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THE RADICAL CHAIN ADDITION OF DIFLUORAMINE TO OLEFINS

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SUMMARY

The addition of difluoramine, HNF_2, to olefins takes place by a radical chain mechanism to give mono-difluoramino adducts. Thus, 1-difluoramino-octane, 2-difluoraminonorbornane, difluoraminocyclohexane and difluoraminocyclopentane were prepared by the reaction of difluoramine with 1-octene, norbornene, cyclohexene and cyclopentene, respectively. Free radical catalysts used included tetrafluorohydrazine (N_2F_4), benzoyl peroxide and methylethylketone peroxide.

INTRODUCTION

The successful synthesis of tetrafluorohydrazine, F_2NNF_2, by Colburn and Kennedy, reported in 1958[1], opened the new field of organic chemistry of difluoramino derivatives. Thus, the difluoramino radical, formed by thermal dissociation of F_2NNF_2, was first added to olefins by Petry and Freeman[2].

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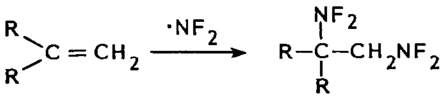
$$F_2N{-}NF_2 \overset{\Delta}{\rightleftharpoons} 2\ {\cdot}NF_2$$



$$R_2C{=}CH_2 \xrightarrow{{\cdot}NF_2} R{-}C(NF_2)(R){-}CH_2NF_2$$

Bumgardner extended the reactivity of the difluoramino radical by photolytic excitation and obtained difluroamino derivatives from even saturated hydrocarbons[3]. The activated difluoramino radical dissociates to fluoronitrene and fluorine which abstracts hydrogen from the hydrocarbon to form an alkyl radical which reacts with a difluoramino radical.

$${\cdot}NF_2 \xrightarrow{h\mu} {\cdot}NF_2^{*} \longrightarrow {\cdot}\ddot{N}F + {\cdot}F$$

$$CH_4 \xrightarrow{{\cdot}F} CH_3{\cdot} \xrightarrow{{\cdot}NF_2} CH_3NF_2$$

The alkylation of difluoramine, HNF_2, by carbonium ions was shown to give the corresponding difluoramino derivative[4]. The addition of HNF_2 to olefins such as isobutylene under acidic conditions gives t-butyldifluoramine, the product expected from Markownikoff addition[5] to the more stable, substituted carbonium ion.

$$R_3C^{\oplus} \xrightarrow{HNF_2} R_3CNF_2 + H^{\oplus}$$

We report here the addition of difluoramine under free-radical conditions to the carbon-carbon double bond.

RESULTS AND DISCUSSION

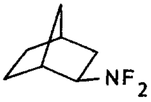
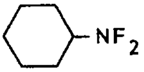
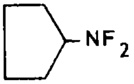
Previous additions of difluoramine to olefins have been postulated to proceed by carbonium ion mechanisms and have resulted in the alkylation of difluoramine by the more substituted or more stable carbonium ion. Here we report the addition of difluoramine to olefins under free radical conditions; the addition to the terminal olefin, 1-octene, to yield 1-difluoraminooctane represents an example of anti-Markownikoff addition of difluoramine to the terminal carbon.

The free radical reagents investigated to initiate the reaction included tetrafluorohydrazine, benzoyl peroxide, methylethylketone peroxide, and azo-bis-isobutyronitrile. Successful addition of HNF_2 was obtained with all of these radical initiators except the azo-bis-isobutyronitrile. The most successful conditions appeared to be with benzoyl peroxide at about 105°C. The reactions were carried out in a dilute solution of the olefin in CCl_4 or CH_2Cl_2 in a Fisher-Porter glass pressure reaction vessel. The HNF_2 and N_2F_4 were condensed from the gas phase into the evacuated reaction vessel at low temperature. When N_2F_4 was used as an initiator, the vicinal bis-difluoramino adduct of the olefin was obtained as a byproduct; however, by using a limited amount of N_2F_4 the yield of the mono-NF_2 product could be made to predominate.

The difluoramino adducts of 1-octene, norbornene, cyclohexene and cyclopentene were obtained. The products were isolated after removal of the excess volatile starting materials such as HNF_2 and N_2F_4, washing with H_2O, taking up in CH_2Cl_2, drying, and removal of the CH_2Cl_2 under vacuum. Characterization of the products was based on the ^{19}F and ^{1}H NMR spectra, infrared spectra, gas chromatography (GC), and C, H, N, and F elemental analyses. The ^{19}F and ^{1}H NMR data are summarized in Table 1.

TABLE 1

Nuclear Magnetic Resonance Data for Difluoramine Adducts

	Chemical Shift [a]		
Structure	^{19}F, ϕ	^{1}H, δ	Coupling Constants, Hz
$CH_3(CH_2)_6CH_2NF_2$	-55.8(t)	3.42 (t,t)	J_{HF} = 30, J_{HH} = 7
	-55.75, -47.75 -69.85, -33.75 (AB,d)	2.43 (t,t)	J_{FAFB} = 562, J_{HF} = 28 J_{HH} = 6
	-41.9(d)	3.25 (t)	J_{HF} = 24
	-51.8(d)		J_{HF} = 32

[a] The negative ^{19}F values, ϕ are observed downfield relative to internal $CFCl_3$; the positive ^{1}H values are δ and observed downfield relative to $Si(CH_3)_4$. The spectral shapes abbreviated as follows: t, triplet; t,t, triplet of triplets; AB, typical AB quartet characteristic of $-NF_2$ adjacent to an asymetric carbon atom; d, doublet.

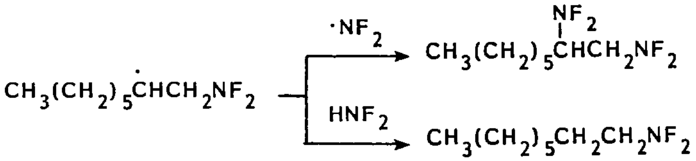
The mechanism of HNF_2 addition to olefins under free radical conditions is postulated to be a typical radical chain process. In fact, the energetics of the reaction closely approximate those of the classical radical chain addition of HBr to olefins[6]. Thus, the reaction consists of an initiation, addition and hydrogen transfer step:

$$\mathrm{R\cdot\ (from\ peroxide) + HNF_2 \longrightarrow RH + \cdot NF_2} \qquad \text{Initiation}$$

$$\mathrm{CH_3(CH_2)_5CH{=}CH_2 + \cdot NF_2 \longrightarrow CH_3(CH_2)_5\dot{C}HCH_2NF_2} \qquad \text{Addition}$$

$$\mathrm{CH_3(CH_2)_5\dot{C}HCH_2NF_2 + HNF_2 \longrightarrow CH_3(CH_2)_5CH_2CH_2NF_2} \qquad \text{Transfer}$$

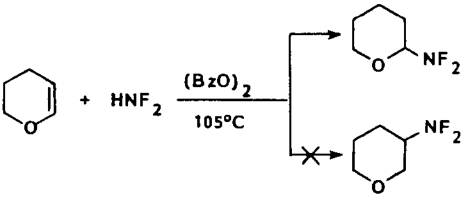
Comparison of the bond energies for the HNF_2 and HBr reactions reveals a close correlation between the energies of the bonds formed in the addition step, C-N (66 kcal/mole) and C-Br (65 kcal/mole), and the bonds broken in the hydrogen transfer step, N-H (92 kcal/mole) and H-Br (87 kcal/mole) The bonds broken, C=C (60 kcal/mole) and the bonds made, C-H (98 kcal/mole), are identical. Using the above bond energies[7] the overall energetics of the two reactions are favorable by -12 kcal/mole for HNF_2 addition and -16 kcal/mole for the HBr addition. The energetics of the two reactions may be even closer since the actual bond dissociation energy of the N-H bond in HNF_2 is probably lower than the 92 kcal/mole value available in standard bond energy tables and thus nearer the 87 kcal/mole value of HBr. When the NF_2 radical from dissociation of N_2F_4 was used as the radical initiator, the reaction consists simply of the addition and hydrogen transfer steps only. The competition then becomes one between the addition-radical reacting with another difluoramino radical or abstracting a hydrogen from HNF_2:



$$\mathrm{CH_3(CH_2)_5\dot{C}HCH_2NF_2} \begin{cases} \xrightarrow{\cdot NF_2} \mathrm{CH_3(CH_2)_5\overset{NF_2}{\overset{|}{C}}HCH_2NF_2} \\ \xrightarrow{HNF_2} \mathrm{CH_3(CH_2)_5CH_2CH_2NF_2} \end{cases}$$

This explains the necessity of keeping the N_2F_4/NHF_2 ratio small if good yields of the HNF_2 olefin adducts are to be realized.

Several limitations of the addition were identified. With dihydropyrane the facile Markownikoff addition[4] took place irreversibly at room temperature and no anti-Markownikoff product was formed:



Furthermore, no radical chain reaction of HNF_2 was obtained with α-methylstyrene; instead the olefin-N_2F_4 adduct was formed. Apparently, the intermediate radical, $\phi\dot{C}(CH_3)CH_2NF_2$, is too stable to abstract a hydrogen from HNF_2. This behavior is reminiscent of the relative difficulty of achieving a radical chain reaction between HCl and propylene as compared to ethylene; in addition isobutylene acted as an inhibitor for the ethylene reaction[8]. In the more substituted olefins the reactivity of the intermediate radical is reduced, increasing the activation energy for the hydrogen transfer step.

The only product reported here for which stereoisomerism is possible is the 2-difluoraminonorbornane. Based on analogy with previous radical reactions of the 2-norbornyl radical[9], the 2-difluoraminonorbornane is assigned the exo configuration.

This reaction is useful as a means of preparing mono-NF_2 compounds not readily prepared by other methods. Furthermore, it illustrates that difluoramine is a relatively facile radical chain transfer agent.

EXPERIMENTAL

General

Caution: Mixtures of difluoramine or tetrafluorohydrazine with organic compounds and oxygen are highly explosive. All reactions with these compounds should only be conducted with adequate shielding and precautions.

NMR (^{19}F) spectra were obtained with a Varian Associates, Model V-3000-B, high resolution spectrometer using a 40 Hz probe; ^1H spectra were obtained on a Varian, Model 60, 60 Hz probe. Infrared spectra were measured on a Perkin Elmer Infracord double-beam instrument using sodium chloride plates. The chemical shift ϕ and δ values of the ^{19}F and ^1H NMR spectra are reported as ppm upfield (negative values are observed downfield) relative to internal $CFCl_3$ and downfield relative to tetramethylsilane, respectively.

Reaction of 1-Octene with Difluoramine in Presence of Tetrafluorohydrazine

A solution of 0.56 g (0.0050 mole) 1-octene in 10 ml of CCl_4 was heated for 3 hours at 100°C with a mixture of N_2F_4 (0.006 mole) and HNF_2 (0.006 mole) in a glass Fisher-Porter pressure vessel. After cooling to room temperature the pressure vessel was opened to a volume of approximately 150 ml; the pressure was 435 mm and the mass spectrum indicated 10% N_2F_4 (0.0004 mole), 10% CCl_4 and 80% HNF_2 (0.003 mole) The volatiles were removed under vacuum, the liquid residue was taken up in CH_2Cl_2, washed with H_2O, dried over $CaCl_2$, filtered, and stripped; yield: 1.19 g of a liquid residue. Both the ratio of the GC peaks and ^{19}F NMR probe areas indicated a ratio of N_2F_4/1-octene adduct to HNF_2/1-octene adduct of approximately 4:1. The N_2F_4/1-octene adduct, $CH_3(CH_2)_5$ $CHNF_2CH_2NF_2$ had the typical $-CH_2NF_2$ ^{19}F triplet pattern centered at ϕ-57.1, J_{HF} = 24 Hz, and a doublet AB pattern typical of an NF_2 group attached to an assymetric carbon with a single proton. The central peaks were centered at ϕ-39 35 (J_{HF} = 20 Hz) and ϕ-36.75 (J_{HF} = 28 Hz) and the wings at ϕ-54 05 and -22.25 ($J_{F_AF_B}$ = 584 Hz). The smaller GC peak was trapped after separation on an SF-96 column at 121°C. The product had a typical $-CH_2NF_2$ triplet at ϕ-55.8 (J_{HF} = 30 Hz); the proton spectrum contained a triplet of triplets centered at δ 3.42 (relative to tetramethylsilane), J_{HF} = 30 Hz, J_{HH} = 7 Hz. The infrared spectrum featured strong NF absorption at 11.5 and 11 9 μ.

Anal. Calcd for $C_8H_{17}NF_2$.C, 58 15, H, 10.37; N, 8.48; F, 23 00. Found: C, 58 6; H, 10.3; N, 8.45; F, 23.4.

Reaction of Norbornene with Difluoramine in Presence of Tetrafluorohydrazine

A solution of 0.47 g (0.005 mole) norbornene in 5 ml CCl_4 was heated at 93°C for 2 hours with 200 ml (0.009 mole) HNF_2 and 50 ml (0.002 mole) N_2F_4. After cooling the contents were expanded into a volume of approximately 150 ml with a pressure of 400 mm. The mass spectrum indicated 66% HNF_2 (0.0023 mole), 26% N_2F_4 (0.001 mole) and 8% CCl_4. The volatiles were removed under vacuum and the liquid residue poured into H_2O and extracted with CH_2Cl_2. After drying over $CaCl_2$ the CH_2Cl_2 was removed on a rotary evaporator to leave a residue of 0.60 g. The ^{19}F NMR spectrum of the residue of the products indicated a mixture of mainly two products with AB quartets. The GC of the products revealed two principal products with the more volatile being present in a ratio of 84:16 This more volatile peak was trapped out and had an ^{19}F doublet AB pattern with the central peaks at ɸ-55.75 and -47.75 and wings at ɸ-69.84 and -33 75 (J_{FAFB} = 562 Hz, J_{HF} = 28 Hz); the ^1H spectrum contained an apparent triplet of triplets centered at δ 3.42 (J_{HF} = 28 Hz, J_{HH} = 6 Hz). The infrared spectrum featured strong NF absorption at 10 75, 11.75, and 12.2 μ.

Anal. Calcd for $C_7H_{11}NF_2$:C, 57.13; H, 7.54; N, 9.52; F, 25 82. Found: C, 56.7; H, 7.55; N, 9.98; F, 25.10.

The ^{19}F spectrum assigned to the bis-difluoramino adduct of norbornene with N_2F_4 was a doublet AB pattern with central peaks at ɸ-58.9 and -54.7 and wings at ɸ-73.3 and -40 3 (J_{FAFB} = 576 Hz, J_{HF} = 24 Hz)

Reaction of Norbornene with Difluoramine in Presence of Benzoyl Peroxide

A solution of 0.94 g (0.01 mole) norbornene in 15 ml CH_2Cl_2 was heated for 2 hours at 108°C with 250 ml (0.011 mole) HNF_2 and 0.36 g (0.0015 mole) benzoyl peroxide. After cooling and expansion approximately 0.00025 mole of HNF_2 remained. The residue after washing was 1.0 g. The GC of the residue only had norbornene and difluoraminonorbornane peaks in the area ratio of 15:85.

Reaction of Cyclohexene with Difluoramine in Presence of Benzoyl Peroxide

A solution of 0.82 g (0.01 mole) cyclohexene in 10 ml CH_2Cl_2 was heated at 106°C for 3 hours with 224 ml (0.01 mole) HNF_2 and 0.24 g (0.001 mole) benzoyl peroxide. Approximately 0.0016 moles of HNF_2 were recovered. The residue was washed with H_2O, taken up in CH_2Cl_2, dried over $CaCl_2$, filtered and stripped to a residue of 0.62 g (some product was identified in the -80°C trap used during the stripping). The GC separation through a 5 foot DOW 11 silicone column at 65°C indicated a single major peak which was trapped out. The ^{19}F spectrum was a doublet centered at ɸ-41.9 (J_{HF} = 24 Hz); the ^1H spectrum had a poorly defined triplet centered at 3.25 (J =

24 Hz). The infrared spectrum featured strong NF absorption peaks at 10 35, 10 9, and 11.8 μ

Anal. Calcd for $C_6H_{11}NF_2$: C, 53.00, H, 8.74; N, 10.31; F, 27.95. Found: C, 52.9; H, 8.59; N, 10.7; F, 29 7.

Reaction of Cyclopentene with Difluoramine in Presence of Benzoyl Peroxide

A solution of 0 68 g (0 01 mole) cyclopentene in 10 ml CH_2Cl_2 was heated 3 hours at 105°C in a glass pressure bottle with 250 ml HNF_2 (0.011 mole) and 0.24 g (0.001 mole) benzoyl peroxide Approximately 0.0008 mole of HNF_2 was recovered as indicated by mass spectral analysis. The liquid residue was washed with H_2O, taken up in CH_2Cl_2, dried over $CaCl_2$, filtered and stripped on a rotary evaporator to yield 0 63 g of residue GC separation at 60°C on a 5 foot DOW 11 silicone column afforded a principal product peak with a ^{19}F doublet at ϕ-51.8 (J_{HF} = 32 Hz) The infrared spectrum featured strong NF absorption at 10 85 and 11.70 μ.

Anal. Calcd for $C_5H_9NF_2$: C, 49.58; H, 7 49; N, 11.57; F, 31.37. Found: C, 49.43; H, 7.64; N, 11.22; F, 31.0.

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