Diphenyliodosyl Trifluoroacetate with Hydrogen Peroxide.—To a stirred suspension of 2.00 g (4.88 mmol) of diphenyliodosyl trifluoroacetate in 10 ml of water at room temperature was added 2.00 g (17.6 mmol) of 30% hydrogen peroxide and the reaction mixture was stirred for 10 min. From the chilled reaction mixture the product was collected by suction filtration, dried, and washed with ether, yielding 1.15 g (2.92 mmol, 60%) of diphenyliodonium trifluoroacetate, mp 190-192°, after two recrystallizations from acetonitrile. Mixture melting point determination and comparison of ir spectra showed this compound to be identical with that obtained from the metathesis reaction described above.

Registry No.—Diphenyliodonium trifluoroacetate, 16668-99-8; *p*-fluoroiodoxybenzene, 16669-00-4.

Allylic Displacements by N_2F_4

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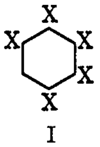
Previous workers, Frazer,[2,3] Petry and Freeman,[4] and others[5] have shown that NF_2 radicals derived from the dissociation of N_2F_4[6] undergo reaction with methyliodide, trifluoromethyl iodide, acetaldehyde, and hydrocarbons by displacement reactions to give CH_3NF_2, CF_3NF_2, $CH_3C(=O)NF_2$, and RNF_2. We have extended this work to the allylic systems by demonstrating the displacement or replacement of allylic proton,[7] bromine,[8,9] and iodine by thermal free-radical reactions to form allyldifluoramines from allyl bromide and iodide, 2,3-dibromo- and 2,3-diodopropene, 1,4-cyclohexadiene, propylene, and piperylene.

These displacements seem to proceed by an SN2 mechanism except possibly in the case of the allyl iodides where products arising from the free allyl radical indicate an SN1 mechanism.

The reactivity of the allyldifluoromines is similar; both N_2F_4 and Br_2 add to the double bond. In the case of N_2F_4 and allyldifluoramine this gives rise to the highly energetic 1,2,3-tris(difluoramino)propane.[9]



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$(X = NF_2)$

In the case of 3-difluoramino-1,4-cyclohexadiene, a second mole of N_2F_4 adds with difficulty to form isomeric pentakisdifluoraminocyclohexanes I.[7]

Historically allyl difluoramine was first found in 1959[9] during attempts to add N_2F_4 to the olefin double bond as reported by workers at Rohm and Haas.[10]

Experimental Section

Allyl Bromide and N_2F_4.[11]—Allyldifluoramine was made from allyl bromide in the vapor phase using a 0.25-in. stainless steel flow reactor[12] under conditions shown in Table I. A high bromide/N_2F_4 ratio gave maximum yields; a low ratio gave considerable quantities of tris-1,2,3-difluoraminopropane[9] owing to addition of N_2F_4 to allyldifluoramine.[13] The presence of free bromine gave rise to 1,2,3-tribromopropane and 2,3-dibromo-1-difluoraminopropane (bp 185), both identified on gc by the use of authentic reference samples.

TABLE I

ALLYLIC DISPLACEMENT CONDITIONS

Feed	Reactor	N_2F_4/ feed ratio	Temp, °C	Pressure, atm	Time	Yield, mol %
Allyl bromide	Flow	1/5	230	1	1 min	52
	Flow	1/1	230	1	1 min	33
Allyl iodide	Static[a]	1	25	1	115 hr	60
2,3-Dibromopropene	Flow	3/1	200	1	0.5 min	...
2,3-Diiodopropene	Static[a]	1/7	25	0.5	110 hr	80

[a] Shielded Pyrex bulb.

Allyldifluoramine boils at 40° and weighs 1.045 g/ml at 23.5° and its vapor density was consistent with the calculated molecular weight. Table II gives gc and nmr analytical data; the infrared spectrum is given in Figure 1.

Allyl Iodide and N_2F_4.—This reaction to give allyldifluoramine was carried out in a Pyrex bulb under conditions given in Table I.

2,3-Dibromopropene and N_2F_4.—2-Bromoallyldifluoramine was made from 2,3-dibromopropene and N_2F_4 under conditions described in Table I.

The product had a boiling point of 130° and a pressure of 24 mm at 21.8°. An impure sample had a molecular weight of 208 *vs.* theoretical 200. Other analyses of samples 91 or 95% pure by gc are given in Table II.

Allene and iodine in CCl_4 was allowed to stand at room temperature in a Pyrex bulb for a day in the presence of an incandescent light. The crude stripped product, 2,3-diodopropene, had the following analysis and was used without further purification.

Anal. Calcd for $C_3H_4I_2$: C, 12.3; H, 1.4; I, 86.4. Found: C, 15.6; H, 2.8; I, 83.6.

2,3-Diiodopropene and N_2F_4.—This reaction was carried out at the ambient conditions shown in Table I. The product, isolated by preparative gc had the properties shown in Table II. In addition to the ^{19}F nmr the proton nmr spectrum showed singlets at +0.44 and 0.80 ppm relative to benzene and a triplet at +2.62 ppm with J_{HF} of 26.3 Hz. These values are consistent with the structure assignment, $CH_2=CI-CH_2NF_2$, where the terminal olefinic protons are nonequivalent.

Propylene and N_2F_4.—This displacement was carried out at 1-min contact time and 300° in the flow reactor. Allyldifluoramine, formed in low yield, was identified in the reaction products by gc and by its conversion into 2,3-dibromodifluoraminopropane (gc spectrum) when the crude products were treated with bromine.

1,4-Pentadiene and N_2F_4.—The reaction with 3 vol. of N_2F_4 in a Pyrex bulb at 150° gave rise to HNF_2[14] in 15% yield based on diene. Distinct peaks at relative retention times

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[11] Purchased from Peninsular Chem Research, Gainesville, Fla.

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[14] Identified by its distinctive infrared spectra. See A. Kennedy and C. B. Colburn, *J. Amer. Chem. Soc.*, **81**, 2906 (1959).

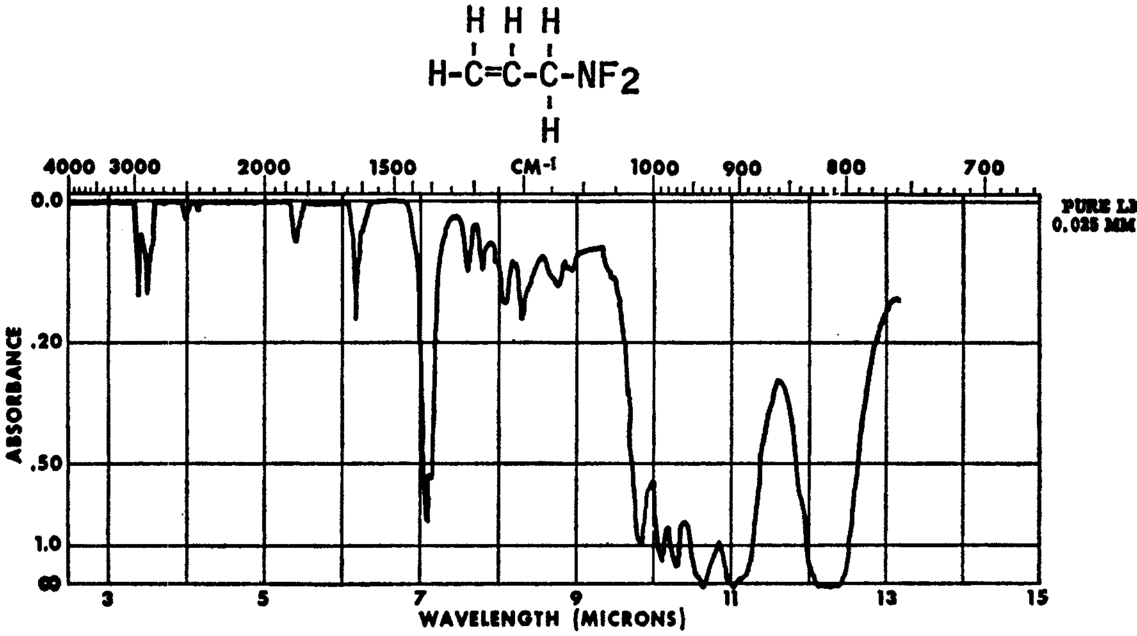

Figure 1.—Infrared spectra of allyldifluoramine.

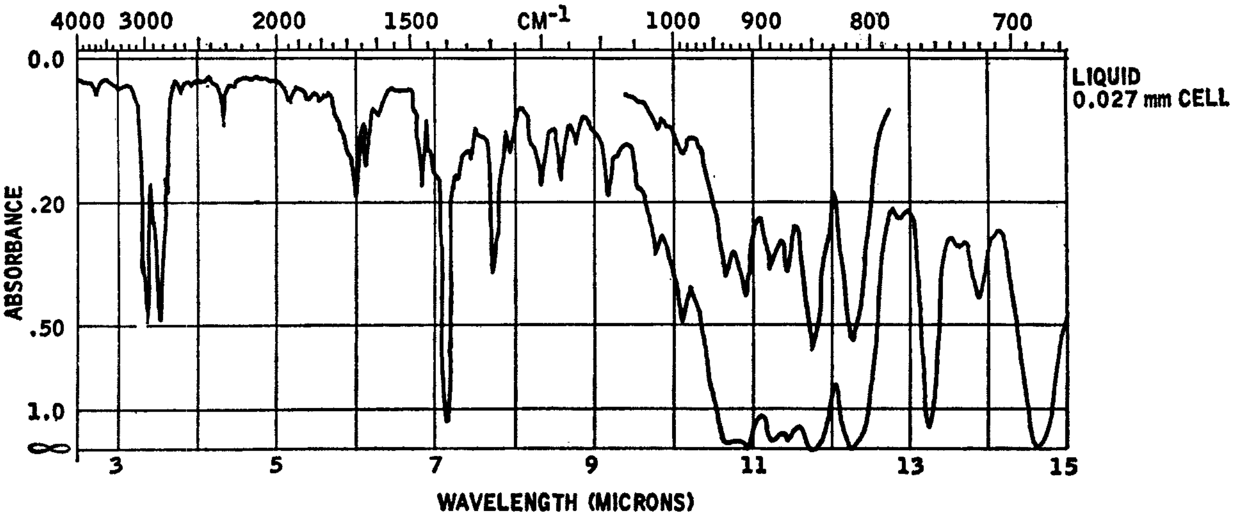

Figure 2.—3-Difluoraminocyclohexadiene-1,4.

TABLE II

PRODUCT CHARACTERIZATION

Product	Relative retention time (benzene)[a]	Elemental analyses, %						^{19}F nmr at 40 MHz	
		C	H	N	F	Br	I	Shift (TFA), ppm	J_{HF}, Hz
Allyldifluoramine	0.23	...	...	...	...	...	...	134.7 (triplet)	29[b]
2-Bromoallyldifluoramine	1.33	...	1.7[c]		19.6	43			
(theory)			(2.3)		(22.1)	(46)			
2-Iodoallyldifluoramine	2.9	17.4	1.99	6.9	17.7		56	134.4 (triplet)	26.3
(theory)		(16.5)	(1.84)	(6.4)	(17.4)		(58)		
3-Difluoramino-1,4-cyclohexadiene	4.5	55.0	5.6	9.5[d]	30.0				
(Theory)		(55.0)	(5.4)	(10.7)	(29.0)				

[a] At 75° on 0.25-in. SS 6-ft tube packed with Dow Corning 200 silicone oil, 30 g/100 g of Chromosorb. [b] Consistent with Bumgardner's observations.[5] [c] H by broad line nmr, F by wet analysis, both on 96% pure (gc) sample. Br value on 91% (gc) pure sample. [d] Low owing to leak in Coleman Analyzer.

0.8 and 1.2 relative to benzene in the gc trace indicated the possibility of the 3- and the 5-difluoraminopentadienes. These products were not investigated further.

1,4-Cyclohexadiene and N_2F_4.—The reaction of N_2F_4 with 1,4-cyclohexadiene at a 7:1 mol ratio was initially observed in a 2-cm Pyrex infrared cell at 440 mm and room temperature. The reaction began immediately on mixing the reagents and proceeded with the appearance of almost exactly 1 mol of HNF_2[14] for each mole of N_2F_4 that disappeared. In 110 hr the HNF_2 formed corresponded almost mole for mole with the cyclohexadiene originally present. Benzene was detected in increasing amounts after the 30th hour.

The principal product from larger scale reactions in Pyrex bulb was isolated in 97.6% purity (2.4% benzene impurity) by preparative gc. In addition to the analyses given in Table II the following properties were measured: mol wt, 124; vapor pressure at 23°, 15.0 mm.

The infrared spectrum of the liquid is given in Figure 2. The ultraviolet spectrum showed no diene conjugation above 2150 Å. The compound was too unstable to allow its convenient study by nmr spectroscopy.

Safety Note.—All the work with N_2F_4 reaction mixtures and products is generally quite hazardous. Extremely brisant explosions are to be expected. Plexiglas shields, shatter proof goggles, heavy leather gloves, lab coats with sleeves, and the the use of small, *i.e.*, 0.5-g, quantities of N_2F_4 are recommended for anyone comtemplating work with these and other N_2F_4 systems.

Registry No.—N_2F_4, 10036-47-2; allyldifluoramine, 16101-17-0; 2-bromoallyldifluoramine, 16101-20-5; 2-iodoallyldifluoramine, 16626-73-6; 3-difluoramino-1,4-cyclohexadiene, 16626-74-7.

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Steric Effects on the Reaction of Propargyl and Allenyl Chlorides with Sodium Methoxide in Methanol[1]

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We have observed that in a series of mixtures of substituted propargyl and allenyl chlorides (III and IV) the position of attack depends on the size of the groups attached to the propargyl position when chloride ion is displaced by sodium methoxide in methanol. A mixture of III and IV with R = methyl or ethyl (60–70% III) yielded only propargyl ethers (VI). A mixture of III and IV with R = isopropyl or *t*-butyl (98% IV) yielded a mixture of propargyl ethers (VI) and allenyl ethers (VII) in the ratios 20:80 and 10:90, respectively. Elimination to form enyne V accompanies the displacement, increasing in importance as the temperature is raised and decreasing in importance as R increases in size (methyl > ethyl > isopropyl). The results are detailed in Table I.

It may be assumed that these product proportions represent the selectivity of attack on intermediate I. The mechanism shown above is believed to be general for tertiary propargyl halides, $RR'CXC\equiv CH$, and the corresponding allenyl halides, $RR'C=C=CHX$, on the basis of earlier work[3] with 3-bromo-3-methyl-1-butyne and 1-bromo-3-methyl-1,2-butadiene. Other workers have noted steric effects on the position of attack on similar molecules.[4,5]

The halide mixtures were obtained by treatment of the propargyl alcohols, II, with hydrochloric acid, calcium chloride, and copper bronze[6] (see Table II). Attempts were made to increase the proportions of IV by rearrangement with a mixture of ammonium chloride, hydrochloric acid, cuprous chloride, and copper powder, but no change was observed. When the cuprous chloride and copper bronze were omitted from the reaction mixture during synthesis, the III:IV ratio increased from 60:40 to 78:22 (R = ethyl) and from 70:30 to 76:24 (R = methyl). The total chloride yield decreased under these conditions to 48% with R = ethyl and 47% with R = methyl. The reaction of II (R = methyl) with thionyl chloride in pyridine[7] gave only 29% of the allenyl chloride and so was not used further.

The reactions of potassium *t*-butoxide and sodium isopropoxide on chloride mixtures with R = methyl were examined with the hope that bulkier nucleophiles would yield allenyl ethers to some extent from these less-hindered chlorides. These reagents gave at least 93% elimination to V even at room temperature. The ether fractions were mixtures containing considerable conjugated material, probably $CH_2=C(t\text{-butyl})CH=CHOR$ which might be formed by rearrangement of the expected allenyl ethers.

Experimental Section

Infrared spectra were obtained on Perkin-Elmer Model 421 and 137 spectrophotometers (usually neat, but occasionally in carbon tetrachloride solution). Bands are designated as strong (s), medium (m), and weak (w). Nuclear magnetic resonance spectra were obtained with a Varian Associates analytical nmr Model A-60, neat or in 10% carbon tetrachloride solutions with tetramethylsilane as the internal standard, and recorded in τ values. The usual designations for singlet (s), doublet (d), triplet (t), multiplet (m), etc., are used and the figure following the letter indicates the number of protons based on the integration. Analytical glpc determinations were carried out on a Perkin-Elmer model 800 instrument with a 10-ft column of 20% 1,2,3-tris(2-cyanoethoxy)propane on 80/100 Chromsorb W at 80–105°. A silicone oil column was somewhat less satisfactory. A Nester-Faust Teflon spinning-band distillation column, Model NFT-60, was used for some of the distillations.

Substituted propargyl alcohols [$(CH_3)_3CCROHC\equiv CH$, II] were prepared from the corresponding ketones and sodium acetylide in liquid ammonia (addition 2 hr, stirring 4 hr more). Reaction mixtures were decomposed with cold aqueous ammonium chloride and extracted with ether. Yields recorded are of once-distilled product which still contained some unreacted ketone; distillation through a spinning-band column removed all but traces of carbonyl impurity. Compounds prepared (R substituent) and their physical and spectral properties are listed below.

R = CH_3: bp 143–144°; $n^{25}{}_D$ 1.4386 (lit.[8,9] bp 142–144°; $n^{20}{}_D$ 1.4440); ir, 3340 (s), 2120 (w), 650 (s) ($C\equiv CH$), 3500 (s), 1320 (s), 1085 (s), cm^{-1} (OH); nmr, τ 8.97 (s, 9), 8.57 (s, 3), 7.54 (s, acetylenic H), 6.93 (s, hydroxyl-H).

R = C_2H_5: bp 88°(60 mm); $n^{25}{}_D$ 1.4428 (lit.[10] bp 94° (90 mm); $n^{20}{}_D$ (1.4456); ir, 3340 (s), 2120 (w), 650 (s) ($C\equiv CH$),

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[2] Dr. Siebe Hoff was supported in part by National Science Foundation Grant GP-5530 and in part by a fellowship from the University of Utrecht, The Netherlands.

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