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DIFLUORAMINE CHEMISTRY

1 July 1961 to 30 September 1961

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CHEMICAL CORPORATION
REACTION MOTORS DIVISION
DENVILLE, NEW JERSEY
DIFLUORAMINE CHEMISTRY

D. Grafstein  
C. Vogel

Report RMD-076-Q3-61  
Contract NOnr 1878(00)

1 July 1961 to 30 September 1961

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ADM-148
FOREWORD

This report was prepared by Thiokol Chemical Corporation, Reaction Motors Division, Denville, New Jersey, under Contract No. N00r 1878(00), ARPA Order No. 186-61. The research reported herein was administered under the direction of the Power Branch, Office of Naval Research, with Mr. R. L. Hanson as project engineer.

This quarterly report covers work conducted during the period of 1 July 1961 to 30 September 1961 on RMD Project 076. The following personnel participated in this research:

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ABSTRACT

The study of the chemistry of the organic NF₂ group was continued. Deuterium exchange studies established that the α-hydrogen atoms in secondary aliphatic bis-difluoramines are not acidic and are not sufficiently labile to permit base catalyzed addition on the α-carbon atom. The C-NF₂ group appears to be inert to free radical bromination conditions and this may allow radical substitution of α-hydrogen.

The unexpected redox reaction between organic bis-difluoramines and permanganate ion was investigated further. Extensive fragmentation of the organic molecules resulted, but the nature of this reaction has not been elucidated. An acid catalyzed reaction was also observed with hydrogen peroxide, but here the NF function appears to act as an oxidizing agent, being reduced to N-H.

Two model gem compounds, 1,1-bis(difluoramino)cyclohexane and 2,2-bis(difluoramino)propane, were prepared. An interesting correlation of mass spectral fragmentation patterns was obtained between the latter compound and the olein-N₂F₄ adducts. These spectra support the previously suggested reversal of the olefin-N₂F₄ reaction in the mass spectrometer and also indicate a fluorine migration process for α-difluoramino carbonium ions.
I. INTRODUCTION

The purpose of this program is to investigate the chemistry of the aliphatic difluoramines, and to a lesser extent the organo iminofluorides, and to define the chemical processes which these new functions can undergo. Initially, four aliphatic bis-difluoramines, prepared by the thermal addition of tetrafluoro-hydrazine to unsaturated hydrocarbons, were chosen as model compounds for this study. With these adducts, a comparison of the chemical behavior of primary, secondary and tertiary carbon difluoramines was undertaken. This comparison was made to separate the intrinsic behavior of the C-NF₂ function from the effects of other groups and structural features.

In the previous quarterly reports, the initial exploratory investigation of the interaction of these model bis-difluoramines with some oxidizing, reducing and solvolytic reagents was described. The C-NF₂ function, per se, was found to be quite stable. This led to the conclusion that some of the reactions previously associated with this function could be attributed instead to the presence of an α-hydrogen atom and the associated ease of dehydrofluorination. The tertiary C-NF₂ group was not affected by strong base and no authentic nucleophilic substitution reaction on F or N could be demonstrated. The NF₂ group was unattacked in a standard hydrogenation reaction and did not react with diborane under hydroboration conditions. The observed reduction of permanganate in both acidic and basic media was of some interest.

During the current report period, emphasis has been placed on a study of the possible labile character of the α-hydrogen atoms in secondary carbon difluoramines and on the nature of the redox reactions with some oxidizing reagents. Two gem bis-difluaramino model compounds were prepared.
II. DISCUSSION

A. Model Aliphatic Bis-difluoramines

The preparation and structural assignment of the four listed model aliphatic bis-difluoramines were described in a previous report.1

I. trans 1, 2-bis(difluoramino)cyclohexane

II. cis 1, 2-bis(difluoramino)cyclohexane

III. trans 2, 5-bis(difluoramino)-2, 5-dimethyl-3-hexene

IV. 1, 2-bis(difluoramino)hexane

The discovery of methods for the synthesis of gem-bis-difluoramines from aldehydes and ketones5 now permits the inclusion of another important class of compounds in this study.

The secondary gem compounds are derived from ketones. Since they do not contain a hydrogen atom on the same carbon atom to which the NF₂ groups are attached, these gem compounds would be expected to display much the same chemical stability as do the tertiary carbon difluoramines. The synthesis of two model gem compounds, 1, 1-bis(difluoramino)cyclohexane (V) and 2, 2-bis(difluoramino)propane (VI), was undertaken. The former compound, V, is isomeric with I and II, and it was of interest to compare their infrared spectra as well as their chemical behavior.

The synthesis of V is quite erratic and very sensitive to reaction conditions. Two attempts to convert cyclohexanone to V using 96% and 97% sulfuric acid as the acid solvent were unsuccessful. A successful synthesis of V was realized using 98% sulfuric acid. Purification of V was effected via gas chromatography at 80°C, removing a small amount of unreacted cyclohexanone from the product. No other products were indicated from the VPC analysis. A comparison of the infrared spectrum of V (Figure 1) with those for its isomers, I and II (see Figures 2 and 3 of Ref 1) revealed substantial shifts in position and intensity.
of the peaks in the 9.5 to 12.0 μ (NF) region. These shifts to lower wavelength in the gem compounds may become useful as a structure diagnostic for the gem vs vicinal relationship. Subsequently, an infrared spectrum for V was published and found to be essentially identical, except for the anomalous peak at 5.8 μ in our sample.

One of the apparent difficulties with the gem synthesis is that cyclohexanone and other ketones are degraded rapidly in concentrated sulfuric acid. A solid intermediate is observed on the cold reactor walls in the cyclohexanone -HNF₂ system. The synthesis of this intermediate, presumably 1-difluoramino-1-cyclohexanol, was attempted before treatment with the HNF₂-H₂SO₄ reagent in the hope that the intermediate would be more stable to concentrated sulfuric acid. In a 5 mmole run, cyclohexanone was treated with difluoramine at room temperature. A smooth uptake of difluoramine was observed, and a viscous oil formed. The oil was not impact sensitive and burned with a sooty flame. Unlike the starting ketone, the oil was not charred by 115% sulfuric acid. Repeating this reaction on a preparative (40 mmole) scale resulted in a violent explosion soon after the HNF₂ was allowed to contact the ketone. At present, no satisfactory explanation can be given for the cause of this explosion.

2, 2-Bis(difluoramino)propane, VI, was synthesized in three individual runs. Using 97% sulfuric acid and the stoichiometric quantity of reactants, a 39% yield of VI was obtained. The product was isolated by distillation (bp 70°C) as a water white liquid. In the subsequent preparations, identical reaction conditions were employed except that 115% sulfuric acid was used. In each run, the yield of VI was 72%. The infrared spectrum of the product, Figure 2, confirmed the assigned structure and also indicated a high degree of purity by the absence of carbonyl and hydroxyl absorption bands. It was noteworthy that VI did not give a positive iodoform test.

We were interested in comparing the mass spectra of the gem compounds with those obtained previously with the N₂F₄-olefin adducts. In the first quarterly report evidence was presented which indicated that the addition of N₂F₄ to olefins is reversed in the mass spectrometer. This was based on the observation with I, II, and III that the most intense m/e peak corresponded to the removal of both NF₂ groups, leaving a hydrocarbon fragment (C₆H₉⁺ for I and II, C₈H₁₄⁺ for III). The data implied that the principal bond breaking process occurred at the C-N bond. Although the breaking of two C-N bonds need not be a related process, it seemed reasonable to suggest that the removal of the first NF₂ unit resulted in an intermediate species which stabilized itself by a preferred elimination of a second NF₂ unit. Such an elimination process would not be expected to occur with a gem or non-vicinal bis-difluoramine.
Figure 1. Infrared Spectrum of 1,1-Bis(difluoromino)cyclohexane

Figure 2. Infrared Spectrum of 2,2-Bis(difluoromino)propane
The mass spectrum for VI is given in Table I. It is evident that, as in other cases, the breaking of one C-N bond is the significant initial ionization process, leaving \((\text{CH}_3)_2\text{CNF}_2^+\) as the ion of highest mass. The hydrocarbon fragment, \(\text{C}_3\text{H}_6^+\), does form but this is no longer the preponderant fragmentation product. Instead, a rearrangement process must dominate, since the most intense m/e peak occurs at mass 65. This peak corresponds to the \(\text{CH}_3\text{CF}_2^+\) cation. The following chart for the fragmentation of VI appears to correlate all the important mass spectral features. We do not mean to imply by this chart that the ions of intermediate mass are being formed first and then are degraded to species of lower mass. Rather, it is suggested that several competitive bond-breaking and rearrangement processes are probably occurring simultaneously, depending on the energy input. An appearance potential study might shed some light on the energetics of the basic ionization processes and indicate the bond-breaking mechanisms.

B. Redox Reactions

The interesting reactions of the organic bis-difluoramines with potassium permanganate in aqueous acetic acid was reported previously.\(^2\) The nature of this reaction was obscured by the fact that only water soluble reaction products and fluoride ion were formed. Our interest in this reaction stems from the belief that a direct attack on the NF\(_2\) group may be involved. An exothermic reaction was also observed between III and sodium permanganate in pyridine solution. Again, neither III nor an NF containing product could be extracted from an aqueous solution of the reaction products.

In an attempt to simplify matters by eliminating the organic solvent, a two-phase reaction was conducted in aqueous sodium hydroxide between III (containing 10% of its isomer) and sodium permanganate (1 to 4 mole ratio). A temperature of 80-90°C was required to maintain reaction, bleaching the purple permanganate color and forming the green color characteristic of manganese ion. Workup of the mixture recovered 80% of unchanged starting material as the only extractable product. Thus, complete oxidation of the reacting molecules had occurred indicating that the first oxidation products are more susceptible to oxidation than the starting material. Qualitative oxidations were also conducted in neutral and strongly acid media forming MnO\(_2\) and Mn\(^{+2}\), respectively.

It might be inferred that the permanganate reaction involved an initial attack on nitrogen forming an amine oxide intermediate, VII, akin to the recently described oxide of nitrogen trifluoride.\(^5\)

\[
\text{VII} \quad \text{R}_3\text{CNF}_2
\]
**TABLE I**

MASS SPECTRUM OF 2, 2-BIS(DIFLUORAMINO)PROPANE

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<tr>
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<tr>
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<tr>
<td>37</td>
<td>C₂H⁺</td>
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</tr>
<tr>
<td>38</td>
<td>C₂H₂⁺, C₂N⁺</td>
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</tr>
<tr>
<td>39</td>
<td>C₃H₃⁺, C₂HN⁺</td>
<td>32.4</td>
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<tr>
<td>40</td>
<td>C₃H₄⁺, C₂H₂N⁺</td>
<td>20.2</td>
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<tr>
<td>41</td>
<td>C₃H₅⁺, C₂H₃N⁺</td>
<td>41.4</td>
</tr>
<tr>
<td>42</td>
<td>C₃H₆⁺</td>
<td>25.1</td>
</tr>
<tr>
<td>43</td>
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<tr>
<td>44</td>
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<tr>
<td>45</td>
<td>CNF⁺</td>
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<td>52</td>
<td>C₃H₂N⁺</td>
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<td>54</td>
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<td>55</td>
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<td>m/e</td>
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<tr>
<td>56</td>
<td>C₂H₄N⁺</td>
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<td>57</td>
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<td>C₂H₃NF⁺</td>
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<td>65</td>
<td>C₂H₃F₂⁺</td>
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<td>66</td>
<td>C₂H₂N₂⁺ (?)</td>
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<tr>
<td>94</td>
<td>C₂H₄NF₂⁺</td>
<td>66.3</td>
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Since permanganate is obviously being reduced by the organic difluoramines, the search for the intermediate organic oxidation products will be continued. An attempt was made to prepare a dioxide from III by treatment with mercuric oxide in refluxing benzene. However, no reaction occurred.

$$\text{(CH}_3\text{)}_2\text{C-CH=CHC(CH}_3\text{)}_2 + 2\text{HgO} \rightarrow \text{(CH}_3\text{)}_2\text{C-CH=CHC(CH}_3\text{)}_2 + 2\text{Hg}$$

Hydrogen peroxide was also investigated since it is known to oxidize amines to amine oxides, difluoramine to oxides of nitrogen and has the advantage over permanganate in not leaving solid decomposition products. First, it was determined that III did not interfere in the ceric IV sulfate titration for peroxide, so that this reagent could be used to follow peroxide consumption.

A reaction was observed between III and 30% hydrogen peroxide in glacial acetic acid. Only a solid silicate was isolated along with a qualitative indication of ammonium ion. No reaction was observed between III and 30% hydrogen peroxide in methanol solution at 65°C. The addition of hydrochloric acid to the methanol system catalyzed a redox reaction forming acetone, an unknown organic residue, and a solid, identified by infrared as ammonium fluorosilicate. The organic residue possessed an ester carbonyl peak but did not contain an NF bond. This reaction was repeated at room temperature in a Kel-F reactor. After three days, 96% of the peroxide was consumed. No solid was produced. Concentration of the aqueous alcohol solution and refrigeration caused the prescription of extremely pure III. No other organic materials could be recovered from the methanol mother liquor. It is significant that although the starting material contained about 10% of the isomer, 4,5-bis(difluoramino)-2,5-dimethyl-2-hexene, none of this isomer nor any of its dehydrofluorinated derivative, 5-difluoramino-4-fluorimino-2,5-dimethyl-2-hexene, could be recovered. Thus, a selective reaction must have occurred.

The observation that ammonium ion is one of the products of the peroxide reaction clearly required that carbon-nitrogen bond cleavage and "reduction" of the N-F bonds have occurred. The formation of ammonia is not consistent with a direct attack on nitrogen and the formation of an amine oxide intermediate. The results are more consistent with a complex redox reaction in which the N-F bond acts as an oxidant for peroxide.
C. Nature of the α-Hydrogen Atoms

The easy dehydrofluorination of primary and secondary carbon difluoramines suggested that the α-hydrogen atom might be sufficiently acidic to permit the utilization of the anion, VIII, as a synthetic intermediate.

\[
\begin{align*}
\text{NF}_2 & \\
\text{R}_2\text{C-H} & \xrightarrow{\text{base}} \left[ \text{R}_2\text{C-NF}_2 \right] & \rightarrow & \text{R}_2\text{C}=\text{NF} + \text{F} \\
\text{VIII}
\end{align*}
\]

This equation assumes that the elimination of hydrofluoric acid is a stepwise rather than a concerted reaction. If the anion, VIII, has any stable existence at all, then it might be used in typical anionic condensation and addition reactions such as hydroxymethylation and Mannich additions.

Several attempts to demonstrate a carbonyl addition reaction with the cyclohexene adducts, I and II, were unsuccessful. Treatment of I and II under neutral and basic conditions with benzaldehyde did not result in addition products. Instead, the aldehyde was recovered and dehydrofluorination was the only recognizable result. Before investigating other possible addition reactions, we decided to apply a more sensitive test for labile hydrogen. If, as postulated, a protonic character can be attributed to the α-hydrogen atom of secondary alkyl difluoramines, then these hydrogen atoms should exchange stepwise with deuterium oxide, as indicated:

On three occasions, the mixture of I and II was treated with a tenfold excess of heavy water in purified dioxane as solvent. Conditions were varied as to time and temperature and, in one experiment, a drop of pyridine was added to make the system more basic. In every case, the cyclohexene adducts were recovered and subjected to analysis. The infrared and mass spectral methods proved that exchange had not occurred. These results argue against a labile, protonic
character for the α-hydrogen atoms, and discourage further attempts at condensation and ionic substitution reactions. Furthermore, the results support a concerted mechanism for the dehydrofluorination process.

Since ionic substitution reactions no longer look promising, our attention has shifted toward possible radical substitution of α-hydrogen. To determine whether the NF₂ group itself is stable under free radical conditions, studies were first initiated with the diteriary difluoramine, III, and the gem compound, VI. No reaction was observed with III using N-bromosuccinimide and benzoyl peroxide as reagents. N-Bromosuccinimide was recovered in 70% yield. Since the styrene - NF₂ adduct is reported to be degraded by these reagents, our results suggest that the α-hydrogen atom may be susceptible to radical substitution. Other radical substitution reactions are now being studied with the cyclohexene adducts and VI.
III. EXPERIMENTAL

A. 2,2-Bis(difluoramino)propane

1. Into an evacuated 200 ml flask equipped with a magnetic stirring bar was placed 10 ml of 97.0% sulfuric acid. Acetone (0.17 gram, 0.003 mole) and 135 ml (0.006 mole) of purified difluoramine were condensed over the sulfuric acid at -110°C. Using a -110°C cold finger, the difluoramine was allowed to reflux for one hour over the sulfuric acid solution which was kept at -10°C to 0°C. Then the temperature of the mixture was allowed to rise to ambient. The products were fractionated through -80°C and -110°C traps. The -80°C trap contained a white solid which was liquid at room temperature and had a vapor pressure of 104 mm Hg. Distillation gave 0.16 gram (39% yield) of 2,2-bis(difluoramino)propane, bp 70°C.

2. The preparation of this gem compound was repeated under identical conditions, except for the concentration of the acid. Using 115% sulfuric acid, the yield of 2,2-bis(difluoramino)propane was 72%. This yield was reproduced in a third preparation. The combined amount of distilled product from the three runs was 0.75 gram.

The infrared spectrum for this gem compound is shown in Figure 2. The mass spectrum (Table I) was obtained at 70 ev using a Model 12 Bendix Time-of-Flight instrument.

B. 1,1-Bis(difluoramino)cyclohexane

Into a 200 ml evacuated flask containing 10 ml of degassed 98% sulfuric acid was condensed 0.5 ml (0.005 mole) of cyclohexanone and 0.008 mole of difluoramine. By means of a cold-finger condenser kept at -100°C, difluoramine was refluxed for 50 minutes over the acid-ketone mixture kept at 15-20°C. Some decomposition was noted in the organic phase as a tarry residue formed. The acid mixture was then poured onto ice, and the mixture was extracted three times with chloroform. The solvent was removed by evaporation, and the residual oil was subjected to purification by gas chromatography at 80°C through our standard didecylphthalate column using Helium as the carrier gas.
The retention time was 89 minutes. No other product was indicated by the VPC analysis, although a small amount of unreacted cyclohexanone was present. The retention time on this column was very close to that for the isomer, cis-1,2-bis(difluoramino)cyclohexane (98 minutes at 78°C). However, the infrared spectrum (Figure 1) clearly indicated the absence of any vicinal isomers.

C. Hydrogen Peroxide and 2,5-Bis(difluoramino)-2,5-dimethyl-3-hexene

1. A solution of 1.07 grams (0.005 mole) of the ditertiary difluoramine (III), 1 ml (0.01 mole) of 30% aqueous hydrogen peroxide and 10 ml of glacial acetic acid was heated at 70°C for one hour and then allowed to stand overnight at room temperature. About one-half the solvent was removed by distillation, and the residue was made basic with ice-cold dilute aqueous sodium hydroxide. The mixture possessed a strong ammoniacal odor, and an inorganic silicate was removed by filtration. The basic solution was extracted with ethyl ether, acidified with cold dilute hydrochloric acid, and extracted again. Evaporation of the ether extracts failed to leave an organic residue.

2. A solution of 1.07 gram (0.005 mole) of III, 2 ml (0.02 mole) of 30% aqueous hydrogen peroxide and 10 ml of anhydrous methanol were stored at room temperature for 24 hours. No consumption of peroxide occurred as shown by titration of an aliquot with the ceric sulfate reagent. The solution was heated at 65°C for 48 hours and again the peroxide was not consumed. Hydrochloric acid (1 ml, 36%) was then added, and the solution was maintained at 65°C for 12 hours. All the peroxide was consumed. A solid, identified as ammonium fluorosilicate, was removed by filtration. Mass spectral analysis of the filtrate identified acetone as one of the reaction products. Evaporation of the solvent gave a yellow pasty residue whose infrared spectrum revealed a carbonyl peak in the ester region but no N-F peaks.

3. A solution of 2.14 grams (0.01 mole) of III, 2 ml (0.02 mole) of 30% hydrogen peroxide, and 1 ml of 36% hydrochloric acid in 20 ml of methanol was allowed to stand at room temperature for three days in a Kel-F tube. At the end of this time, titration of an aliquot revealed that 96% of the peroxide had been consumed. The solution was then heated at 50°C for three hours and titrated again to reveal that 97% of the peroxide had been consumed. No solid had formed. After concentrating the solution to about half its original volume, the residue was placed in a refrigerator for two days. A white precipitate formed which was isolated by decantation. The solid melted just above room temperature and was identified by gas chromatography, mass spectroscopy, and infrared analysis as extremely pure III, free of any isomers. Neither the 4,5-isomer, which comprised about 10% of the starting III, nor any other organic material was recovered from the alcohol solution.
D. Sodium Permanganate and 2,5-Bis(difluoramino)-2,5-dimethyl-3-hexene

A solution of 5.68 grams (0.04 mole) of sodium permanganate in 20 ml of water was added dropwise with stirring to a mixture of 2.14 grams (0.01 mole) of III in 10 ml of water containing 2 grams (0.05 mole) of sodium hydroxide. After the first three drops of the permanganate reagent had been added, the solution turned green, but no further reaction was noted after additional drops of reagent were added. The mixture was then heated with stirring to 80-90°C, and the permanganate addition was completed with reaction over a four hour period. At the end of this time, the mixture was a deep blue color. The reaction mixture was cooled to 0°C, acidified with ice-cold dilute sulfuric acid, and the color was bleached with sodium sulfite solution. A two phase system resulted. The organic phase was the lighter. The mixture was extracted with ethyl ether. The ether solution was washed with water and dried over sodium sulfate. Filtration and evaporation of the solvent gave 1.72 grams (80%) of starting material. Gas chromatography revealed that the recovered material was still a mixture of the two isomers, qualitatively richer in III.

E. Attempted Deuterium-Hydrogen Exchange with 1,2-Bis(difluoramino)cyclohexane

1. A solution of 0.43 gram (0.0025 mole) of the cis and trans mixture of 1,2-bis(difluoramino)cyclohexane in 5 ml of purified dioxane was treated with 0.5 ml (0.027 mole) of deuterium oxide (D_2O > 99.5%). The resulting solution was allowed to stand at 25°C for three hours. The solvent was then removed under vacuum. Only nondeuterated starting material was recovered as indicated by infrared and mass spectral analyses.

2. This reaction was run exactly as above except that the solution was heated at 70°C for 2 hours and then allowed to stand at room temperature overnight. Analysis again revealed that no exchange had occurred.

3. A third reaction was conducted as in 1, except that one drop of pyridine was added. A red color gradually developed, and the solution was allowed to stand overnight. Workup and analysis again revealed that no exchange had occurred. Only the unchanged adducts were recovered, and there was no indication of a dehydrofluorinated product.
F. Benzaldehyde and 1,2-Bis(difluoramino)cyclohexane

A solution containing 0.93 gram (0.005 mole) of 1,2-bis(difluoramino)-
cyclohexane and 1.06 grams (0.01 mole) of benzaldehyde in 10 ml of anhydrous
methanol was prepared. Sodium bicarbonate (0.84 gram, 0.01 mole) was
suspended in the solution, and the mixture was allowed to stand for 24 hours
under nitrogen. A small amount of gas was evolved. Filtration of the mixture
and distillation recovered 0.83 gram (78%) of benzaldehyde.

G. Mercuric Oxide and 2,5-Bis(difluoramino)-2,5-dimethyl-3-hexene

A mixture of 1.07 grams (0.005 mole) of III, 3.0 grams (0.013 mole) of
mercuric oxide and 10 ml of dry benzene was stirred for twenty hours at room
temperature. The mixture was then refluxed for five hours. No reaction was
indicated by the absence of free mercury. Workup of the mixture recovered
only the starting materials.

H. N-Bromosuccinimide, Benzoyl Peroxide, and 2,5-Bis(difluoramino)-
2,5-dimethyl-3-hexene

A mixture of 3.56 grams (0.02 mole) of N-bromosuccinimide and 0.02
gram of benzoyl peroxide was added portionwise to a refluxing solution of 2.14
grams (0.01 mole) of III and 0.02 gram of benzoyl peroxide in 10 ml of dry
benzene. After each portion was added, the solution frothed. When the ad-
tion was completed, the solution was refluxed for four hours and then allowed
to stand overnight at room temperature. A solid precipitated. It was filtered,
washed with ligroin, and dried. The solid weighed 2.5 grams and was identified
as unreacted N-bromosuccinimide by its mp 175-180°C, lit mp 180-182°C,
and by mixed melting point. The yield of recovered NBS was 70%.

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SECTIONS 793 AND 794. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW.
IV. FUTURE WORK

1. Prepare additional quantities of the gem and olefin-N$_2$F$_4$ model compounds.

2. Study radical substitution reactions on $\alpha$ and $\beta$ hydrogen, particularly halogenation and nitration.

3. Elucidate the permanganate reduction reaction.

4. Study the interaction of the model compounds with organometallics.

5. Prepare 1,2-bis(fluorimino)cyclohexane and investigate its chemistry.
V. REFERENCES


2. Thiokol Chemical Corporation, Reaction Motors Division, RMD-076-Q2-61, June, 1961.

3. Aerojet-General Corporation, Special Report, Contract NOr 2655(00), March, 1961.


6. Thiokol Chemical Corporation, Reaction Motors Division, RMD-2075-F1, December, 1960.

