Chemistry of Tetrafluorohydrazine. V. Synthesis of N-Difluoramino-Substituted Hydrazines

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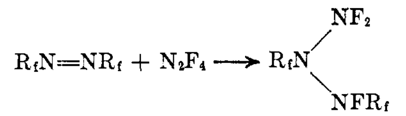
Ultraviolet irradiation of a mixture of N_2F_4 and hexafluoroazomethane gives the N-difluoramino-substituted hydrazine, $CF_3N(NF_2)NFCF_3$. The corresponding NNF_2 compound is obtained from decafluoroazoethane. These adducts are thermally unstable, and their decomposition to starting materials was studied by infrared spectroscopy.

In reported reactions of N_2F_4 involving its dissociation into NF_2 radicals, olefins gave 1,2-bis(difluoramino)ethanes,[1] acetylenes gave vinyldifluoramines and their rearrangement products,[2] and sulfur- and oxygen-containing compounds led to the corresponding species with the difluoramino group attached to the sulfur and oxygen atoms, respectively.[3] We report here the synthesis of N-difluoramino-substituted hydrazines.

The products were obtained by reaction of N_2F_4 with perfluoroazoalkanes in the presence of ultraviolet light (eq 1).[4] Irradiation of an equimolar mixture of hexafluoroazomethane and N_2F_4 at 25° gave



$$R_fN{=}NR_f + N_2F_4 \longrightarrow R_fN(NF_2)NFR_f \qquad (1)$$

Ia, $R_f = CF_3$
b, $R_f = C_2F_5$

Ia in ~50% yield. The product was purified by gas chromatography to give Ia as a colorless gas. Its physical properties are listed in Table I.

TABLE I
PHYSICAL PROPERTIES OF $CF_3N(NF_2)NFCF_3$

Bp, °C	+19° (vapor pressure)
Vapor pressure equation	$\log p_{mm} = -1267/T + 7.19$
Trouton constant	19.9
Heat of vaporization	5797 cal/mol

The F^{19} nmr spectrum of Ia was obtained at −62° (Table II).

The infrared spectrum of Ia was obtained on the vapor in a cell cooled at −46 to −80° (Figure 1b). Principal absorption bands in the N–F region are located at 10.2 and 11.3–11.5 μ with weaker absorptions at 10.8 and 11.8 μ. Figure 1a shows the infrared spectrum obtained after the cell was allowed to warm to 25° (1 hr). The bands at 7.9 and 8.35 μ are characteristic of the C–F stretching bands of hexafluoroazomethane (Figure 2), and the 9.75-μ band is characteristic of SiF_4 arising from decomposition of N_2F_4 in glass. Hence, these infrared data showed the decomposition of Ia to starting material.

TABLE II
F^{19} NMR SPECTRA OF N-DIFLUORAMINO-SUBSTITUTED HYDRAZINES

Compound	F^{19} chemical shift, cps[a-c]
$CF_3N(NF_2)NFCF_3$ (Ia)	−5325 (s, NF_2)
	+840 (s, NF)
	+3650 (d, CF_3)[d]
	+4270 (s, CF_3)
$C_2F_5N(NF_2)NFC_2F_5$ (Ib)	−5390 (m, NF_2)
	+400 (s, NF)
	+4835 (d, m, CF_3)[e]
	+6245 (t, m, CF_2)[f]

[a] All spectra were run neat using an external reference of $CFCl_3$. [b] All the resonances of the fluorine attached to nitrogen are relatively broad peaks, owing to the quadripolar relaxation of the N^{14} nucleus, and fine spin–spin couplings with other fluorines are obscured. [c] Singlets, doublets, triplets, and multiplets are denoted as s, d, t, and m, respectively. [d] The doublet splitting was not well defined. [e] The CF_3 peak was split into a doublet and an additional multiplet; the spectrum was not precisely interpreted; [f] The CF_2 peak was split into a triplet and an additional multiplet. The spectrum was not precisely interpreted.

Mass spectrometric analysis of Ia showed the positive ion fragments expected from a mixture of hexafluoroazomethane (70%) and N_2F_4 (30%), indicating the complete decomposition of Ia in the mass spectrometer.

Similarly, irradiation of a mixture of decafluoroazoethane and N_2F_4 has given the corresponding N-difluoramino-substituted hydrazine (Ib), in 36% yield. This product was also purified by gas chromatography to give Ib as a pale yellow liquid with an estimated boiling point of 77° (vapor pressure data).

The F^{19} nmr spectrum was obtained at −80° (Table II). The relative area ratios of the peaks (2:1:6:4) agree with the assigned structure.

Attempts to obtain the mass spectrum of Ib were not successful, and only cracking patterns attributable to decafluoroazoethane and N_2F_4 were observed.

The infrared spectrum of Ib was determined on the vapor in a cell cooled at −20° (Figure 3). Principal N–F absorption bands were observed at 10.2, 11.0, and 11.7 μ with weaker bands at 10.7 and 11.3 μ. The cell was warmed to 25° and allowed to stand for 30 min. The spectrum (Figure 3) now showed the characteristic C–F stretching bands of decafluoroazoethane (Figure 4) with additional bands attributable to SiF_4 (9.75 μ) and NO_2 (6.2 μ). The spectrum was unchanged after an additional 16 hr at 25°.

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(1) R. C. Petry and J. P. Freeman, Abstracts of the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, p 46s; A. J. Dijkstra, J. A. Kerr, and A. F. Trotman-Dickenson, *J. Chem. Soc., A*, 582 (1966); 105 (1967); H. Cerfontain, *ibid.*, 6602 (1965); T. E. Stevens and W. H. Graham, *J. Amer. Chem. Soc.*, **89**, 182 (1967); F. A. Johnson, C. Haney, and T. E. Stevens, *J. Org. Chem.*, **32**, 466 (1967); G. N. Sausen and A. L. Logothetis, *ibid.*, **33**, 2330 (1968); T. S. Cantrell, *ibid.*, **32**, 911 (1967); T. E. Stevens, *ibid.*, **32**, 670 (1967); S. K. Brauman and M. E. Hill, *J. Amer. Chem. Soc.*, **89**, 2127, 2131 (1967). For leading references to pertinent work, see papers I and II in this series, A. L. Logothetis, *J. Org. Chem.*, **31**, 3686 (1966); A. L. Logothetis and G. N. Sausen, *ibid.*, **31**, 3689 (1966).

(2) G. N. Sausen and A. L. Logothetis, *ibid.*, **32**, 2261 (1967); R. C. Petry, C. O. Parker, F. A. Johnson, T. E. Stevens, and J. P. Freeman, *ibid.*, **32**, 1534 (1967).

(3) For leading references to the synthesis and characterization of these compounds see paper III in this series, G. N. Sausen and A. L. Logothetis, *ibid.*, **32**, 2261 (1967).

(4) R. C. Petry and J. P. Freeman, *J. Amer. Chem. Soc.*, **83**, 3912 (1961), describe the reaction of N_2F_4 with azoisobutane to give *t*-butyldifluoramine.

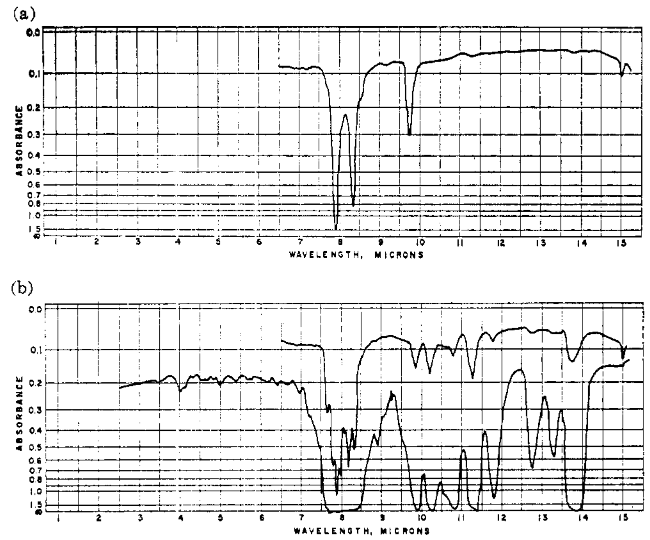

Figure 1.—Infrared spectrum of $CF_3N(NF_2)NFCF_3$: (a) 25°; (b) −46 to −80°.

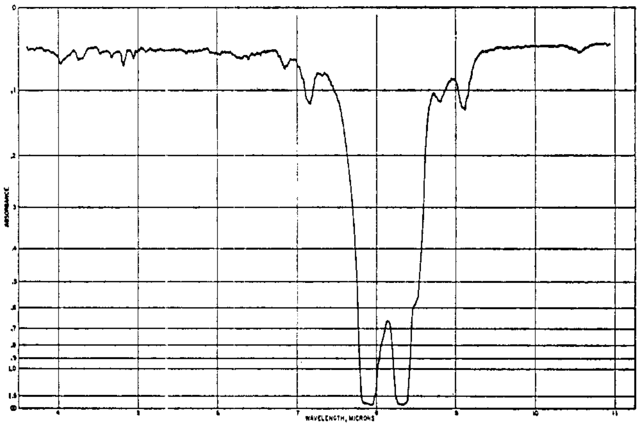

Figure 2.—Infrared spectrum of $CF_3N{=}NCF_3$.

Discussion

The mechanism of this difluoramination reaction undoubtedly involves photolytic decomposition of N_2F_4 *via* an excited difluoramino radical[5] to give a fluorine radical which subsequently adds to the azo bond (eq 2–4). No products corresponding to the direct addition of N_2F_4 to the azo group have been observed.

$$\cdot NF_2 \xrightarrow{h\nu} \cdot NF_2^* \rightarrow \cdot F + [NF] \qquad (2)$$

$$R_fN{=}NR_f + F\cdot \longrightarrow R_fNF\underset{\cdot}{N}R_f \qquad (3)$$

$$R_fNF\underset{\cdot}{N}R_f + N_2F_4 \longrightarrow I + \cdot NF_2 \qquad (4)$$

Thermal cleavage of the reaction products would lead to starting materials as observed in both mass spectrometric and infrared analyses of the products.

$$\begin{tikzcd} R_fN(NF_2)NFR_f \arrow[r] & R_f\underset{\cdot}{N}NFR_f \arrow[d, "-F"] & + \cdot NF_2 \arrow[d] \\ & R_fN{=}NR_f & 0.5N_2F_4 \end{tikzcd} \qquad (5)$$

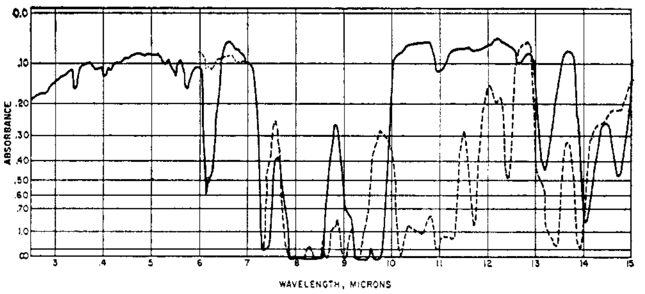

Figure 3.—Infrared spectrum of $C_2F_5N(NF_2)NFC_2F_5$: ----, −20°; ——, 25°.

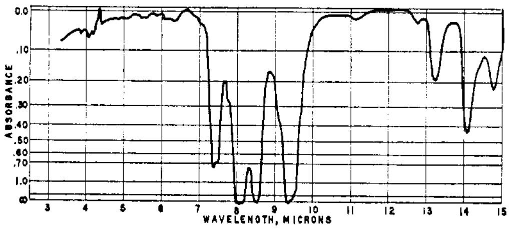

Figure 4.—Infrared spectrum of $C_2F_5N{=}NC_2F_5$.

An approximately 2:1 ratio of azo compound to N_2F_4 would be expected, and this agrees with the mass spectrometric results obtained on Ia.

The bond energy of the F_2N–N bond in I and hence its thermal stability might be expected to be low in light of the low bond dissociation energy of the N–N bond in N_2F_4 (19.8 kcal/mol)[6] and nitrosodifluoramine (10 kcal/mol).[7]

Experimental Section[8]

General Procedure.—*Caution must be exercised in the handling of N_2F_4.*[2] Irradiations were carried out behind a shield. *Remote operation during N_2F_4 reaction is imperative, and adequate shielding is essential* for work-up of the products.

2-Difluoramino-3-fluoro-2,3-diazahexafluorobutane (Ia).—A 150-ml quartz reactor was evacuated, charged with 0.47 g (2.8 mmol) of hexafluoroazomethane[9,10] and 0.30 g (2.9 mmol) of N_2F_4, and irradiated at 25° for 1.25 hr. The product gases were transferred to a cylinder cooled at −196°. Two such runs were combined, and volatile products were removed by applying vacuum at −95° (1–2 mm). The residue, 1.0 g, analyzed by gas chromatography[8] on a 6-ft column at 0°, was found to consist of 67% Ia (gc elution time, 3.0 min; 50% yield),[11] 22% unchanged hexafluoroazomethane, and small amounts of NF_3 and N_2F_4. The volatile fraction consisted mainly of *cis-* and *trans*-N_2F_2, NF_3, and N_2O, with *smaller amounts* of nitrogen, unchanged N_2F_4, $CF_3N{=}NCF_3$, and Ia. The product was further purified

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[5] This mechanism was proposed by C. L. Bumgardner, *Tetrahedron Lett.*, 3683 (1964), to explain the reaction products obtained from irradiation of 2-butene and 2-butyne with N_2F_4. The same mechanism was used to explain the formation of FSO_2NF_2 from SO_2 and N_2F_4 [C. L. Bumgardner and M. Lustig, *Inorg. Chem.*, **2**, 662 (1963), and FSO_3NF_2 from SO_3 (M. Lustig, C. L. Bumgardner, and J. K. Ruff, *ibid.*, **3**, 917 (1964)]. See also, A. L. Logothetis, G. N. Sausen, and R. J. Shozda, *ibid.*, **2**, 173 (1963), for the formation of SF_5NF_2 from the photochemical reaction of SF_4 with N_2F_4, and G. W. Fraser and J. M. Shreeve, *ibid.*, **4**, 1497 (1965), for the preparation of $F_2NC({=}O)F$ by irradiation of CO and N_2F_4.

[6] C. B. Colburn, *Endeavour*, **24**, 138 (1965).

[7] F. A. Johnson and C. B. Colburn, *Inorg. Chem.*, **2**, 24 (1963).

[8] Infrared spectra were measured on a Perkin-Elmer recording spectrophotometer, Model 21 and Infracord Model 135. Fluorine nmr spectra were obtained with a high-resolution spectrometer and associated electromagnet (Varian Associates) operating at 56.4 Mc/sec and approximately 14,000 G. Spectra were calibrated in terms of displacements in cycles per second (cps) from the F^{19} resonance of $CFCl_3$. Negative frequency displacements are for resonances at lower field than the reference. The irradiations were carried out with a low-pressure mercury resonance lamp connected to a 60-ma, 6000-V transformer emitting mostly at 2537 Å. The gas chromatographic analyses were carried out on a 0.25-in. column, packed with 20% ethyl ester of perhalooctanoic acid (Kel-F Acid 8114, 3M Co. trademark) on firebrick. Helium carrier gas flow was 60 ml/min.

[9] W. J. Chambers, C. W. Tullock, and D. D. Coffman, *J. Amer. Chem. Soc.*, **84**, 2337 (1962).

[10] J. A. Young and R. D. Dresdner, *J. Org. Chem.*, **28**, 833 (1963), described the thermal decomposition of perfluoroazoalkanes at 350–500° in the presence of N_2F_4 to give N,N-difluoramines.

[11] G. N. Sausen, U. S. Patent 3,149,165 (1964).

by gas chromatography to give Ia as a colorless gas, which was conveniently stored in glass at −78°.

3-Difluoramino-4-fluoro-3,4-diazadecafluorohexane (Ib).—A 400-ml quartz reactor was charged with 1.63 g (6.1 mmol) of decafluoroazoethane[9] and 0.74 g (7.1 mmol) of N_2F_4, and the tube was irradiated at 25° for 1.0 hr. The reaction tube was cooled at −80°, and the volatile products were removed by applying vacuum (1–2 mm). The residual yellow liquid, analyzed by gas chromatography[8] on a 6-ft column at 25°, was found to consist of 61% unchanged decafluoroazoethane (gc retention time, 1.4 min) and 36% Ib (gc retention time, 5.2 min). The product was purified by gas chromatography on the same column to give Ib as a pale yellow liquid. The product could be stored indefinitely at −78°.

Registry No.—Ia, 1840-66-0; Ib, 3829-29-6; $CF_3N{=}NCF_3$, 372-63-4; $C_2F_5N{=}C_2H_5$, 756-00-3; tetrafluorohydrazine, 10036-47-2.

Acknowledgment.—The author is indebted to members of the Physical and Analytical Division for gas chromatography, infrared, mass spectral, and nmr analyses.

Free-Radical 1:5 Rearrangement of the Trichloromethyl Group[1,2]

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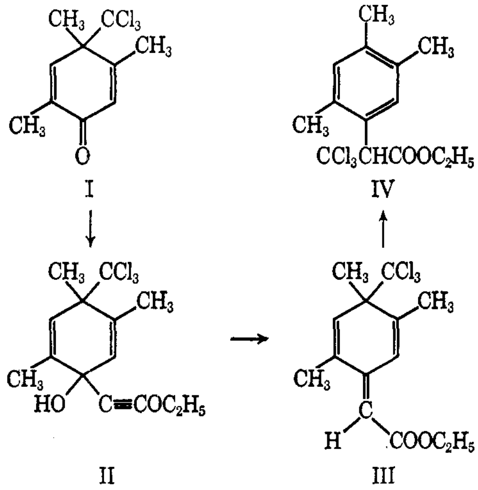
(+)-4-Trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone (I) produces (+)-1-ethoxyethynyl-4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienol (II) on treatment with ethoxyethynylmagnesium bromide followed by water. Treatment of (+)-II with acid yields (−)-ethyl 4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienylideneacetate (III). On pyrolysis or photolysis of active III inactive ethyl α-(2,4,5-trimethylphenyl)-β,β,β-trichloropropionate (IV) is formed. Reaction of active I with ethylmagnesium bromide followed by treatment of the product with dilute acid and then heating affords inactive 2,4,5-trimethyl-β,β,β-trichloroisopropylbenzene (VIII). The free-radical nature of these rearrangements is demonstrated and discussed. Resolution of I was accomplished by reaction with active α-(isopropylidenaminooxy)propionic acid (V).

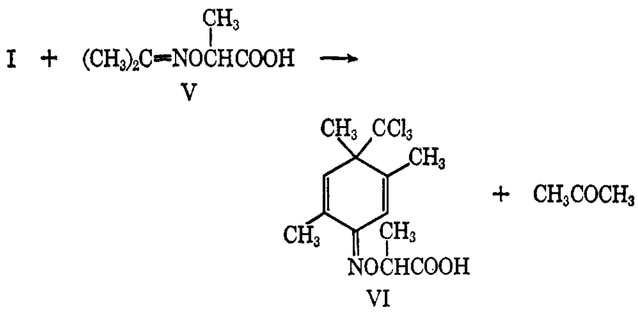
In earlier studies on the behavior of trichloromethyl groups in 4-methyl-4-trichloromethyl-2,5-cyclohexadienones, 1,5 migrations had been observed in several cases.[3] The work herein reported was initiated with the intent to find out more about the mechanism involved in the transformation of 4-trichloromethyl-2,4,5-trimethyl-2,5-cyclohexadienone (I)[4] to ethyl α-(2,4,5-trimethylphenyl)-β,β,β-trichloropropionate (IV) *via* the expected intermediate compounds, II and III (Scheme I).

SCHEME I



Since I and IV each had an asymmetric carbon (but different ones), the use of optically active I was deemed of interest. Accordingly I was resolved by reaction with active α-isopropylidenaminooxypropionic acid (V)[5] to yield a mixture of isomers of VI which was separated by fractional recrystallization. On heating with levulinic acid,[6] the pure isomer of VI was converted into active I. Thus the reagent, V, may prove of value for the resolution of other ketones (Scheme II).

SCHEME II



On treatment of active I with ethoxyethynylmagnesium bromide and work-up of the reaction mixture[3c] racemic IV was obtained. Since it was expected that active IV would be obtained, further study of the rearrangement was undertaken. By careful treatment of a similar reaction mixture with cold water, II was obtained in optically active form when active I was used. Because of experimental difficulties in handling II, no pure isomer was obtained. Hence, it is not known if a single diastereoisomer of II was present or not.[7]

On treatment with acid under mild conditions II could be transformed into III which was also active. However, on warming III to about 85° in cyclohexane

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[1] This work formed part of the Ph.D. thesis (1967) of R. Layton who was the recipient of a National Institutes of Health Predoctoral Fellowship, 1966–1967. Kinetic data are listed in the thesis.

[2] Supported in part by a grant from the National Science Foundation.

[3] (a) K. von Auwers and W. Jülicher, *Chem. Ber.*, **55**, 2167 (1922); (b) M. S. Newman and R. L. Tse, *J. Org. Chem.*, **21**, 638 (1956); (c) M. S. Newman and J. A. Eberwein, *ibid.*, **29**, 2516 (1964).

[4] M. S. Newman, D. Pawellek, and S. Ramachandran, *J. Amer. Chem. Soc.*, **84**, 995 (1962).

[5] M. S. Newman and W. B. Lutz, *ibid.*, **78**, 2469 (1956).

[6] C. H. DePuy and B. W. Ponder, *ibid.*, **81**, 4629 (1959).

[7] M. S. Newman, J. Eberwein, and L. L. Wood, Jr., *ibid.*, **81**, 6454 (1959), showed that only one isomer was formed on treatment of 4-methyl-4-trichloromethyl-2,5-cyclohexadienone with phenylmagnesium bromide.