor coil. The exit line from the reactor was passed through a series of cold traps cooled in the order -80° , -130° and -196° . In practice, the organic materials from the reactor were always collected in the -80° trap while excess N_2F_4 was collected in the -196° trap. Reactions were started by first flushing the system at a given temp with He and while maintaining the He flow at the desired level both the N_2F_4 and isobutane flows were started. For instance, at a reactor temp of 250° and a constant He flow of 32 cc/min, N_2F_4 was introduced at the rate of 65 cc/min and isobutane at 10 cc/min. Reaction time was 46 min at which point the flows of N_2F_4 and isobutane were stopped and the He flow continued for 15 min. Contents of the -196° trap were expanded into a 2 l. bulb and examined. Mass spec analysis showed the presence of N_2F_4 , and minor quantities of isobutane, difluoramine, and silicon tetrafluoride. The major part of the organic materials contained in the -80° trap were transferred through a second series of traps cooled

to -80° , -130° and -196° in order to ensure removal of any dissolved N_2F_4 . After opening to the air remotely, the contents (0.7 g) of the -80° trap were removed and isolated by gas chromatograph. Conversion of isobutane to products [assuming mono(difluoramines)] was 25%. Characterization data on these products are shown in Table 1. In those instances where liquid hydrocarbons were employed, the substrate was introduced into the feed line from a calibrated power driven syringe at a point just prior to its entrance into the heated reactor.

Structural assignments were made on the basis of the F^{19} and H^1 NMR spectral data. For instance, isobutane yielded products I-IV (Table 1). The F^{19} NMR spectrum of I showed a singlet at -55.9ϕ



(broad peak) indicative of the primary difluoramino group. Its proton spectrum has signals as a triplet ($J = 30$ c/s) of doublets ($J = 7$ c/s) centered at τ 6.65 arising due to the coupling of the methylene H-atoms with fluorine and a doublet ($J = 7$ c/s) centered at τ 8.92 attributed to the Me groups. Compound II showed a singlet at -27.7ϕ for the tertiary difluoramino group in its F^{19} NMR spectrum. The proton spectrum displayed a triplet ($J = 2$ c/s) centered at τ 8.88 for the Me groups. A triplet centered at -62.7ϕ and a singlet at -26.8ϕ were noted in the F^{19} spectrum of III. These signals were attributed to a primary and tertiary difluoramino group respectively. Signals in the form of a triplet ($J = 29$ c/s) centered at τ 6.18 (for $-CH_2NF_2$) and a singlet at τ 8.58 (for CH_3-) were noted in its proton spectrum. Finally, compound IV showed a triplet ($J = 27$ c/s) centered at -54.4ϕ for the primary difluoramino groups in its F^{19} spectrum. The proton spectrum of IV displayed a triplet ($J = 30$ c/s) of doublets ($J = 7$ c/s) centered at τ 6.92 ($-CH_2NF_2$) and a doublet ($J = 7$ c/s) centered at τ 9.28 ($-CH_3$). Data of this type considered in conjunction with the elemental analysis data were employed in making structural assignments to the remaining products from the hydrocarbon reactions reported in Table 1.

The reactions of dialkyl ethers with tetrafluorohydrazine were conducted under similar conditions. Data on these products are found in Table 2. The structures of the ether products were confirmed by F^{19} and proton NMR spectroscopy.

Methyl difluoraminoethyl ether (V) displayed a singlet at τ 6.22 for the methyl protons and a triplet ($J = 24$ c/s) centered at τ 5.30 for the methylene protons of the $-CH_2NF_2$ group in its proton NMR spectrum. A broad peak centered at -32.6ϕ was observed in its F^{19} NMR spectrum attributed to the $-CH_2NF_2$ group. A broad peak at -32.0ϕ and a triplet ($J = 45$ c/s) centered at $+153.7 \phi$ attributed to the $-CH_2NF_2$ and $-CH_2F$ groups, respectively, were found in the F^{19} NMR spectrum of VI. The proton NMR spectrum of VI displayed a triplet ($J = 23$ c/s) centered at τ 5.02 representing the protons of the $-CH_2NF_2$ group and a doublet ($J = 45$ c/s) centered at τ 4.42 for the protons of the $-CH_2F$ group. The proton NMR spectrum of VII showed a triplet ($J = 21$ c/s) centered at τ 5.25 while a triplet ($J = 21$ c/s) centered at 31.3ϕ was observed in its F^{19} NMR spectrum, both indicative of the $-CH_2NF_2$ grouping. Compound VIII was characterized by a triplet ($J = 24$ c/s) centered at -28.6ϕ in its F^{19} NMR spectrum ($-CH_2NF_2$) and a triplet ($J = 24$ c/s) centered at τ 4.82 ($-CH_2-$ protons) and a singlet at τ 4.82 ($-OH$ proton) in its proton NMR spectrum. The OH proton signal was covered by the center of the triplet ($-CH_2-$ protons) but upon warming the OH peak shifted upfield from the triplet center.

Compound IX was characterized as showing a single peak at -25.3ϕ ($>CHNF_2$) in its F^{19} NMR spectrum. A peak centered at τ 8.72 representing both Me group protons (signals overlap), a complicated signal centered at τ 6.68 attributed to the methylene protons (difficult to resolve clearly due to overlap of the methine proton) and a triplet ($J_{HF} = 18$ c/s) of quadruplets ($J_{HH} = 7$ c/s) centered at τ 5.45 for the methine proton was found in its proton NMR spectrum.* Ethyl 2-difluoraminoethyl ether (X) was characterized by the following data. Its F^{19} NMR spectrum showed a triplet centered at -55.7ϕ ($-CH_2NF_2$) while the proton NMR spectrum showed a triplet ($J = 7$ c/s) centered at τ 8.97 (Me protons), a quadruplet ($J = 7$ c/s) centered at τ 6.65 (methylene protons of the Et group), a singlet centered at τ 6.45 (CH_2- protons of the β -difluoramino Et group) and a triplet ($J = 28$ c/s) centered at τ 6.65 ($-CH_2NF_2$ protons) being overlapped by the signals from both sets of methylene protons. Compound XI showed signals as a triplet centered at -55.7ϕ ($-CH_2NF_2$) and a singlet centered at -23.9ϕ ($>CHNF_2$) in its F^{19} NMR spectrum. The proton NMR spectrum was complicated by overlapping of the peaks with the Me protons centered at τ 8.72. The remaining peaks clump together and center at τ 5.78.

* The chemical shift of the methine hydrogen has been reported as τ 5.62 with similar coupling constants.⁵

Acknowledgement—The interpretation of NMR spectra by Mrs. Carolyn Haney is gratefully acknowledged. The technical assistance of Mr. H. H. Hill is appreciated.

REFERENCES

- ¹ This work was carried out under the support of the U.S. Army Missile Command, Redstone Arsenal, Alabama, under Army Ordnance Contract DA-01-021 ORD-11909.
- ² Deceased.
- ³ J. P. Freeman, *Free Radicals in Inorganic Chemistry* No. 36; p. 128. Advances in Chemistry Series, American Chemical Society, Washington, D.C.
- ⁴ C. L. Bumgardner, *Tetrahedron Letters* 3683 (1964).
- ⁵ M. J. Czesla, K. F. Mueller and O. Jones, *Ibid.* 813 (1966).
- ⁶ A. J. Dijkstra, Ph.D. Thesis, University of Leiden, 1965.
- ⁷ H. Cerfontain, *J. Chem. Soc.* 6602 (1965).
- ⁸ A. L. Logothetis, U.S. Patents 3,196,167 (20 August 1965) and 3,215,709 (2 November 1965).
- ⁹ J. P. Freeman and R. C. Petry, *J. Org. Chem.* **32**, 4034 (1967).
- ¹⁰ S. F. Reed, Unpublished work.
- ¹¹ J. Grzechowiak, J. A. Kerr and A. F. Trotman-Dickenson, *Chem. Comm.* 109 (1965).
- ¹² J. W. Frazer, *J. Inorg. Nucl. Chem.* **16**, 23 (1960).
- ¹³ J. P. Freeman and W. H. Graham, *J. Am. Chem. Soc.* **90**, 121 (1968).
- ¹⁴ J. Grzechowiak, J. A. Kerr and A. F. Trotman-Dickenson, *J. Chem. Soc.* 5080 (1965).