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.

Acknowledgment.—This research was supported by the Advanced Research Projects Agency, Propellant Chemistry Office, and was monitored by Army Ordnance, under Contract No. DA-30-069-ORD-2487. Thanks are owed to Dr. R. E. Swarbrick for his analytical interpretation of nmr spectra.

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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[1] This research was supported by Grant GP-5530 from the National Science Foundation.

[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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[5] H. D. Hartzler, *J. Amer. Chem. Soc.*, **88**, 3155 (1966).

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[8] I. A. Favorskaya, *Zh. Obshch. Khim.*, **18**, 52 (1948); *Chem. Abstr.*, **42**, 4905 (1948).

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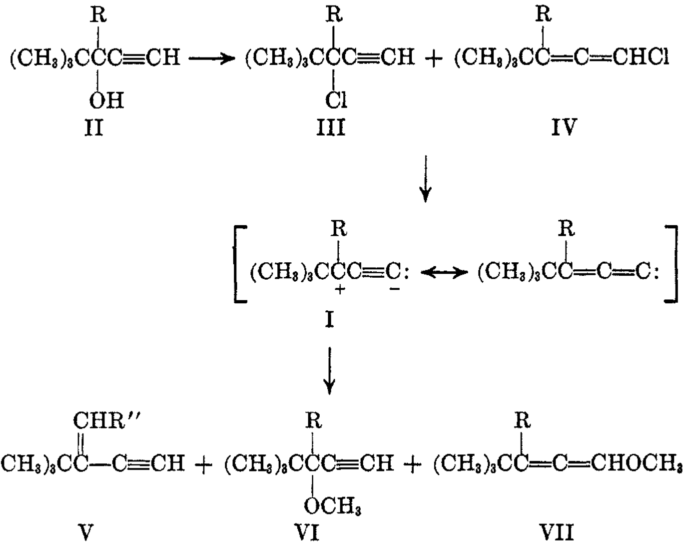


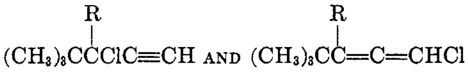
TABLE I

REACTIONS OF MIXTURES OF $(CH_3)_3CCRClC{\equiv}CH$ (III) AND $(CH_3)_3CCR{=}C{=}CHCl$ (IV) WITH 100% EXCESS OF CH_3ONa IN CH_3OH

Starting material		Conditions		Products, %[a]			
R	III:IV	Temp, °C	Time, hr	III and IV	V	VI	VII
CH_3	67:33	Room temperature	288	12[b]	40	48	
		65	15		Mainly		
C_2H_5	60:40[c]	Room temperature	288	28[b]	30	42	
		65	15		Mainly		
$CH(CH_3)_2$	2:98	Room temperature	288	Mainly	Minor	*d*	*d*
		65	15	~5	40	11	44
$C(CH_3)_3$	2:98	Room temperature	288	Mainly		Trace	Trace
		65	15	Trace		10	90

[a] The numbers represent proportions of products and errors may be as high as ±10% of the figures given. A single distillation of the reaction mixture usually gave a distillate that accounted for over 90% of starting materials but with R = $C(CH_3)_3$ the yield was about 80%. [b] This appeared to be entirely allenyl chloride IV. [c] A second experiment with III:IV = 78:22 under the same conditions gave the same product distribution but recovered IV was somewhat less. [d] The VI:VII ratio could not be determined as precisely as in the next experiment, but was approximately 20:80 in agreement with the latter.

TABLE II



$(CH_3)_3CCRClC{\equiv}CH$ AND $(CH_3)_3CCR{=}C{=}CHCl$

III IV

			Ratio of III:IV		Anal, %					
					Calcd			Found		
R	Bp, °C (mm)	Yield, %	Nmr	Glpc	C	H	Cl	C	H	Cl
CH_3	56–57 (29)[a]	68	67:33	70:30	66.43	9.06	24.51	66.57	9.15	24.43
C_2H_5	68–69 (21)	69	60:40		68.12	9.56	22.34	68.40	9.65	22.12
	63 (15)	48[b]	78:22	78:22				68.25	9.66	22.67
$CH(CH_3)_2$	65 (11)	74		2:98	69.54	9.92	20.53	69.76	10.06	19.93
$C(CH_3)_3$	56 (3)[c]	72		2:98	70.75	10.25	18.99	70.82	10.33	18.93

[a] Reported[7] for IV (R = CH_3): bp 62–63° (15 mm) and bp 91–92° (110 mm). [b] Cuprous chloride and copper bronze were omitted in this synthesis. [c] Reported[7] for IV [R = $C(CH_3)_3$]: bp 72–74° (15 mm).

3500 (s), 1320 (s), 1100 cm^{-1} (s) (OH); nmr, τ 8.97 (s), 8.91 (t), 8.45 (q), 7.57 (s, acetylenic H), 7.41 (s, hydroxyl H); the 8.97 and 8.91 peaks total 12 protons, the methylene peak at 8.45 integrates for two.

R = $CH(CH_3)_2$: bp 98° (60 mm); $n^{25}D$ 1.4487 (lit.[9] bp 174.5–176°, 65–68° (16 mm); $n^{20}D$ 1.4421–1.4423); ir, 3350 (s), 2125 (w), 600 (s) (C≡CH), 3550 (s), 1320 (s), 1110 (m), cm^{-1} (OH); nmr, τ 8.88 (s), 8.92 (d), 8.00 (q, 1) 7.60 (s, acetylenic H), 7.57 (s, hydroxyl H); the 8.88 and 8.92 peaks total 15 protons and the 7.60 plus 7.57 peaks total two protons.

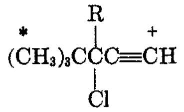
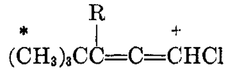
R = $C(CH_3)_3$: bp 75° (14 mm); $n^{25}D$ 1.4560 (lit.[9] bp 74–75° (14 mm); $n^{20}D$ 1.4589; ir, 3350 (s), 2120 (w), 600 (s) (C≡CH), 3600 (s), 1300 (s), 1085 (s) cm^{-1} (OH); nmr, 8.82 (s, 18), 7.71 (s, acetylenic H), 7.57 (s, hydroxyl H).

Substituted propargyl and allenyl chlorides III and IV were prepared on approximately one-fourth mole scale by the method of Hennion and Boisselle[6] except that the reaction mixture was stirred for 1.5–2.5 hr and then extracted twice with ether. The work-up of the ethereal layer was essentially as described[6] except that a column packed with glass beads was used. The propargyl product with R = methyl is a semisolid and attempts at distillation through the spinning-band column were unsuccessful.

No reaction occurred when hydrogen chloride was passed through 0.3 mol of II (R = CH_3) in 250 ml of pentane at −75° for 3 hr and only very slow reaction occurred in ether at −50° or in nitromethane at −30° in similar experiments.

Reactions of Mixtures of III and IV with Sodium Methoxide in Methanol.—The chloride mixtures were dissolved in a 100% excess of 2 *N* sodium methoxide in methanol and the reaction carried out under conditions given in Table I. Reaction mixtures were poured into ice–water and extracted with ether; the ether extracts were washed with a saturated aqueous solution of sodium chloride dried over anhydrous sodium sulfate, concentrated, and

TABLE III
SPECTRAL DATA[a]

Compd	R	Infrared,[b] cm⁻¹	Nmr *	Nmr +	Nmr R
 $(CH_3)_3CC(R)(Cl)C{\equiv}CH$	CH_3	3350 (w) 2130 (w)	8.82 (s)	7.48 (s)	8.21 (s)
	C_2H_5	3330 (s) 2130 (w)	8.83 (s)	7.48 (s)	8.80 (t, CH_3)[c] 8.15 (q, CH_2)
 $(CH_3)_3CC(R){=}C{=}CHCl$	CH_3	1960 (m)	8.90 (s)	4.10 (q), $J = 2.5$ cps	8.17 (s)
	C_2H_5	1960 (m)	8.90 (s)	3.97 (t), $J = 2.5$ cps	8.80 (t, CH_3)[c] 8.15 (q, CH_2)
	$HC(CH_3)_2$	1955 (s)[d]	8.90 (s)	3.97 (s)	8.85 [d, $(CH_3)_2$] 7.70 (q, HC)
	$C(CH_3)_3$	1940 (m)[d]	8.78 (s)	4.10 (s)	8.78 (s)

[a] These spectra were determined on mixtures of III and IV; *J* values were often difficult to determine with any accuracy and are not then reported. Integrations were in agreement with the assignments made. [b] All of these compounds showed a strong band at 740–750 cm⁻¹ attributed to the C–Cl band. [c] Bands for the ethyl groups of III and IV overlap so badly that the same average values are given for both. [d] A very weak band at 3310 cm⁻¹ is attributed to 2% of III present.

distilled under reduced pressure through a 45-cm column packed with glass beads. With R = methyl or ethyl only propargyl ethers, VI, were detected either with experiments carried only part way (where essentially only III had reacted) or to completion. The starting chlorides and the methyl ethers boil so close together that efficient separation was not attained on the scale employed. Only with R = methyl was separation of quite pure propargyl ether VI possible. In all other cases the spectra and analyses were of the mixtures indicated.

R = Methyl.—The higher boiling fraction came over at 51–59° (31 mm) and contained 20% of starting chlorides (glpc and nmr spectra); spectra indicated that this recovered chloride was essentially all allenic. Careful redistillation of this fraction through the spinning-band column gave material of bp 56° (31 mm) with ir absorptions at 3340 (s), 2110 (w), 2840 (m), 1130 (s) cm⁻¹. Glpc indicated the presence of 1% of the allenyl chloride IV (R = CH_3) and this gave weak ir bands at 735 and 1945 cm⁻¹. The nmr spectrum of the ether showed peaks at τ 8.98 (s, 9), 8.70 (s, 3), 7.62 (s, 1) and 6.71 (s, 3); this is in excellent agreement with the assigned structure.

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. For $C_9H_{16}O$ containing 1% $C_8H_{13}Cl$: C, 76.94; H, 11.39. Found: C, 76.94; H, 11.32.

R = Ethyl.—The higher boiling fraction, bp 67–70° (27 mm), contained 36% starting chloride, mainly allenic, on the basis of glpc and nmr spectra. Infrared absorptions were at 3335 (s), 2110 (w), 1110 (s), and 2840 cm⁻¹ (m) for the ether; bands for chloride impurity as recorded for IV (R = C_2H_5). The nmr peaks for the *t*-butyl hydrogens and for the methyl hydrogens of the ethyl group overlapped in the τ 9.0 region. The acetylenic hydrogen, 7.51 (s), the methylenic hydrogens, 7.37 (q) and the methoxyl hydrogens, 6.70 (s) were in proper proportions.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.85; H, 11.76. For $C_{10}H_{18}O$ containing 35% $C_9H_{15}Cl$: C, 74.46; H, 10.98. Found: C, 74.54; H, 10.93.

R = Isopropyl.—The higher boiling fraction from the run at reflux temperature, bp 68–69° (13 mm), was free from starting chloride within the error of spectral and analytical determinations. Nmr spectroscopy indicated that it was a mixture containing 80% of the allenyl ether and 20% of the propargyl ether. Infrared absorptions of the mixtures were at 1935 (s), 3340 (m), 2850 (m), 1140 (s) cm⁻¹. In the nmr spectrum the region around τ 9.00 has a complicated band pattern because *t*-butyl and isopropyl methyls for the two compounds give bands which do not coincide; other bands for VII (R = isopropyl) are at τ 7.90 (q), 6.96 (s), and 3.52 (s) with area ratios close to 1:3:1 and for VI (R = isopropyl) are at 7.69 (s) and 6.72 (s) with a ratio of 1:3. The tertiary hydrogen on the isopropyl group was obscured.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.40; H, 11.81.

R = *t*-Butyl.—The higher fraction from the run at reflux temperature, bp 66–68.5° (7 mm), had the following ir bands: 1940 (s), 3340 (w), 1080 (s), 735 (w) cm⁻¹. The 7.35-cm⁻¹ band indicated the presence of a little unreacted chloride. Nmr peaks for VII (R = *t*-butyl) were at 9.00 (s), 6.90 (s), 3.65 (s); for VI (R = *t*-butyl) they were at 9.00 (s), 6.72 (s), 7.69 (s). The nmr spectrum suggests that the fraction was a 90:10 mixture of VII and VI. An analysis was not obtained.

The instability of the allenyl ethers to glpc separation should be mentioned.

Registry No.—Sodium methoxide, 124-41-4; methanol, 67-56-1; III (R = CH_3), 16487-11-9; III (R = C_2H_5), 16487-12-0; IV (R = CH_3), 16487-13-1; IV (R = C_2H_5), 16487-14-2; IV [R = $CH(CH_3)_2$], 16487-15-3; IV [R = $C(CH_3)_3$], 16487-16-4; VI (R = CH_3), 16487-17-5; VI (R = C_2H_5), 16487-18-6; VI [R = $CH(CH_3)_2$], 16487-19-7; VI [R = $C(CH_3)_3$], 16487-20-0; VII [R = $CH(CH_3)_2$], 16487-21-1; VII [R = $C(CH_3)_3$], 16487-22-2.

The Addition of 2,4-Dinitrobenzenesulfenyl Chloride to Allenes[1,2]

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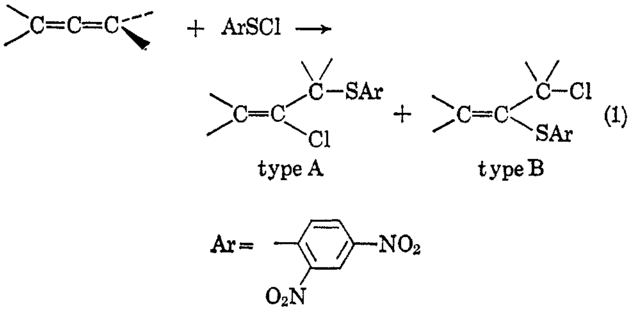
In the reaction of unsymmetrical allenes with 2,4-dinitrobenzenesulfenyl chloride (DBSC), two orientations of adducts are possible at each double bond. These are of two types, as shown in eq 1. We recently



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[1] This work was presented in part before the Intrascience Conference on the Chemistry of Sulfenyl Compounds, Santa Monica, Calif., Nov 1967.

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