(6) The addition of carbethoxynitrene to allene and 1,1-dimethylallene gives low yields of allenimines: E. M. Bingham and J. C. Gilbert, *J. Org. Chem.*, **40**, 224 (1975).
(7) The reaction of cyanoallene with phenyl azide leads to a triazole, possibly via an intermediate methylenetriazoline: W. Ried and H. Mengler, *Justus Liebigs Ann. Chem.*, **678**, 95 (1964).
(8) J. K. Crandall, W. W. Conover, and J. B. Komin, *J. Org. Chem.*, **40**, 2043 (1975).
(9) For a review on triazoles, see *Adv. Heterocycl. Chem.*, **16**, 33 (1974).
(10) W. Regel and W. von Philipsborn, *Helv. Chim. Acta*, **51**, 871 (1968).
(11) For a review on tin hydride reactions see H. G. Kuivila, *Synthesis*, **2**, 449 (1970).
(12) For a recent review on the Claisen rearrangement see *Org. React.*, **22**, 7 (1975).
(13) R. Huisgen, L. Mobius, and J. Szeimies, *Chem. Ber.*, **98**, 1138 (1965).
(14) G. Pourcelot, *C. R. Acad. Sci.*, **260**, 2847 (1965).
(15) T. Kaal and Kh. Sossi, *Uch. Zap. Tartu. Gos. Univ.*, **95**, 179 (1960); *Chem. Abstr.*, **56**, 5868 (1962).

Solvolysis of Haloallenes. The Question of Nucleophilic Solvent Assistance

Melvyn D. Schiavelli,* Ted C. Germroth, and Joseph W. Stubbs

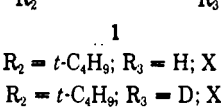
Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185

Received October 29, 1975

The solvolysis rates of 14 di- and trisubstituted bromoallenes are reported. Solvent effects in ethanol and trifluoroethanol, methyl/hydrogen ratios, and the effect of solvent nucleophilicity on relative rates and α- and β- secondary isotope effects are discussed. Increases in the magnitude of $(k_H/k_D)_\alpha$ and $(k_H/k_D)_\beta$ with decreasing solvent nucleophilicity are analogous to the behavior of highly hindered secondary brosylates. These data are interpreted in terms of a rate-limiting elimination step from an ion-pair intermediate. The relative rate of isomeric propargyl and allenyl systems is also discussed.

In earlier work we have reported that di- and trisubstituted chloro- and bromoallenes exhibit solvolytic behavior typical of an unimolecular bond heterolysis as the slow step.[1] These compounds exhibit m values between 0.80 and 1.06, k_{Br}/k_{Cl} leaving group ratios of 20–58, $\Delta S^{\ddagger}$ of −10 to +9.0 eu, ρ values for aryl-substituted chloroallenes of −2.0, CH_3/H rate ratios in 60E of $10^{4.5}$, and apparently "normal" α and β secondary isotope effects.

Since disubstituted haloallenes exhibit solvolytic reactivity in aqueous ethanol on the order of reactivity of secondary carbinyl systems, we were led to assess the possible involvement of nucleophilic solvent assistance in our system. To this end we have prepared the following substituted haloallenes, **1a–n**, and measured the rates of solvolysis in a variety of solvents. The results of this investigation are compiled in Table I. Tables II and III present the isotope effects based on the data in Table I and the isotopic purity of the deuterated samples. Deuterated and undeuterated compounds were solvolyzed in paired conductance cells. The bridge and digital clock were interfaced with a computer allowing no less than 100 points to be taken per cell. Rate constants were calculated using a nonlinear least-squares program. Each reaction exhibits excellent first-order behavior through better than 4 half-lives.



1

a, $R_1 = R_2 = t\text{-}C_4H_9$; $R_3 = H$; X = Br
b, $R_1 = R_2 = t\text{-}C_4H_9$; $R_3 = D$; X = Br
c, $R_1 = t\text{-}C_4H_9$; $R_2 = CH_3$; $R_3 = H$; X = Br
d, $R_1 = t\text{-}C_4H_9$; $R_2 = CH_3$; $R_3 = D$; X = Br
e, $R_1 = t\text{-}C_4H_9$; $R_2 = CD_3$; $R_3 = H$; X = Br
f, $R_1 = R_2 = CH_3$; $R_2 = H$; X = Br
g, $R_1 = R_2 = CH_3$; $R_3 = D$; X = Br
h, $R_1 = R_2 = CD_3$; $R_3 = H$; X = Br
i, $R_1 = R_3 = t\text{-}C_4H_9$; $R_2 = CH_3$; X = Cl
j, $R_1 = R_3 = t\text{-}C_4H_9$; $R_2 = CD_3$; X = Cl
k, $R_1 = R_3 = t\text{-}C_4H_9$; $R_2 = CH_3$; X = Br
l, $R_1 = R_3 = t\text{-}C_4H_9$; $R_2 = CD_3$; X = Br
m, $R_1 = R_2 = t\text{-}C_4H_9$; $R_3 = CH_3$; X = Br
n, $R_1 = t\text{-}C_4H_9$; $R_2 = R_3 = CH_3$; X = Br

Results and Discussion

The question of nucleophilic solvent assistance has been approached through a study of the effect of solvent nucleophilicity on (a) α and β secondary isotope effects, (b) the CH_3/H ratio, (c) the relative rate of model compounds, and (d) the presence or absence of a rate–product correlation in the presence of azide ion.[2] In this paper we will focus only on the effect of changing solvent nucleophilicity on the reactivity of the haloallenes reported here. The effect of added salts on this reaction will be reported later.

Effect of Solvent Nucleophilicity on Rate. It has been suggested that in those systems where nucleophilic solvent assistance is important (such as secondary carbinyl derivatives) such assistance is manifested in markedly changing rate ratios between solvent assisted substrates and those incapable of assistance usually owing to steric inhibition.[3] An elegant example of this behavior was reported by Schleyer et al. These workers reported 2-propyl tosylate/2-adamantyl tosylate rate ratios which varied from $10^{-1.6}$ in TFA to 10^3 in 100E and interpreted this behavior as consistent with substantial solvent assistance in 2-propyl tosylate not present (or marginally present) in the weakly nucleophilic solvents. The 2-adamantyl tosylate shows no solvent assistance due to steric interactions and is therefore a good model of a nonassisted secondary carbinyl system. On the other hand, *tert*-alkyl halides exhibit a constant rate ratio over a variety of solvents. For example, the *t*-BuCl/1-adamantyl Br rate ratio remains constant throughout 19 solvents of widely varying polarity and nucleophilicity.[4]

Table I
Conductometric Rate Constants for Solvolysis of 1

Compd[a]	Temp, °C	Solvent[b]	10^4 k, sec^{-1} [c,d]
1a	74.37 ± 0.03	50E	0.276 ± 0.002
		70T	2.26 ± 0.02
1b		50E	0.219 ± 0.005
		70T	1.90 ± 0.01
1c	64.14 ± 0.02	97T	0.679 ± 0.006
	64.14 ± 0.02	60E	0.287 ± 0.008
	60.20 ± 0.01	70T	2.44 ± 0.001
	64.22 ± 0.02	50E	0.897 ± 0.009
1d	60.20 ± 0.01	70T	2.03 ± 0.007
	64.22 ± 0.02	50E	0.758 ± 0.007
1e	64.14 ± 0.02	97T	0.529 ± 0.003
	64.14 ± 0.02	60E	0.251 ± 0.006
	60.20 ± 0.01	70T	2.07 ± 0.03
	64.22 ± 0.02	50E	0.773 ± 0.005
1f	64.17 ± 0.02	97T	0.672 ± 0.009
	64.15 ± 0.02	60E	1.06 ± 0.02
	54.24 ± 0.01	70T	1.93 ± 0.01
	54.24 ± 0.01	50E	1.08 ± 0.01
1g	64.17 ± 0.02	97T	0.536 ± 0.020
	54.24 ± 0.01	70T	1.60 ± 0.02
	54.24 ± 0.01	50E	0.916 ± 0.009
1h	64.17 ± 0.02	97T	0.524 ± 0.007
	64.15 ± 0.02	60E	0.838 ± 0.009
	54.24 ± 0.01	70T	1.52 ± 0.007
	54.24 ± 0.01	50E	0.842 ± 0.002
1i	44.05	70E	0.440 ± 0.01
		60E	1.24 ± 0.01
		50E	3.94 ± 0.02
1j	15.3	97T	6.05 ± 0.03
	44.05	60E	1.105 ± 0.005
1m	24.63	80E	0.263 ± 0.003
		70E	0.970 ± 0.03
		60E	3.57 ± 0.10
	44.05	80E	3.16 ± 0.04
1n	24.62	80E	5.88 ± 0.08

[a] 2–5 × 10^{-4} M. [b] 50E represents 50:50 (v/v) ethanol–water; 70T represents 70:30 (w/w) trifluoroethanol–water; etc. [c] Average of triplicate determinations paired with appropriate deuterated compound. Occasionally quintuplicate determinations were performed. [d] Errors listed are standard deviations calculated in the usual manner for 95% confidence limits.

Table II
α Isotope Effects for Solvolysis of 1

	Temp, °C	Solvent	k_H/k_D[a,b]	$\Delta\Delta F^{\ddagger}/D$[a]
1a/1b	74.37	50E	1.28 ± 0.03	168
		70T	1.20 ± 0.01	126
1c/1d	64.22	50E	1.20 ± 0.01	121
	60.20	70T	1.218 ± 0.009	130
1f/1g	64.17	97T	1.28 ± 0.05	169
	54.24	70T	1.23 ± 0.02	136
	54.24	50E	1.20 ± 0.01	118

[a] Corrected to 100% deuteration at the temperature listed. [b] Errors listed are standard deviations for quotients calculated in the usual manner for 95% confidence limits. It should be noted that measured k_H/k_D values for each paired run were usually reproducible to better than 0.7% error, e.g., k_H/k_D = 1.20 ± 0.008.

Table III
β Isotope Effects for Solvolysis of 1

	Temp, °C	Solvent	$k_H k_{CD_3}$[a]	$\Delta\Delta F^{\ddagger}/CD_3$[d]
1c/1e	64.14	97T	1.33 ± 0.02[b]	192
	64.14	60E	1.17 ± 0.04[b]	103
	60.20	70T	1.21 ± 0.02[b]	125
	64.22	50E	1.18 ± 0.01[b]	114
1f/1h	64.17	97T	1.33 ± 0.02[c]	96
	64.15	60E	1.31 ± 0.04[c]	92
	54.24	70T	1.33 ± 0.01[c]	92
	54.24	50E	1.33 ± 0.04[c]	93
1i/1j	15.3	97T	1.121 ± 0.009[b]	72
	44.1	60E	1.13 ± 0.01[b]	80
1k/1l	24.62	60E	1.21 ± 0.03[b]	111
	45.30	80E	1.23 ± 0.02[b]	132

[a] See footnote b, Table II, for an explanation of errors. [b] Corrected to 100% deuteration, i.e., to three deuteriums/molecule. [c] Corrected to 100% deuteration, i.e., to six deuteriums/molecule. [d] Value listed is per *one* trideuteromethyl group at the temperature of the measurement.

The major exceptions to this behavior are the rates of 1-Adam Br solvolysis in aqueous TFE solutions, where consistently high rates (relative to Y values) are observed. These are apparently due to the greater electrostatic solvation or H bonding of the TFE to the leaving group. In the case of di- and trisubstituted haloallenes, protonation of the allene moiety precludes any solvolysis study in acidic solvents such as TFA. Nonetheless, within this constraint several trends are noticeable from a study of the solvent dependence of the rate. Table IV shows the steric dependence of the 97T/60E rate ratio (rate ratio at constant Y value) for several tri- and disubstituted haloallenes.[5]

Table V lists the relative rates for a variety of allenyl halides to allow comparison with saturated systems of comparable reactivity.

It should be noted that a marked change in this rate ratio between two compounds means also that the relative rate of solvolysis of these compounds changes with solvent. The compounds studied show substantial changes in 97T/60E rate ratios depending upon the steric size of the groups attached to the allene moiety, the 97T/60E rate ratio increasing with steric bulk, particularly at C-3. Within the series of trisubstituted chloroallenes studied the relative rates show a much steeper dependence on steric size of attached groups in 60E than in 97T. For example, the highly hindered compound tri-*tert*-butylchloroallene solvolyzes 1.7 times as slowly as 1,3-di-*tert*-butyl-3-methylchloroallene in 97T but nearly seven times as slowly in 60E. Disubstituted bromoallenes show an identical but somewhat muted behavior with the less hindered 3,3-dimethylbromoallene (**1f**), solvolyzing at the same rate as 3-methyl-3-*tert*-butylbromoallene (**1c**) in 97T but nearly four times faster in 60E. Such behavior may be interpreted as arising from increased nucleophilic solvent assistance in aqueous ethanol for less hindered substrates such as **1f**. The involvement of such assistance is clearly less important in the less nucleophilic TFE solutions. It is unlikely that such solvent assistance occurs by an in-plane route at C-1 owing to the lack of precedent for in-plane nucleophilic substitution in vinylic systems.[15] Thus, if a k_S process is involved, it probably occurs at the 3 position ("allylic position"). The question of direct displacement at C-1 is under investigation. Nucleophilic addition–elimination schemes are ruled out by the lack of dependence on pyridine concentration up to a fivefold excess and the observation of normal m values, e.g., **1f** and **1c** exhibit m = 0.88 and 0.90, respectively, in aqueous ethanol. In view of the "normal" behavior of these compounds with regard to classical SN1 criteria such as m values, $\Delta S^{\ddagger}$, CH_3/H ratios, k_{Br}/k_{Cl} ratios, and particularly the magnitude and solvent independence of the α and β secondary isotope effects (vide infra), it appears unlikely that the enhanced sensitivity of the rate of solvolysis to steric bulk in ethanol over TFE is due primarily to solvent assistance. Rappoport et al. have shown recently that vinylic substrates show unusual solvent effects in aqueous TFE, manifested as a nonlinear dependence of either log k vs. X_{H_2O} or log k vs. $Y_{t\text{-BuCl}}$.[16] These workers attribute the ob-

Table IV
$(TFE/E)_Y$ Ratios for $R_1R_2C{=}C{=}C(X)R_3$

Registry no.	R_1	R_2	R_3	X	Solvent	Rate ratio
37892-65-2	*t*-Bu	*t*-Bu	*t*-Bu	Cl	97T/60E	900
2115-12-0	*t*-Bu	Ph	*t*-Bu	Cl	97T/60E	280
	t-Bu	Me	*t*-Bu	Cl	97T/60E	12
	t-Bu	*t*-Bu	H	Br	70T/50E	8.2[a]
	t-Bu	Me	H	Br	97T/60E	2.4[b]
					70T/50E	3.7[b]
	Me	Me	H	Br	97T/60E	0.63[c]
					70T/50E	1.8[c]

[a] At 75°. [b] At 64°. [c] At 54°.

Table V
Relative Rates of Solvolysis of Saturated and Unsaturated Halides in 80% Ethanol at 25°

Compd	Rel rate	Ref
$(Ph)_2CHCl$	192	6
$(t\text{-Bu})(CH_3)C{=}C{=}C(CH_3)Br$	65	7
$(CH_3)_2CClC{\equiv}CCH_3$	60	8
$CH_3CH_2C{\equiv}CC(CH_3)_2Cl$	54	9
$(CH_3)_3CBr$	40	6
$(CH_3)_2CHC{\equiv}CC(CH_3)_2Cl$	38	9
$PhCH(CH_3)Br$	22	10
$(t\text{-Bu})(CH_3)C{=}C{=}C(t\text{-Bu})Br$	4.1	7
$CH_3CH_2C(CH_3)_2Cl$	1.8	11
$PhCH(CH_3)Cl$	1.2	10
$(CH_3)_3CCl$	1.0	5
$HC{\equiv}CC(CH_3)_2Br$	0.5	12
$HC{\equiv}CC(CH_3)_2Cl$	0.025	9
$(CH_3)_2C{=}C{=}C(H)Br$	0.011	7
$(CH_3)_2CHBr$	0.008	3
$(CH_3)_2CHCl$	2×10^{-4}	13
2-Adamantyl Br	1.2×10^{-5}	3
$CH_2{=}C{=}HBr$	4×10^{-7}	14

servation of high, low, or negative m values in TFE either to a balance between decreasing solvent electrophilicity and increasing dielectric constant with increasing X_{H_2O} or to an increase in the fraction of ion pairs leading to product forming dissociated ions with increasing H_2O content. In the present case **1c** and **1f** show a very steep dependence on $Y_{t\text{-BuCl}}$ in TFE. Even when compared against log $k_{\text{Adam-Br}}$[4] or log $k_{\text{AnC(X)=CMe}_2}$[16] in aqueous TFE the resulting two-point solvent dependence is also steep. This suggests that unusual solvent effects in TFE may be operative in our system as well. In addition, a common ion rate depression has been observed in at least one chloroallene solvolysis, thus implicating ion pairs on these solvolysis. In the present case, a complete study of the effect of added salts, in particular the presence or absence of a rate–product correlation in the presence of added Nu^-, should provide substantial information in this area. Such a study is currently underway.

Finally, *tert*-butyl chloride exhibits rates of solvolysis in aqueous trifluoroethanol which are slower than expected when compared to the rate of 1-adamantyl bromide solvolysis. It has been suggested that this results from a shift to rate-limiting elimination in TFE.[2,4,5,16] The isotope effects reported here support such an explanation in this case as well.

Secondary Isotope Effects. Shiner et al. have suggested that the degree of solvent dependence of α and β secondary isotope effects is an excellent mechanistic probe for the involvement of k_S processes in solvolysis reactions.[2] Both *tert*-butyl chloride and α-phenylethyl chloride exhibit α and β isotope effects independent of the solvent nucleophilicity.[2] Shiner has reported also that the hindered secondary system 2-adamantyl tresylate exhibits α secondary isotope effects invariant (k_H/k_D = 1.225 ± 0.001) with solvent nucleophilicity.[17]

The isotope effects reported here are consistent with a limiting mechanism of solvolysis for disubstituted bromoallenes. The magnitudes of the α isotope effects (Table II) are the largest ever reported for halide leaving groups. They do not, however, approach the maximum value, k_H/k_D = 1.32, for an $sp^2 \rightarrow sp$ change estimated by the method of Shiner and Hartshorn.[18]

It must be noted that the use of the α secondary isotope effect in this system to assess the amount of k_S behavior is severely restricted since nucleophilic assistance at the 3 position results in increased s character in the C–H bond at the reaction center, thus increasing $(k_H/k_D)_\alpha$ while nucleophilic assistance at the 1 position, i.e., the reaction center, would lead to a lowered $(k_H/k_D)_\alpha$. While nucleophilic attack by solvent at C-1 may be unlikely on the neutral substrate, it is certainly possible in the tight ion pair where developing charge has been delocalized to both C-1 and C-3. β effects would then seem to be the probe of choice. The magnitude of the α effects observed rules out any carbene mechanism where proton loss is slow or where proton loss is a fast equilibrium step.[19]

The β effects (Table III) are remarkably constant from 50E to 97T, being somewhat smaller per CD_3 in the less hindered case, **1f/1h**, than in the hindered system **1c/1e**. Comparable behavior is observed in the solvolysis of several tertiary alkyl chlorides owing to a rather large fraction of olefin formation in the Me branch.[11] The increase in the β effect for **1c/1e** in 97T is analogous to the increase in β effect for *tert*-butyl chloride in 97T.[2,5,20] This has been explained as the result of increased involvement of rate-limiting elimination from an ion pair in this solvent and is manifested by an increased olefin fraction in 97T in this case as well. Reliable product studies are not yet available for our system. The β isotope effects observed in our system also preclude any mechanism involving removal of the terminal proton, since the base-assisted solvolysis of **1f** exhibits k_H/k_{d_6} = 1.15 in 80E.[19] Schleyer has suggested that variations in secondary isotope effects with solvent nucleophilicity may be too small to detect in certain cases, thus necessitating the very accurate measurement of rates, i.e., to a precision better than ±1%. The errors in the isotope effects reported here are calculated from the usual equation for the standard deviation of a quotient. In fact the measured k_H/k_D in each case of paired runs showed deviations usually one order of magnitude better than that reported.[22] It appears therefore that in spite of the low reactivity of 3,3-dimethylbromoallene, $k_{1f}/k_{i\text{-PrBr}}$ = 1.4 in 80E at 25°, a limiting mechanism of solvolysis is operative and supported by at least four commonly accepted mechanistic criteria. Work is now in progress to determine whether the limiting mechanism holds throughout the series $R_2C{=}C{=}C(R)Br$, $R_2C{=}C{=}CHBr$, $R(H)C{=}C{=}CHBr$, $CH_2{=}C{=}CHBr$.

Allenyl vs. Propargyl Halide Solvolysis. An interesting comparison is now possible between the reactivity of **1f** and 3-methyl-3-bromo-1-butyne. The propargyl isomer solvolyzes about 45 times faster than the allenyl isomer. Stang et al.[14] reported that propargyl bromide solvolyzed 4000 times as rapidly as allenyl bromide in 50E. They concluded that the difference in reactivity was due to the difference in ground-state energy as well as to differences in transition-state geometry. The smaller $k_{\text{propargyl}}/k_{\text{allenyl}}$ ratio observed here implies that the ground-state energy difference may be smaller than might be expected, since **1f** and 3-methyl-3-bromo-1-butyne both might be expected to rely heavily on the tertiary center for carbonium stabilization and thus have energetically similar transition states.

Experimental Section

Infrared spectra were obtained using a Perkin-Elmer Model 337 infrared spectrophotometer. Preparative gas–liquid chromatography was performed on a Hewlett-Packard chromatograph, Model 5750. The NMR spectra were run on an Hitachi Perkin-Elmer R-20B nuclear magnetic resonance spectrometer, 60 MHz. Elemental analyses were performed by Atlantic Microlabs, Inc., Atlanta, Ga. Mass spectral analyses were performed by Professor Donald Hunt, University of Virginia.

Materials. 2,2,2-Trifluoroethanol (Halocarbon) was purified according to Shiner et al.[5] or Rappoport.[16] Ethanol was dried according to Wiberg.[23] 2,2,4,4-Tetramethyl-3-pentanone (Chemical Samples) was used without further purification. 3-Methyl-3-butyn-2-ol (Eastman) and 3,4,4-trimethyl-1-pentyn-3-ol (Farchan) were distilled prior to use.

3,3-Dimethyl-2-butanone-*1-d*$_3$ was prepared by three exchanges in 0.25 *M* NaOD–D_2O followed by pentane extraction and distillation. It was used without further purification, NMR (CCl_4) 1.1 ppm (s).

4,4-Dimethyl-3-*tert*-butyl-1-pentyn-3-ol was prepared using the procedure of Beumel and Harris[24] by adding 250 mmol of di-*tert*-butyl ketone dropwise to 25 g (250 mmol) of lithium acetylide–ethylenediamine in 250 ml of dry tetrahydrofuran in a flamed-out apparatus under dry N_2 at 35°C (maintained during addition by cooling). This mixture was allowed to react overnight with stirring and was then hydrolyzed with 100 ml of water. The contents were brought to a gentle boil for 1 hr, extracted with hexane, dried, and distilled: bp 85–90° (13 Torr); ir (neat) 3270 (C≡CH), 3500 (OH), 2090 cm^{-1} (w, C≡C).

1-Bromo-4,4-dimethyl-3-*tert*-butylpenta-1,2-diene (1a) was prepared using the procedure of Landor et al.[25] with the following proportions: 10.5 g (67 mmol) of 4,4-dimethyl-3-*tert*-butyl-1-pentyn-3-ol, 11.4 g of cuprous bromide, 6.1 g of ammonium bromide, 0.7 g of copper powder, 24 ml of 48% w/w HBr. The progress of the reaction was followed by watching the disappearance of the OH peak in the ir at 3500 cm^{-1}, which disappeared entirely after 5 days. The allene was then isolated and distilled: bp 89° (3.4 Torr) [lit. bp 80–81° (6 torr)];[25] ir (neat) 1920 cm^{-1} (C=C=C); NMR (CCl_4) 1.20 (s, 18), 5.80 ppm (s, 1). Anal. Calcd for $C_{11}H_{19}Br$: C, 57.14; H, 8.23; Br, 34.56. Found: C, 57.33; H, 8.34; Br, 34.29.

4,4-Dimethyl-3-*tert*-butyl-1-pentyn-3-ol-*1-d* was prepared by allowing 4.5 g of the undeuterated title compound to stir overnight in a 0.25 *M* NaOD–D_2O solution. This procedure was repeated three times and the recovered title alcohol was then distilled, yielding 2.4 g of the alcohol: bp 90–95° (12 Torr); ir (neat) 2555 cm^{-1} (C≡CD); NMR (CCl_4) 1.16 ppm (s).

1-Bromo-4,4-dimethyl-3-*tert*-butylpenta-1,2-diene-*1-d* (1b) was prepared identically with the undeuterated allene described above: bp 87° (3.4 Torr); ir (neat) 1900 cm^{-1} (C=C=C); NMR (CCl_4) 1.22 ppm (s). Mass spectral analysis yielded 0.95 D/molecule.

1-Bromo-3,4,4-trimethylpenta-1,2-diene (1c) was prepared by the procedure of Landor and Patel,[25] using 250 mol of 3,4,4-trimethyl-1-pentyn-3-ol: bp 55–58° (3.0 Torr) [lit. bp 57–61° (10 Torr)];[2] ir (neat) 1939 cm^{-1} (C=C=C); NMR (CCl_4) 5.68 (1, m), 1.85 ppm (9, s).

3,4,4-Trimethyl-1-pentyn-3-ol-*1-d* was prepared by allowing 13.4 g (116 mmol) of the undeuterated title compound to stir overnight in 0.25 *M* NaOD–D_2O solution prepared by adding 10 mmol (0.23 g) of sodium to 40 ml of D_2O. The alcohol was removed by syringe and the procedure repeated twice. The alcohol was then distilled: bp 72–73° (19 Torr); ir (neat) 3340 (OH), 2560 (C–D), 1980 cm^{-1} (C≡C); NMR (CCl_4) 1.03 (s, 9), 1.39 ppm (s, 3).

1-Bromo-3,4,4-trimethylpenta-1,2-diene-*1-d* (1d) was prepared by the following procedure of Landor et al.,[25] using the proportions 5.66 g of 3,4,4-trimethyl-1-pentyn-3-ol-*1-d*, 7.63 g of cuprous bromide, 3.8 g of ammonium bromide, 0.5 g of copper powder: bp 79–83° (6 Torr); ir (neat) 1933 (C=C=C), 2695 cm^{-1} (C–D); NMR (CCl_4) 5.72 (m, 1), 1.12 (s, 9), 1.83 ppm (d, 3). Mass spectral analysis gave 0.934 D/molecule.

3-Methyl-d_3-4,4-dimethyl-1-pentyn-3-ol was prepared by the method of Olah and Pittman:[26] bp 68–70° (20 Torr); ir (neat) 3400 (OH), 3260 cm^{-1} (≡CH), 3270 (C–D), 2090 cm^{-1} (C≡C); NMR (CCl_4) 1.03 (s, 9), 1.00 ppm (s, 1).

1-Bromo-3-methyl-d_3-4,4-dimethylpentadiene (1e) was prepared as described for **1c**: bp 56–57° (6 Torr); ir (neat) 3010 (=CH), 1925 cm^{-1} (C=C=C); NMR (CCl_4) 1.1 (s, 9), 5.73 ppm (s, 1). Mass spectral analysis gave 2.62 D/molecule.

1-Bromo-3-methylbuta-1,2-diene (1f) was prepared by the procedure of Landor and Patel:[25] bp 62–64° (38 Torr), [lit. bp 53–54° (60 Torr)];[2] ir (neat) 1958 cm^{-1} (s) (C=C=C); NMR (CCl_4) 1.80 (s, 9), 5.68 ppm (m, 1).

3-Methyl-1-butyn-3-ol-*1-d* was prepared by allowing 16.8 g (200 mmol) of the undeuterated title compound to stir overnight in a 0.25 *M* NaOD–D_2O solution. The solution was then extracted with 3 × 50 ml of ether, the ether evaporated, and the procedure repeated twice. Distillation yielded 5.5 g of alcohol: bp 100–102°; ir (neat) 1960 (C≡C), 2560 (C≡CD), 2470 cm^{-1} (OD); NMR (CCl_4) 1.5 ppm (s).

1-Bromo-3-methylbuta-1,2-diene-*1-d* (1g) was prepared using the procedure of Landor et al.,[25] using the proportions 5.5 g (66 mmol) of 3-methyl-1-butyn-3-ol-*1-d*, 3.3 g of cuprous bromide, 2.6 g of ammonium bromide, 0.13 g of copper powder, and 16 ml of 48% w/w HBr: bp 40–45° (47 Torr); ir (neat) 1920 (C=C=C), 2255 cm^{-1} (C=C=C–D); NMR (CCl_4) 1.84 ppm (s). Mass spectral analysis gave 0.894 D/molecule.

3-Methyl-d_3-butyn-3-ol-*4-d*$_3$ was prepared according to the method of Beumel and Harris.[24] Acetone-d_6 (Aldrich) (10 g, 16.2 mmol) was allowed to react with 17.2 g (17.2 mmol) of lithium acetylide ethylenediamine (Ventron) in THF. Work-up and distillation afforded a 62% yield of the title compound: bp 100–101°; ir (neat) 3250 (OH), 2200 (C–D), and 2090 cm^{-1} (C≡C); NMR (CCl_4) 2.27 (s) and 3.29 ppm (s).

1-Bromo-3-methyl-d_3-butadiene-*4-d*$_3$ (1h) was prepared as for **1f**. Preparative GC (10 ft × 0.5 in., SE-30 on Chromosorb W, 95°) afforded the title compound: ir (neat) 1940 cm^{-1} (C=C=C); NMR (CCl_4) 6.15 ppm (s). Analysis of CH_3 by NMR yielded 0.84 H/2CD_3. Mass spectral analysis gave 5.16 D/molecule.

2,2,3,6,6-Pentamethyl-4-heptyn-3-ol was prepared by the method of Olah and Pittman.[26] The product (24.8 g) was obtained in 90% yield: bp 73–76° (3 mm); ir (neat) 3470 (OH), 2240 cm^{-1} (C≡C); NMR (CCl_4) 0.99 (s, 9), 1.21 (s, 9), 1.33 (s, 3), 2.01 ppm (s, 1).

3-Chloro-2,2,5,6,6-pentamethyl-3,4-heptadiene (1i) was prepared by the method of Jacobs and Fenton.[27] 2,2,3,6,6-Pentamethyl-4-heptyn-3-ol (9.2 g, 50 mmol) was added to cold anhydrous ether. Thionyl chloride (3.6 ml, 5.9 g, 50 mmol) and 8.0 ml (7.9 g, 100 mmol) of pyridine in ether were quickly added with stirring, which was continued for 1 hr at 0°. The precipitate was filtered out of the reaction mixture and the organic layer washed three times with 100 ml of 5% sodium bicarbonate and twice with 50 ml of water. The organic layer was dried as above and vacuum distilled to give four fractions, 45–62°, 62–68°, 68–75°, 75–81° (4 mm). These fractions were found to contain varying proportions of the chloroallene and the ene-yne elimination product on the basis of ir and NMR spectra. Further separation was carried out using preparative gas chromotography: ir (neat) 1950 cm^{-1} (C=C=C); NMR (CCl_4) 1.07 (s, 9), 1.08 (s, 9), 1.11 (s, 9), 1.23 (s, 9), 1.74 (s, 3), 5.03 ppm (s, 2).

2,2,6,6-Tetramethyl-3-methyl-d_3-4-heptyn-3-ol was prepared by the method of Olah and Pittman.[26] Butyllithium in hexane (20%, 43 ml, 90 mmol) was chilled in an ice bath and 11.4 ml (7.7 g, 93 mmol) of *tert*-butylacetylene in 20 ml of hexane added dropwise. The solution was diluted with anhydrous diethyl ether, followed by slow addition of 9.1 g (90 mmol) of 3,3-dimethyl-*1-d*$_3$-2-butanone in anhydrous ether. The reaction mixture was gently refluxed for 2 hr and then cooled to 0° before addition of an excess of water to hydrolyze the lithium salt. After separation of the aqueous and organic layers, the latter was washed with two 50-ml portions of saturated sodium chloride solution, filtered through anhydrous magnesium sulfate, and stored over this drying agent overnight. Filtration followed by evaporation of solvent and vacuum distillation yielded 13.2 g (79%) of product: bp 73.5–75.5° (3 mm); ir (neat) 3470 (OH), 2250 (C≡C), 2080–2140 cm^{-1} (C–D), no residual ketone band; NMR (CCl_4) 0.98 (s, 9), 1.19 (s, 9), 1.83 ppm (s, 1).

3-Chloro-2,2,6,6-tetramethyl-5-methyl-d_3-3,4-heptadiene (1j) was prepared as described for the undeuterated compound, **1i**. Preparative GLC (10 ft × 0.5 in., SE-30 on Chromosorb W, 125°) afforded the title compound, ir (neat) 1960 cm^{-1} (C=C=C). Mass spectral analysis yielded 2.53 D/molecule.

3-Bromo-2,2,5,6,6-pentamethyl-3,4-heptadiene (1k) was prepared by adding 6.1 g (33 mmol) of 2,2,5,6,6-pentamethyl-3-heptyn-5-ol to a mixture of 5.7 g (40 mmol) of cuprous bromide, 2.8 g of ammonium bromide, 0.4 g of copper powder, and 12 ml of 48% w/w HBr warmed to 40°. The progress of the reaction was followed by watching the appearance of the 1940-cm^{-1} peak in the ir due to the allenyl stretch. After 3.5 hr the mixture was cooled and filtered and the residue washed with ether and extracted. The ether layer

was washed with 48% HBr until the lower layer showed no violet coloration. The ether layer was then filtered through $MgSO_4$–$NaHCO_3$ mixture and distilled: bp 78–79° (3.2 Torr); ir 1939 cm^{-1} (C=C=C); NMR (CCl_4) 1.07 (s, 9), 1.12 ppm (s, 9).

3-Bromo-2,2,6,6-tetramethyl-5-methyl-d_3-3,4-heptadiene (**1l**) was synthesized by the procedure of Marvel et al.[28] 2,2,6,6-Tetramethyl-3-methyl-d_3-4-heptyn-3-ol (5.7 g, 30 mmol) was dissolved in petroleum ether and 1.0 ml (2.85 g, 10 mmol) of phosphorus tribromide added. The reacting mixture was allowed to stir overnight, after which two layers were separated. The organic one was washed twice with 50 ml of saturated sodium bicarbonate and once with 100 ml of water. The organic solution was filtered through and dried over anhydrous magnesium sulfate. After filtering, the solvent was stripped by rotary evaporation. Vacuum distillation afforded 3.4 g (46%) of product: bp 80–84.5° (3 mm); ir (neat) 1947 (C=C=C), 2065–2140 cm^{-1} (C–D), no alcohol band; NMR (CCl_4) 1.09 (s, 9), 1.14 (s, 9), 1.74 ppm (m, 0.5). Anal. Calcd for $C_{12}H_{18}D_3Br$: C, 58.07; H and D, 8.56 (based on production of water); Br, 32.20. Found: C, 58.69; H, 8.64; Br, 32.16. Mass spectroscopic deuterium analysis yielded 2.50 D/molecule.

5,5-Dimethyl-4-*tert*-butyl-2-hexyn-4-ol was prepared by slowly bubbling propyne gas through 66 mmol (30 ml of 2.2 *M*) *n*-butyllithium in 120 ml of hexane with stirring under N_2 at room temperature. After 20 min 8.5 g (66 mmol) of di-*tert*-butyl ketone in 50 ml of diethyl ether was added dropwise and the mixture was refluxed for 30 min. After cooling, water was added dropwise to hydrolyze the mixture and the ether layer was washed with water and filtered through $MgSO_4$. The ether was then evaporated and the residue was distilled: bp 83–88° (3.1 Torr); ir (neat) 3470 (OH) and 2220 cm^{-1} (C≡C); NMR (CCl_4) 1.14 (s, 18), 1.83 ppm (s, 3).

2-Bromo-5,5-dimethyl-4-*tert*-butyl-2,3-hexadiene (**1m**) was prepared by adding 0.96 ml (2.73 g, 10.1 mmol) of PBr_3 to 5.5 g (30.2 mmol) of 5,5-dimethyl-4-*tert*-butyl-2-hexyn-4-ol in 75 ml of petroleum ether and allowing it to stir overnight in an ice bath. The mixture was then hydrolyzed with 40 ml of water. The ether layer was washed twice with 40 ml of saturated $NaHCO_3$ solution and then 30 ml of water and filtered through $MgSO_4$. The ether was evaporated and the residue distilled: bp 87–89° (2.9 Torr); ir (neat) 1940 cm^{-1} (C=C=C); NMR 1.24 (s, 18), 2.21 ppm (s, 3). Anal. Calcd for $C_{12}H_{21}Br$: C, 58.78; H, 8.63; Br, 32.59. Found: C, 59.48; H, 8.74; Br, 31.93.

4,5,5-Trimethyl-2-hexyn-4-ol was prepared by the method described for 5,5-dimethyl-4-*tert*-butyl-2-hexyn-4-ol using 66 mmol (30 ml of 2.2 *M*) of *n*-butyllithium and 6 g (60 mmol) of *tert*-butyl methyl ketone. The isolated alcohol was then distilled: bp 93° (18 Torr); ir (neat) 2220 (C≡C), 3420 cm^{-1} (OH); NMR (CCl_4) 0.97 (s, 9), 1.3 (s, 3), 1.8 ppm (s, 4).

2-Bromo-4,5,5-trimethylhexa-2,3-diene (**1n**) was prepared using the procedure of Landor et al.[25] using the following proportions: 3.4 g (24.3 mmol) of 5,5-dimethyl-2-hexyn-4-ol, 4.1 g of cuprous bromide, 2.0 g of ammonium bromide, 0.3 g of copper powder, and 8.7 ml of 48% w/w HBr. The reaction was kept at 30° for 1.5 hr. Distillation afforded the title compound, bp 78° (6 Torr). It was then purified by preparative GLC (SE-30 on Chromosorb W, 10 ft × 0.5 in., 155°), ir (neat) 1943 cm^{-1} (C=C=C). This compound decomposed rapidly (1 day) on standing at 0°.

Kinetic Studies. Kinetic solvents were prepared by weight from conductivity water and purified organic soolvents. Conductivity measurements were performed in paired cells using a Wayne Kerr autobalance universal bridge, B642, and a Chronolog Model 32001 digital clock interfaced with a Wang 600 advanced programable calculator. Solvent was allowed to equilibrate for 20 min in the conductance cells before initiating a kinetic run. From 0.5 to 1.3 μl of desired haloallene (preweighed syringe) was then introduced into the cell with stirring. Each kinetic sample was purified by preparative GLC on SE-30 (10 ft × 0.5 in.) prior to use. One hundred or more points were taken for each cell over 4–5 half-lives. Rate constants were obtained using an exponential least-squares program written in our laboratories for the Wang 600. In all other respects, rate constants were determined as described earlier.[1] Temperature control and measurement were accomplished using a PRT regulated proportional temperature controller and a Hewlett-Packard quartz thermometer.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for the partial support of this research. The senior author wishes to thank the Research Corporation for assistance in purchasing the equipment necessary for this study and Professor Donald Hunt for analysis of the deuterated samples.

Registry No.—**1a**, 10575-75-4; **1b**, 57444-15-2; **1c**, 10575-72-1; **1d**, 57444-16-3; **1e**, 57444-17-4; **1f**, 6214-32-0; **1g**, 57444-18-5; **1h**, 57444-19-6; **1i**, 51211-93-9; **1j**, 57444-20-9; **1k**, 51038-84-7; **1l**, 57444-21-0; **1m**, 57444-22-1; **1n**, 57444-23-2; 2,2,2-trifluoroethanol, 75-89-8; ethanol, 64-17-5; 4,4-dimethyl-3-*tert*-butyl-1-pentyn-3-ol, 33420-19-8; 4,4-dimethyl-3-*tert*-butyl-1-pentyn-3-ol-*1-d*, 57444-24-3; 3,4,4-trimethyl-1-pentyn-3-ol-*1-d*, 57444-25-4; 3,4,4-trimethyl-1-pentyn-3-ol, 993-53-3; 3-methyl-d_3-4,4-dimethyl-1-pentyn-3-ol, 57444-26-5; 3-methyl-1-butyn-3-ol-*1-d*, 10313-04-9; 3-methyl-1-butyn-3-ol, 115-19-5; 3-methyl-d_3-butyn-3-ol-*4-d*$_3$, 57444-27-6; 2,2,3,6,6-pentamethyl-4-heptyn-3-ol, 36187-02-7; 2,2,6,6-tetramethyl-3-methyl-d_3-4-heptyn-3-ol, 57444-28-7; 5,5-dimethyl-4-*tert*-butyl-2-hexyn-4-ol, 57444-29-8; propyne, 74-99-7; di-*tert*-butyl ketone, 815-24-7; 4,5,5-trimethyl-2-hexyn-4-ol, 5187-21-3; *tert*-butyl methyl ketone, 75-97-8.

References and Notes

(1) M. D. Schiavelli, S. C. Hixon, H. W. Moran, and C. T. Boswell, *J. Am. Chem. Soc.*, **93**, 6989 (1971); M. D. Schiavelli, R. P. Gilbert, W. A. Boynton, and C. J. Boswell, *ibid.*, **94**, 5061 (1972); M. D. Schiavelli and P. L. Timpanaro, *J. Org. Chem.*, **38**, 3054 (1973); M. D. Schiavelli and D. Ellen Ellis, *J. Am. Chem. Soc.*, **95**, 7916 (1973).
(2) For a review of this field in saturated systems see J. Milton Harris, *Prog. Phys. Org. Chem.*, **11**, 1 (1974), numerous references cited therein; V. J. Shiner, Jr., in "Isotope Effects in Chemical Reactions", C. J. Collins and N. S. Bowman, Ed., Monograph No. 167, American Chemical Society, Washington, D.C., 1970, Chapter 2.
(3) J. L. Fry, C. J. Lancelot, L. K. M. Lam, J. M. Harris, R. C. Bingham, D. J. Raber, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 2540 (1970); P. v. R. Schleyer, J. L. Fry, L. K. M.Lam, and C. J. Lancelot, *ibid.*, **92**, 2542 (1970); S. H. Liggero, J. O. Harper, P. v. R. Schleyer, A. P. Krapcho, and D. E. Horn, *ibid.*, **92**, 3789 (1970).
(4) D. J. Raber, R. C. Bingham, J. M. Harris, J. L. Fry, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **92**, 5977 (1970).
(5) For an early study of the use of trifluoroethanol in solvolysis reactions see V. J. Shiner, Jr., W. Dowd, R. D. Fisher, S. R. Hartshorn, M. A. Kessick, L. Milakofsky, and M. W. Rapp, *J. Am. Chem. Soc.*, **91**, 4838 (1969).
(6) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **70**, 846 (1948).
(7) Present work.
(8) V. J. Shiner, Jr., and G. S. Kriz, *J. Am. Chem. Soc.*, **86**, 2643 (1964).
(9) A. Buroway and E. Spinner, *J. Chem. Soc.*, 3752 (1964).
(10) V. J. Shiner, Jr., W. E. Buddenbaum, B. L. Murr, and G. Lamaty, *J. Am. Chem. Soc.*, **90**, 418 (1968).
(11) V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **75**, 2925 (1953); **83**, 240 (1961).
(12) V. J. Shiner, Jr., and J. W. Wilson, *J. Am. Chem. Soc.*, **84**, 2402 (1962).
(13) H. G. Richey, Jr., and J. M. Richey in "Carbonium Ions", Vol. II, G. A. Olah and P. v. R. Schleyer, Ed., Wiley-Interscience, New York, N.Y., 1970, pp 931–949.
(14) P. J. Stang, C. D. Lee, R. J. Hargrove, and T. E. Dueber, *Tetrahedron Lett.*, 2519 (1971).
(15) Z. Rappoport, *Adv. Phys. Org. Chem.*, **7**, 1 (1969).
(16) Zvi Rappoport and J. Kaspi, *J. Am. Chem. Soc.*, **96**, 4518 (1974).
(17) V. J. Shiner and R. D. Fisher, *J. Am. Chem. Soc.*, **93**, 2553 (1971).
(18) S. R. Hartshorn and V. J. Shiner, Jr., *J. Am. Chem. Soc.*, **94**, 9002 (1972).
(19) V. J. Shiner, Jr., and J. S. Humphrey, Jr., *J. Am. Chem. Soc.*, **89**, 622 (1967).
(20) V. J. Shiner, Jr., B. L. Murr, and G. Heinemann, *J. Am. Chem. Soc.*, **85**, 2413 (1963).
(21) J. M. Harris, R. E. Hall, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **93**, 2551 (1971).
(22) If one applies the usual method of calculation of the standard deviation of a quotient

$$k_H/k_D^2 = \frac{1}{k_D^2}\left[k_H^2 + (k_H/k_D)^2 k_D^2\right]$$

and assumes rate constants corresponding to $t_{1/2} \approx 100$ min and $k_H/k_D = 1.15$ then a precision of ±1% in rate constants yields a standard deviation in k_H/k_D of ±1.3% and a precision of ±0.5% in rate constants yields a standard deviation in k_H/k_D of ±0.65%. This strongly indicates the need for precise determination of rate constants and accurate reporting of *statistical* errors.
(23) K. B. Wiberg, "Laboratory Technique in Organic Chemistry", McGraw-Hill, New York, N.Y., 1960.
(24) O. F. Beumel and R. F. Harris, *J. Org. Chem.*, **29**, 1872 (1964).
(25) S. R. Landor, A. N. Patel, P. F. Winter, and P. M. Greaves, *J. Chem. Soc. C*, 1223 (1966).
(26) C. V. Pittman, Jr., and G. A. Olah, *J. Am. Chem. Soc.*, **87**, 5632 (1965).
(27) T. L. Jacobs and D. M. Fenton, *J. Org. Chem.*, **30**, 1808 (1965).
(28) J. H. Ford, C. D. Thompson, and C. S. Marvel, *J. Am. Chem. Soc.*, **57**, 2619 (1935).