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ADVANCED OXIDIZER RESEARCH (U)

SEMIANNUAL REPORT RMD-5043-66

Report Period: 1 January 1966 to 30 June 1966

Office of Naval Research Contract No. NONr 4364(00)

July 31, 1966

GROUP 4
DOWNGRADED AT 3-YEAR INTERVALS:
DECLASSIFIED AFTER 12 YEARS

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Thiokol
CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVER, NEW JERSEY

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ADVANCED OXIDIZER RESEARCH (U)

SEMIANNUAL REPORT RMD-5043-66

Report Period: 1 January 1966 to 30 June 1966

Office of Naval Research Contract No. NONr 4364(00)

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GROUP 4
Downgraded at 3 year
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David J. Mann
David J. Mann
Director of Research

FOREWORD

This report was prepared by the Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, and summarizes work in the area of advance oxidizer chemistry conducted over the period from January 1, 1966 to June 30, 1966. This research was sponsored by the Office of Naval Research with Mr. Richard L. Hanson serving as Scientific Officer.

Contributors to the work described in this report are as follows:

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Report RMD 5043-66

ABSTRACT - INORGANIC CHEMISTRY

$N_2F_3AsF_6$ was observed to be compatible with the perchlorates; $KClO_4$, NH_4ClO_4 , and $(CH_3)_4NClO_4$, in the solid state. Metathesis with perchlorates in liquid sulfur dioxide at $-50^\circ C$ was unsuccessful because of reaction of $N_2F_3AsF_6$ with the solvent to product $NOAsF_6$. $N_2F_3AsF_6$ reacts rapidly with the strongly acidic solvent, HSO_3F .

Fluorination of Cl_2NF over CsF at low temperatures gave only known compounds. The attempted preparation and in situ fluorination of CF_3OCl was unsuccessful. The fluorination of a purple $Cl_2-O_2AsF_6$ adduct at $-80^\circ C$ produced an unidentified volatile product, in addition to ClO_3F and oxides of chlorine.

INTRODUCTION

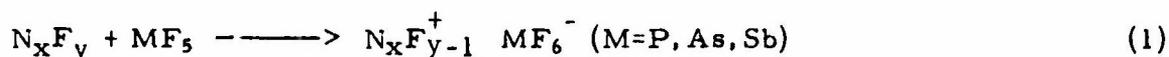
This program is an investigation of the chemistry of compounds containing certain combinations of nitrogen, oxygen, fluorine, and chlorine, that have been identified by theoretical calculations as most desirable for liquid and solid rocket oxidizers. Our ultimate objective is to uncover new liquid or solid structures containing such energetic combinations as; O-F, N-F, O-N-F, Cl-F, O-Cl-F, and Cl-O.

During the past six months we have continued efforts initiated during the previous year to prepare $N_2F_3ClO_4$ by metathesis from $N_2F_3AsF_6$. In addition we have begun a study of the fluorination of various chlorine compounds as an approach to new inorganic liquid oxidizers. A minor effort has been devoted to some aspects of the chemistry of organic N-F compounds. This "organic phase" will not be continued during the remainder of the current year.

DISCUSSION - INORGANIC CHEMISTRY

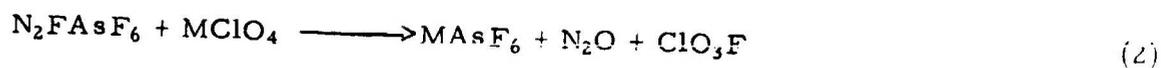
A. Attempts to Prepare $N_2F_3ClO_4$

Last year we studied extensively the reaction of N_2F_4 with AsF_5 , from which one obtains a stable solid adduct of composition, $N_2F_4 \cdot AsF_5$. The F^{19} n. m. r. and infrared spectra of the adduct are consistent with an ionic structure, $N_2F_3^+ AsF_6^-$ (Ref 1). Thus the $N_2F_4-AsF_5$ adduct is one of a growing family of ionic compounds having N-F cations, which are obtained by reactions of simple covalent inorganic NF compounds with Group V pentafluorides (eq. 1). Among other cations

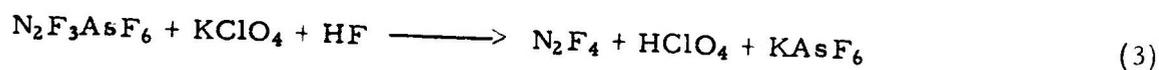


that have been reported recently are N_2F^+ (Refs 2, 3, 4), ONF_2^+ (Ref 5), and NF_4^+ (Ref 6, 7).

Although the existence of stable hexafluoroarsenates of N-F cations is of academic interest, their value to oxidizer research rests on whether they may undergo metathesis without decomposition of the N-F cation. In the case of N_2F^+ (Ref 2) we found that attempted metathesis with oxygen-containing salts results in the conversion of N_2F^+ to N_2O (eq. 2). Investigation of the reaction of $N_2F_3AsF_6$



with perchlorates was initiated last year. It was observed that HF solutions of $\text{N}_2\text{F}_3\text{AsF}_6$ yields N_2F_4 (eq. 3) upon addition of KClO_4 (Ref 1). We have now attempted



the use of SO_2 and HSO_3F as liquid media for the preparation of $\text{N}_2\text{F}_3\text{ClO}_4$.

Unfortunately, both of these solvents were found to react extensively with the N_2F_3^+ ion.

1) Compatibility of $\text{N}_2\text{F}_3\text{AsF}_6$ with Dry Perchlorates

Approximately equimolar mixtures of $\text{N}_2\text{F}_3\text{AsF}_6$ with KClO_4 , NH_4ClO_4 , and $(\text{CH}_3)_4\text{NClO}_4$, respectively were examined by infrared and X-ray after the mixtures had been ground for 1-2 hours under dry nitrogen. In each case, visual observation indicated no reaction and this was confirmed by the infrared and X-ray spectra that were obtained.

2) Reaction of $\text{N}_2\text{F}_3\text{AsF}_6$ with Perchlorates in Sulfur Dioxide

It has been reported that $\text{N}_2\text{F}_4 \cdot \text{SbF}_5$ is sufficiently stable in SO_2 below -45°C to permit one to obtain an F^{19} n. m. r. spectrum of the adduct (Ref 5).

Therefore, we thought it possible that SO_2 might serve as an inert reaction medium for N_2F_3^+ salts at low temperatures.

The insoluble perchlorate, NH_4ClO_4 , was suspended in an SO_2 solution of excess $\text{N}_2\text{F}_3\text{AsF}_6$ for two hours at -50°C . The suspension was filtered and an infrared spectrum of the insoluble residue was obtained. There was no evidence of cation exchange. That is, the characteristic absorptions of the N_2F_3^+ cation were not present.

Sulfur dioxide was added to mixtures of $\text{N}_2\text{F}_3\text{AsF}_6$ and the soluble perchlorate, $(\text{CH}_3)_4\text{NClO}_4$, at -196°C in both glass and Kel-F reactors. The pale yellow solutions which formed at -50°C were either filtered or decanted, and both soluble and insoluble solid fractions were examined by infrared and X-ray. In each run the soluble fraction was identified by X-ray as virtually pure $(\text{CH}_3)_4\text{NAsF}_6$. The insoluble fraction was predominantly NOClO_4 .

At this point, we decided to determine the extent of reaction of SO_2 with $\text{N}_2\text{F}_3\text{AsF}_6$ at -50°C . A sample of the salt still exhibited strong N_2F_3^+

absorptions in the infrared (1500 cm^{-1} , 1300 cm^{-1} , 1100 cm^{-1} , 900 cm^{-1}) after recovery from solution in SO_2 at -50°C . However, the X-ray pattern (Table I) of the same sample showed that extensive conversion to NOAsF_6 had occurred by interaction with the solvent.

TABLE I Diffraction Pattern of $\text{N}_2\text{F}_3\text{AsF}_6$ (Principal Lines)

| <u>Before Dissolving in SO_2</u> | | <u>After Recovery from SO_2 Solution at -50°C</u> | |
|--|-----------------------------|--|-----------------------------|
| <u>d, Å</u> | <u>I/ I₀</u> | <u>d, Å</u> | <u>I/ I₀</u> |
| 5.37 | 40 | 5.37 | 40 |
| - | - | *4.73 | 30 |
| 4.44 | 100 | 4.43 | 100 |
| - | - | *4.05 | 40 |
| 3.38 | 90 | 3.39 | 90 |
| - | - | *2.86 | 15 |

*Principal lines of NOAsF_6

Although this has not been confirmed by an examination of the volatile products, it is probable that the reaction proceeds as shown in equation (4).



It is furthermore quite reasonable, on the basis of present observations, to assume that the decomposition of the N_2F_3^+ cation in the attempted metathesis with Me_4NClO_4 in SO_2 is due to reaction with the solvent as shown in (4). The yellow color

observed in the solution may be indicative of some perchlorate decomposition, but it is obviously a minor reaction since virtually all of the initial perchlorate is recovered as NOClO_4 . The formation of NOClO_4 is easily explained by the reaction shown in (5).



We are in the process of searching for a solvent medium in which we may determine unequivocally whether N_2F_3^+ and ClO_4^- can coexist. During this report period we observed that the strongly acidic solvent, HSO_3F , is not compatible with $\text{N}_2\text{F}_3\text{AsF}_6$. Other possible solvents to be examined include; BrF_5 , SOF_2 , CF_2O , CF_3OF , and $(\text{CF}_3)_2\text{CO}$.

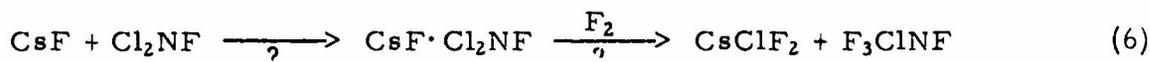
B. Fluorination Studies

The work with Group V pentafluoride adducts of simple NF compounds is directed primarily toward the synthesis of new solid oxidizers. We have recently initiated a study of the fluorination and oxyfluorination of chlorine containing compounds, which is directed toward the synthesis of new liquid oxidizers. We

intend to examine the reactions of F_2 , OF_2 , and O_2F_2 with a variety of simple chlorine containing compounds, and their complexes with CsF and AsF_5 .

1) Fluorination of Cl_2NF

The fluorination of Cl_2NF in the presence of CsF was examined as a possible route to F_3ClNF , as shown in equation (6). The reactants were stored



at $-78^\circ C$ in a stainless steel cylinder for one week. $ClNF_2$, NF_3 , and N_2F_2 were the only volatile products of the reaction.

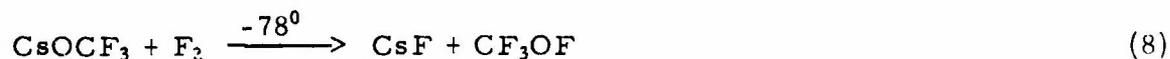
Arsenic pentafluoride behaved as a fluorinating agent rather than forming a complex with Cl_2NF , producing $ClNF_2$ and AsF_3 .

2) Attempted Preparation and In Situ Fluorination of CF_3OCl

An attempt was made to fluorinate the presumably unstable compound, CF_3OCl , at reduced temperatures as an approach to new chlorine oxyfluorides (eq. 7). $CsOCF_3$ was prepared at room temperature by the reaction



of COF_2 with CsF . The solid was exposed to an equimolar quantity of Cl_2 for twenty-four hours at -78°C , and then fluorine was added. The CsOCF_3 was simply converted to CF_3OF (eq. 8), and Cl_2 was recovered quantitatively.



3) Reaction of " $\text{Cl}_2 \cdot \text{O}_2\text{AsF}_6$ " with Fluorine

Chlorine forms an uncharacterized purple complex with O_2AsF_6 which is stable at -78°C (Ref 8). An investigation of the fluorination of this adduct has been initiated with the view of preparing Cl-O-F compounds. In our initial experiment, O_2AsF_6 was treated with Cl_2 at -78°C in order to form the complex. Excess F_2 was added and the reaction mixture stored at -78° for five days. The infrared spectrum of the gaseous products showed the presence of ClO_2 and an unidentified component. Mass spectroscopic analysis showed the presence of Cl_2 , O_2 , and ClO_2 . No O_2AsF_6 was recovered. Attempts to isolate and identify the unknown component in the products are in progress.

EXPERIMENTAL

Attempted Reaction of Ammonium Perchlorate with $N_2F_3AsF_6$ in Sulfur Dioxide

Ammonium perchlorate which had been dried in vacuo for 30 hours was mixed for one hour with $N_2F_3AsF_6$ in an agate mortar under dry nitrogen. Samples of the mixture were examined by X-ray and infrared. Both analyses indicated the presence of unreacted $N_2F_3AsF_6$.

In an inert atmosphere box, approximately one millimole (0.12 g) of dry NH_4ClO_4 and a threefold excess of $N_2F_3AsF_6$ were added to one leg of an "H-shaped" glass reactor. The legs of the reactor were connected by a tube containing a sintered glass filter disc. The reactor was attached to a vacuum system, evacuated and then cooled to $-196^{\circ}C$. Sulfur dioxide was condensed on the solid mixture and then the $-196^{\circ}C$ bath was removed to allow the sulfur dioxide to melt. A good portion of the solid was observed to dissolve in the SO_2 at its melting point (-73°). A -50° bath was placed under the reactor. After 2-3 hours the solution was forced through the filter disc (with N_2 pressure) to the other leg of the reactor. The SO_2 was then distilled out of the reactor.

An infrared spectrum of the insoluble solid fraction showed that it was virtually pure NH_4ClO_4 , there was a weak AsF_6^- absorption at 700 cm^{-1} , but no trace of the N_2F_3^+ ion. The soluble fraction, as expected in view of the large initial excess, was predominantly $\text{N}_2\text{F}_3\text{AsF}_6$.

Attempted Reaction of $(\text{CH}_3)_4\text{NClO}_4$ with $\text{N}_2\text{F}_3\text{AsF}_6$

$(\text{CH}_3)_4\text{NClO}_4$ was obtained by mixing saturated aqueous solutions of $(\text{CH}_3)_4\text{NBr}$ and $\text{Ba}(\text{ClO}_4)_2$. The $(\text{CH}_3)_4\text{NClO}_4$ was obtained as a milky white precipitate (solubility 1.6g/100 ml) which was washed with ice water and dried in vacuo at 120°C . The infrared spectrum of the solid exhibited a sharp ClO_4^- band at 1080 cm^{-1} in addition to bands characteristic of $(\text{CH}_3)_4\text{N}^+$. Its X-ray pattern [4.171 (S), 5.85 (M), 4.84 (M)] was identical to the A. S. T. M. pattern of $(\text{CH}_3)_4\text{NClO}_4$. A sample of $(\text{CH}_3)_4\text{NClO}_4$ was shown to be unreactive toward $\text{N}_2\text{F}_3\text{AsF}_6$ in the dry state by X-ray and infrared analysis of an equimolar mixture formed by mechanical agitation for two hours.

In a dry nitrogen box, one millimole (0.17 g) $(\text{CH}_3)_4\text{NClO}_4$ and approximately

1.5 millimoles $N_2F_3AsF_6$ (0.41 g) were added to the glass reactor described previously, and treated with SO_2 at $-50^\circ C$ as was done in the experiment with NH_4ClO_4 . The soluble solid fraction was examined by infrared and X-ray. The spectra obtained were identical to those of an authentic sample of $(CH_3)_4NAsF_6$. The major X-ray lines of $(CH_3)_4NAsF_6$ are: 6.07 (S), 5.08 (M), 4.35 (V.S.), 2.04 (M). The infrared of the insoluble solid fraction showed weak bands at 1300 cm^{-1} , 1100 cm^{-1} , and 930 cm^{-1} that might be due to $N_2F_3^+$, a very weak AsF_6^- absorption at 700 cm^{-1} , and a strong broad perchlorate band at $1100-1050\text{ cm}^{-1}$. The X-ray pattern indicated a mixture of $NOClO_4$ and $(CH_3)_4NAsF_6$.

Since it is known that $N_2F_3AsF_6$ decomposes slowly to $NOAsF_6$ in glass, the reaction of $N_2F_3AsF_6$ with $(CH_3)_4NAsF_6$ in SO_2 was repeated several times in a Kel-F reactor. However, in each case the result was identical to that obtained in glass; namely, $NOClO_4$ was the major component of the insoluble fraction.

$N_2F_3AsF_6$ was dissolved in SO_2 in a Kel-F tube and held at -50° for two hours. The solid recovered from this solution exhibited $N_2F_3^+$ absorptions at 1500 cm^{-1} , 1300 cm^{-1} , 1100 cm^{-1} , and 900 cm^{-1} in the infrared. Its X-ray pattern,

however, indicated that it was approximately a 60:40 mixture of $N_2F_3AsF_6$ and $NOAsF_6$.

Fluorination of Dichlorofluoramine

Approximately 2 millimoles of dichlorofluoramine (Ref 9) was condensed onto CsF in a 300 ml. stainless steel cylinder at -196^0 and 10 millimoles of fluorine were added. The cylinder was allowed to stand at -78^0 for one week. Fluorine was then pumped out of the cylinder at -196^0 . Examination of the residual gas at room temperature by infrared and mass spectroscopy indicated the presence of CIN_2 , NF_3 , and N_2F_2 .

Reaction of CsF with COF_2

(a) To .188 g. (12.4 mmole) of CsF in Fischer-Porter aerosol compatibility tube was added 25 ml. of dry CH_3CN . The reaction mixture was cooled to -196^0C and 12.4 mmole COF_2 introduced. The reaction mixture was stored at ambient temperature overnight. No change in pressure was observed. However, the gaseous fraction was found to be a mixture of CF_4 and CO_2 . The CH_3CN was

removed in vacuo and the solid product pumped on for several hours to yield 1.95 g. of crystalline material. Thermal decomposition of this solid yielded CH_3CN .

(b) To 0.94 g. (6.2 mmole) of CsF in 20 ml. of CH_3CN at -196°C was added 6.2 mmole of $(\text{CF}_3)_2\text{C}=\text{O}$. After stirring the reaction mixture at room temperature a solution was obtained. To this solution was added 6.2 mmole of COF_2 . After stirring at room temperature the gaseous fraction was sampled and found to be a mixture of COF_2 and $(\text{CF}_3)_2\text{C}=\text{O}$. Evaporation of the solvent in vacuo yielded 1.32 g. of a white solid which upon thermal decomposition liberated $(\text{CF}_3)_2\text{C}=\text{O}$, COF_2 and CH_3CN .

(c) A 125 ml. stainless steel bomb was charged with 10 g. (65.7 mmole) of CsF and some stainless steel balls. Then 5 mmoles of COF_2 was added and the reaction mixture was placed in a wrist shaker for 4 hours after which time an 80 percent drop in pressure was observed. The residual pressure was due to CO_2 and CF_4 . Upon thermal decomposition, a sample of the solid product liberated only COF_2 .

Reaction of CsOCF_3 with Cl_2/F_2

To a mixture of CsF and 5 mmoles of CsOCF_3 prepared as outlined above in

paragraph (c), was added at -196°C 2.5 mmole of Cl_2 . The reaction mixture was allowed to warm to -78°C and stored overnight. The reaction mixture was cooled to -196°C and a large excess of F_2 was added. After standing at -78°C for 5 days, the reactor was cooled to -196°C and the unreacted F_2 removed. The residual material was fractionated and characterized as Cl_2 and CF_3OF .

Reaction of $\text{Cl}_2 \cdot \text{O}_2\text{AsF}_6$ with F_2

A stainless steel cylinder was charged with 0.55 g. (2.5 mmole) of O_2AsF_6 , evacuated and then cooled to -196°C . Then 2.5 mmole of Cl_2 was added and the reaction mixture was allowed to stand overnight at -78°C . The reactor was again cooled to -196°C and a large excess of F_2 was added. After standing 5 days at -78°C the unreacted F_2 was removed and the gaseous products were collected at -78°C , -95°C and -196°C . An uncharacterized component was present in both the -95°C fraction and the -196°C fraction. The products identified include; Cl_2 , O_2 , ClO_2 , CO_2 (which is an impurity in the Cl_2), and COF_2 .

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ABSTRACT - ORGANIC NF CHEMISTRY

No stable adducts could be isolated in the reactions of >C-NF_2 and >C=NF compounds with AsF_5 or BF_3 . Attempts to synthesize N-fluorooxaziranes from ketofluorimines were unsuccessful. CF_3OF does not form adducts with AsF_5 or BF_3 .

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DISCUSSION - ORGANIC NF CHEMISTRY

Earlier reports (Refs 1, 2) in this area have dealt with the reactions of alkyldifluoramines with a variety of reagents, with the preparation and chemical properties of bis(difluoramino)cyclohexenes, and with the reactions of the keto-fluorimino group. The latter study was directed toward determining the scope of the active hydrogen addition reaction which is characteristic of perfluoroguanidine.

This report presents results of investigations of three aspects of organic difluoramine chemistry; namely, the synthesis of C-N-F cations by fluoride addition to AsF_5 and/or BF_3 , the synthesis of N-fluorooxaziranes, and the synthesis of $\text{C}_x\text{F}_y\text{O}_n^+$ salts to serve as intermediates in the preparation of C-ONF₂ compounds.

Since the results in each of these areas were not encouraging, no further work with organic N-F compounds is planned for the remainder of the program.

A. Reaction of Organic N-F Compounds with Lewis Acids

Inorganic fluorine compounds, such as N_2F_2 , have been shown (Ref 1 and 3) to react with fluoride ion acceptors to give new inorganic cations (eq. 1).

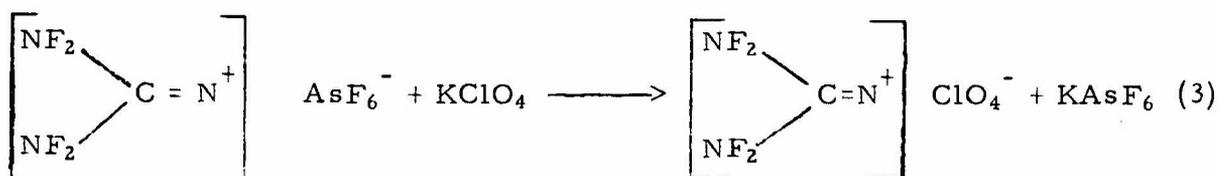
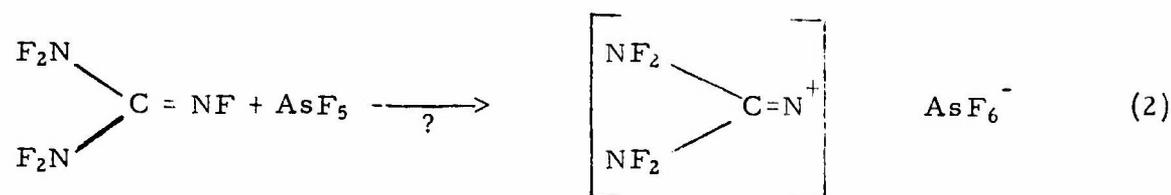


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An investigation of the extension of this type reaction to organic N-F compounds has been explored as a route to new and potentially valuable oxidizer structures (eqs. 2 and 3).

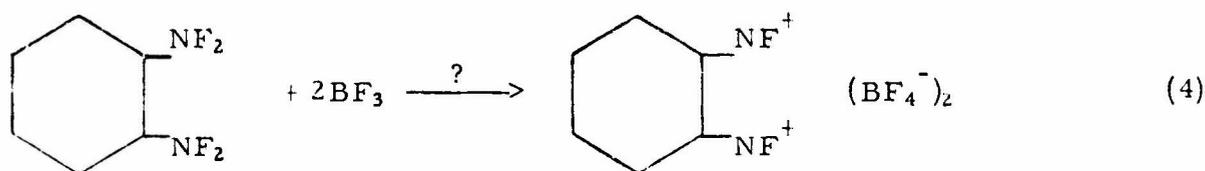


In exploratory runs with N, N, N'-trifluoropentoxyformamidine and with 1,2-bis(difluoramino)cyclohexane indications of fluoride ion abstraction were obtained although extensive decomposition also occurred (Ref 2).

Since BF₃ could be expected to react less vigorously than AsF₅ with organic N-F compounds several experiments were conducted with BF₃ and 1,2-bis(difluoramino)-cyclohexane (eq. 4). When the reaction was conducted in the absence

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of a solvent a solid product was obtained but extensive decomposition occurred (Ref 3).

When the reaction was conducted in CH_2Cl_2 at 0°C a yellow intractable solid was obtained which slowly turned to a dark resinous mass at ambient temperatures.

This dark resinous mass was obtained immediately when the reaction was conducted in liquid SO_2 . Because of the intractable nonhomogeneous nature of the reaction product, meaningful analytical data could not be obtained. However, the presence of boron in the solid product, as indicated by a flame test, was confirmed by mass spectroscopic analysis. Moreover, the boron present in the product is retained when it is heated in vacuo at 50°C , suggesting that it is present as BF_4^- .

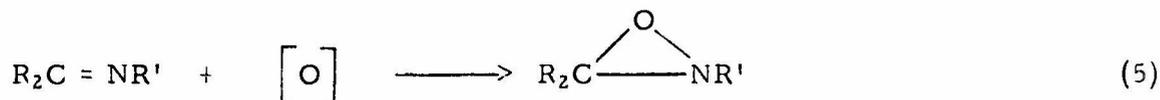
Similar results were obtained when the reaction was conducted with 1,2-bis(difluorimino)cyclohexane.

B. Peroxide Oxidation of Ketofluorimines

The oxidation of alkylimines with peroxides (eq. 5) to yield oxazirane

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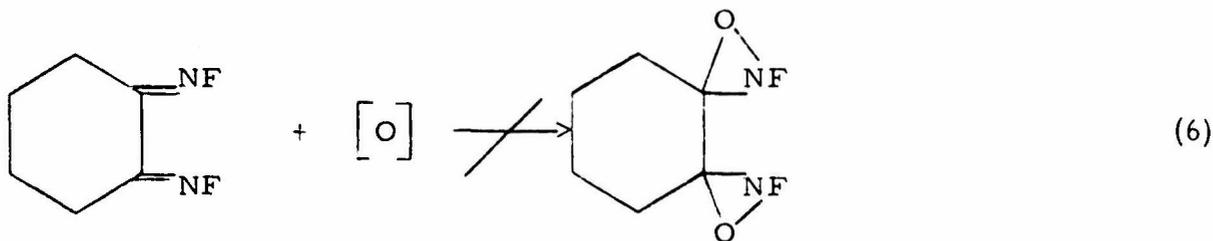
derivatives has been reported (Ref 4, 5). Application of this reaction to the



preparation of N-fluorooxaziranes has been briefly explored (Ref 3). No reaction

was found to occur between trifluoropentoxylformamidine and benzoylperoxide in

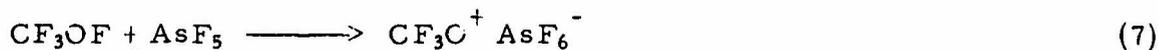
CH₂Cl₂ at 25°C (Ref 3). Similarly no reaction, (eq. 6) was observed between



1,2-bis(difluorimino)cyclohexane and benzoylperoxide at 25° or at elevated temperatures.

C. Attempted Preparation of CF₃O⁺ Salts

The preparation of CF₃O⁺ salts by the reaction of CF₃OF with fluoride ion acceptors (eq. 7) was explored as a model system in the development of an ionic route to F_xC(ONF₂)_{4-x} compounds (eq. 8).



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No reaction occurred between CF_3OF and BF_3 . However, a trace amount of solid was obtained from an equimolar mixture of CF_3OF and AsF_5 which exhibited an AsF_6^- absorption in the infrared at 700 cm^{-1} . Appreciable quantities of this solid were not obtained, even when an excess of AsF_5 was employed and the reaction time was extended. It was concluded therefore, that the solid was not an adduct of CF_3OF and AsF_5 , but rather a product of the reaction of AsF_5 with some minor impurity in the system.

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EXPERIMENTAL

1. Reaction of 1,2-Bis(difluoramino)cyclohexane with BF₃

(a) To a solution of 0.41 g. (2.20 mmole) of 1,2-bis(difluoramino)-cyclohexane in 10 ml. CH₂Cl₂ at -196°C was added 4.40 mmoles of BF₃. The reaction mixture was stirred at -30°C for 2.5 hours, filtered and the pasty yellow solid was pumped on in vacuo for 1 hour. Heating the solid in vacuo at 50°C was accompanied by considerable darkening of the solid but no BF₃ was evolved.

(b) A solution of 0.20 g. (1.07 mmole) of 1,2-bis(difluoramino)cyclohexane in 10 ml. of SO₂ was prepared and cooled to -196°C. Then 2.14 mmoles of BF₃ was added and the reaction mixture was warmed to -30°C. The solution immediately became dark brown. After removing the SO₂ in vacuo a brown tacky mass was obtained.

2. Reaction of 1,2-Bis(difluorimino)cyclohexane with BF₃

To a solution of 0.35 g. (2.39 mmole) of 1,2-bis(difluorimino)cyclohexane in 12 ml. of CH₂Cl₂ at -196°C was added 4.8 mmole of BF₃. The reaction mixture was stirred for several hours at 0°C. A brown insoluble oil first formed and

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subsequently congealed into a brown tacky resinous mass.

3. Reaction of 1,2-Bis(difluorimino)cyclohexane with Benzoylperoxide

(a) To a solution of 0.50 g. (3.4 mmole) of 1,2-bis(difluorimino)cyclohexane in 50 ml. of CH_2Cl_2 at 40°C was added dropwise a solution of 1.90 g.

(6.8 mmole) of benzoylperoxide in 100 ml. of CH_2Cl_2 . The reaction mixture was refluxed 4 hours, washed with Na_2CO_3 and CH_2Cl_2 layer stored over Na_2CO_3 .

Finally the CH_2Cl_2 was evaporated to yield a pasty mass consisting of unreacted benzoylperoxide and 1,2-bis(difluorimino)cyclohexane.

(b) To a solution of 0.35 g. (2.39 mmole) of 1,2-bis(difluorimino)cyclohexane in 75 ml. of dichloroethane at 80°C was added dropwise a solution of 1.30 g.

(5.68 mmole) of benzoylperoxide in 100 ml. of dichloroethane. The reaction mixture was refluxed for several hours, cooled, and washed with Na_2CO_3 . The organic phase was dried over Na_2CO_3 and subsequently evaporated to give a pasty

mass. This solid was washed with chilled Freon-113 and characterized as

unreacted benzoylperoxide. The Freon filtrate upon evaporation yielded 0.36 g.

of a red-brown liquid which consisted primarily of unreacted 1,2-bis(difluorimino)-

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cyclohexane but whose infrared spectrum had uncharacterized absorptions at 6.1-6.2 and 6.9-7.0.

4. Reaction of CF_3OF with BF_3

Equimolar amounts of CF_3OF and BF_3 were condensed in a Kel-F tube at -196°C and then allowed to warm slowly to room temperature. The gases were recondensed several times. No evidence for reaction was observed and the CF_3OF and BF_3 were recovered.

5. Reaction of CF_3OF and AsF_5

(a) Equimolar amounts of CF_3OF and AsF_5 were condensed in a Kel-F reactor and then allowed to warm slowly to room temperature. The mixture was recondensed several times. After standing at room temperature overnight a trace amount of solid was obtained which exhibits the characteristics AsF_6^- absorption in the infrared. The gaseous fraction consisted of unreacted reagents.

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(b) A 3:1 mole ratio of AsF_5 to CF_3OF was condensed in a Kel-F reactor at -196°C and then stored overnight at -78°C . The reaction mixture was allowed to warm slowly to room temperature. After standing at ambient temperature for several hours only a trace amount of solid was obtained.

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