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ARPA Order No. 186-61
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DIFLUORAMINE CHEMISTRY

Report Period: 20 January 1961 to 31 March 1961

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68

DIFLUORAMINE CHEMISTRY

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ARPA- Report RMD 076-Q1-61

Order No. 186-61

Contract NOnr 1878(00)

20 January 1961 to 31 March 1961

22142
68
TIPOR A

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RMD 076-Q1

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ABSTRACT

Substantial quantities of the pure 1:1 tetrafluorohydrazine adducts of 1-hexene, cyclohexene, and 2,5-dimethyl-2,4-hexadiene were prepared. The latter two adducts were resolved into isomers, and structural assignments have been made. As a result, the following pure compounds are now available for the study of C-NF₂ chemistry:

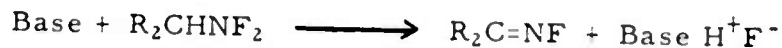
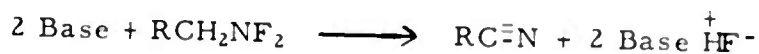
- | | |
|---|-------|
| trans 1,2-bis(difluoramino)cyclohexane | (I) |
| cis 1,2-bis(difluoramino)cyclohexane | (II) |
| trans 2,5-bis(difluoramino)-2,5-dimethyl-3-hexene | (III) |
| 1,2-bis(difluoramino)-n-hexane | (IX) |

The reactions of these compounds with a variety of reagents are under investigation. Nucleophilic reagents such as alkoxide, t-amine, and iodide primarily cause dehydrofluorination of primary and secondary difluoramines, although other reactions are also observed. Tertiary organic difluoramines apparently are not attacked by these reagents.

Evidence is presented which shows that the addition reaction of tetrafluorohydrazine to olefins is reversed in the mass spectrometer.

I. INTRODUCTION

There are very few well characterized reactions of the aliphatic difluoramines or organoimino fluorides. As a result, our knowledge of the chemical behavior of organic NF compounds is meager. Previous studies (Ref 1) with aliphatic difluoramines containing a hydrogen or a unsaturation disclosed a strong tendency for fluoride elimination or rearrangement. Thus, primary and secondary aliphatic difluoramines undergo dehydrofluorination to yield nitriles and imino fluorides, respectively.



The dehydrofluorination reaction is probably initiated by removal of an α proton by a base with a concurrent or subsequent elimination of fluoride ion. Preliminary evidence suggests that the ease of dehydrofluorination is strongly dependent upon the structure of the aliphatic difluoramine, the strength of the attacking base, and the presence of activating functions on the α carbon atom. Fluorine migration, akin to an allylic rearrangement, has been noted with vinyl difluoramines which are unstable to the formation of β -fluoralkyl imino fluorides (Ref 8). The mechanism for this rearrangement is unknown.



A reaction of C-NF₂ compounds which appears to be characteristic of the NF₂ group is the oxidation of iodide to iodine. The stoichiometry of this redox reaction is not predictable (cf. Ref 2).

Although halogenoid properties have been attributed to the NF₂ group, none of the usual transformations of the organic halides such as organometallic formation, displacement or elimination reactions has been demonstrated with the C-NF₂ group. Also, no substitution or displacement reactions on the fluorine atom of the N-F bond have been described. Thus, a wide area of fruitful research remains to be explored.

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It is the purpose of this program to investigate the chemistry of the aliphatic difluoramines, and to a lesser extent the organo iminofluorides, in order to define the chemical processes which these new functions can undergo.

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II. DISCUSSION

A. Preparation and Characterization of Aliphatic bis-Difluoramines

The initial purpose of this work has been concerned with the preparation of suitable aliphatic bis-difluoramines to supply raw materials for the study of C-NF₂ chemistry. Aliphatic bis-difluoramines are conveniently prepared by the thermal addition of tetrafluorohydrazine to alkenes. 1-Hexene, cyclohexene, and 2,5-dimethyl-2,4-hexadiene were chosen as the starting olefins for the first portion of this work, since their respective N₂F₄ adducts would be expected to be stable, distillable liquids, and each adduct would represent a different kind of C-NF₂ compound. From these adducts a comparison of the behavior of primary, secondary and tertiary NF₂ groups can be made, and this may permit us to distinguish the reactions characteristic of the NF₂ group, independent of the presence of a hydrogen. Both the batch-wise bulb method and the continuous reactor previously described (Ref 1) were used in these preparations.

1,2-bis(Difluoramino)cyclohexane

1,2-bis(Difluoramino)cyclohexane was prepared initially by the bulb reaction of tetrafluorohydrazine with cyclohexene. The early experiments, which show a wide variation in yield, are tabulated in Table I. More recent preparations, both in the bulb reactor and in the continuous reactor, are given in the experimental section. The cyclohexene adduct is a water white, impact insensitive liquid which is easily vacuum distilled, although some decomposition is noted during distillation at higher temperature (> 90°C). A portion of the adduct was triply distilled, and the following properties were measured: bp 46-47°C/6 mm, 118°C/135 mm; $n_D^{27.5}$ 1.4107; d_{25} 1.289g/cc.

Anal. Calcd. for C₆H₁₀F₄N₂: C, 38.71; H, 5.41; N, 15.05; F, 40.83
Found: C, 38.70; H, 5.61; N, 14.86; F, 40.83

Isolation of Cis and Trans 1,2-bis(Difluoramino)cyclohexane

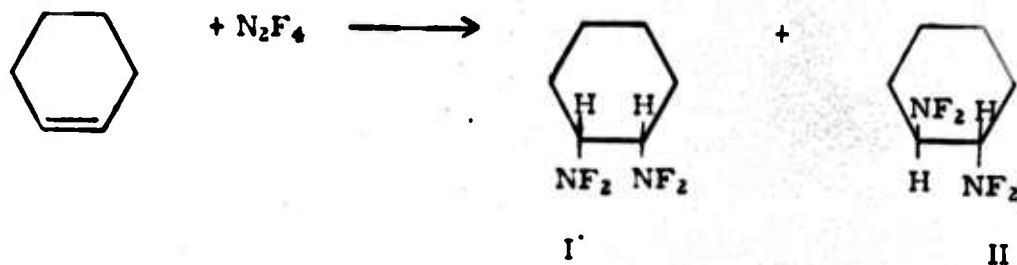
Because of its cyclic structure, cyclohexene adducts could be expected to exist in geometrical forms, i. e. cis (I) and trans (II) isomers:

TABLE I
PREPARATION OF 1,2-BIS(DIFLUORAMINO)CYCLOHEXANE

Ex. No. L-374-	Time (hr)	Temp (°C)	Crude Product (grams)	Crude Yield* (%)
44	3	120	2.7	55
47	4	140-145	1.2	24
50	3	120-130	3.28	65
52	3	120-130	1.4	28
56	4	140-145	2.2	44
58	4	140	2.2	44
60	3	125	3.56	71
62	4	120-125	3.1	61
64	2	120-125	3.0	60
66	4	120-125	2.45	50

NOTE: Reactants were 2.2 grams (27 mmoles) cyclohexene and 3.08 grams (31.2 mmoles) 95% N_2F_4 .

* Based on C_6H_{10} charged.



A crude sample of 1,2-bis(difluoramino)cyclohexane was separated by gas chromatography into two pure components. At $78^\circ C$, column retention times were 49 and 98 minutes (Figure 1). The components were assigned a trans and cis configuration, respectively, based on their infrared spectra and volatilities. These spectra are shown as Figures 2 and 3. As can be seen, the spectra are very similar. The assignment of the cis configuration to the smaller component (98 minutes) is based in part on the presence of the 13.79μ peak in Figure 3 and the absence of this peak in Figure 2.

The components were confirmed as isomers by means of their mass spectra (Table II). The cracking patterns are almost identical. As is usual with these materials, neither component showed a parent peak (m/e 186), but both showed the same highest fragment (m/e 134) corresponding to the removal of one NF_2 group. It may be significant that in both components a strong peak ($r. i. = 100$) appears at m/e 81. This corresponds to the $C_6H_9^+$ moiety and suggests that one of the principal bond breaking reactions is the cleavage of the C-N bond, possibly regenerating the olefin as an intermediate. Some physical constants of the isomers are: trans, d_{25} 1.275 g/cc, n_D^{25} 1.4095; cis, d_{25} 1.293 g/cc, n_D^{25} 1.4125.

Using a larger preparative column, ten liquid cc of the trans-cis mixture were cleanly separated at $135^\circ C$, retention times being 20 and 43 minutes, respectively. Although this method of separation is tedious and limited to relatively small quantities, it appears to be the only practical purification procedure available. Alternative methods for separating the isomers are being investigated. Thus far, liquid phase partition chromatography on a silica column does not appear promising. However, we have some evidence that the mixture can be partially resolved by fractional distillation.

TABLE II

MASS SPECTRA OF CIS AND TRANS
1, 2-BIS(DIFLUORAMINO)CYCLOHEXANE

m/e	Relative Intensities		m/e	Relative Intensities	
	I Trans	II Cis		I Trans	II Cis
36	0.1	0.1	61	7.8	8.8
37	1.1	1.7	62	3.0	5.3
38	4.0	6.2	63	1.3	1.3
39	48.8	63.5	64	1.0	1.1
40	17.4	22.3	65	11.7	12.9
41	91.4	107.3	66	8.6	10.3
42	31.3	34.7	67	60.3	66.7
43	9.0	10.5	68	16.8	19.4
44	1.8	3.3	69	9.0	10.3
45	2.4	2.9	70	1.8	1.6
46	5.9	7.8	71	1.4	1.3
47	19.2	22.6	72	2.8	3.2
48	8.8	10.2	73	45.3	46.7
49	0.7	0.8	74	10.0	10.3
50	2.1	2.8	75	1.9	1.8
51	7.0	9.4	76	0.9	-
52	6.3	8.2	77	4.6	4.7
53	30.4	35.3	78	1.5	2.0
54	23.3	26.6	79	15.6	15.9
55	26.8	29.3	80	9.7	10.3
56	8.3	7.4	81	100.0	100.0
57	1.9	1.8	82	15.6	16.5
58	1.1	1.4	83	1.7	2.0
59	22.6	24.5	84	1.0	1.0
60	4.1	4.7	85	2.3	2.4

TABLE II (cont)

m/e	Relative Intensities		m/e	Relative Intensities	
	I Trans	II Cis		I Trans	II Cis
86	6.0	6.4	96	6.3	6.5
87	5.2	5.3	97	1.7	1.7
88	2.0	2.0	98	1.6	1.7
89	0.6	0.6	99	5.9	5.8
90	0.4	0.4	100	2.5	2.7
91	0.4	0.4	102	0.2	0.2
92	1.8	1.7	106	0.4	0.4
93	2.1	2.3	110	0.1	0.2
94	6.9	7.0	111	0.3	0.3
95	2.9	3.0	112	0.8	0.7
			114	6.0	6.1
			115	7.3	7.2
			134	3.3	3.4

1

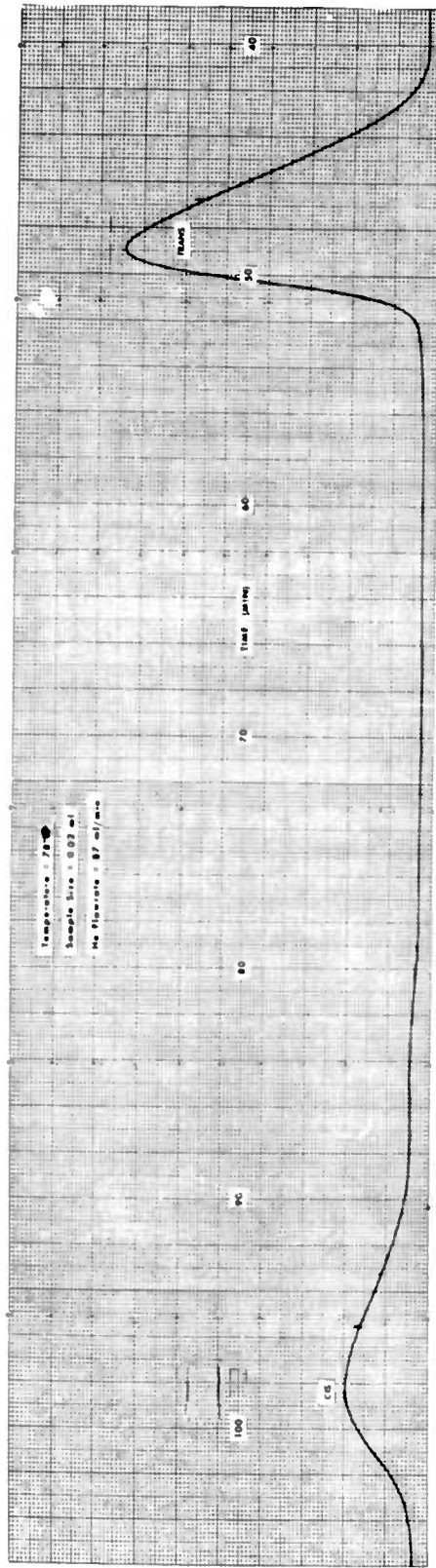
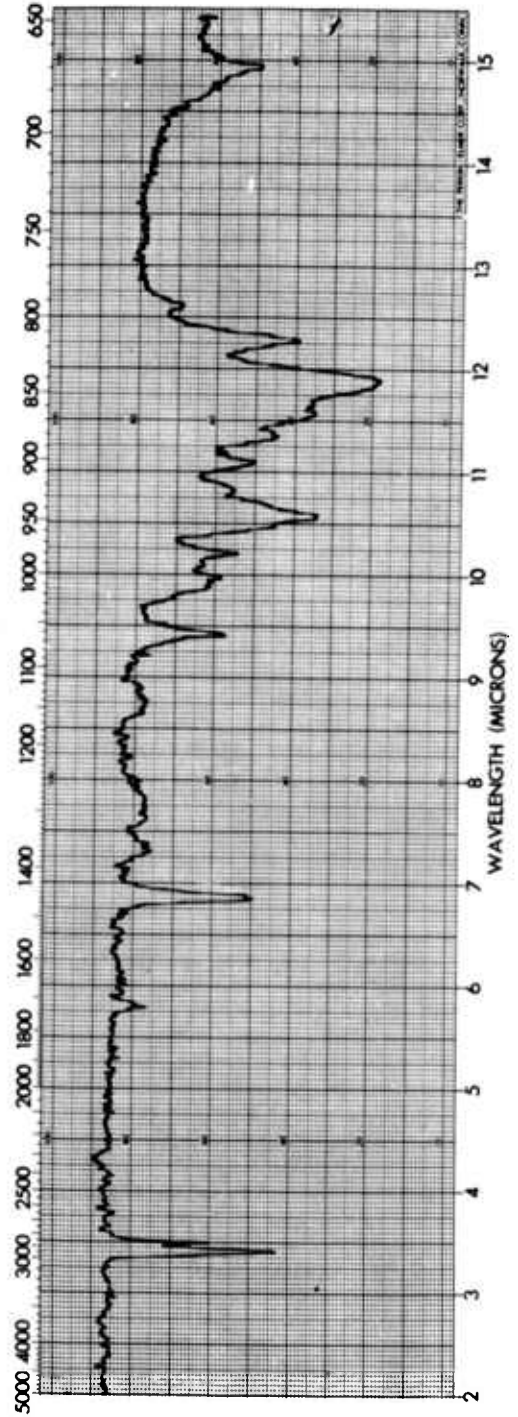


Figure 1. Vapor Phase Chromatographic Separation of Trans and Cis 1,2-bis(Difluoramino)cyclohexanes



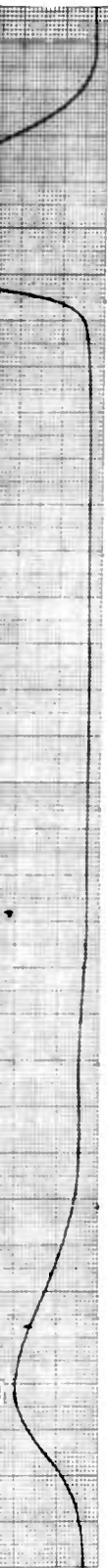


Figure 1. Vapor Phase Chromatographic Separation of Trans and Cis 1,2-bis(Difluoramino)cyclohexanes

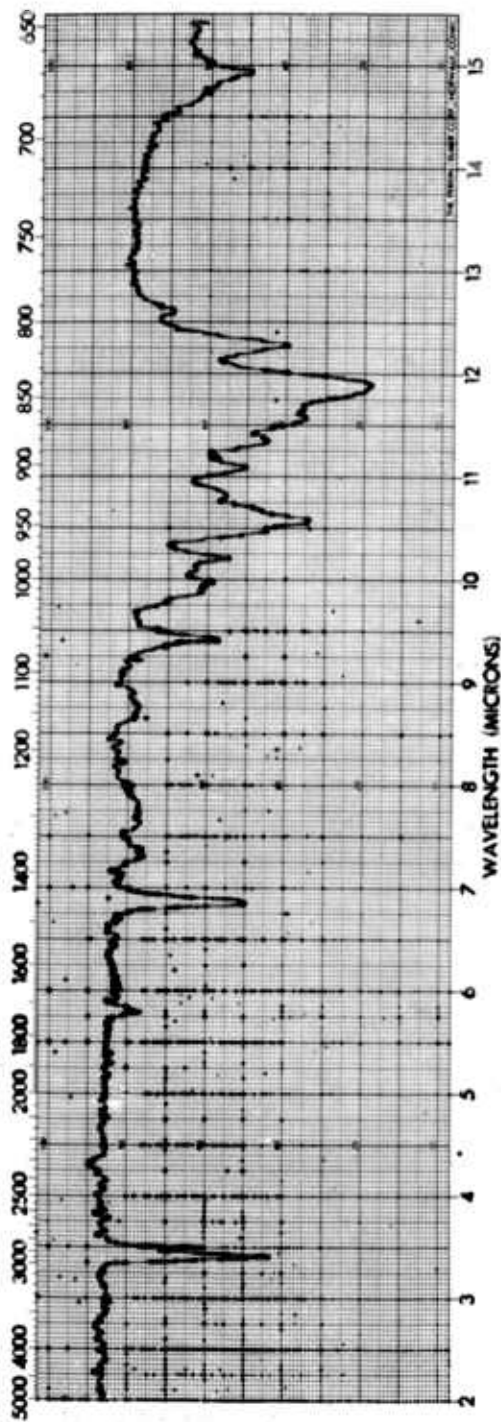


Figure 2. Infrared Spectrum of Trans 1,2-bis(Difluoramino)-cyclohexane

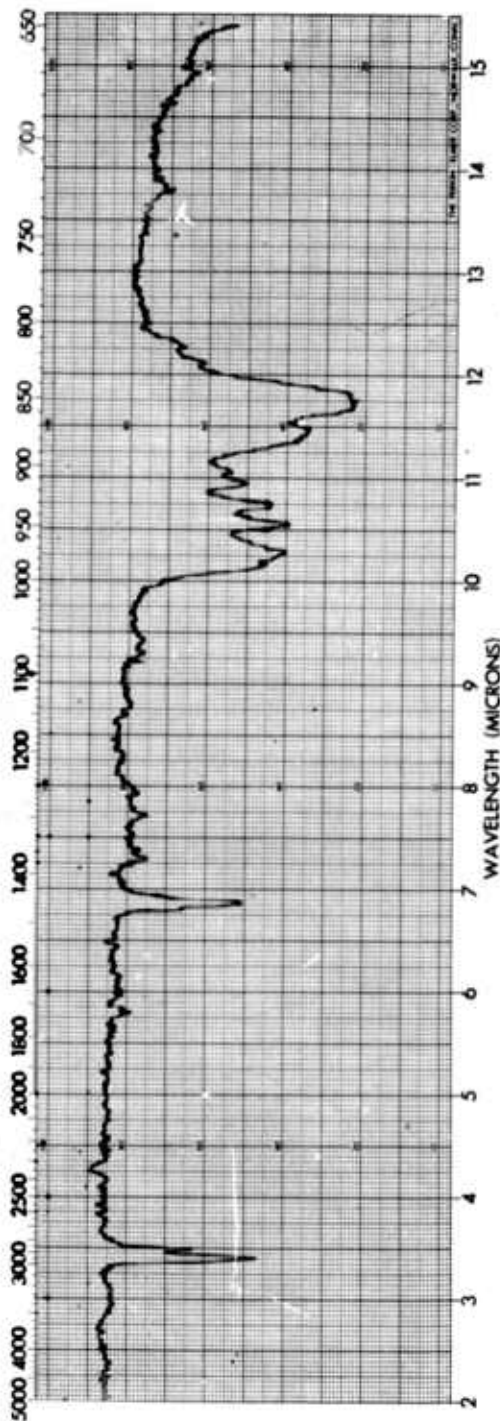


Figure 3. Infrared Spectrum of Cis 1,2-bis(Difluoramino)-cyclohexane

2

TABLE III
REACTION OF 2, 5-DIMETHYL-2, 4-HEXADIENE WITH N_2F_4

Ex. No. L-352-	Time (hr)	Temp (°C)	Crude Product (grams)	Crude Yield* (%)
66	4	140-145	2.4	45
68	3.5	100-105	3.67	68
72	8	110	1.25	23
102	4	110-120	3.85	72
104	4	120-135	4.99	93.2
106	4	130-135	4.22	79
108	4	130-135	4.89	90
110	4	130-135	2.45	46

NOTE: Reactants were 85% N_2F_4 (32.3 mmoles) and hexadiene (25 mmoles).

* Based on amount of hexadiene charged.

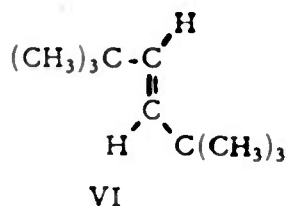
A subsequent set of five runs (see Experimental) gave 16 grams of distilled mono-adduct. This represented a 61% yield. Its physical properties were: bp 92°C/35 mm, n_D^{23} 1.4077.

Anal. Calcd. for $C_8H_{14}F_4N_2$: C, 44.85; H, 6.59; N, 13.08; F, 35.48
Found: C, 44.96; H, 6.60; N, 13.00; F, 35.86

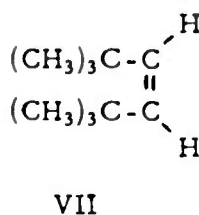
A sample of the second batch of mono-adduct was subjected to gas chromatography and partially resolved into two components, a low melting solid and a liquid. The separation was not clean cut since the peak retention times (50 and 53 minutes at 78°C) were too close and the very small second peak (liquid) overlapped the much larger first peak (solid).

The solid was assigned the trans configuration (III) based initially on its high yield, volatility, and relatively high melting point. Subsequent chemical studies (see below) would appear to strongly support this assignment. The impure liquid (not completely free of III) was at first thought to be the cis isomer (IV), but this assignment was subsequently found to be incompatible with the infrared spectra and apparent reactivity. The infrared spectra of the trans adduct III (Figure 4), and the liquid (Figure 5) are quite similar, except for a double bond peak at 5.98 μ and a peak at 12.28 μ in the latter.

The trans adduct III may be formally compared to trans tertiary butyl ethylene (VI). This molecule was prepared by F. L. Howard, et al. (Ref 3).



The corresponding cis isomer (VII) has been described by G. F. Hennion and T. F. Barrigan (Ref 4).



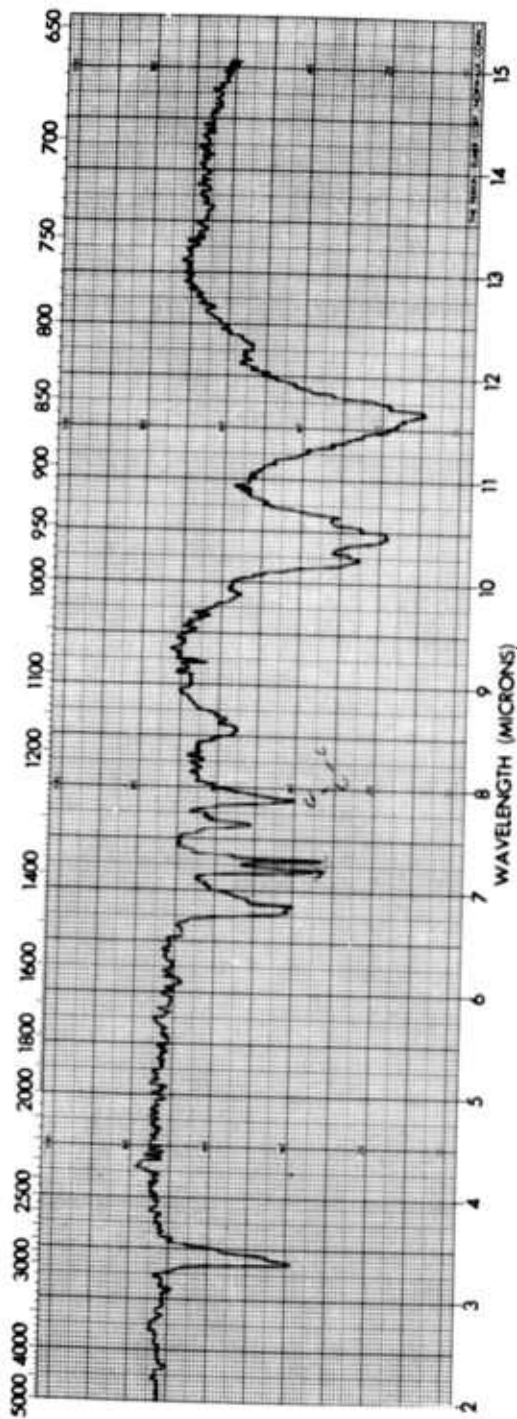


Figure 4. Infrared Spectrum of Trans 2,5-bis(Difluoramino)-2,5-dimethyl-3-hexene

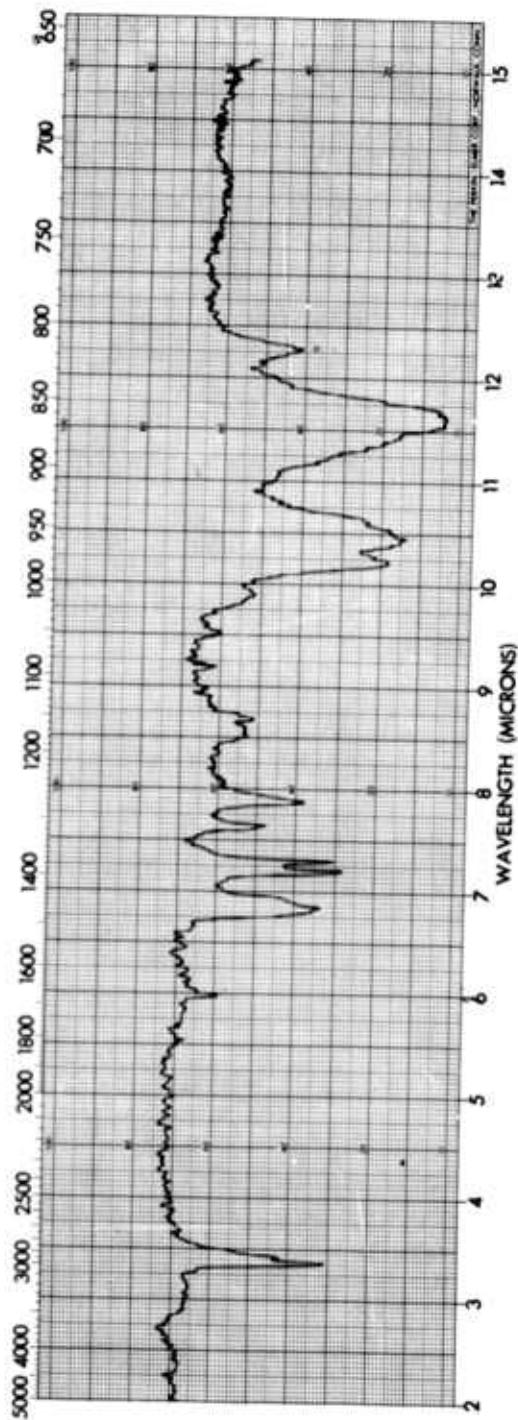


Figure 5. Infrared Spectrum of 4,5-bis(Difluoramino)-2,5-dimethyl-2-hexene

TABLE IV

MASS SPECTRA OF TRANS 2, 5-BIS(DIFLUORAMINO)-
2, 5-DIMETHYL-3-HEXENE AND
4, 5-BIS(DIFLUORAMINO)-2, 5-DIMETHYL-2-HEXENE

m/e	Relative Intensities		m/e	Relative Intensities	
	III	V		III	V
26	4.9	2.0	60	2.0	0.9
27	58.6	22.3	61	17.1	3.2
28	41.8	19.7	62	4.1	0.8
29	64.8	17.5	63	1.0	0.6
30	3.9	1.4	65	3.6	4.3
31	0.7	0.3	66	13.8	3.2
32	3.3	2.4	67	12.1	8.7
33	4.8	2.2	68	7.9	4.4
36	0.2	-	69	55.0	7.6
37	0.6	-	70	6.6	1.3
38	2.3	1.3	71	1.6	0.4
39	33.5	21.1	73	2.5	0.8
40	0.3	4.9	74	6.6	1.3
41	113.0	43.8	75	4.9	0.7
42	24.3	10.5	76	1.1	-
43	63.3	17.3	77	2.3	2.8
44	3.9	3.0	78	-	0.8
45	0.8	-	79	4.9	3.2
46	2.9	1.7	80	2.6	1.6
47	30.2	6.4	81	14.6	5.0
48	7.4	1.4	82	5.6	3.3
51	3.3	4.2	83	9.8	1.7
52	2.5	3.3	84	2.0	0.5
53	13.1	13.9	85	0.8	-
54	7.8	6.3	86	0.9	0.4
55	85.5	23.1	87	1.3	0.7
56	20.4	14.4	88	2.8	0.4
57	10.5	2.8	89	0.8	0.2
58	1.6	0.6	91	0.5	0.9
59	5.9	2.9	92	-	0.5

TABLE IV (cont)

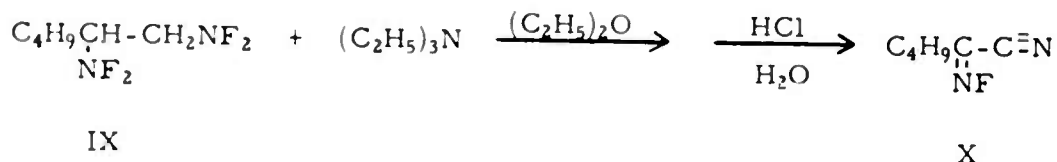
m/e	Relative Intensities		m/e	Relative Intensities	
	III	V		III	V
93	1.0	1.6	109	-	7.9
94	1.6	2.5	110	<u>100.0</u>	<u>100.0</u>
95	19.4	9.2	122	2.3	0.6
96	6.1	6.4	124	3.8	3.2
97	6.1	1.1	126	0.8	0.3
98	-	0.6	128	1.7	1.4
100	-	0.5	139	0.5	-
106	-	0.2	142	0.2	0.3
107	-	0.9	147	0.5	0.3
108	-	2.2	153	0.5	0.1
			159	0.7	-
			162	13.1	12.6

work has been done on the characterization of the reaction products. No one has bothered to determine the behavior of the C-NF₂ group to hydrogenation, reduction, nucleophilic substitution or oxidation. Some work has been done on the oxidation of iodide to iodine (Ref 7) by organodifluoramines but neither the reaction products nor the stoichiometry has been characterized.

The synthesis of aliphatic compounds containing 1^o, 2^o, and 3^o NF₂ groups should provide the tool for studying C-NF₂ chemistry. The tertiary difluoramines are particularly important since the complications due to a hydrogen (i.e. dehydrofluorination) are not present.

1,2-bis(Difluoramino)hexane and Triethylamine

The reaction of 1,2-bis(difluoramino)hexane (IX) with triethylamine was reported (Ref 1) to yield a fluorimino-nitrile, X, identified by its infrared features, a strong C=NF absorption at 5.8 μ, a C≡N band at 4.5 μ and an NF band at 11-12 μ. This reaction was repeated in ethyl ether solvent, and a chromatographically pure sample of iminofluoride-nitrile was isolated after removal of excess triethylamine with hydrochloric acid. It was of interest to note that the strong 5.8 μ band previously observed was no longer present in the pure product and this suggests that the previous sample contained a carbonyl by-product, probably an aldehyde.



Anal. Calcd. for C₆H₉N₂F: C, 56.24; H, 7.06; N, 21.86; F, 14.83
 Found: C, 55.25; H, 7.31; N, 21.73; F, 15.35

1,2-bis(Difluoramino)hexane with Sodium Iodide and with Methanol

A very complex reaction was observed when IX was treated with sodium iodide in refluxing methanol. About two moles of iodine were liberated per mole of IX. An oil was isolated from the reaction mixture after the iodine was removed with aqueous sodium sulfite. The oil gave an infrared spectrum very similar to X, except that a strong 5.76 μ band was again present. However, the product was resolved into three components by means of gas chromatography. Infrared analysis of the three components indicates that the products

The above results indicate that III is inert to strong base and that V is attacked by strong base. This is entirely consistent with the assigned structures. Furthermore, base treatment permits us to remove the small amount of V and isolate pure III from the isomer mixture. It is also significant that III, which cannot undergo dehydrofluorination, does not appear to oxidize iodide to iodine in methanol.

III. EXPERIMENTAL

Preparation of 1,2-bis(Difluoramino)cyclohexane

Cyclohexene (2.7 ml, 0.027 mole) was charged under a constant stream of nitrogen into a 2-liter flask attached to a glass vacuum system. The cyclohexene was cooled to -196°C and degassed. Tetrafluorohydrazine (96% pure, 0.0312 mole, 259 mm Hg) was introduced, and the reactants were heated to 125°C and kept at that temperature for three hours. After this time, the flask was cooled to -196°C , and any noncondensable gases were stripped off under vacuum. The crude product was condensed in a trap cooled with Dry Ice and then collected for distillation. The yield of crude 1,2-bis-(difluoramino)cyclohexane was 3.6 grams (70%). This yield was reproduced three times out of five runs. The other two runs gave only black-brown viscous polymers due to an air leak.

Preparation of 1,2-bis(Difluoramino)cyclohexane in Flow Reactor

A stream of nitrogen diluted N_2F_4 -cyclohexane mixture was passed through a coil reactor (60 cc capacity) kept at 140°C . The flowrates were: N_2 , 16 cc/min; liquid C_6H_{10} , 0.066 cc/min; and N_2F_4 , 11.1 cc/min. This gave a $\text{C}_6\text{H}_{10}/\text{N}_2\text{F}_4$ mole ratio of 1:1. The crude product was collected in a trap cooled at 0°C . A one-day run produced 8-10 grams of crude product. The product contained unknown volatile substances, which sometimes caused ignition. In one instance, the crude product, stored under nitrogen at 0°C , detonated. It proved to be difficult to work with the flow reactor due to the buildup of deposits which tended to plug the coil.

Preparation of Trans 2,5-bis(Difluoramino)-2,5-dimethyl-3-hexene and 4,5-bis(Difluoramino)-2,5-dimethyl-2-hexene

Under an atmosphere of argon, 2.75 grams (25 mmole) of 2,5-dimethyl-2,4-hexadiene were charged into a two liter bulb. The olefin was then frozen at -196°C , and then the bulb was evacuated. Tetrafluorohydrazine (32 mmole) was introduced, and the reaction flask was heated to $120-150^{\circ}\text{C}$ for four hours. At the end of this time, the mixture was cooled to -196°C and the noncondensable

gases were pumped off. The residue was distilled into a Dry Ice trap and collected. Five identical runs were made giving 18.6 grams of crude adduct. This was distilled, bp 92°C/35 mm, to give 16.25 grams (61% yield) of the isomer mixture, $n_D^{23} = 1.4077$.

Separation of Geometrical isomers

Gas chromatography of the cyclohexene and dimethylhexadiene adducts was conducted on a Model 154-C Perkin-Elmer Vapor Fractometer. Conditions were:

Column: di-n-decyl phthalate (25%) on fire brick (30-60 mesh), six foot length

Carrier Gas: Helium

Temperature: 78°C

Preparative separation of the cyclohexene adducts was accomplished under the same conditions except that the temperature was 135°C.

IV. FUTURE WORK

1. Study the reactions of the organodifluoramines with strong bases, strong nucleophilic reagents, oxidizing and reducing reagents.
2. Hydrogenate trans 2,5-bis(difluoramino)-2,5-dimethyl-3-hexene to the corresponding hexane.
3. Study the chlorination and nitration of primary and secondary difluoramines.
4. Prepare 1,1-bis(difluoramino)cyclohexane and determine its behavior to iodide and other reagents. Study the chemistry of the gem bis-difluoramino group and determine its possible effects on other functions such as β hydrogen.

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