

Tetrafluorohydrazine Reactions with Unsaturated Nitrogen Compounds^{1a}SAMUEL F. REED, JR., AND MAX LUSTIG^{1b}*Rohm and Haas Company, Redstone Research Laboratories, Huntsville, Alabama 35807*

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Addition reactions of tetrafluorohydrazine with a number of types of unsaturated nitrogen compounds have been demonstrated to occur in the expected manner. Unsaturated amides, carbamates, isocyanates, nitriles, and nitro compounds were investigated. Diallylic-substituted nitrogen compounds formed cyclic bis(difluoramines) as well as the tetrakis(difluoramines). Only the nitro compounds failed to react.

During the past few years, several reports^{2,3} have appeared in the literature describing the addition of tetrafluorohydrazine (N_2F_4) to olefins, including a rather comprehensive study by Petry and Freeman.² Since only limited studies have been reported on the N_2F_4 addition to olefinic nitrogen-containing compounds,⁴ we have extended this reaction to include unsaturated amides, carbamates, isocyanates, nitriles, and nitro compounds. The present work describes the addition reactions and characterization of products.

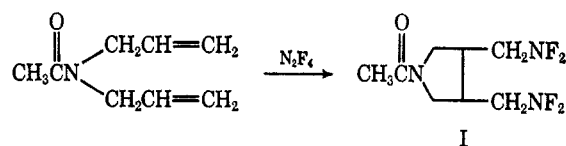
Although several experimental techniques are suitable for conducting the N_2F_4 -olefin reactions, the preparative work was conveniently carried out under pressure in inert solvents such as carbon tetrachloride, chlorobenzene, and Freon 113. Fischer-Porter aerosol pressure tubes were used as reaction apparatus in a remote-controlled environment. Reaction temperatures ranged from 30 to 110° depending upon the reactivity of the olefinic substrate. In many instances, products were isolated by distillation or preparative gas chromatography; however, a number of products were judged to be nonvolatile or too explosive in character for distillation and were analyzed as a crude product or purified by column chromatography over silica gel. Characterization and identification of the products (Table I) were based on infrared and ¹⁹F nmr spectral data and elemental analysis. The ¹⁹F absorption of the difluoramino groups occurred at relatively low fields (ϕ -25 to -50).⁵ Groups attached to primary carbon appeared near ϕ -50 while groups attached to secondary carbon appeared near ϕ -35. Coupling (J_{HF}) of fluorines on nitrogen with α -hydrogen atoms ranged between 27 and 30 cps. Infrared absorption for the difluoramino group was observed in the 800-1000-cm⁻¹ region for all adducts. The common functional groups displayed absorption at characteristic frequencies.

Amides.—Several unsaturated amides, when treated with N_2F_4 in inert solvents, gave the expected addition compounds in moderate yields. They were usually obtained as viscous oils which were not amendable to distillation. In these cases, the products were purified by chromatography over silica gel using carbon tetrachloride or benzene as the eluting solvent. These products displayed characteristic infrared spectra and gave reasonably consistent elemental analysis.

Some difficulty was experienced when N_2F_4 was allowed to react with acrylamide and its N-alkyl or di-

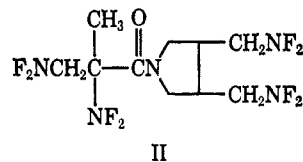
alkyl derivatives due to polymerization of the substrates at reaction temperatures. The only success realized was with N,N-diethylacrylamide which gave a 56% yield of the addition compound along with polymeric materials. Even this yield could not be duplicated consistently. Similar difficulties had previously been observed when acrylic anhydride or acryloyl chloride was treated with N_2F_4 , although N_2F_4 is considered to be a very effective radical trap.²

Both N,N-diallylacetamide and N,N-diallylmethacrylamide failed to yield the corresponding tetrakis- or hexakis(difluoramino) derivatives when treated with excess N_2F_4 , as would be expected by direct addition of N_2F_4 to all sites of unsaturation. N,N-diallyl-



acetamide gave a bis(difluoramino) of structure I arising through a concomitant addition and cyclization reaction. This structure was assigned on the basis of the elemental analysis and ¹⁹F and ¹H nmr spectra. The ¹⁹F nmr spectrum displayed only overlapping triplets centered at ϕ -56.7 (-CH₂NF₂) for the *cis* and *trans* isomers. No absorption due to olefinic protons was observed in the ¹H nmr spectrum.

Similarly, N,N-diallylmethacrylamide gave a tetrakis(difluoramino) derivative (II), arising *via* the addi-



tion-cyclization reaction. Identification was based on both elemental analysis and ¹⁹F and ¹H nmr spectral data as described in the above case. The ¹⁹F resonance absorptions were noted at ϕ -54.3 (triplet -CH₂NF₂) and at -27.5 (singlet C-NF₂) whereas the -CH₂NF₂ group attached to the ring showed two overlapping triplets centered at ϕ -56.5 and -56.8. No vinyl protons were present by ¹H nmr spectral analysis. Compounds containing the 1,6-heptadienyl-type system are known⁶ to undergo cyclization when treated with N_2F_4 or other radical reagents. A small quantity of a second product, apparently the normal tetrakis(difluoramino), was obtained but could not be freed of the cyclic addition compound for adequate analysis.

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TABLE I
CHARACTERIZATION DATA ON N₂F₄-OLEFIN ADDITION COMPOUNDS

Olefin	Registry no.	N ₂ F ₄ adduct	Mp or bp (mm), °C	nd	Calcd, %			Found, %				
					C	H	F	C	H	F		
N-Allylacetamide		<chem>F2NCH2CH(NF2)CH2NHCOCH3</chem>			29.45	4.43	37.43	20.69	29.68	4.70	31.22	20.45
N,N-Diallylacetamide		<chem>F2NCH2CH(NF2)C(CH2)2NCH3</chem>			39.51	5.35	31.27	17.28	39.19	5.52	31.63	18.05
Methacrylamide	19639-82-8	<chem>F2NCH2C(CH3)(NF2)CONH2</chem>	70-71		25.39	3.69	40.21	22.22	25.26	3.49	40.44	22.69
N-Phenylmethacrylamide		<chem>F2NCH2C(CH3)(NF2)CONHC6H5</chem>			45.30	4.16	28.65	15.84	45.47	4.21	28.95	15.55
N-Methylolmethacrylamide		<chem>F2NCH2C(CH3)(NF2)CONHCH2OH</chem>			27.40	4.12	34.68	19.18	28.37	4.46	34.60	19.27
N-Allylmethacrylamide		<chem>F2NCH2C(CH3)(NF2)CONHCH2CH(NF2)CH2NF2</chem>			25.20	3.31	45.65	21.02	25.50	3.44	45.41	21.40
N,N-Diallylmethacrylamide		<chem>F2NCH2C(CH2)2NCH(NF2)CN</chem>			32.15	4.04	40.72	18.76	32.30	4.17	41.09	19.03
N,N-Diethylacrylamide		<chem>F2NCH2CH(NF2)CON(CH2CH3)2</chem>			36.35	5.62	32.87	18.27	36.53	5.76	32.60	18.09
Allyltrifluoroacetamide		<chem>CF3CONHCH2CH(NF2)CH2NF2</chem>			23.34	2.33			23.63	2.32		
Ethyl N-allylcarbamate	19639-83-9	<chem>CH3CH2OCONHCH2CH(NF2)CH2NF2</chem>	95 (1)	1.4119	30.90	4.76	32.50	18.02	30.52	4.65	32.60	17.97
Ethyl N,N-diallylcarbamate		<chem>CH3CH2OCON(CH2)2NCH(NF2)CH2NF2</chem>		1.4414	39.56	5.49	26.37	15.38	39.00	5.57	27.10	15.72
Allyl carbamate	19639-84-0	<chem>F2NCH2CH(NF2)CH2OCONH2</chem>	55-60		23.41	3.41	37.07	20.49	23.19	3.52	36.94	20.72
Vinyl isocyanate	15811-73-1	<chem>F2NCH2C(CH2)(NF2)NCO</chem>	49 (52)	1.4169	20.81	1.73	43.93	24.27	20.70	1.89	43.66	24.47
Allyl isocyanate	19639-86-2	<chem>F2NCH2CH(NF2)CH2NCO</chem>	36-38 (13)	1.4140	25.65	2.67	40.60	22.45	25.51	2.79	40.35	22.69
Allyl isothiocyanate	19639-87-3	<chem>F2NCH2CH(NF2)CH2NCS</chem>	53-54 (0.75)	1.4752	23.65	2.43	37.46	20.67	23.81	2.48	37.28	20.84
Methacrylonitrile	19639-88-4	<chem>F2NCH2C(CH2)(NF2)CN</chem>	44-45 (11)	1.3700	28.07	2.92	44.44	24.55	27.90	2.80	44.29	24.68
3-Butenenitrile	19639-89-5	<chem>F2NCH2CH(NF2)CH2CN</chem>	56-58 (1)	1.3915	28.04	2.92	44.41	24.55	28.31	2.76	44.53	24.43
1,4-Dicyano-2-butene	19639-49-7	<chem>NCCNCH(NF2)CH(NF2)CH2CN</chem>			34.28	2.86	36.18	21.65	34.49	2.69	36.27	21.43
5-Cyano-1,3-pentadiene	19639-50-0	<chem>F2NCH2CH(NF2)CH=CHCH2CN</chem>	88 (1)		36.55	3.56	38.54	21.33	36.61	3.38	38.77	21.61
1-Cyano-2,5-hexadiene		<chem>F2NCH2CH(NF2)CH2CH(NF2)CH(NF2)CH2CN</chem>			26.67	2.88	48.22	22.22	26.85	2.91	47.99	22.62
4,4-Dicyano-1,6-heptadiene		<chem>NC(C#N)C(CH2)2NCH(NF2)CH2NF2</chem>			43.31	4.38	30.26	22.30	43.09	4.35	30.49	22.56

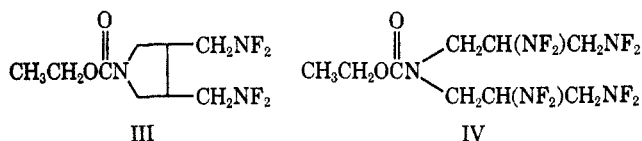
* Major product from the reactions. † Isolated as a mixture.

TABLE II
 EXPERIMENTAL DATA FOR N₂F₄-OLEFIN REACTIONS

Olefin type	Olefin (mmol)	Solvent (ml)	Temp, °C	Time, hr	Yield, %
Amides	N-Allylacetamide (25)	C ₆ H ₅ Cl (50)	90	4.5	75
	N,N-Diallylacetamide (14)	CCl ₄ (50)	{ 30 100	15.0 4.0	91 ^a
	Methacrylamide (100)	Tetrachloroethene (50)	75	5.2	83
	N-Phenylmethacrylamide (43)	C ₆ H ₅ Cl (50)	78	3.5	91
	N-Methylmethacrylamide (55)	CCl ₄ (50)	70	4.5	80
	N-Allylmethacrylamide (20)	CCl ₄ (50)	80	21.0	82 ^b
	N,N-Diallylmethacrylamide (10)	CCl ₄ (50)	80	20.0	80 ^b
	N,N-Diethylacrylamide (50)	C ₆ H ₅ Cl (25)	80	2.5	56
	Allyltrifluoroacetamide (59)	Freon 113	60	6.0	65
	Carbamates	Ethyl N-allylcarbamate (52)	Freon 113	40-100	6.0
Ethyl N,N-diallylcarbamate (59)		Freon 113	60	6.0	
Allyl carbamate (50)		C ₆ H ₅ Cl (25)	100	24.0	93
Isocyanates	Vinyl isocyanate (100)	CCl ₄ (50)	70	4.0	68
	Allyl isocyanate (50)	C ₆ H ₅ Cl (50)	100	5.4	81
	Allyl isothiocyanate (50)	CCl ₄ (50)	80	6.0	84
Nitriles	Methacrylonitrile (50)	CCl ₄ (50)	80	5.0	83
	3-Butenenitrile (100)	CCl ₄ (50)	90	12.0	81
	1,4-Dicyano-2-butene (42)	CCl ₄ (50)	92	2.0	21
	5-Cyano-1,3-pentadiene (25)	CCl ₄ (25)	{ 30 60 90	0.5 0.5 1.0	93 ^a
	1-Cyano-2,5-hexadiene (30)	CCl ₄ (25)	92	23.5	76 ^b
	4,4-Dicyano-1,6-heptadiene (25)	CCl ₄ (25)	90	6.0	97 ^a
Nitro compounds	Nitroethylene (25)	CCl ₄ (25)	70	2.0	No reaction
	2,3-Dinitro-2-butene (25)	CCl ₄ (25)	70-90	2.0	No reaction

^a Bis(difluoramine). ^b Tetrakis(difluoramine).

Carbamates.—The simple olefinic carbamates reacted normally with N₂F₄ to give the expected bis(difluoroamino) derivatives. Addition-cyclization was again observed when ethyl diallylcarbamate reacted with N₂F₄. The cyclic product (III) represented approx-

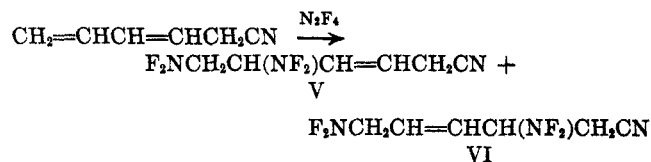


imately 90% of the mixture with the remaining 10% being the tetrakis(difluoramine) (IV) arising through straight addition of N₂F₄ to the sites of unsaturation. The cyclic product (*cis-trans* isomers) (III) was isolated pure by elution chromatography over silica gel. The ¹⁹F nmr spectrum of III showed triplets centered at ϕ -56.1 and -56.2 (-CH₂NF₂), whereas the simple adduct IV showed a triplet centered at ϕ -56.8 (CH₂NF₂) and a multiplet centered at ϕ -38.8 (CHNF₂). Both infrared and ¹H nmr spectra were consistent with the assigned structures.

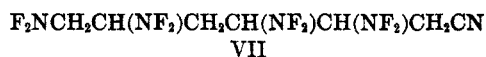
Isocyanates.—Tetrafluorohydrazine reacted with the olefinic isocyanates to give the bis(difluoramines) in good yield. These products were readily distillable to clear liquids. Allyl isocyanate reacted slowly at lower temperatures. Yields of 7, 25, and 81% were obtained from reactions conducted at 80, 90, and 100° over a 5-hr period. The isocyanate and isothiocyanate addition products reacted normally with alcohols yielding carbamates and underwent hydrolysis readily to give the substituted ureas.

Nitriles.—Tetrafluorohydrazine reacted with the simple unsaturated nitriles to give the bis(difluoramines) in high yields except for 1,4-dicyano-2-butene which reacted slowly to give a 21% yield of the adduct. Acrylonitrile gave a product prone to decompose on

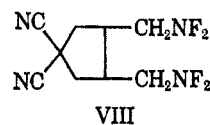
standing and it was found difficult to obtain acceptable analysis of this material. A mixture of bis(difluoramine) was obtained from 5-cyano-1,3-pentadiene which represented the 1,2- and 1,4-addition products (V and VI) due to 1,2 or 1,4 addition across the conju-



gated double-bond system. This mixture was resistant to further reaction under our conditions.² In contrast 1-cyano-2,5-hexadiene gave the expected tetrakis(difluoramine) (VII) and illustrates the greater ease of



N₂F₄ addition to a nonconjugated diene over addition to a conjugated diene. Cyclization was observed when N₂F₄ was treated with 4,4-dicyano-1,6-heptadiene. The major product VIII (*cis-trans* isomers) was char-



acterized by its ¹⁹F nmr spectrum and elemental analysis. Triplets centered at ϕ -56.8 and -56.2 were observed in the spectrum. No evidence of olefinic protons was observed in the ¹H nmr spectrum.

Nitro Compounds.—The two nitro compounds, nitroethylene and 2,3-dinitro-2-butene, did not react with N₂F₄ or were extremely sluggish. Only nitroethylene absorbed N₂F₄; however, the reaction was limited and after 2 hr a pressure increase was noted followed by termination of the reaction. The product

mixture containing NF_2 compounds continued to decompose on standing at room temperature which precluded any attempts toward isolation. Weakly nucleophilic olefins have previously been shown to resist the N_2F_4 addition reaction.²

This study has shown that olefinic nitrogen compounds undergo the addition of N_2F_4 in the expected manner. It has been further demonstrated that compounds containing the 1,6-heptadienyl structure are prone to undergo an addition-cyclization reaction with the ultimate formation of bis(difluoramino) derivatives. It is important to stress the explosive character of these reaction mixtures and products. Mixtures of organic materials and N_2F_4 are potentially explosive and the products are impact-sensitive materials; hence, the experimental work should be performed with requisite precautions.

Experimental Section

Most olefins were purchased from commercial sources and used as received. The tetrafluorohydrazine employed was of 95–99% purity containing CF compounds as impurities. Infrared spectra were obtained with a Perkin-Elmer Infracord spectrophotometer using a sodium chloride prism while nmr spectra were obtained with a Varian Associates Model V-4310 high-resolution spectrometer using a 40-Mc probe (^{19}F). An Aerograph Instrument, Model A-100-C, with a dinonyl phthalate on Chromosorb column was used for all gas chromatography work. The general

experimental technique used in all reactions is described for the reaction of tetrafluorohydrazine with *N,N*-dimethylmethacrylamide. Experimental data for the other reactions are presented in Table II.

Tetrafluorohydrazine-*N,N*-Dimethylmethacrylamide.—As a typical preparative example, a thick-walled glass Aerosol tube with high-pressure fittings containing 25 ml of carbon tetrachloride and 25 mmol of *N,N*-dimethylmethacrylamide was attached to a high-pressure stainless steel manifold and the system de-aerated by alternately evacuating to low pressure and flushing with nitrogen. The system was then charged with N_2F_4 to 65 psi, placed in an oil bath at 85°, and heated for 6 hr. The pressure was maintained between 30 and 65 psi by frequently recharging the system as necessary. On cooling the excess N_2F_4 was vented, the tube was flushed thoroughly with nitrogen, and the contents were transferred to a round-bottomed flask. On evaporation of the solvent, a dark liquid residue remained which was distilled at reduced pressure on an 18-in. Holtzman column to give 4.9 g (90%), bp 53° (0.6 mm), n_D^{20} 1.4262, of *N,N*-dimethyl-2-methyl-2,3-bis(difluoramino)propionamide. Its infrared spectrum showed absorption at 1665 ($-\text{C}=\text{O}-$) and 800–1000 cm^{-1} (NF_2). The ^{19}F nmr spectrum showed signals as a triplet centered at ϕ 54.3 (CH_2NF_2) and a singlet at 26.7 (CNF_2).

Anal. Calcd for $\text{C}_8\text{H}_{11}\text{F}_4\text{N}_2\text{O}$: C, 33.12; H, 5.07; F, 35.00; N, 19.35. Found: C, 33.61; H, 5.03; F, 34.77; N, 19.66.

Registry No.—Tetrafluorohydrazone, 10036-47-2; *N,N*-dimethyl-2-methyl-2,3-bis(difluoramino)propionamide, 19639-91-9.

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The Mechanism of Alcoholysis of Carboxylic Acid Halides in the Presence of Triethylamine

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The alcoholysis of carboxylic acid halides in the presence of triethylamine and a hydrocarbon solvent proceeds by two competing pathways, an elimination-addition process involving a ketene intermediate and a substitution process involving an acyl quaternary ammonium intermediate. Evidence for the ketene intermediate was obtained by performing the reaction in the presence of methanol-*d* and measuring the proportion of monodeuterated ester (in the absence of polydeuterated ester). The products obtained from the isomeric butenoyl chlorides provide further evidence for the competitive processes and suggest the interconversion of the two intermediates. The effects of the leaving group and of the structure of the acyl halide are also presented.

The reaction of acyl chlorides, possessing α hydrogens, with tertiary amines is an old and commonly used method for the synthesis of ketenes,¹ and is often used for *in situ* generation as in cycloadditions² and other reactions typical of ketenes. Having demonstrated the role of sulfene intermediates in the triethylamine-induced alcoholysis of sulfonyl chlorides,³ the mechanism of alcoholysis of acid chlorides in the presence of triethylamine was investigated by like methods and is reported herein. To determine the relative participation of ketene intermediates, the alcoholysis was carried out using methanol-*d* (MeOD). The ester arising from the reaction of ketene with methanol-*d* would be monodeuterated. The absence of dideuterated ester would preclude deuterium incorporation by simple exchange.

Results

A number of carboxylic acid halides and acetic anhydride were treated with ordinary methanol and methanol-*d* in the presence of triethylamine. The procedure involved adding a solution of the acid halide to a stirred solution of methanol and triethylamine in an inert solvent (pentane, hexane, or octane) at 0°. The identity of the esters was verified by comparison of physical properties with literature values and by nmr⁴ analysis. Nmr analysis was also used to show that deuterium incorporation occurred on the carbon α to the carbonyl carbon. The esters were subjected to low voltage mass spectral analysis⁵ (used to eliminate the P – 1 peak) to determine the amount of deuterium incorporation⁶ and

(4) The nmr spectra were obtained using a Varian A-60 or A-60A spectrometer at a sweep width of 500 cps with tetramethylsilane (TMS) as internal standard.

(5) Mass spectra were run at the Purdue Mass Spectral Center on a Hitachi RMU-6a instrument.

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