1973

A Kinetic Examination of 1,3-Di-t-butyl-3-methylbromoallene Solvolysis

Dwight Ellen Foster Ellis
College of William & Mary - Arts & Sciences

Recommended Citation

Ellis, Dwight Ellen Foster, "A Kinetic Examination of 1,3-Di-t-butyl-3-methylbromoallene Solvolysis" (1973). *Dissertations, Theses, and Masters Projects.* William & Mary. Paper 1539624809.
https://dx.doi.org/doi:10.21220/s2-pphx-9k80

A KINETIC EXAMINATION OF 1,3-DI-*T*-BUTYL-3-METHYLBROMOALLENE SOLVOLYSIS

A Thesis
Presented to
The Faculty of the Department of Chemistry
The College of William and Mary in Virginia

In Partial Fulfillment
Of the Requirements for the Degree of
Master of Arts

---

wight
by
D. Ellen Ellis
1973

APPROVAL SHEET

This thesis is submitted in partial fulfillment of
the requirements for the degree of

MASTER OF ARTS

D. Ellen Ellis
Author

Approved, May 1973

Melvyn D. Schiavelli
Melvyn D. Schiavelli, Ph.D.

Randolph A Coleman
Randolph A. Coleman, Ph.D.

Richard L Kiefer
Richard L. Kiefer, Ph.D.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS

The author wishes to express her appreciation to Professor Melvyn D. Schiavelli for his patience, guidance, and criticism, and to Professors Randolph A. Coleman and Richard L. Kiefer for their thorough reading and critical examination of this manuscript.

List of Tables

List of Figures

Figure Page

List of Figures (cont'd)

ABSTRACT

The solvolysis of 1,3-di-*t*-butyl-3-methylbromoallene has been determined to follow an S_N1 mechanism in aqueous alcohol by examination of the kinetics of the reaction. Excellent first order kinetics were observed by conductimetric measurement. In 80% aqueous ethanol at 45°, the β-secondary deuterium isotope effect, k_H/k_D, equals 1.23 for the 1,3-di-*t*-butyl-3-d_3-methylbromoallene isotopic variant. The value of $\Delta S^\ddagger$ is -0.7eu and $\Delta H^\ddagger$ is 23.2 kcal/mole at 25°. The Grunwald-Winstein *m* value is 0.87. This compound shows an 18-fold rate enhancement over tri-*t*-butylbromoallene solvolysis. Tri-*t*-butylbromoallene has an *m* value of 1.06 (45°), $\Delta S^\ddagger$ value of 9.0 eu (25°), and $\Delta H^\ddagger$ value of 26.0 kcal/mole in aqueous ethanol. An element effect, k_{Br}/k_{Cl} = 14.6, is also reported for the latter compound.

A KINETIC EXAMINATION

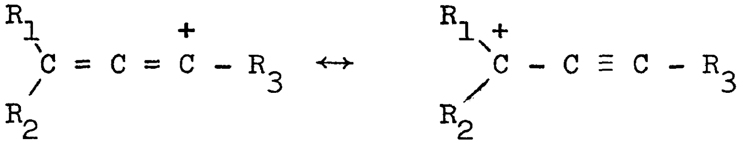
OF

1,3-DI-*T*-BUTYL-3-METHYLBROMOALLENE

SOLVOLYSIS

INTRODUCTION

The subject of vinyl cations as reaction intermediates has been studied by many workers[1-4] in recent years, but the extension of this study to the allenyl cation and its resonance form, the propargyl cation

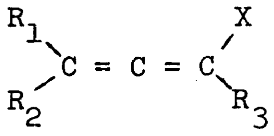


allenyl cation propargyl cation

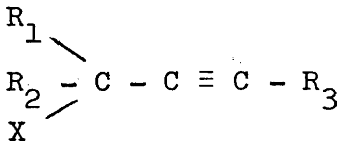
has received relatively little attention. This laboratory has undertaken an investigation of its reactivity through a series of solvolysis reactions of allenyl halides[5,6], which are listed in Figure 1. Beginning with those compounds expected to be most reactive in an S_N1 mechanism, the triaryl substituted haloallenes, Schiavelli and coworkers have demonstrated the applicability of a rate determining ionization to the solvolysis of each of the series through tri-*t*-butylchloroallene, IIIf, (Figure 1). The present work extends the series to 3-bromo-2,2,5,6,6-pentamethyl-3,4-heptadiene (1,3-di-*t*-butyl-3-methylbromoallene, Ia) in an effort to further elucidate the solvolytic reactivity of

Figure 1

Allenyl and Propargyl Halides Solvolyzing by an S_N1 Mechanism



A



P

		R_1	R_2	R_3	X
I a	A	*t*-Bu	Me	*t*-Bu	Br
b	A	*t*-Bu	*t*-Bu	*t*-Bu	Br
II a	A	Ph	Ph	Ph	Cl
b	A	Ph	Ph	p-ClPh	Cl
c	A	Ph	Ph	p-CH_3Ph	Cl
d	A	Ph	Ph	p-CH_3OPh	Cl
e	A	p-CH_3Ph	p-CH_3Ph	Ph	Cl
III a	A	Ph	*t*-Bu	*t*-Bu	Cl
b	A	Ph	*t*-Bu	Ph	Cl
c	A	*t*-Bu	*t*-Bu	Ph	Cl
d	A	*t*-Bu	Ph	*t*-Bu	Cl
e	A	*t*-Bu	Ph	*t*-Bu	Br
f	A	*t*-Bu	*t*-Bu	*t*-Bu	Cl
IV a	P	Me	Me	H	Cl
b	P	Me	Me	Me	Cl
c	P	Me	Me	Et	Cl
d	P	Me	Me	*i*-Pr	Cl
e	P	Me	Me	*t*-Bu	Cl
V	P	*t*-Bu	H	*t*-Bu	OTs
VI a	P	Me	Me	H	Br
b	P	CD_3	CD_3	H	Br
c	P	Me	Me	D	Br
d	A	CD_3	CD_3	H	Br
e	A	CD_3	CD_3	Me	Br
f	A	Me	Me	CD_3	Br

Table I

Selected Kinetic Parameters for S_N1 Solvolysis Reactions

COMPOUND	SOLVENT (v/v)	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ eu	m
II a	80:20 DMK:H_2O[a]	20.2	-10.7	0.69[b]
b	80:20 DMK:H_2O	21.1	- 8.80	
d	DMK - H_2O			0.77[b]
III a				0.87[c]
b	60:40 DMK:H_2O	19.4	-11.7	0.95[c]
c	50:50 DMK:H_2O	20.2	-10.4	1.13[c]
d				1.04[c]
e				0.90[c]
f	50:50 DMK:H_2O	23.4	- 5.0	1.22[d]
IV b	80:20 EtOH:H_2O	20.6	- 4.6[e]	
c		20.6	- 4.6[e]	
d		21.5	- 2.1[e]	
e		21.4	- 2.8[e]	
V	HOAc, NaOAc	26.47	3.59[f]	

[a] Acetone (dimethylketone)
[b] Reference 5, 26°
[c] Reference 6, 35°
[d] Reference 6, 55°
[e] Reference 16, 25°
[f] Reference 17, 40°

haloallenes in aqueous ethanol or acetone.

The triarylchloroallenes[5], II, were shown to follow first order kinetics unaffected by 1250-fold excess of triethylamine in aqueous acetone solvolysis. That the reaction is insensitive to added strong nucleophile is demonstrated by the excess of triethylamine. A Hammett plot of ρ *vs* σ^+ yielded $\rho = -2.0$, indicative of positive charge development at or before the rate determining step. A parameter showing reaction sensitivity to solvent polarity, the Grunwald-Winstein *m* value[7] was found to be 0.69 ± 0.6 for IIa at 26°. This value is comparable to that found for other S_N1 reactions and helps to eliminate an S_N2 process, (Table I).

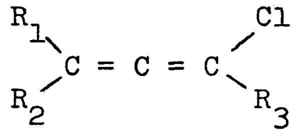
The Arrhenius activation parameters are also consistent with an S_N1 mechanism. The entropy of activation is generally a good mechanistic indicator. S_N2 pathways show large negative (~ -20 eu) $\Delta S^\ddagger$ due to conjunction of two reactants and concomitant increase in order. S_N1 reactions might therefore be expected to show large positive values, as they indeed do, in the gas phase. In solution, however, solvent ordering about the ionic species usually results in an overall small negative $\Delta S^\ddagger$ (-10 to 0 eu). Concerted elimination reactions and the Hennion mechanism do involve large (~ 20 eu) positive entropy change to the transition state.

A measure of the stability of the intermediate ion, the selectivity ratio (k_{-1}/k_{H_2O}), was determined to be between 5 and 13, which is on the order of the values found for benzhydrylchloride in aqueous acetone[8] or 2,2-diphenylbromoethylene in aqueous dimethylformamide.[9]

Evidence for a unimolecular dissociation pathway for the next compounds in the series, the aromatic and *t*-butyl substituted haloallenes[6], has been found in relative rates of reaction of the chloro- and bromo-derivatives of 1,3-di-*t*-butyl-3-phenylhaloallene, IIId and IIIe respectively. This element effect, $k_{Br}/k_{Cl} = 56$, suggested that the carbon-halogen bond, carbon-bromine being weaker, is broken in a rate determining step. Each of these compounds, III, showed rate enhancements relative to the tri-*t*-butyl case, IIIf, consistent with the proposed mechanism in view of charge delocalization through the aromatic rings (Table II). The amount of acceleration was thought to vary with the availability of a configuration in which the rings were coplanar with the allenyl system, coplanarity being a necessary condition for π electron delocalization. The Grunwald-Winstein m values for these compounds in aqueous acetone ranged between 0.87 for IIIa and 1.22 for IIIf (Table I). The activation parameters were very similar to those observed for the triaryl system (Table I) with the exception of IIIf, which showed the high m value and relatively less negative $\Delta S^{\ddagger}$, -5.0 eu, consistent with increased steric hinderance to direct solvation and decreased charge delocalization due to the absence of aromatic substituents. Product analysis gave results suggesting increased hinderance to solvation, also. Triphenylchloroallene solvolysis resulted exclusively

Table II

Relative Rates of Solvolysis for Phenyl and *t*-Butyl Substituted Chloroallenes



COMPOUND

	R_1	R_2	R_3	k_{rel}
II a	Ph	Ph	Ph	345^a
III a	Ph	Ph	*t*-Bu	87.6^b
III b	Ph	*t*-Bu	Ph	10.6^b
III c	*t*-Bu	*t*-Bu	Ph	14.4^b
III d	*t*-Bu	Ph	*t*-Bu	1.84^b
III f	*t*-Bu	*t*-Bu	*t*-Bu	1.00^b

[a] Reference 5.

[b] Reference 6.

in the propargyl alcohol[5] from attack on the more stable propargyl cation resonance form[2,10], some types of which have, in fact, been observed spectroscopically.[11-13] However, solvolysis of tri-*t*-butylchloroallene produced the propargyl alcohol in smaller amounts, equal to approximately 80% of the total isolated product. The remaining 20% was the unsaturated ketone arising from water addition at the less hindered allenyl cation[6] (Figure 2).

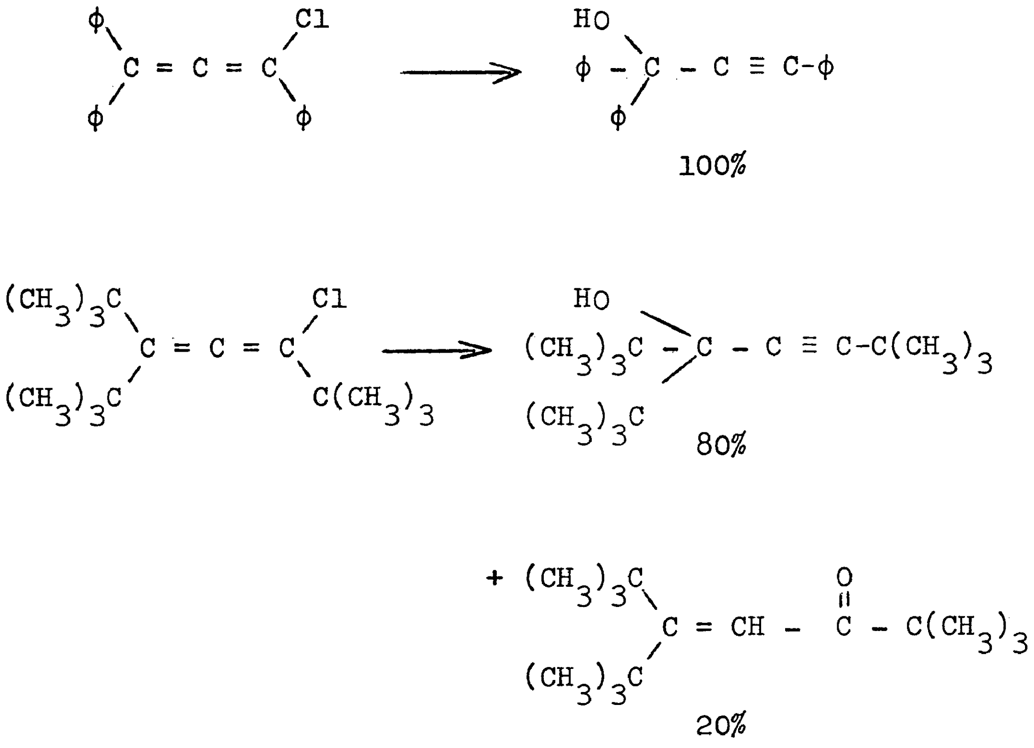
Other investigations in this area have centered on the propargyl form, which is the more reactive of the two under solvolysis conditions.[14,15] Burawoy and Spinner[16], in an investigation of the alkyl substituted compounds, IV, concluded that all but IVa reacted through an S_N1 process in 80% aqueous ethanol and were affected very little by added base. The values of $\Delta H^{\ddagger}$ (20.6 kcal/mole) and $\Delta S^{\ddagger}$ (-4.6 eu for IVb) are also consistent with those expected for the proposed mechanism (Table I).

Macomber[17] has studied 1,3-di-*t*-butylpropargyl tosylate, V, under acetolysis conditions, dry acetic acid containing one equivalent of sodium acetate. The reaction was observed to proceed *via* an allenyl-propargyl cation with a rate constant of 1.34×10^{-5} sec^{-1} at 40° and to have an unusual, small positive $\Delta S^{\ddagger}$ (3.59 eu), judged to be due to the stability of the cation. Approximately 99% of the products observed could be accounted for by reactions of the propargyl cation.

Shiner and coworkers have done extensive work on deuterium isotope effects in solvolysis reactions, including some on propargyl halides.[18-22] Secondary isotope effects are thought to be due to differences in activation

Figure 2

Solvolysis Products of Triphenyl and Tri-*t*-butylchloroallene in Aqueous Acetone



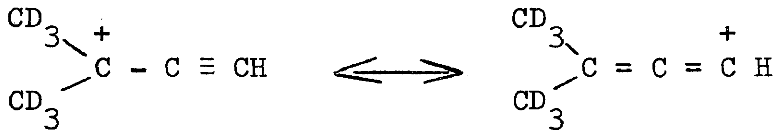
energies originating principally from changes in the bending modes of C-H and C-D vibrations.[23] The overall effect has been described[24] as having three interrelated components: (1) a steric effect due to the shorter bond length of C-D as compared to C-H; (2) an inductive effect arising because the C-D bond is more polar than that of C-H; and (3) a hyperconjugative effect contributed to the lesser polarizability of the C-D bond. The third appears to be the dominant effect, even when hybridization changes are involved.[19,25-27]

Shiner's group[18] demonstrated that VIa reacts by a carbonium ion mechanism in 80% aqueuous ethanol at 25°. This conclusion was based largely on the classical normal salt effect, and the small mass law effect with added bromide ion. The β-secondary isotope effect obtained by comparison to VIb is 1.84, but by comparison to VIc is approximately 1.0. This is consistent with later studies[28,29] showing the steric dependence of the β-secondary isotope effect, i.e. the effect is minimal when the carbon-deuterium bond is at an angle of 90° with the p orbital where positive charge is developing and is optimized when this angle is 0° or 180°. They also observed a β-secondary isotope effect when VIb was solvolyzed with added base, proceeding through a zwitterion-carbene intermediate, equal to 1.31. This was explained relative to the S_N1 case by less C-Br bond breakage and less total charge development in the predominant resonance form (Figure 3). In a later work[28], the same type of effect for the allenyl analog, VId, was equal to 1.15. Substitution of a methyl group for the terminal hydrogen in neutral solvolysis[20], VIe, lowers the observed k_H/k_D to 1.66 by increasing charge delocalization from C_2 relative to VIb. An isotope effect of 1.09 has been measured for deuterium substitution in this methyl group, VIf. Comparison of these values to those for saturated and vinyl cations may be made in Table III.

Figure 3

Comparison of Transition States for Neutral and Basic Solvolysis of 3-Bromo-3-methyl-1-butyne

neutral solvolysis



basic solvolysis

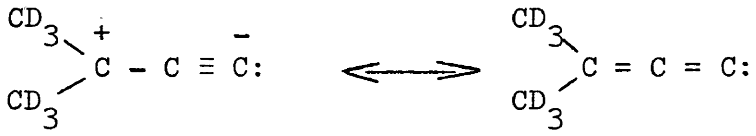


Table III

Secondary Deuterium Isotope Effects

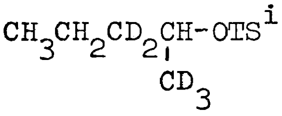
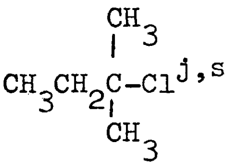
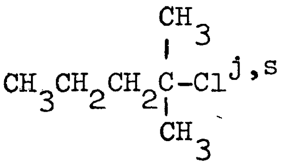
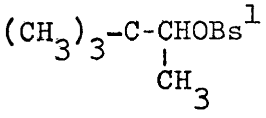
COMPOUND	REACTION[a] CONDITIONS	α-EFFECT	β-EFFECT
CH_3CH_2OBs[c]	80% ETOH, 100°	d_2 1.09 (32)	d_3 1.01 (3)
$CH_3CH_2OSO_2CF_3$[c]	HOAC, 25°	d_2 1.12 (34)	d_3 1.11 (21)
$(CH_3)_2CHOTs$[d]	H_2O, 30°		d_6 1.55 (43)
$(CH_3)_2CHBr$[e]	ETOH, ETO^-, 25°		d_6 1.13 (0.2)
$(CH_3)_3C$-Cl	60% ETOH, 25°[f]		d_3 1.33 (56.3)
			d_6 1.71 (53.0)
			d_9 2.33 (55.7)
	50% ETOH, 25°[g]		d_9 2.368 (56.7)
	70% TFE[h], 25°[g]		d_9 2.493 (60)
 $CH_3CH_2CD_2CH(CD_3)$-OTS[i]	80% ETOH, 50°		d_5 1.40 (43.2)
 $CH_3CH_2C(CH_3)_2$-Cl[j,s]	80% ETOH, 25°		d_3 1.34 (57.7)
			d_2 1.40 (102)
			d_6 1.77 (56.4)[k]
 $CH_3CH_2CH_2C(CH_3)_2$-Cl[j,s]	80% ETOH, 25°		d_2 1.34 (202)
 $(CH_3)_3$-C-$CH(CH_3)OBs$[l]	50% ETOH, 25°	d_1 1.159 (87)	d_3 1.205 (37)
			γ-d_9 1.003 (0.2)

Table III (cont'd)

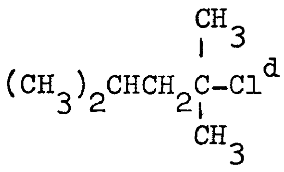
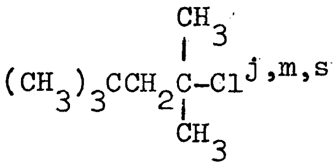
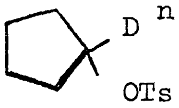
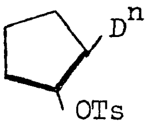
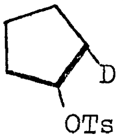
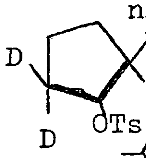
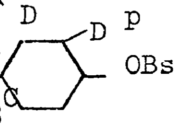
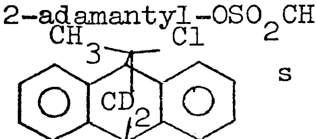
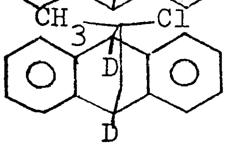
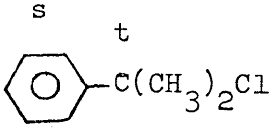
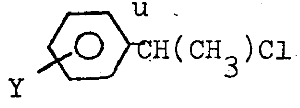
COMPOUND	REACTION[a] CONDITIONS	α-EFFECT	β-EFFECT
 $(CH_3)_2CHCH_2C(CH_3)_2\text{-}Cl^{d}$	80% ETOH, 25°		d_3 1.34 (57.8) d_2 1.47 (114)
 $(CH_3)_3CCH_2C(CH_3)_2\text{-}Cl^{j,m,s}$	80% ETOH, 25°		d_3 1.40 (66.4) d_2 1.08 (22.8)
	HOAc, NaOAc, 50°	d_1 1.15 (90)	
	HOAc, NaOAc, 50°		d_1 1.16 (110)
	HOAc, NaOAc, 50°		d_1 1.22 (127)
	HOAc, NaOAc, 50°		d_4 2.06 (116)
	50% ETOH, 35°		d_1 1.44 (223)
2-adamantyl-tosylate[q]	60% ETOH, 75°	d_1 1.168 (92)	
2-adamantyl-$OSO_2CH_2CF_3$[q,r]	50% ETOH, 25°	d_1 1.225 (120)	
	60% ETOH, 45°		d_2 1.14 (41.4)
	60% ETOH, 45°		d_2 0.986 (-4.5)
	80% ETOH, 25°		d_6 1.48 (38.7)
	80% ETOH, 25°		

Table III (cont'd)

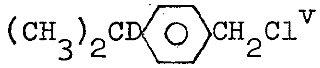
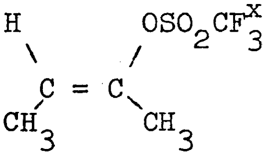
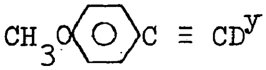
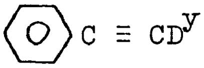
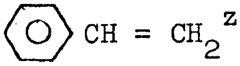
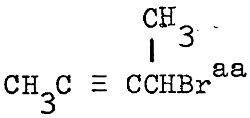
COMPOUND	REACTION[a] CONDITIONS	α-EFFECT	β-EFFECT
Y = m-CH_3			d_3 1.22 (39.3)
p-F			d_3 1.21 (37.6)
p-CH_3			d_3 1.20 (36.0)
p-CH_3	acetolysis,50°[w]		d_3 1.36 (66)
p-phenoxy			d_3 1.16 (29.3)
p-methoxy			d_3 1.11 (20.6)
H			d_3 1.22 (39.3)
H[g]	60% ETOH, 25°		d_3 1.226 (40.2)
 [v]	90% ETOH, 0°		d_3 1.025 (19.4)
	acetolysis, 50°[w]		d_3 1.15 (29)
 [v]	90% ETOH, 0°		d_2 1.009 (2.4)
 [v]	90% ETOH, 0°		d_1 0.998 (-1.2)
 [x]	80% ETOH, 100°		d_1 1.20 (135)
 [y]	H_2SO_4 solutions, 25°		d_1 1.07 (40.1)
 [y]	H_2SO_4 solutions, 25°		d_1 1.11 (61.8)
 [z]	43.4% $HClO_4$, 25°	d_1 0.98 (-4.0)	d_2 1.03 (8.8)
 $CH_3C \equiv C\overset{CH_3}{C}HBr$ [aa]	50% ETOH, 25°	d_1 1.101 (57.0)	d_3 1.200 (35)
			γ-d_3 1.081 (15)

Table III (cont'd)

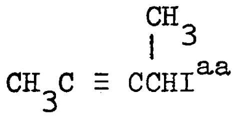
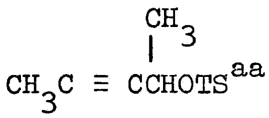
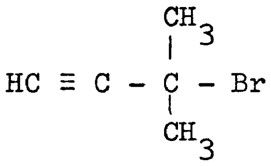
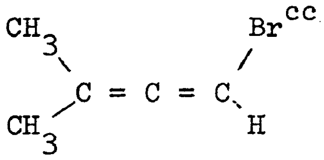
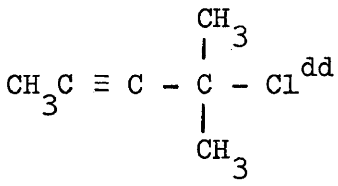
COMPOUND	REACTION[a] CONDITIONS	α-EFFECT	β-EFFECT
	70% TFE, 25°[h]	d_1 1.123 (68.7)	d_3 1.280 (48.7)
			γ-d_3 1.108 (20.2)
 $CH_3C \equiv CCH(CH_3)I$[aa]	50% ETOH, 25°	d_1 1.087 (49.4)	d_3 1.278 (48.4)
	70% TFE, 25°[h]	d_1 1.089 (50.5)	d_3 1.283 (49.2)
 $CH_3C \equiv CCH(CH_3)OTs$[aa]	60% ETOH, 25°	d_1 1.213 (114)	d_3 1.241 (42.6)
			γ-d_3 1.104 (19.5)
	70% TFE, 25°[h]	d_1 1.226 (121)	d_3 1.281 (48.9)
			γ-d_3 1.109 (20.4)
 $HC \equiv C-C(CH_3)_2-Br$	80% ETOH, 25°[bb]		d_6 1.84 (60.2)
	⁻OH, 80% ETOH, 25°[cc]		d_6 1.31 (26.7)
 [cc]	⁻OH, 80% ETOH, 25°		d_6 1.15 (13.8)
 $CH_3C \equiv C-C(CH_3)_2-Cl$[dd]	80% ETOH, 25°		δ-d_3 1.10 (18.8)
	80% ETOH, 25°		d_6 1.70 (22.7)

Table III (cont'd)

[a] Percentages given are volume percent in water.

[b] ΔΔF cal/mole D in parentheses.

[c] A. Streitwieser, Jr., C.L. Wilkins, and E. Kiehlmann, J. Am. Chem. Soc., 90, 1598 (1968).

[d] K.T. Leffek, J.A. Llewellyn, and R.E. Robertson, Can. J. Chem., 38, 1505 (1960).

[e] V.J. Shiner, Jr., J. Am. Chem. Soc., 74, 5285 (1950).

[f] V.J. Shiner, Jr., B.L. Murr, and G. Heinemann, J. Am. Chem. Soc., 85, 2413 (1963).

[g] V.J. Shiner, Jr., W. Dowd, R.D. Fisher, R.S. Hartshorn, M.A. Kessick, L. Milakofsky, and M.W. Rapp, J. Am. Chem. Soc., 91, 4838 (1969).

[h] 2,2,2-trifluoroethanol, weight percent.

[i] E.S. Lewis and C.E. Boozer, J. Am. Chem. Soc., 76, 791 (1954).

[j] V.J. Shiner, Jr., J. Am. Chem. Soc., 83, 240 (1961).

[k] C.G. Swain and E.R. Thornton, Tetrahedron Letters, 6, 211 (1961).

[l] V.J. Shiner, Jr., R.D. Fisher, and W. Dowd, J. Am. Chem. Soc., 91, 7748 (1969).

[m] V.J. Shiner, Jr., J. Am. Chem. Soc., 78, 2653 (1956).

[n] Reference 23.

[p] V.J. Shiner, Jr., and J.G. Jewett, J. Am. Chem. Soc., 87, 1382 (1965).

[q] J.M. Harris, R.E. Hall, and P.V.R. Schleyer, J. Am. Chem. Soc., 93, 2551 (1971).

[r] V.J. Shiner, Jr., and R.D. Fisher, J. Am. Chem. Soc., 93, 2553 (1971).

[s] Reference 28.

[t] C.G. Swain and E.R. Thornton, J. Am. Chem. Soc., 84, 817 (1962).

Table III (cont'd)

[u] Reference 25.

[v] V.J. Shiner, Jr., and C.J. Verbanic, J. Am. Chem. Soc., 79, 373 (1957).

[w] E.S. Lewis and G.M. Coppinger, J. Am. Chem. Soc., 76, 4495 (1954).

[x] P.J. Stang and R. Summerville, J. Am. Chem. Soc., 91, 4600 (1969).

[y] Reference 29.

[z] W.M. Schubert and B. Lamm, J. Am. Chem. Soc., 88, 120 (1966).

[aa] Reference 22.

[bb] Reference 19.

[cc] Reference 21.

[dd] Reference 20.

EXPERIMENTAL

Infrared spectra were taken using a Beckman Infrared Spectrophotometer Model 5A or Beckman Acculab 6 Spectrophotometer on neat samples in sodium chloride cells. Nmr spectra were run on an Hitachi-Perkin-Elmer R-20B Nuclear Magnetic Resonance Spectrometer, 60 Mc/sec, as approximately 20% solutions in carbon tetrachloride, with an internal trimethylsilane reference. Analyses were performed by Atlantic Microlabs, Inc., Atlanta, Georgia.

Materials

1. Conductivity water used in kinetic studies was obtained by passing distilled water through a Bantam Demineralizer, Model BD-1, with a mixed bed resin. Water conductance was less than 10 micromhos at all times.

2. Absolute ethanol was obtained from U.S. Industrial Chemicals Co., Reagent Quality, and used without further purification. Opened solvent was stored over Linde 3A Molecular Sieves and usually used within two weeks.

3. Thionyl chloride was purified by the procedure of Fieser and Fieser.[30]

4. Phosphorus tribromide, Eastman yellow label, was used without further purification.

5. 3,3-Dimethyl-2-butanone, Eastman yellow label, was used without further purification.

6. 2,2,4,4-Tetramethyl-3-pentanone was obtained from Chemical Samples Co. (99% purity) and was used without further purification.

7. 3-Bromo-2,2,5,6,6-pentamethyl-3,4-heptadiene was obtained from F.L. Griffith[31] and used without further purification: b.p. 35-37°C (0.3mm); ir (neat) 1950 cm^{-1} (C = C = C) and no O-H band (Figure 4); nmr (CCl_4) 1.74 ppm (s,3) 1.12 ppm (s,9) 1.07ppm (s,9) (Figure 5). Anal. calcd. for $C_{12}H_{21}Br$: C, 58.78%; H, 8.63%; Br, 32.59%. Found: C, 58.84%; H, 8.69%; Br, 32.69%.

8. 3,3-Dimethyl-2-butanone-1-d_3 was prepared by M.D. Schiavelli[32], to whom the author is indebted, and was stored over anhydrous magnesium sulfate. Nmr (CCl_4) 0.74 ppm (s,18) x 10 sensitivity, 1.68 ppm (m,0.5) (Figure 6). Non-deuterated compound: 0.74 ppm (s,18) 1.68 ppm (s,3) (Figure 6).

9. 2,2,6,6-Tetramethyl-3-methyl-d_3-4-heptyn-3-ol was prepared by the method of Olah and Pittman.[33] Forty-three ml (90 m moles) of 20% butyllithium in hexane was chilled in an ice bath and 11.4 ml (7.7 g, 93 m moles) *t*-butylacetylene in 20 ml hexane added dropwise. The solution was diluted with anhydrous diethyl ether, followed by slow addition of 9.1 g (90 m moles) 3,3-dimethyl-1-d_3-2-butanone in anhydrous ether. The

reaction mixture was gently refluxed for two hours and then cooled to 0°C 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 soultion, filtered through anhydrous magnesium sulfate and stored over this drying agent overnight. Filtration followed by rotary evaporation of solvent and vacuum distillation yielded 13.2 g (79%) of product; b.p. 73.5-75.5°C (3 mm); ir (neat) 3470 cm^{-1} (O-H) 2250 cm^{-1} ($C \equiv C$) 2080-2140 cm^{-1} (C-D) no residual ketone band (Figure 7); nmr (CCl_4) 0.98 ppm (s,9) 1.19 ppm (s,9) 1.83 ppm (s,1) (Figure 8).

10. 3-Bromo-2,2,6,6-tetramethyl-5-methyl-d_3-3,4-heptadiene was synthesized by the procedure of Marvel et. al.[34] 5.7 g (30 m moles) of 2,2,6,6-tetramethyl-3-methyl-d_3-4-heptyn-3-ol was dissolved in petroleum ether and 1.0 ml (2.85 g, 10 m moles) phosphorous 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 saturated sodium bicarbonate and once with 100 ml 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: b.p. 80-84.5°C (3 mm); ir (neat) 1947 cm^{-1} ($C = C = C$) 2065-2140 cm^{-1} (C-D) no alcohol band (Figure 9); nmr (CCl_4) 1.09 ppm (s,9) 1.14 ppm (s,9) x 20 sensitivity 1.74 ppm (m, 0.5) (Figure 10). 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 was generously supplied by Professor Donald Hunt[35]; d_3, 72% ± 4%; d_2, 15%; d_1, 7%; d_0, 6%; 2.5 D/molecule.

11. 2,2,3,6,6-Pentamethyl-4-heptyn-3-ol was prepared by a method identical to that for the previous propargyl alcohol (see 9, above). The product (24.8 g) was obtained in 90% yield: b.p. 73-76°C (3 mm); ir (neat) 3470 cm^{-1} (O-H) 2240 cm^{-1} ($C \equiv C$) no ketone band (Figure 11); nmr (CCl_4) 0.99 ppm (s,9) 1.21 ppm (s,9) 1.33 ppm (s,3) 2.01 ppm (s,1) (Figure 12).

12. 3-Chloro-2,2,5,6,6-pentamethyl-3,4-heptadiene was prepared by the method of Jacobs and Fenton.[36] 9.2 g (50 m moles) of 2,2,3,6,6-pentamethyl-4-heptyn-3-ol was added to cold anhydrous ether. 3.6 ml (5.9 g, 50 m moles) thionyl chloride and 8.0 ml (7.9 g, 100 m moles) pyridine in ether were quickly added with stirring, which was continued for one hour at 0°C. The precipitate was filtered out of the reaction mixture and the organic layer washed three times with 100 ml 5% sodium bicarbonate and twice with 50 ml water. The organic layer was dried as above and vacuum distilled to give four fractions 45-62°C, 62-68°C, 68-75°C, 75-81°C (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) 3050 cm^{-1} ($=CH_2$) 2190 cm^{-1} ($C \equiv C$) 1950 cm^{-1} ($C = C = C$) 1595 cm^{-1} ($C = C - C \equiv C$), (Figure 13); nmr (CCl_4) 1.07 ppm (s,9) 1.08 ppm (s,9) 1.11 ppm (s,9) 1.23 ppm (s,9) 1.74 ppm (s,3) 5.03 ppm (s,2), (Figure 14).

13. 3-Bromo-2,2,6,6-tetramethyl-5-*t*-butyl-3,4-heptadiene was prepared by F.L. Griffith[31], to whom the author is indebted. The sample had been vacuum distilled: b.p. 42-44.5°C (0.1 mm); m.p. 35°; ir (CCl_4) 1920 cm^{-1} (C = C = C) no alcohol band (Figure 15); nmr (CCl_4) 1.14 ppm (s,9) 1.19 ppm (s,18), (Figure 16). <u>Anal.</u> Calcd. for $C_{15}H_{27}Br$: c, 62.17%; H, 9.47%; Br, 27.81%. Found: C, 62.74%; H, 9.39%; Br, 27.73%.

14. 2,2,6,6-Tetramethyl-3-*t*-butyl-4-heptyn-3-ol was prepared by the method of Olah and Pittman[33] using 6.5 ml (5.3 g, 37 m moles) of 2,2,4,4-tetramethyl-3-pentanone. The product obtained was a white crystalline solid, 6.0 g (72%): m.p. 56.5-58.0°C; ir (CCl_4) 3600 cm^{-1} (O-H) 2220 cm^{-1} ($C \equiv C$) 1695 cm^{-1} (C = O), (Figure 17). The sample was used in further synthesis without additional purification.

15. 3-Chloro-2,2,6,6-tetramethyl-5-*t*-butyl-3,4-heptadiene was prepared by the method of Jacobs and Fenten[36] previously outlined. The vacuum distilled product yielded 1.5 g (20%): b.p. 78-82°C (1.5 mm) 62-65°C (0.4 mm); ir (neat) 1945 cm^{-1} (C = C = C) no alcohol band, (Figure 18); nmr (CCl_4) 1.03 ppm (s,a) 1.10 ppm (s,18), (Figure 19).

<u>Kinetic Studies</u>

Conductivity measurements following hydronium ion and bromide ion production were made on a Wayne Kerr Autobalance Universal Bridge B642 using a conductivity cell from Fisher Scientific Co. with a cell constant of approximately 0.17 cm^{-1}. The cell was immersed in an ethylene glycol or water constant temperature bath during each run. All glassware was oven-dried before use and sample stock solutions were sealed with parafilm and stored in the refrigerator to prevent water contamination and decomposition. At the beginning of each run 5 ml of the stock solution and an appropriate amount of absolute ethanol were pipetted into a 50 ml volumetric flask, which was capped and equilibriated to a given temperature. The conductivity water was also equilibriated at bath temperature and subsequently pipetted into the reaction mixture. Timing was begun when approximately half of the water had been added. The volumetric flask was inverted several times to mix reactants and the conductivity cell rinsed three times with the reacting solution. Finally, the cell was filled, inserted in the bath, and readings begun.

A sample first order kinetics plot of log $(C_\infty - C_t/C_\infty - C_v)$ vs. t, where C_t is the conductivity in micromhos and t is the time in minutes, may be seen in Figure 20. The value of the rate constants and the standard derivation for each run were calculated using LSG, a computer program by D.E. Detar[37], for which sample output follows (Table IV). Approximate values for the rate constant in sec^{-1} (estimated as 0.693/half life, sec.), C_∞ and C_o as well as all time and conductivity measurements comprised the data submitted. Activation parameters were calculated using ACTENG[37], by submission of temperature and rate constant data and estimations of the variation in each to the computer. A typical output follows (Table V). A sample Arrhenius plot and Grunwald-Winstein plot may also be found in Figures 21 and 22, respectively.

Figure 4

Infrared Spectrum of 3-Bromo-2,2,5,6,6-pentamethyl-3,4-heptadiene

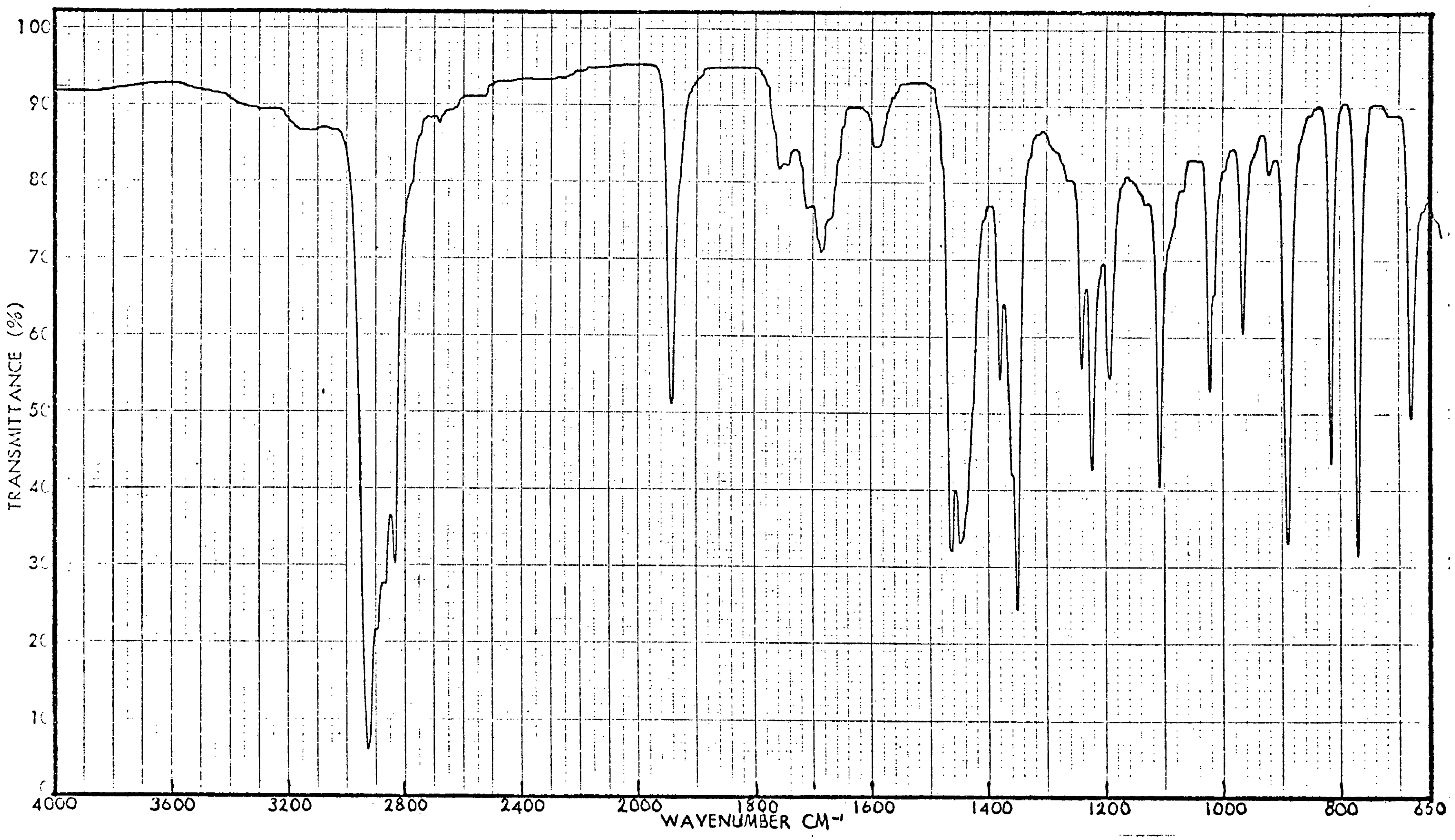


Figure 5

Nmr Spectrum of 3-Bromo-2,2,5,6,6-pentamethyl-3,4-heptadiene

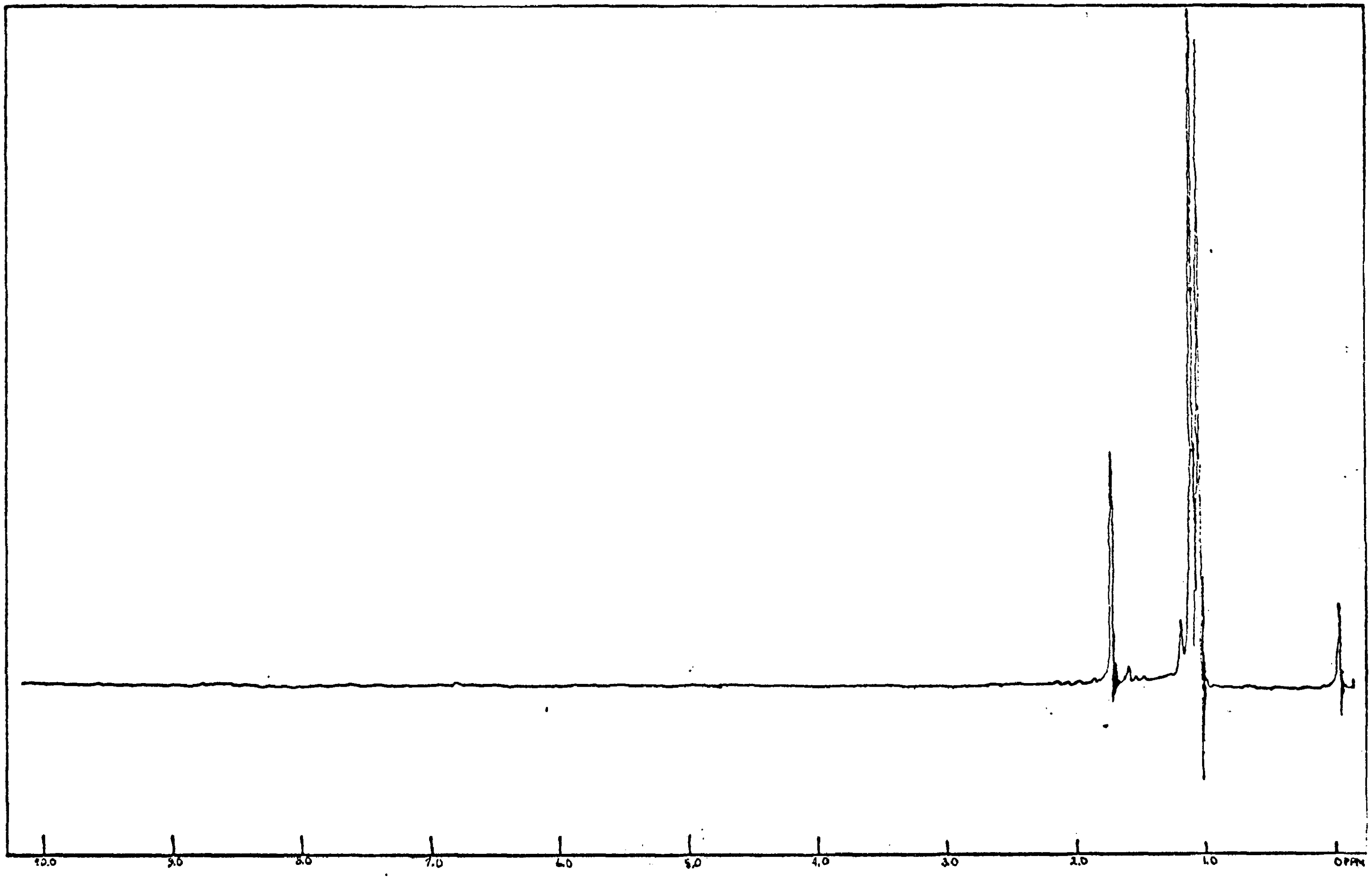


Figure 6

Nmr Spectra of 3,3-Dimethyl-2-butanone-1-d_3^a and 3,3-Dimethyl-2-butanone^b

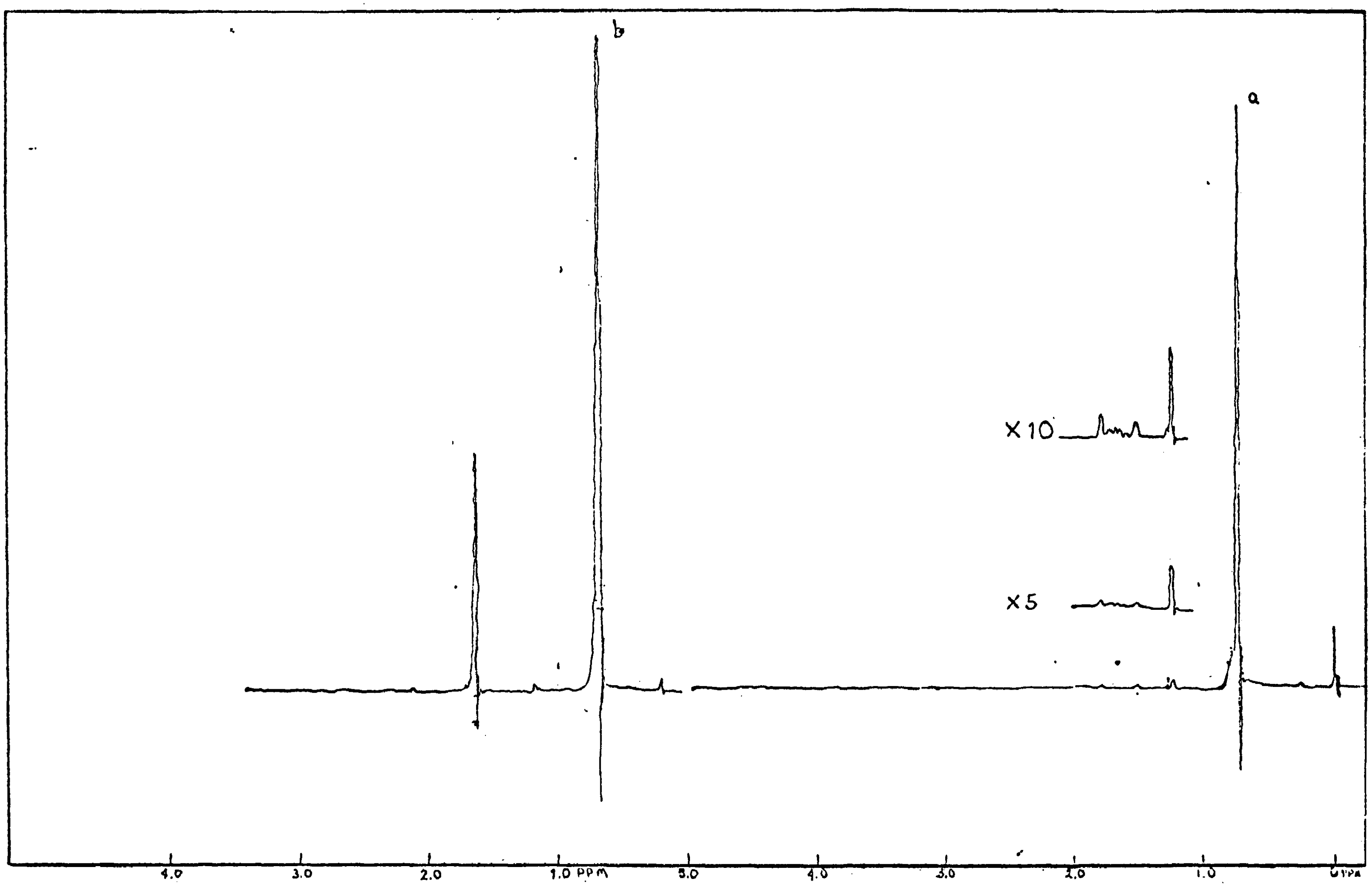


Figure 7

Infrared Spectrum of 2,2,6,6-Tetramethyl-3-methyl-d_3-4-heptyne-3-ol

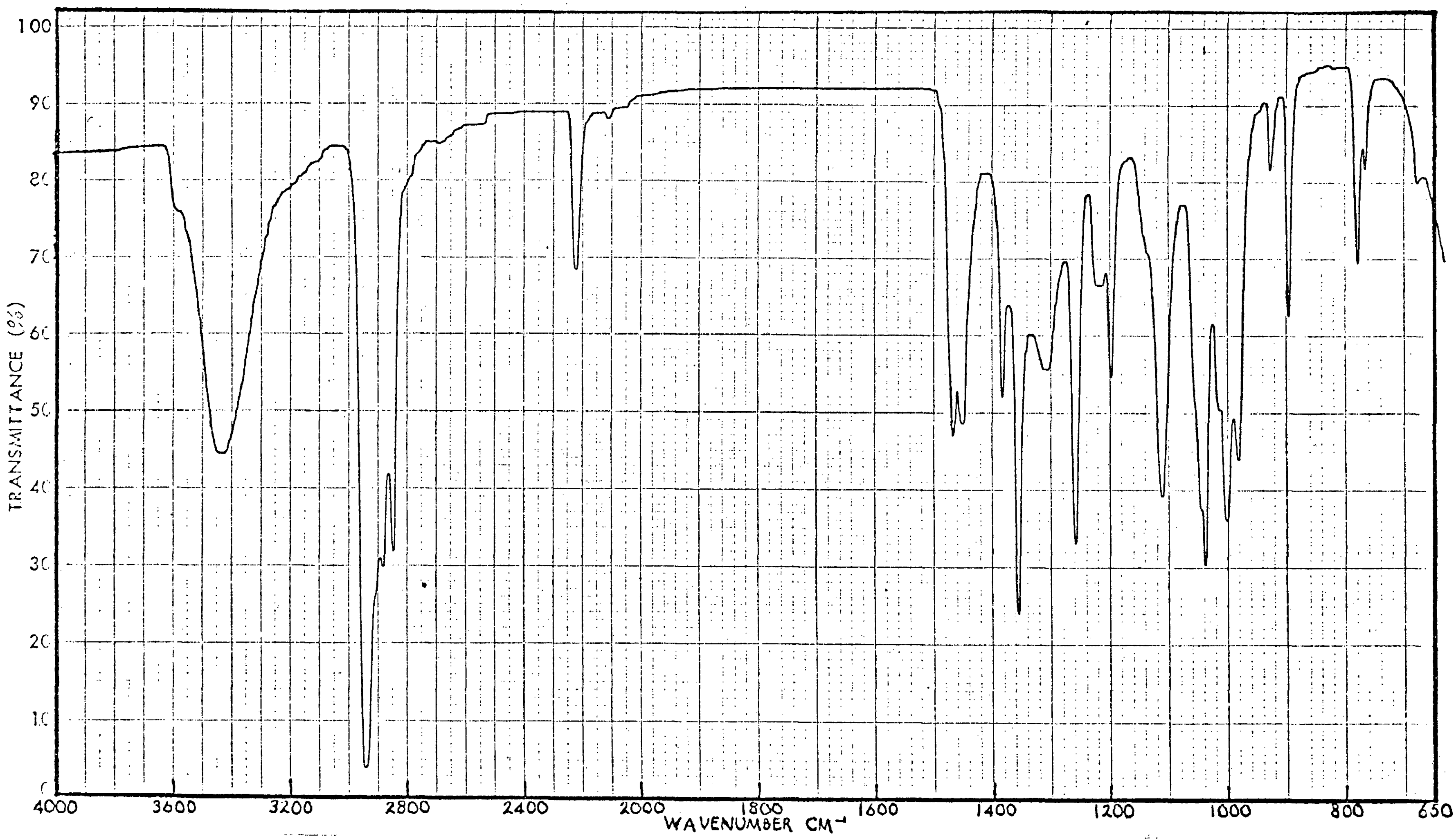


Figure 8

Nmr Spectrum of 2,2,6,6-Tetramethyl-3-methyl-d_3-4-heptyne-3-ol

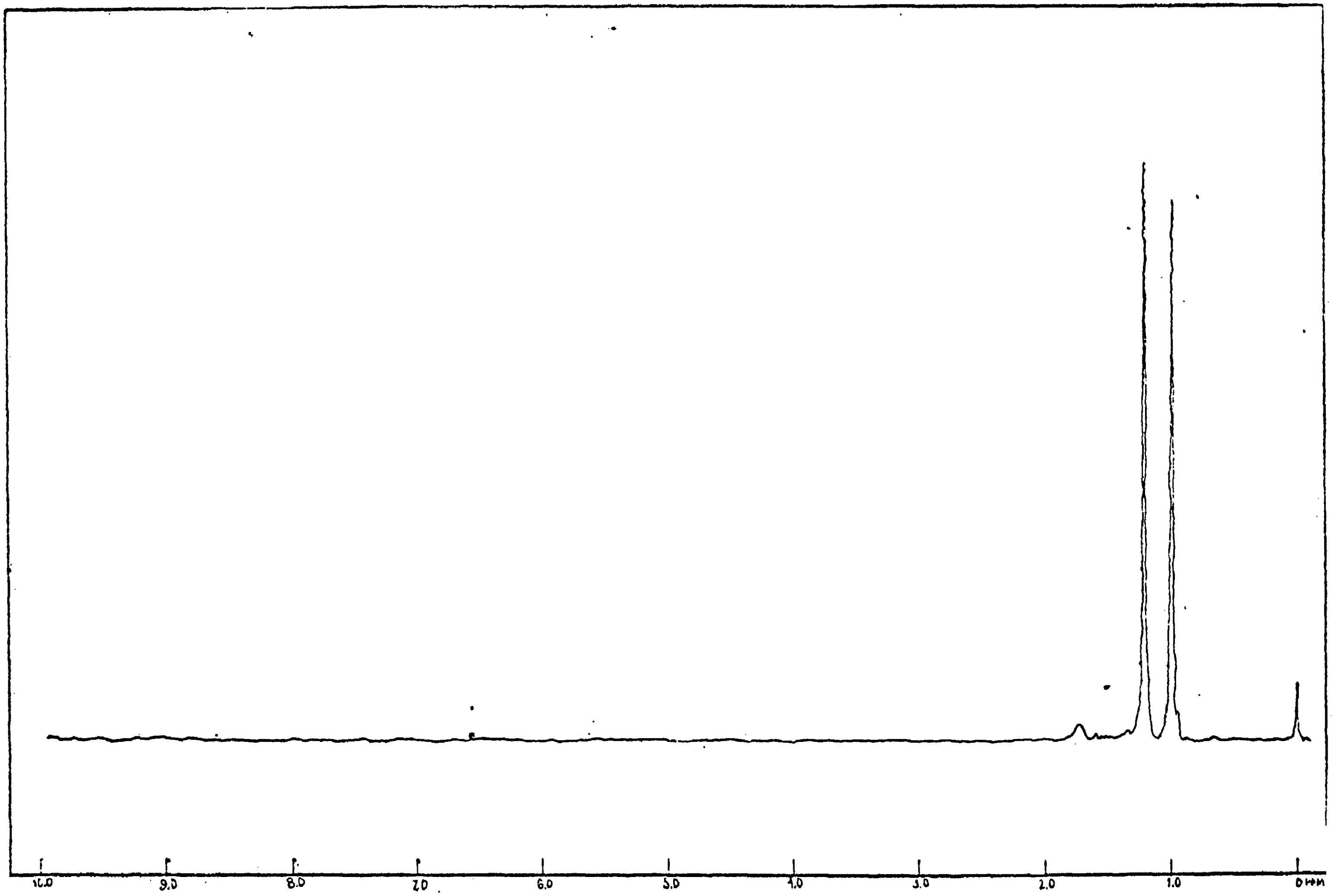


Figure 9

Infrared Spectrum of 3-Bromo-2,2,6,6-tetramethyl-5-methyl-d_3-3,4-heptadiene

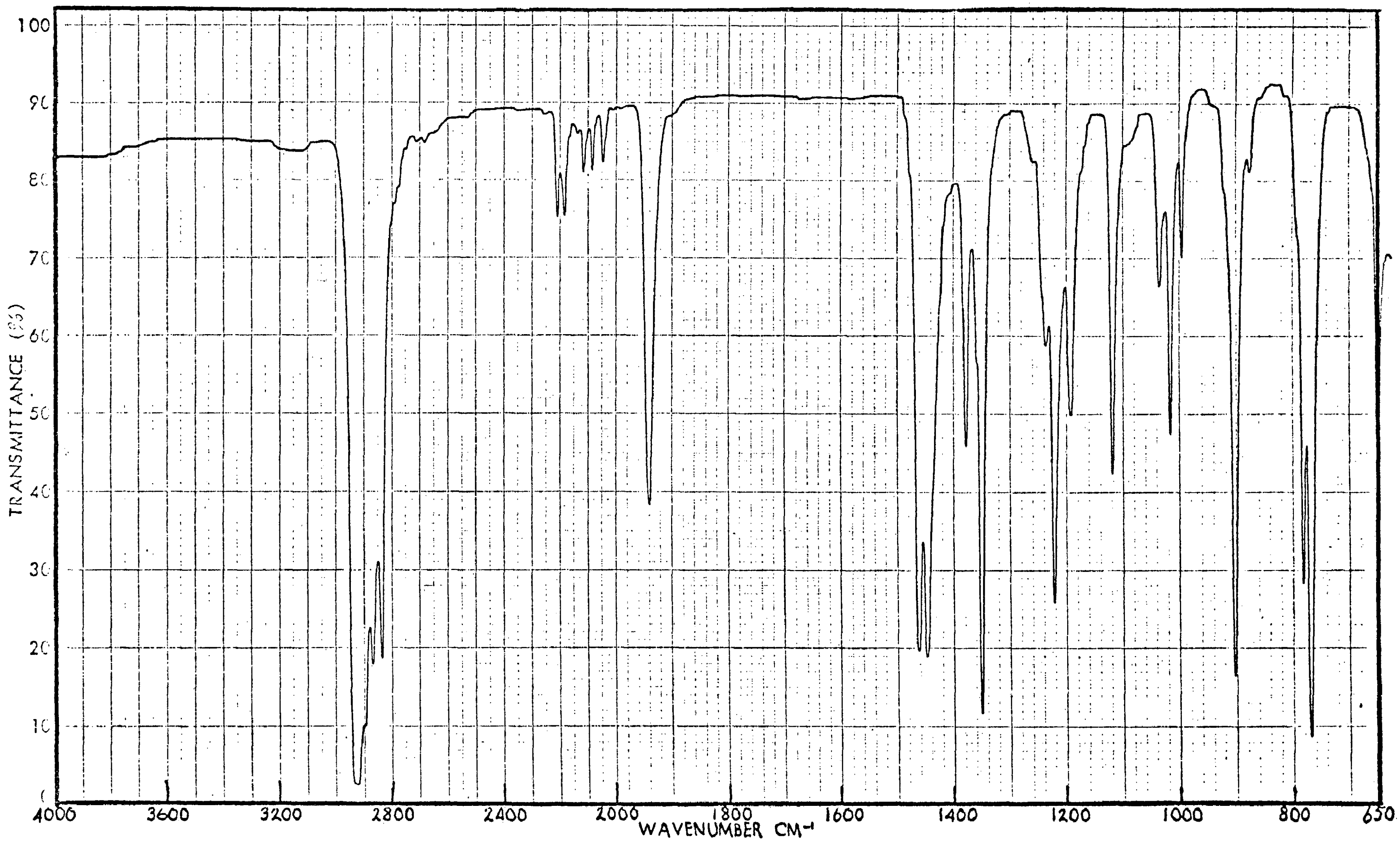


Figure 10

Nmr Spectrum of 3-Bromo-2,2,6,6-tetramethyl-5-methyl-d_3-3,4-heptadiene

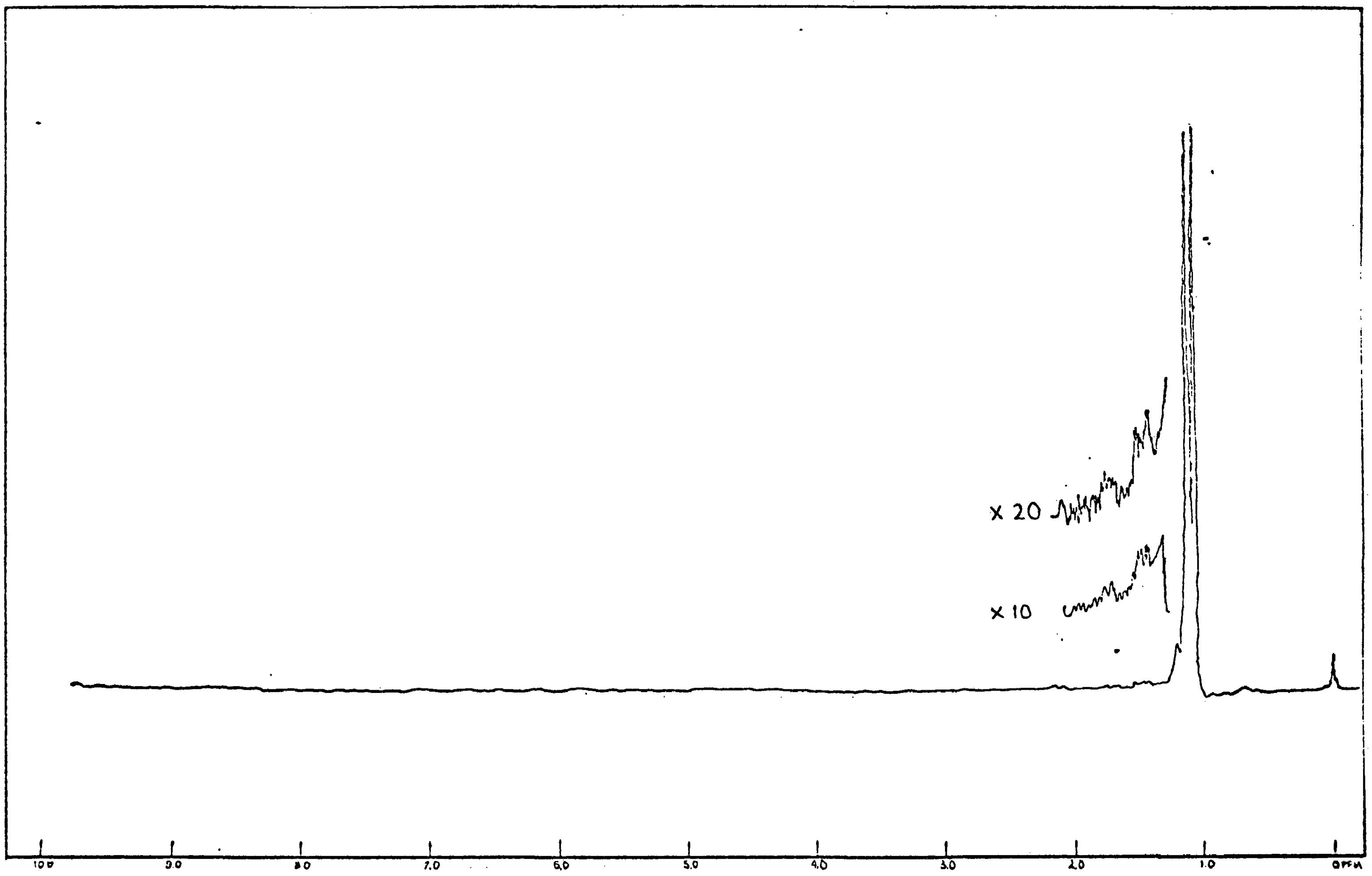


Figure 11

Infrared Spectrum of 2,2,3,6,6-Pentamethyl-4-heptyne-3-ol

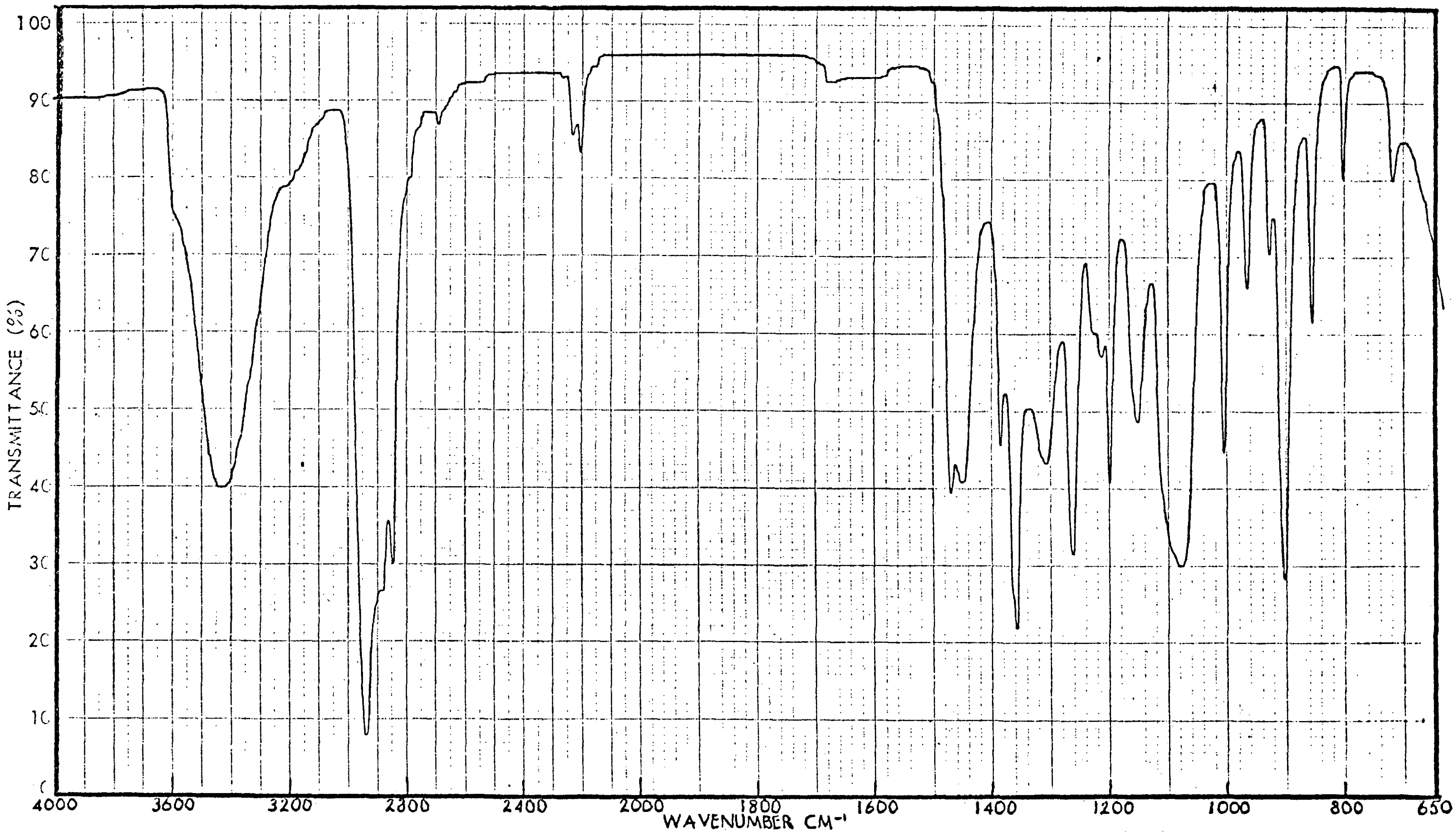


Figure 12

Nmr Spectrum of 2,2,3,6,6-Pentamethyl-4-heptyne-3-ol

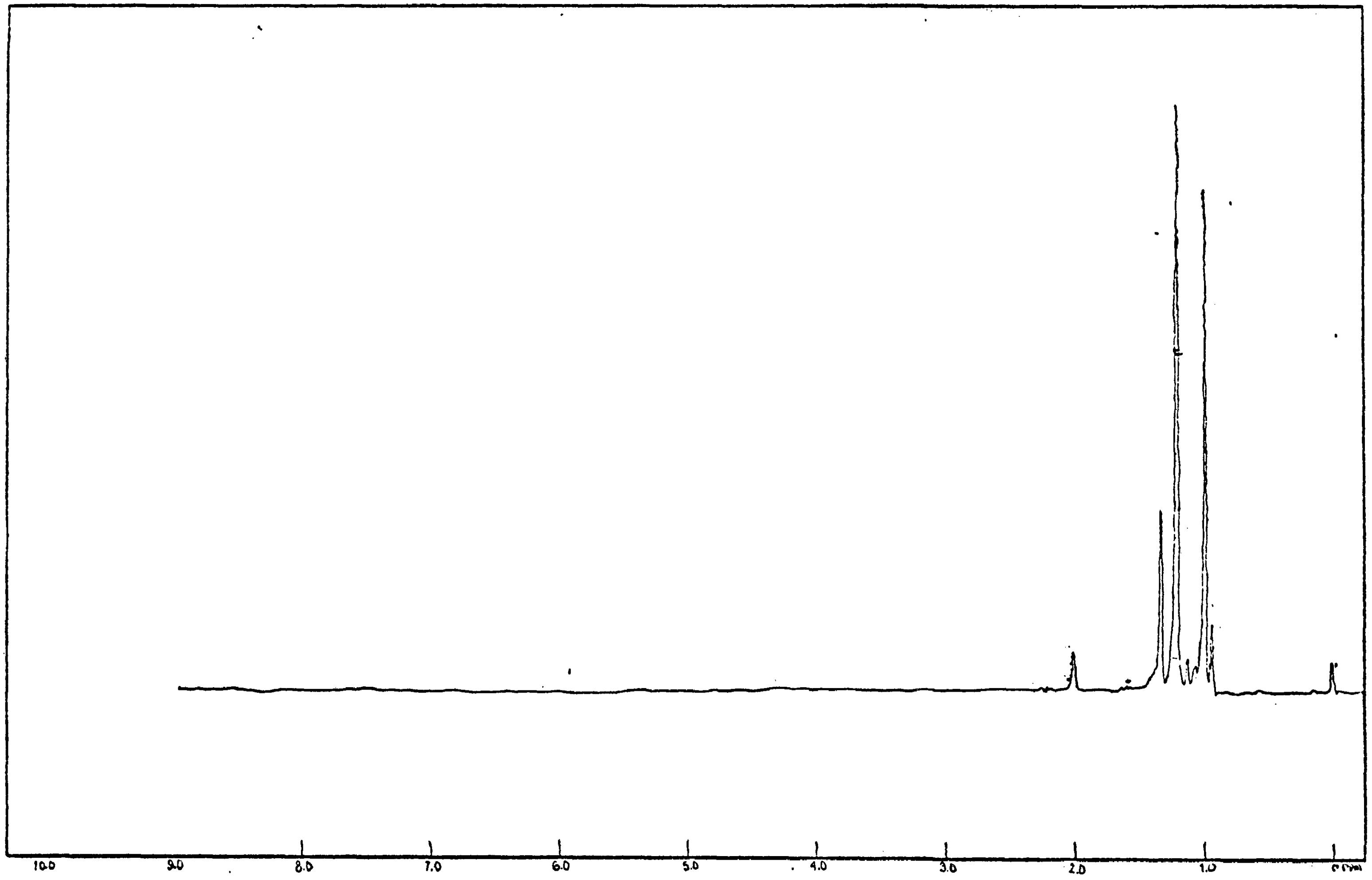


Figure 13

Infrared Spectrum of Products from Reaction of

2,2,3,6,6-Pentamethyl-4-heptyne-3-ol and Thionyl Chloride

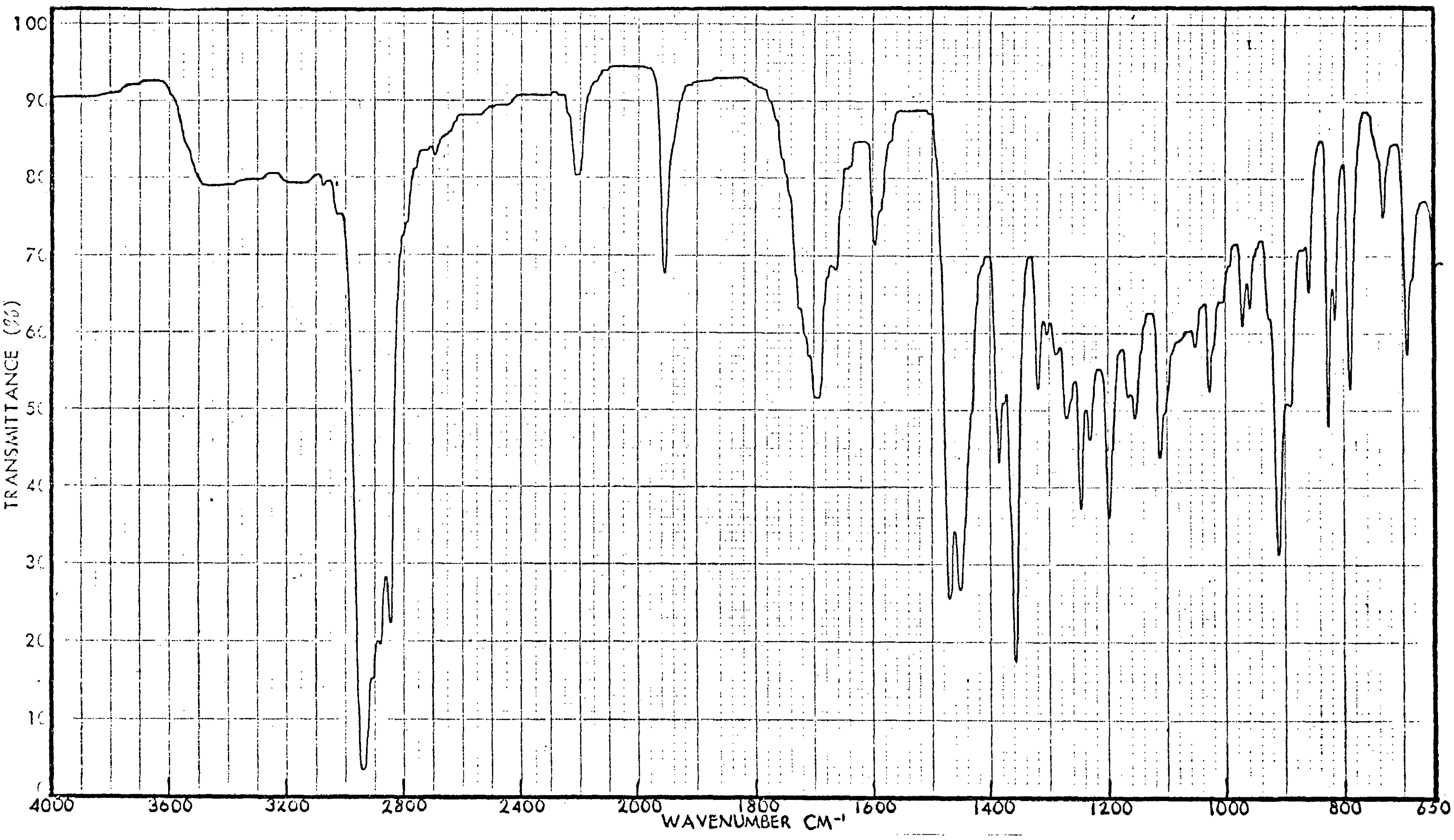


Figure 14

Nmr Spectrum of Products from Reaction of

2,2,3,6,6-Pentamethyl-4-heptyne-3-ol and Thionyl Chloride

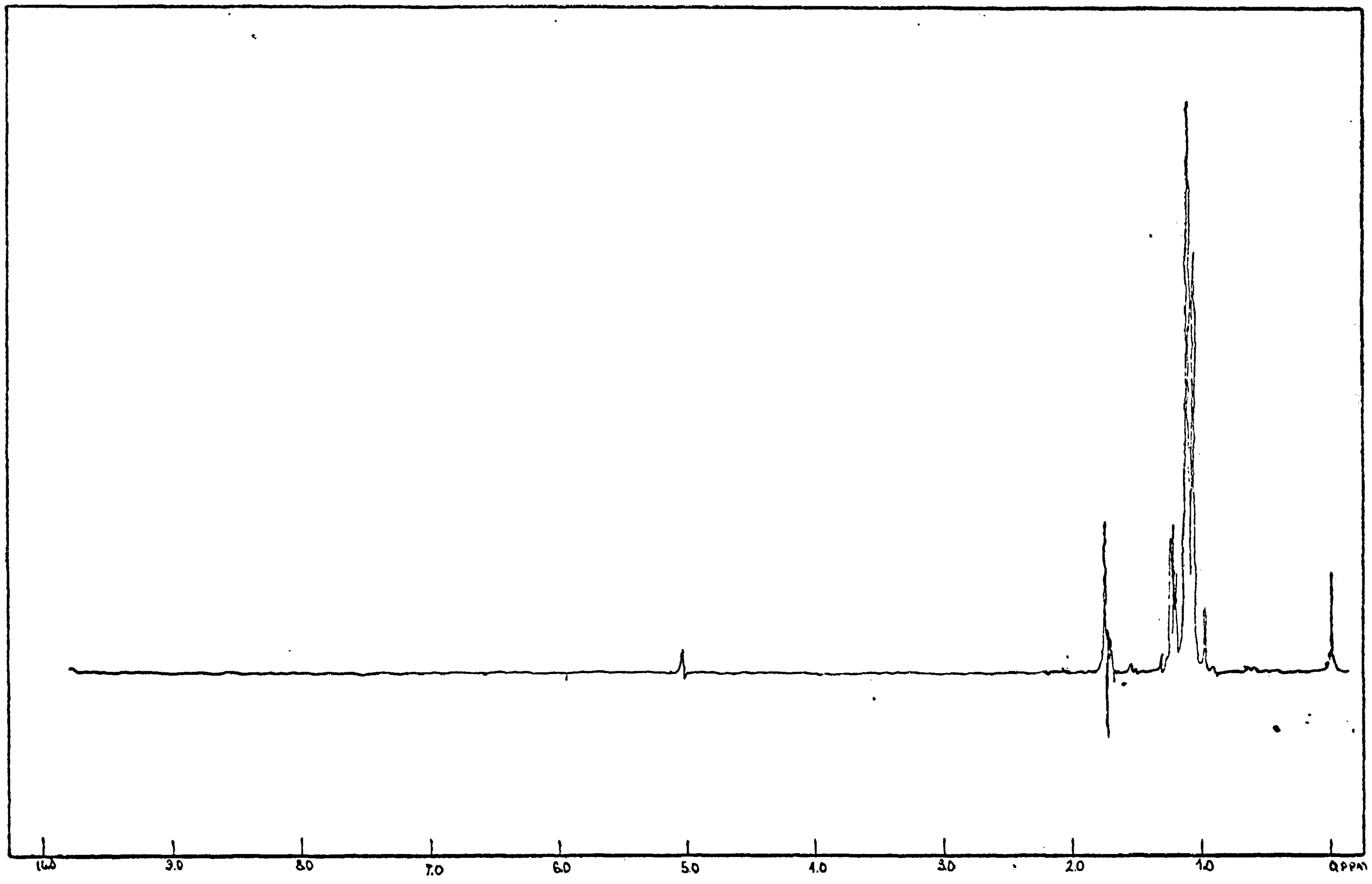


Figure 15

Infrared Spectrum of 3-Bromo-2,2,6,6-tetramethyl-5-*t*-butyl-3,4-heptadiene

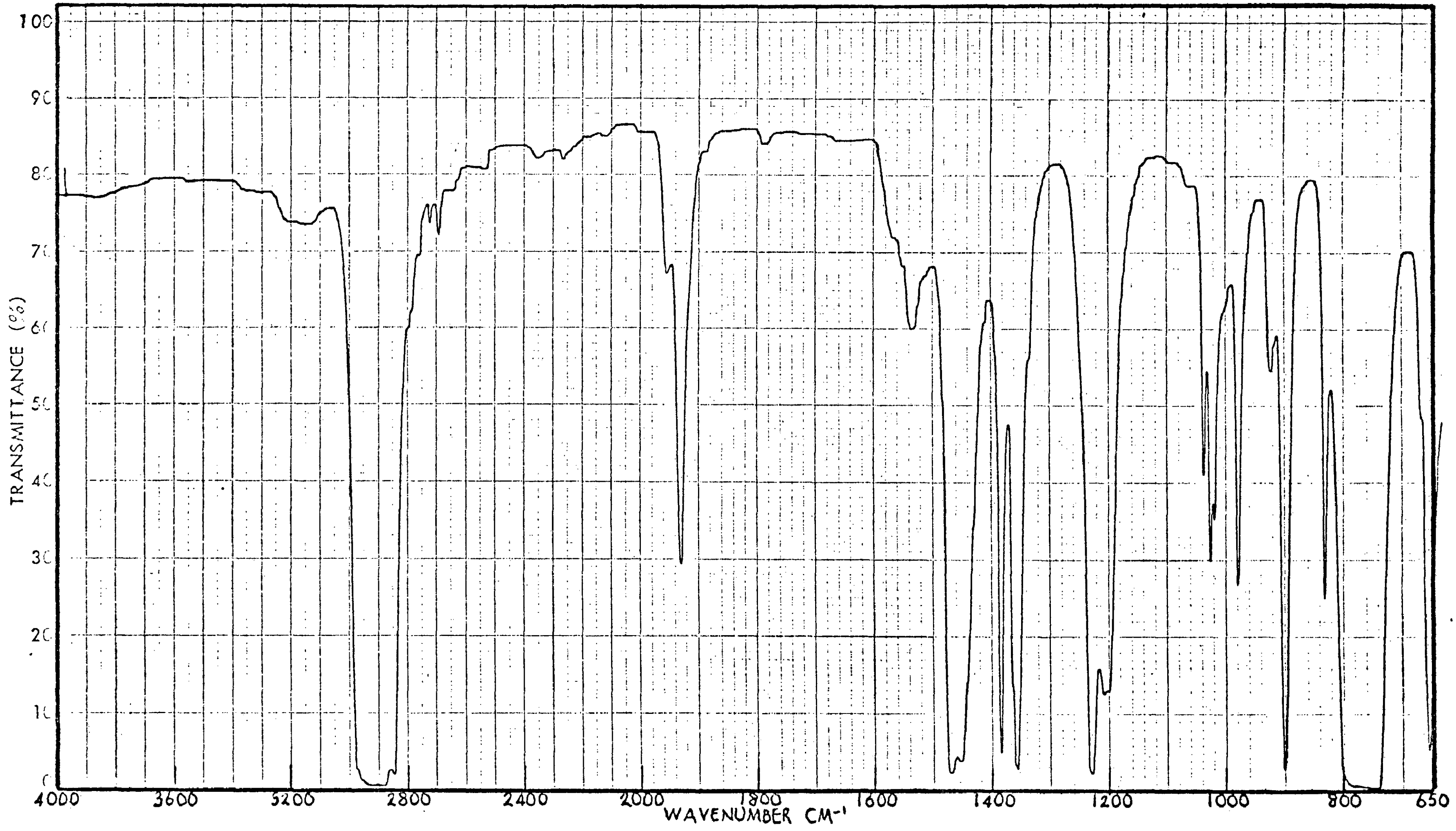


Figure 16

Nmr Spectrum of 3-Bromo-2,2,6,6-tetramethyl-5-*t*-butyl-3,4-heptadiene

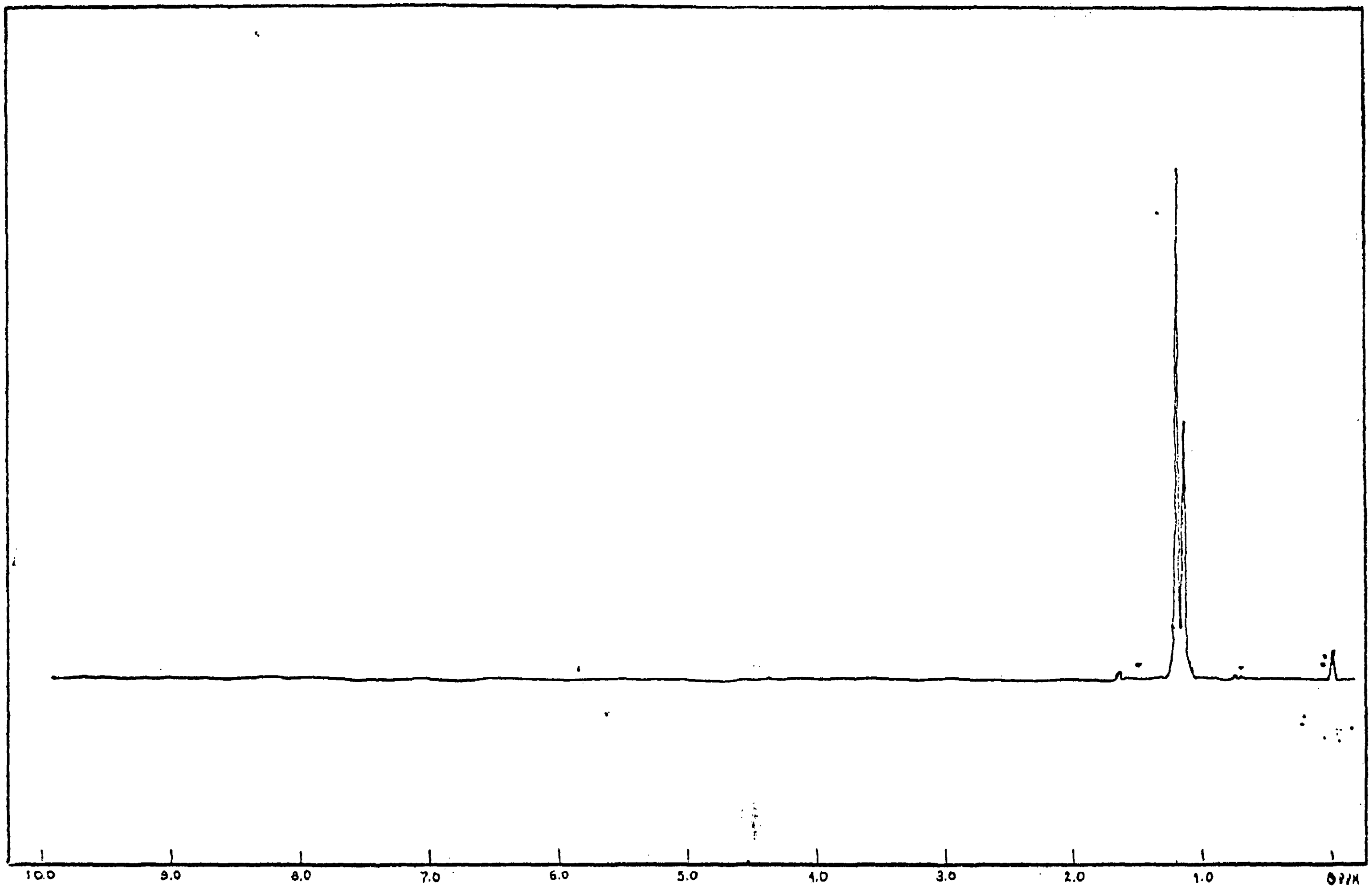


Figure 17

Infrared Spectrum of 2,2,6,6-Tetramethyl-3-*t*-butyl-4-heptyne-3-ol

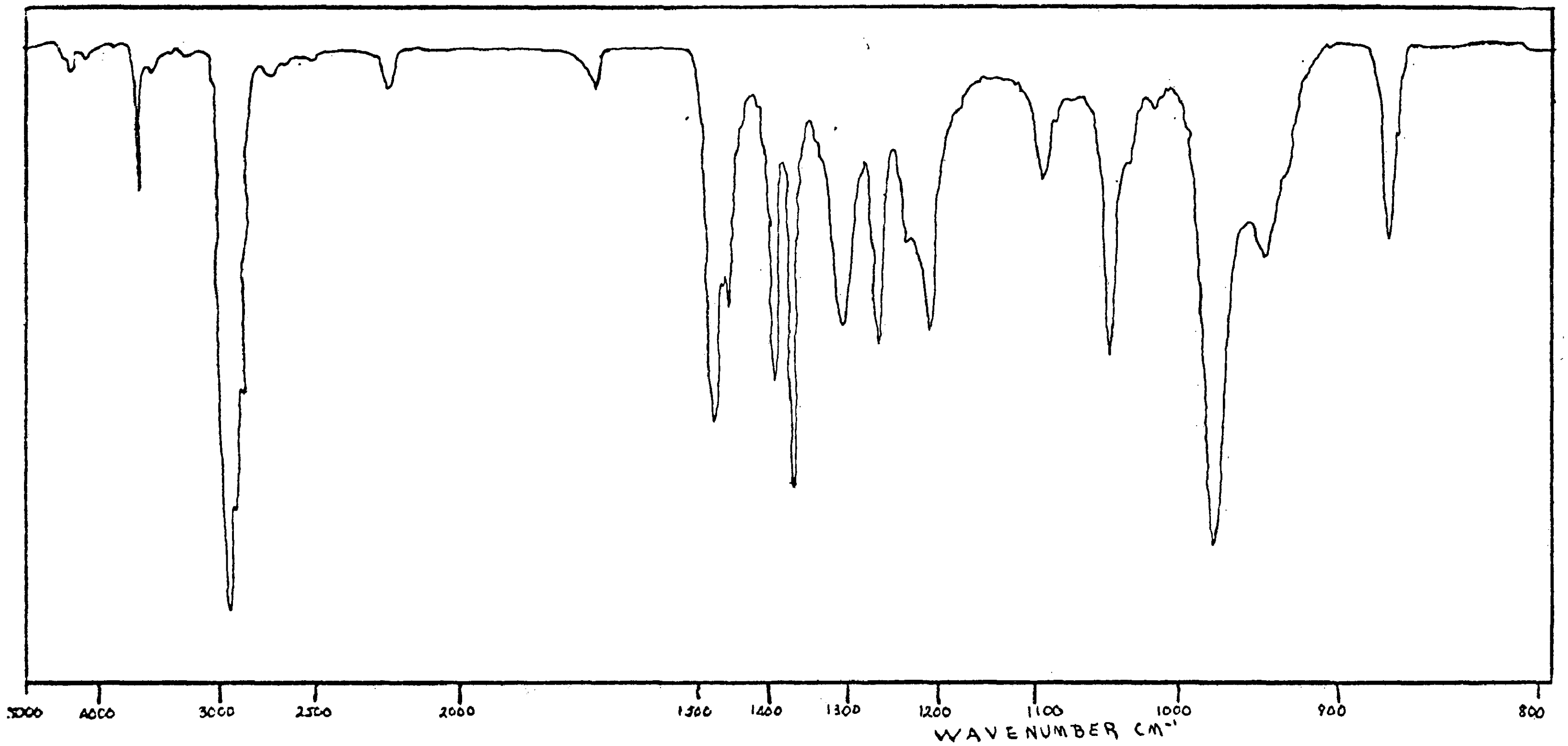


Figure 18

Infrared Spectrum of 3-Chloro-2,2,6,6-tetramethyl-5-*t*-butyl-3,4-heptadiene

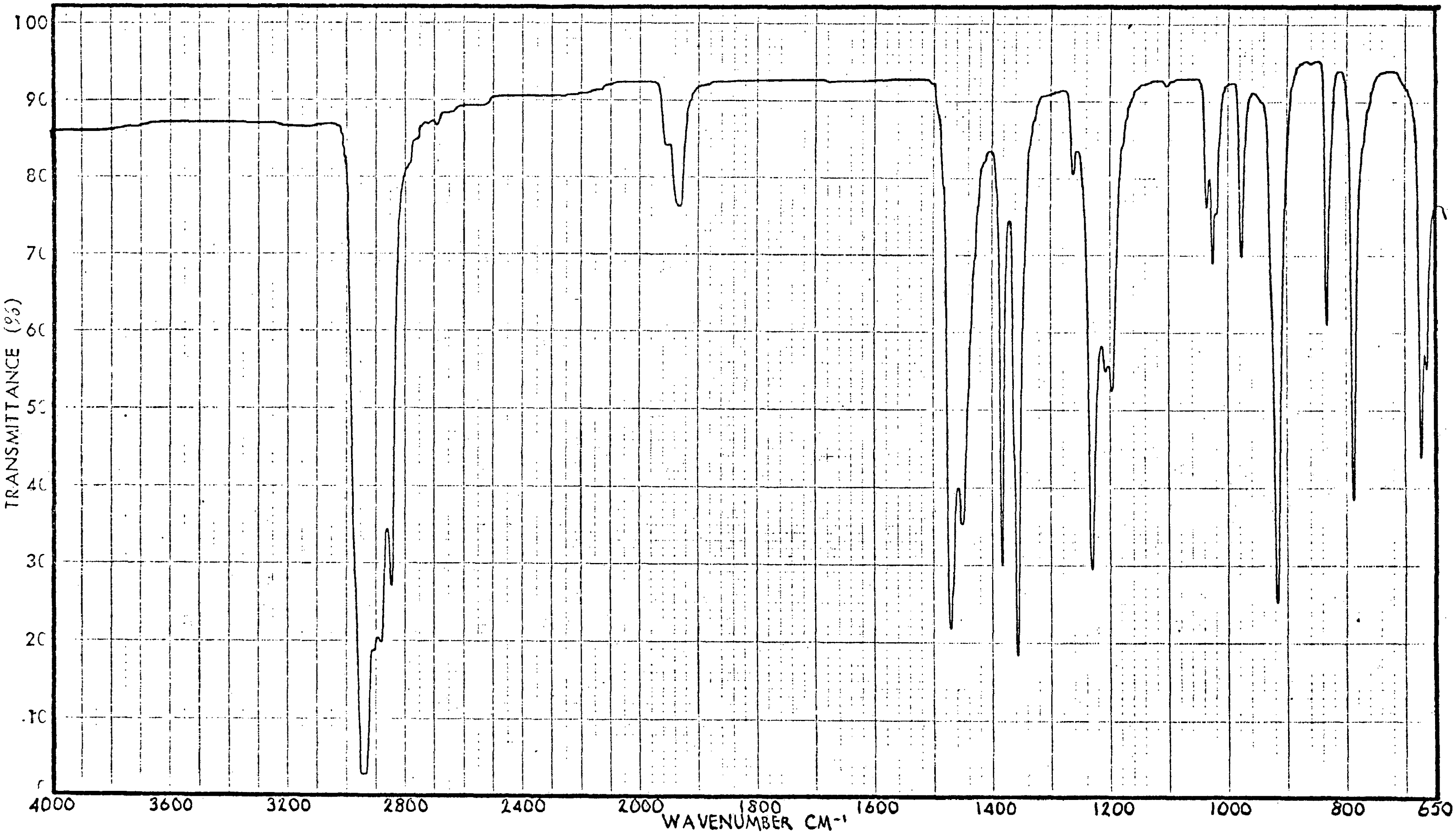


Figure 19

Nmr Spectrum of 3-Chloro-2,2,6,6-tetramethyl-5-*t*-butyl-3,4-heptadiene

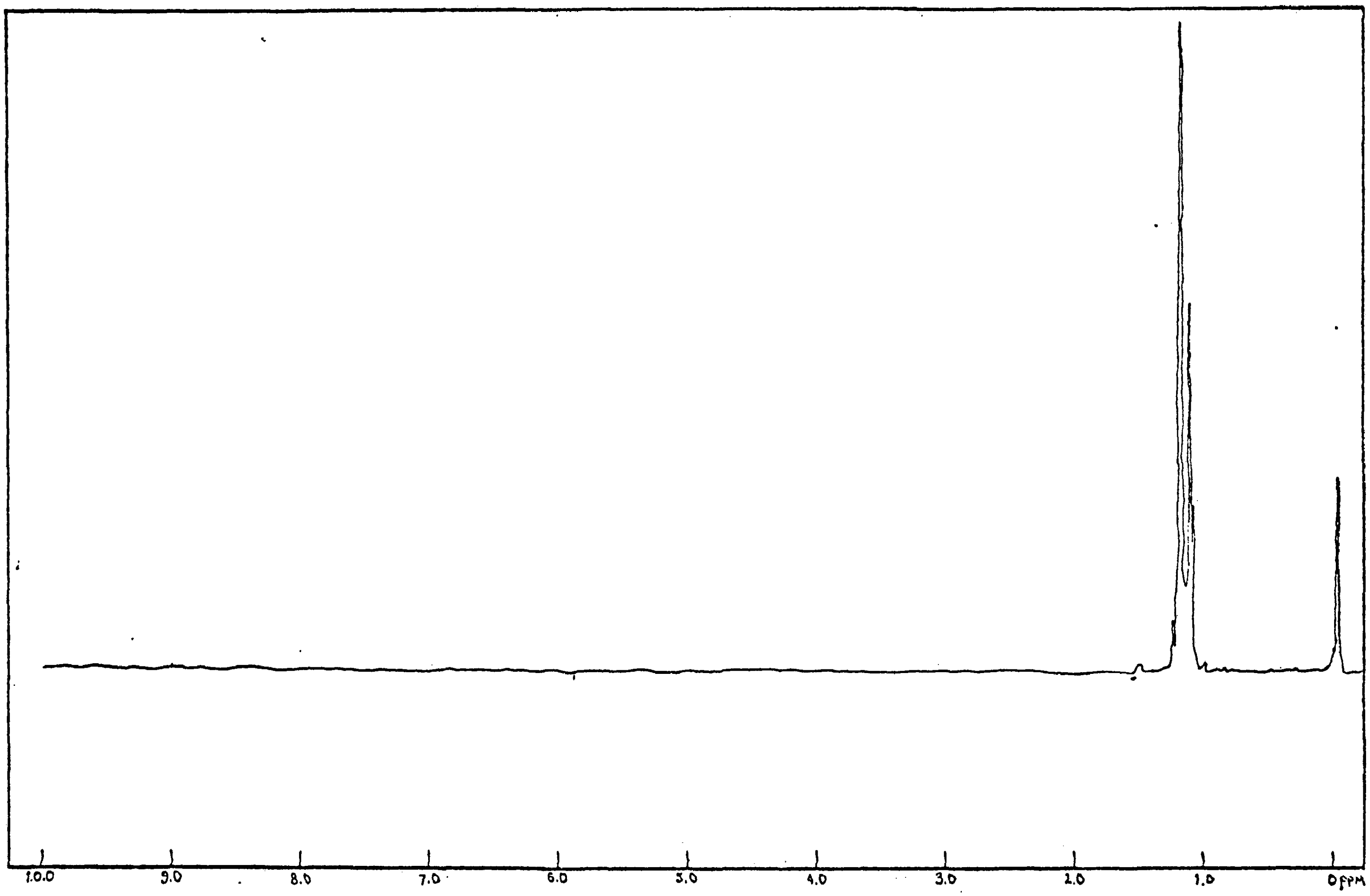


Figure 20

Sample First Order Kinetic Plot

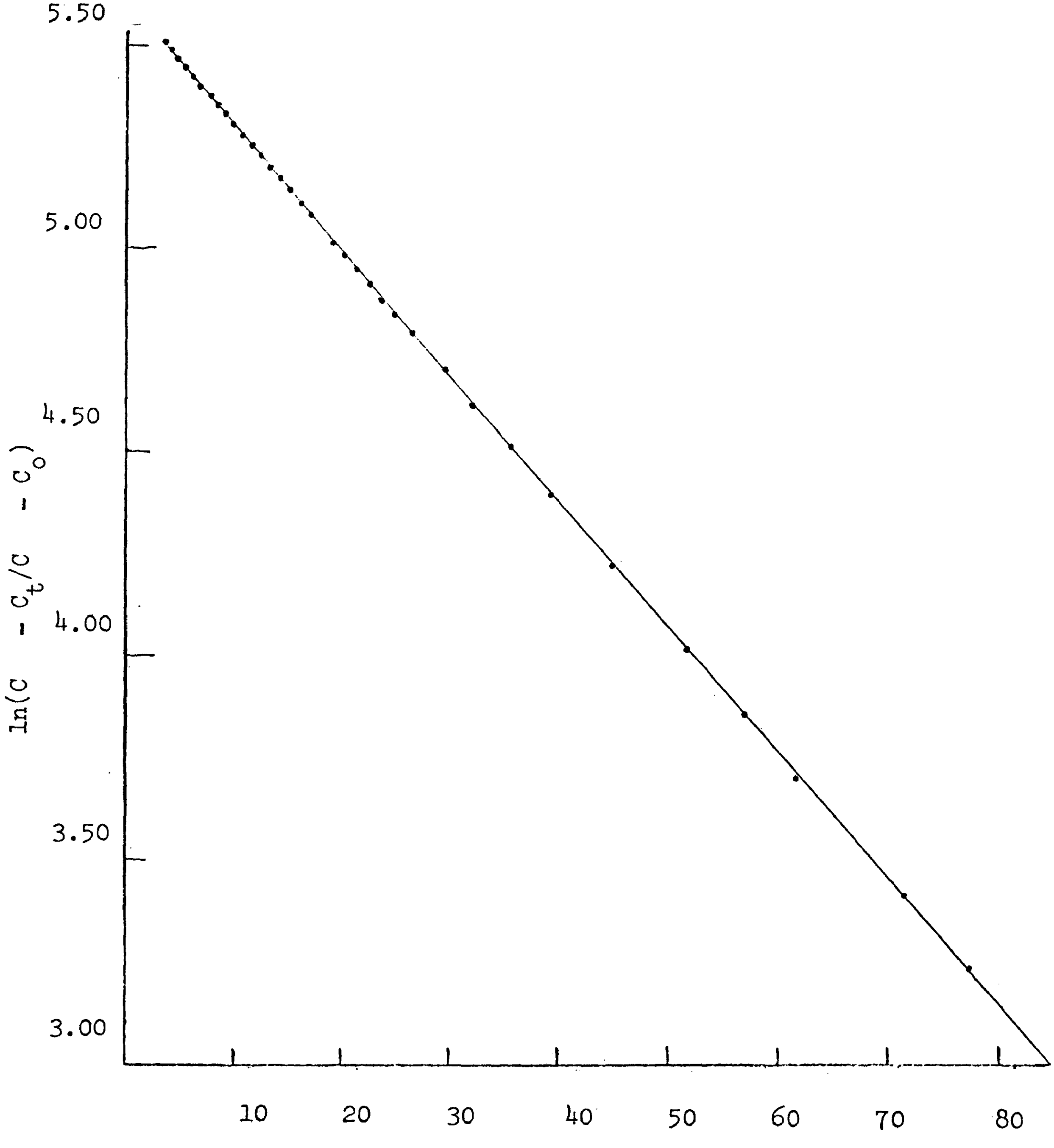


Figure 21

Sample Arrhenius Plot

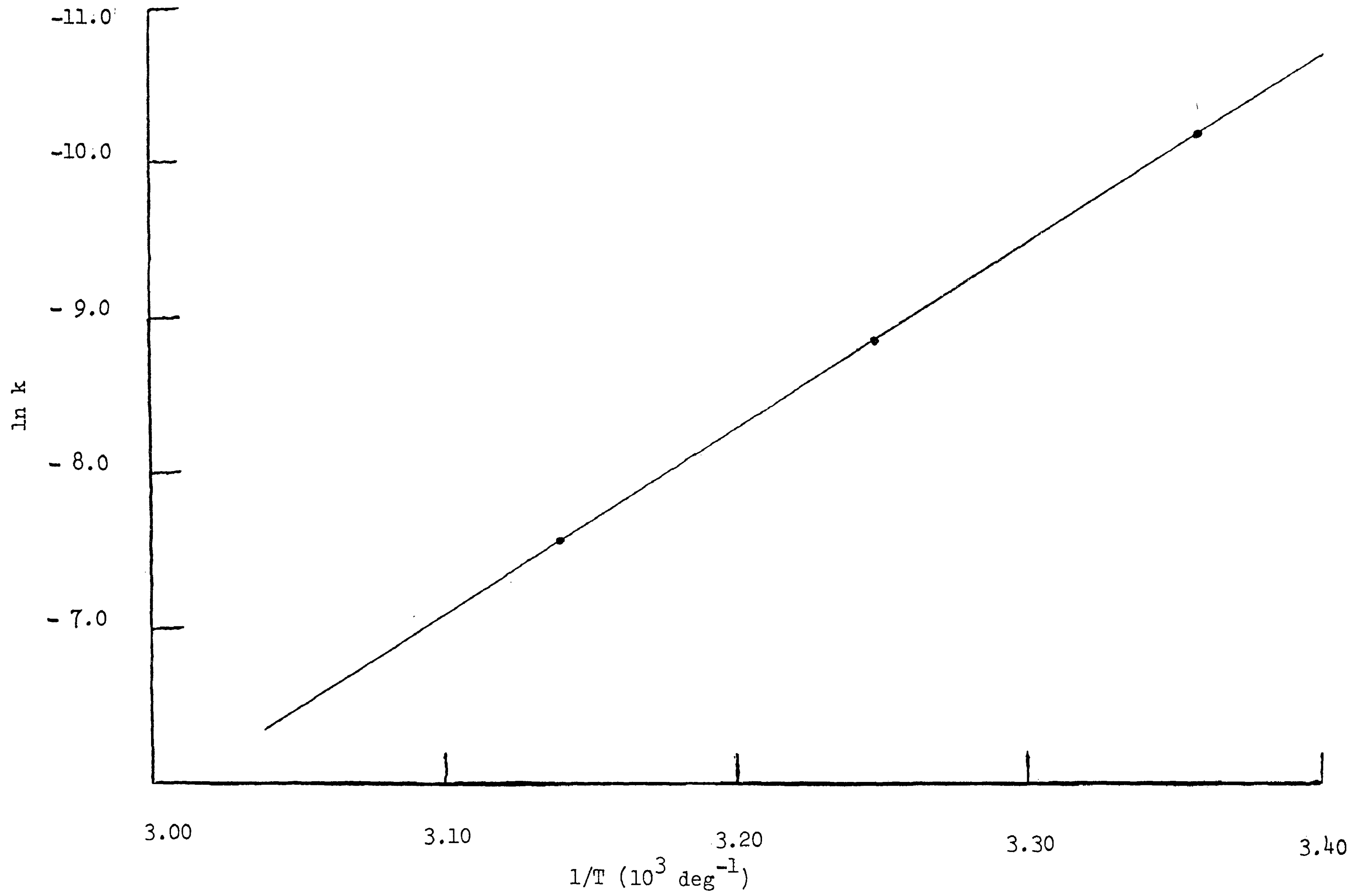


Figure 22

Sample Grunwald-Winstein Plot

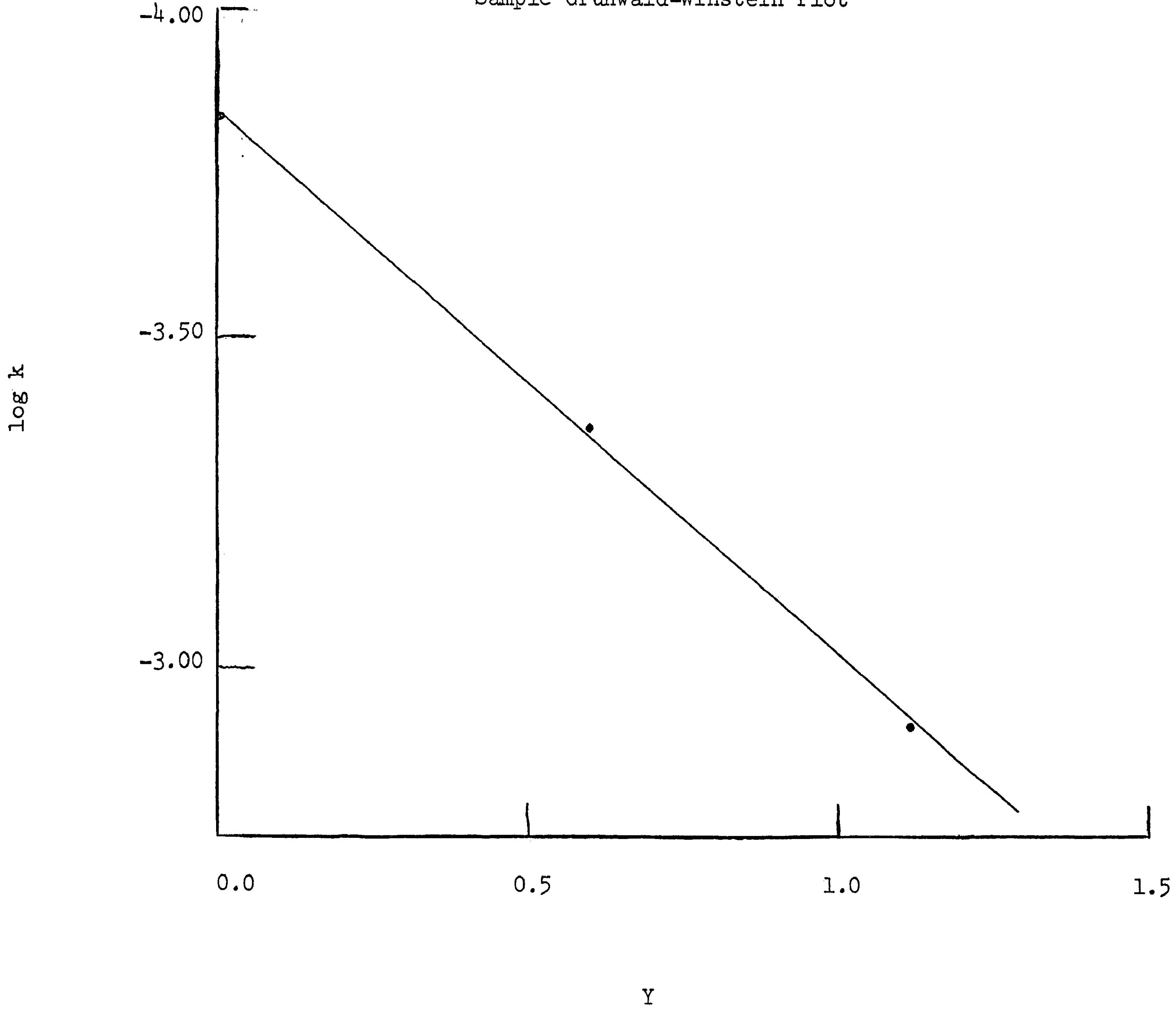


Table IV

Sample Output from LSG Program[a]

Time (min.)	Percent Reacted	Conductance Observed (micromhos)	Conductance Calculated Fit (micromhos)
1.99	5.96	490	490.1
2.64	7.82	540	540.18
3.28	9.63	590	591.7
3.91	11.37	640	639.9
4.58	13.18	690	690.1
5.24	14.93	740	738.6
5.94	16.75	790	788.9
6.64	18.53	840	838.1
7-38	20.37	890	889.1
8.13	22.19	940	939.5
8.90	24.02	990	990.1
9.69	25.85	1040	1041
10.48	27.63	1090	1090
11.30	29.44	1140	1140
12.15	31.27	1190	1191
13.18	23.42	1250	1250
13.89	34.86	1290	1290
14.98	37.02	1350	1350
15.74	38.48	1390	1390
17.68	42.05	1490	1489
19.77	45.67	1590	1590
22.02	49.32	1690	1690
24.41	52.92	1790	1790
26.97	56.50	1890	1889
29.75	60.07	1990	1988
32.92	63.79	2090	2091
37.37	68.44	2220	2220
42.13	72.75	2340	2339
47.30	76.77	2450	2451
52.19	80.02	2540	2541
57.26	82.92	2620	2621
67.63	87.60	2750	2750
86.13	92.99	2900	2900

Table IV (cont'd)

Time (min.)	Percent Reacted	Conductance Observed (micromhos)	Conductance Calculated Fit (micromhos)
103.50	95.90	2980	2980
128.60	98.11	3040	3041
210.00	99.85	3091	3089

$k = 5.14 \times 10^{-4} \text{sec}^{-1}$

[a] 5.47×10^{-4}M 3-Bromo-2,2,5,6,6-pentamethyl-3,4-heptadiene in 80:20 ethanol water (v/v) at 45.32°C.

Table V

Sample Output from ACTENG Program[a]

	FINAL VALUE	STANDARD DEVIATION
Arrhenius A	1.20×10^{13} sec^{-1}	2.53×10^{12}
Arrhenius E_a	23.8 kcal/mole	0.13
$\Delta S^{\ddagger}$	-0.7 eu	0.4
$\Delta H^{\ddagger}$	23.2 kcal/mole	0.13

Calculated Arrhenius Rate Constants

TEMPERATURE (°C)	RATE CONSTANT (sec^{-1})
25.00	4.03×10^{-5}
35.00	1.49×10^{-4}
45.00	5.06×10^{-4}
55.00	1.60×10^{-3}

[a] 3-Bromo-2,2,5,6,6-pentamethyl-3,4-heptadiene in 80:20 ethanol:water (v/v) solutions.

RESULTS

First order kinetic rate constants, the average of triplicate determinations are tabulated in Table VI.

The Grunwald-Winstein *m* value for 1,3-di-*t*-butyl-3-methylbromoallene is 0.87 ± 0.009 at 25°, 0.81 ± 0.01 at 35°, and 0.72 ± 0.05 at 45° (two points only) in aqueous ethanol. For tri-*t*-butylbromoallene, $m = 1.06 \pm 0.02$ at 45° in the same solvent.

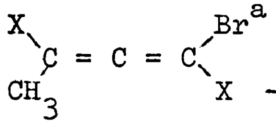
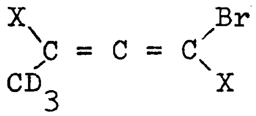
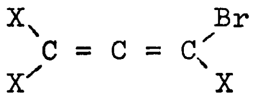
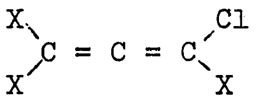
The activation parameters for these compounds are reported in Table VII.

The element effect k_{Br}/k_{Cl} for tri-*t*-butylhaloallene was determined to be 14.6 in 50:50 ethanol:water, at 45.32°C. It may also be noted that the rate of reaction is increased 18-fold by replacement of the *t*-butyl group on C_3 with a methyl group (70:30 ethanol:water, 45.32°C).

The β-secondary isotope effects for d_3 substitution on the 3-methyl group were determined under four different solvent and temperature conditions. Corrected to 100% deuteration, these values are listed in Table VIII.

Table VI

First Order Kinetic Rate Constants in Aqueous Ethanol

COMPOUND	TEMPERATURE, °C	SOLVENT COMPOSITION ETHANOL:WATER (v/v)	10^4k, sec^{-1}
 $(X)(CH_3)C=C=C(Br)(X)$ [a]	45.32 ± 0.02	90:10	1.49 ± 0.03
		80:20	5.15 ± 0.04
	34.68 ± 0.02	80:20	1.47 ± 0.02
		70:30	4.28 ± 0.03
		60:40	12.1 ± 0.1
	24.58 ± 0.01	80:20	0.376[b]
		70:30	1.14 ± 0.02
		60:40	3.64 ± 0.06
 $(X)(CD_3)C=C=C(Br)(X)$	45.32 ± 0.02	90:10	1.22 ± 0.01
		80:20	4.31 ± 0.04
	24.57 ± 0.01	70:30	0.980 ± 0.004
		60:40	3.10 ± 0.04
 $(X)_2C=C=C(Br)(X)$	45.32 ± 0.02	70:30	0.733 ± 0.004
		60:40	2.52 ± 0.05
		50:50	9.71 ± 0.02[c]
	24.62 ± 0.01	50:50	0.610 ± 0.005[c]
 $(X)_2C=C=C(Cl)(X)$	45.33 ± 0.02	50:50	0.666 ± 0.02[c]

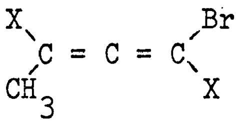
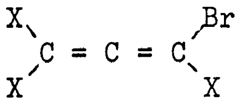
[a] 4.0 - 5.7 x 10^4M; X represents a *t*-butyl group.

[b] One run only.

[c] Duplicate determination.

Table VII

Activation Parameters for 1,3-Di-*t*-butyl-3-methylbromoallene and Tri-*t*-butylbromoallene

COMPOUND[d]	SOLVENT ETHANOL:WATER (v/v)	$\Delta F^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger a}$ (eu)	$\Delta H^{\ddagger}$ (kcal/mole)	E_a (kcal/mole)
 $X(CH_3)C=C=C(Br)X$	80:20	23.4 ± 0.1	-0.7 ± 0.4	23.2 ± 0.1	23.8 ± 0.1
	70:30	22.7 ± 0.1	-2.3 ± 1.0[b]	22.1 ± 0.1	22.7 ± 0.1
 $X_2C=C=C(Br)X$	50:50	23.3 ± 0.1	9.0 ± 0.4[c]	26.0 ± 0.1	26.6 ± 0.1

[a] At 25°.

[b] Third point extrapolated using Grunwald-Winstein *m* value at 45°.

[c] Two points only.

[d] X represents a *t*-butyl group.

Table VIII

β-Secondary Deuterium Isotope Effects for 1,3-Di-*t*-butyl-3-methylbromoallene

TEMPERATURE (°C)	SOLVENT ETHANOL:WATER (v/v)	k_H/k_D	ΔΔF (cal/D)
45.32 ± 0.02	90:10	1.26	47.1
	80:20	1.23	43.6
24.57 ± 0.01	70:30	1.19	35.2
	60:40	1.22	39.2

CONCLUSION

It may reasonably be concluded that the solvolysis of 1,3-di-*t*-butyl-3-methylbromoallene, Ia, in aqueous ethanol solutions proceeds by an S_N1 mechanism, though a more detailed analysis of ion pair behavior is not possible on the basis of present information. Measured values for the β-secondary isotope effect, the Grunwald-Winstein *m* value and $\Delta S^\ddagger$ will each be examined in turn and shown to be consistent with the proposed mechanism and with previous work in this area. The excellent first order kinetics observed are prerequisite to this conclusion, but do not eliminate the possibility that "pseudo" first order kinetics are actually ocurring. The two are indistinguishable under the flooded conditions in which the solvent is one of the reactants.

Activation Parameters

The observed values for $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for Ia in 80% aqueous ethanol at 25° are 23.2 ± 0.1 kcal/mole and -0.7 ± 0.4 eu, respectively. The magnitude of these parameters in 70% aqueous ethanol at 25° is 22.1 ± 0.1 kcal/mole and -2.3 ± 1.0 eu, respectively, well within the range of other values observed for similar S_N1 reactions in each case (Table IX). Anticipated $\Delta S^\ddagger$ values for addition-elimination reactions, S_N2, S_N2', and solvent addition across a double bond are much more negative than the above, as would be addition of water to form the anion (Figure 23). However, $\Delta S^\ddagger$ for elimination-addition reactions not leading to a charged transition state (Figure 24) should be large positive numbers. A rather special case of the latter type is the Hennion mechanism for basic solvolysis.[14,18,38] This type of reaction involves initial abstraction of an acetylenic hydrogen from a propargyl (or allenyl) halide, followed by rate determining halide ions to form the zwitterzion-carbene (Figure 25) and this is not structurally feasible in this case. This mechanism also involves a large positive $\Delta S^\ddagger$ (Table IX).

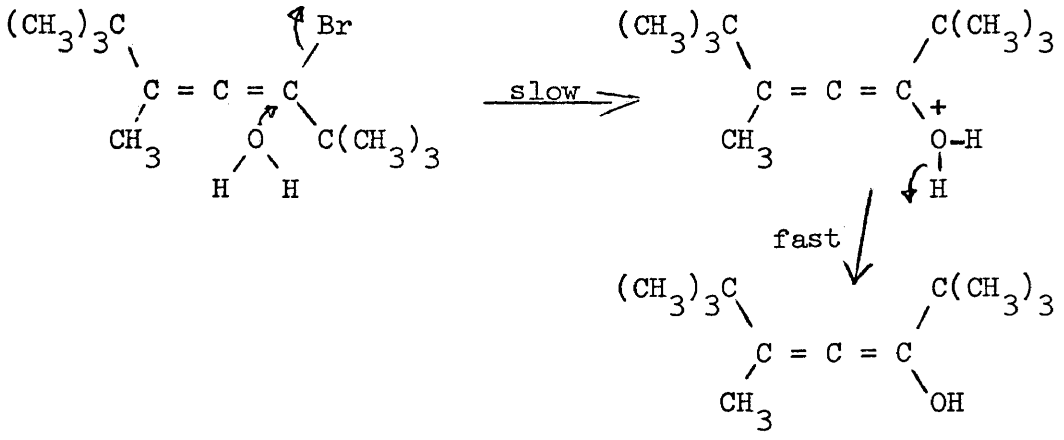
A limiting value for the $\Delta S^\ddagger$ of each reaction type cannot be established, as may be seen in Table IX, for the value may vary considerably for a given compound with temperature and solvent composition. The parameter is still a valuable guideline within these limitations. Of those mechanisms generally considered to be possible for solvolysis reactions[1], the measured value of $\Delta S^\ddagger$ is most consistent with an S_N1 process.

For the structurally analogous compound 1,3,3-tri-*t*-butylbromoallene, $\Delta S^\ddagger$ was determined to be 9.0 eu ± 0.4 eu in 50% aqueous ethanol at 25°. This positive $\Delta S^\ddagger$ is unusual, and the most positive measured to date for a solvolysis reaction of this type, although positive values are not unknown. A value of 4.5 ± 0.9 eu had previously been

Figure 23

Addition-Elimination Mechanisms

1a. Classical S_N2:



b. S_N2':

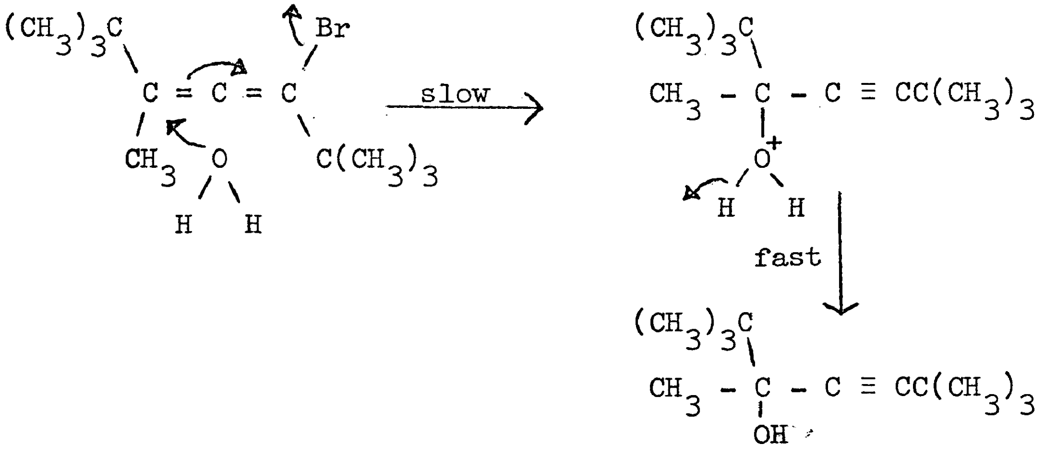
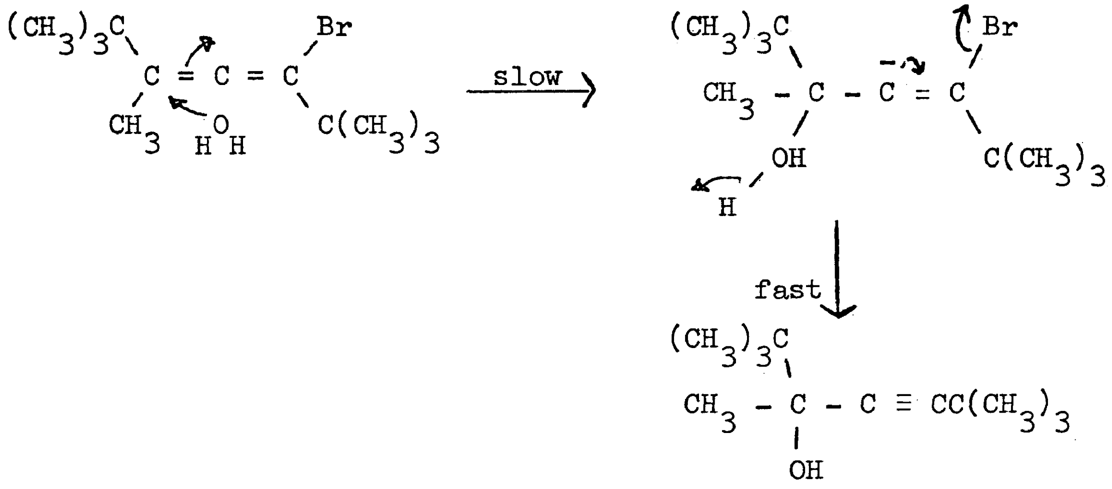


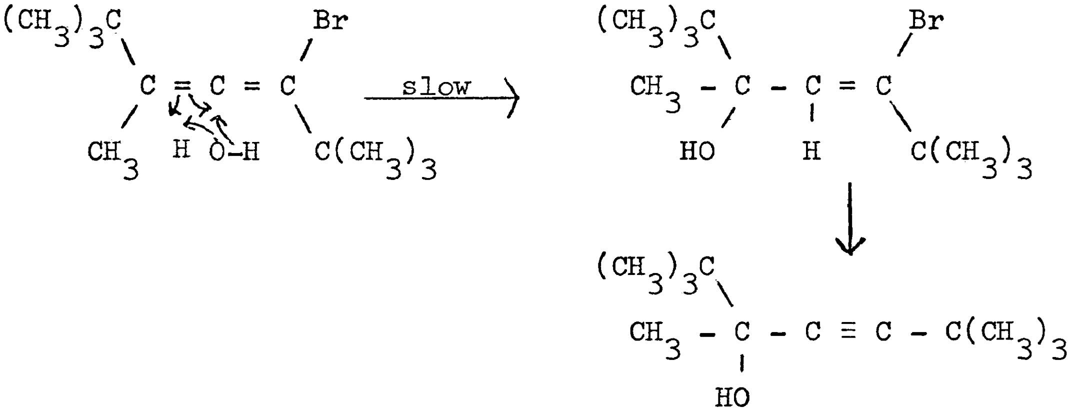
Figure 23 (cont'd)

2. Carbanion formation:



3. Water addition across a double bond:

a.



b.

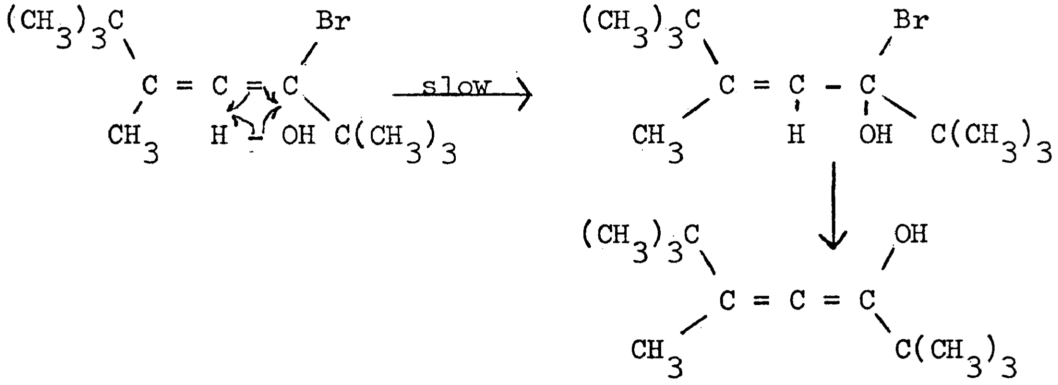
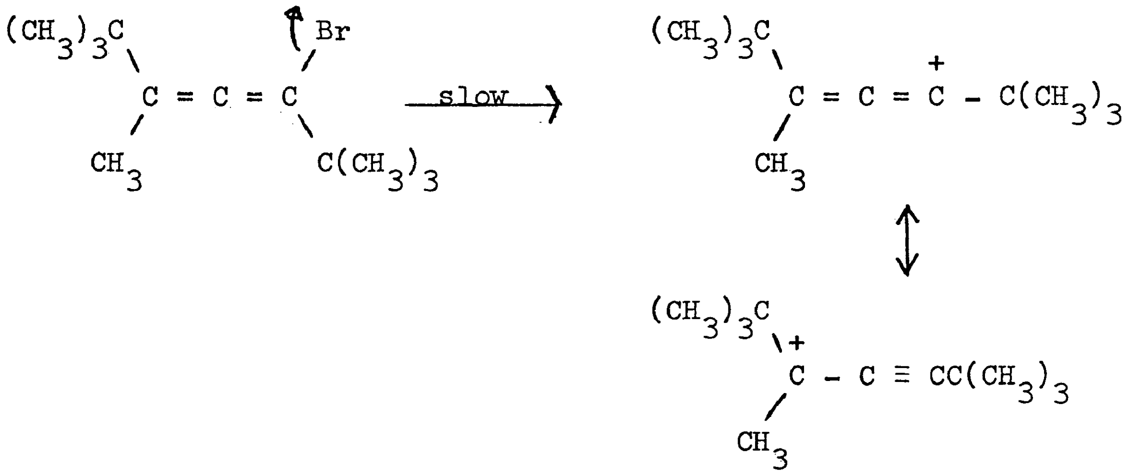


Figure 24

Elimination-Addition Mechanisms

1. Classical S_N1:



2. Halo-hydroelimination:

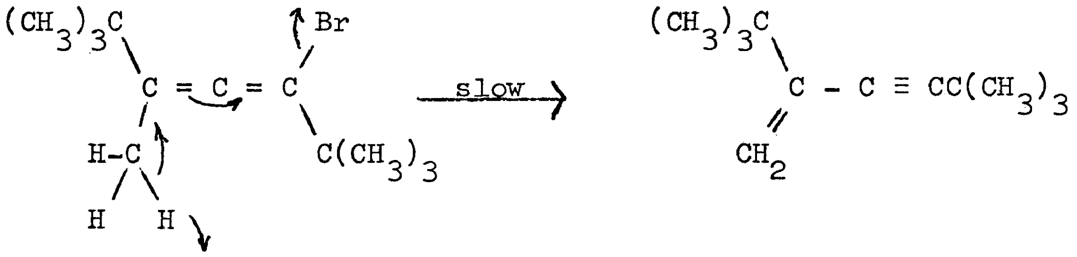


Table IX

Activation Parameters for Solvolysis Reactions

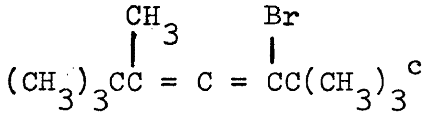
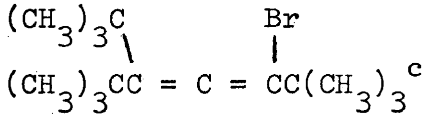
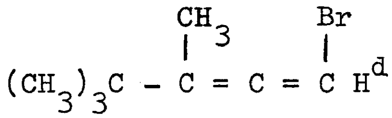
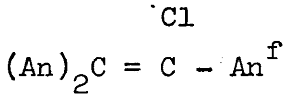
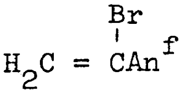
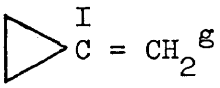
COMPOUND	REACTION CONDITION[a]	$\Delta H^{\ddagger}$ (kcal/mole)	$\Delta S^{\ddagger b}$ (eu)
 $(CH_3)_3C\overset{CH_3}{C}=C=\overset{Br}{C}C(CH_3)_3{}^{c}$	80% ETOH	23.2	-0.7
 $(CH_3)_3C\overset{(CH_3)_3C}{C}=C=\overset{Br}{C}C(CH_3)_3{}^{c}$	50% ETOH	26.0	9.0
 $(CH_3)_3C-\overset{CH_3}{C}=C=\overset{Br}{C}H^{d}$	70% TFE	21.9	-9.9
$CH_2=C=CHBr^{e}$	50% ETOH	24.9	-23.4
$H-C\equiv CCH_2Br^{e}$	50% ETOH	20.7	-20.9
 $(An)_2C=\overset{Cl}{C}-An^{f}$	80% ETOH	26.8	-14.0
 $H_2C=\overset{Br}{C}An^{f}$	80% ETOH	27.0	-7.0
	77.5% MeOH	23.3	-21.2
$CH_3CH_2OTs^{h}$	HOAc	24.4	-16.7

Table IX (cont'd)

[a] Aqueous solutions, volume percent.

[b] Calculated at 25°.

[c] This work.

[d] Reference 44, weight percent 2,2,2-trifluoroethanol.

[e] C.V. Lee, R.J. Hargrove, T.E. Dueber, and P.J. Stang, *Tetrahedron Letters*, 2519 (1971).

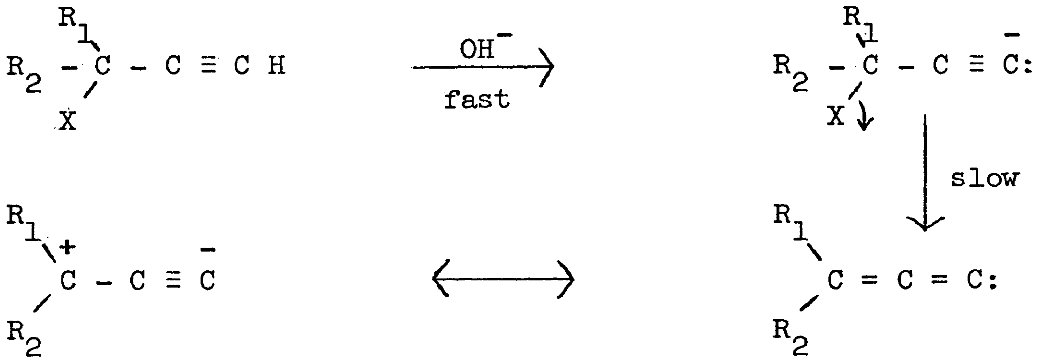
[f] Reference 42.

[g] S.A. Sherrod and R.G. Bergman, *J. Am. Chem. Soc.*, *91*, 2115 (1969).

[h] Reference 48.

Figure 25

The Hennion Mechanism for Solvolysis in Base



found for the chloro analog of this compound (40:60, acetone:water, 25°).[39] Macomber measured $\Delta S^{\ddagger}$ for the acetolysis for 1,3-di-*t*-butyl propargyl tosylate, V, at 3.6 eu.[17] He suggested that this was due to the high stability of the cation, but may also have some dependence upon the steric hinderance to solvation expected of this series substituted with bulky *t*-butyl groups.

Solvent Effects

The Grunwald-Winstein *m* parameter[7] was employed to measure reaction sensitivity to solvent changes. The magnitude of *m* is assigned on the basis of an empirical, linear free energy relationship, $\log k = \log k_0 + mY$. The value of *m* is measured relative to $m = 1.0$ for the reference reaction of *t*-butylchloride solvolysis in 80% aqueous ethanol at 25°C. The "Y" value is equal to 0.0 for this solvent and has been determined for many other solvent systems, as well. The relationship is best applied only within a given solvent system of varying proportions, as it was to aqueous ethanol solutions in this study.

The *m* value for Ia is 0.87 ± 0.009 at 25°C and decreases to 0.72 ± 0.05 at 45°. This, too, is well within the range (greater than 0.5) of the carbonium ion mechanism (Table I). The magnitude of the observed values is indicative of some reaction sensitivity to the change in solvent polarity induced by varying the proportions of ethanol and water. This presumably arises from charge development in the transition state. S_N2-type reactions show smaller values for *m*, generally less than 0.5 (Table X).

For a closely related system, tri-*t*-butyl-bromoallene, Ib, solvolysis at 45° in aqueous ethanol, *m* was measured at 1.06 ± 0.02. Tri-*t*-butylchloroallene has also been determined to have an *m* value of 1.22 in aqueous acetone at 55°.[6] The decrease in sensitivity from tri- to the di-*t*-butyl substituted compound may be due in part to increased hyperconjugative charge delocalization *via* the C-H bonds in the 3-methyl group of Ia.[27] However, this structural change should also allow for increased solvation, in opposition to previous explanations of low *m* values on the basis of low solvation.[40-42] The low values for the solvolysis of these triarylvinyl halides may be due more to the elevated temperatures employed, charge delocalization through aromatic resonance, and non-S_N1 processes than hitherto supposed.

In a further investigation of this system, solvolysis was carried out in 2,2,2-trifluoroethanol (TFE) - water solutions. The compositions of these solutions was so ordered as to have a similar "Y" value to other solvent systems already examined. However, the TFE solution has much less nucleophilic character than ethanol[43] and any part of the reaction proceeding by initial nucleophilic attack would lead to an overall rate depression. Rate enhancement by a factor of roughly 800-1000 was instead observed for tri-*t*-butylchloroallene.[44] This is much larger than that previously observed for 1-phenylethyl chloride[43] (Table X), *t*-butyl chloride[45,46] (Table X), or 2-adamantyl tosylate[47] (k_{TFE}/k_{ETOH} = 7.8). On the other hand, nucleophilic solvent-assisted isopropyl tosylate solvolysis has a rate ratio, k_{TFE}/k_{ETOH}, equal to 0.33, showing rate retardation with decreased nucleophilicity. In a similar study

Table X

Solvent and Isotope Effects for Solvolysis Reactions

COMPOUND	SOLVENT[a]	TEMPERATURE	$\frac{k_{TFE}}{k_{ETOH}}$ /m	ISOTOPE EFFECTS[b] β	 γ
$(CH_3)_3C - \overset{CH_3}{\overset{\vert}{C}} = C = C(Br)C(CH_3)_3$	70% ETOH	25°	/0.87	1.19(35.2)	
$H\text{-}C \equiv CC(CH_3)_2Br^c$	80% ETOH	25°	/	1.84(60)	
$CH_3C \equiv C(CH_3)_2Cl^d$	80% ETOH	25°	/0.95	1.655(50)	1.092(9)
$CH_3C \equiv CCH(CH_3)Br^e$	50% ETOH	25°	0.73/	1.200(35)	1.08(15)
$H\ D\ C = C(Ph)OSO_2F^f$	90% ETOH	50°	0.625^g/ 0.56	1.45(220)	
$Ph\ CH(CH_3)Cl^h$	60% ETOH	25°	6.2/0.91	1.226(40)	
$(CH_3)_3\ C\ Cl^h$	50% ETOH	25°	1.07/1.00	2.368(56.7)	
$(CH_3)_2CHOBs^i$	70% TFE[j]	25°	$0.2/0.44^k$	1.537(42.4)	
ETOTs[l]	aqueous ETOH	50°	$0.01^g/0.25$	1.11(10.3)	

Table X (cont'd)

[a] Aqueous solutions (v/v).

[b] $\Delta\Delta F$ cal/D in parentheses.

[c] Reference 19.

[d] Reference 20.

[e] Reference 22.

[f] Reference 40. Isotope effect is for acetolysis.

[g] k_{HOAC}/k_{ETOH}.

[h] Reference 43.

[i] V.J. Shiner, Jr., R.D. Fisher, and W. Dowd, J. Am. Chem. Soc., 91, 7748 (1969).

[j] Weight percent aqueous solution.

[k] m value from aqueous ethanol.

[l] Reference 48. Isotope effect is for acetolysis.

using acetic acid as the solvent of lesser nucleophilicity, $k_{HOAC}/k_{ETOH} = 0.01$ was observed for ethyl tosylate and ethyl triflate[48] compared to 7.7 for 2-adamantyl tosylate.[49] Other compounds are now being investigated to determine if the unusually large effect exists throughout the alkyl allenyl series.

In summary then, the magnitude of the Grunwald-Winstein *m* parameter measured for 1,3-di-*t*-butyl-3-methyl-bromoallene renders improbable an uncharged transition state, but does not eliminate the possibility of initial nucleophilic attack leading to a more or less stable carbanion. From the results of similar solvolysis in TFE, one may conclude that this is unlikely, but the considerable rate enhancement observed is unexplained for the present. The carbonium ion mechanism remains most consistent with experimental evidence.

β-Secondary Deuterium Isotope Effects

Deuterium substitution on or around the proposed reaction site may be used principally to determine if a given carbon-hydrogen bond is broken in a rate-determining step. This "primary" isotope effect is by far the largest of the possible carbon-deuterium interactions since the rate-retarding difference in bond energies is most directly involved in the transition state. However, "secondary" isotope effects on α, β, or even more remote carbon atoms may also be observed. These effects are somewhat sensitive to conditions at the reaction site through the steric, inductive, and hyperconjugative interactions previously described. A β-secondary isotope effect was consequently measured for 1,3-di-*t*-butyl-3-methylbromoallene, Ia, as an additional indicator of mechanism.

Rate constants for the 1,3-di-*t*-butyl-3-methyl-d_3-bromoallene were measured and compared to the undeuterated form. Though this compound is actually deuterium substituted on the δ-carbon, an effect closer to the values for β-substitution in the propargyl systems is observed (Tables III and X) due to the existence of the propargyl resonance form.

β-deuterium isotope effects are generally much larger in S_N1 reactions, where interaction with an empty p-orbital is possible, than in S_N2 reactions, involving the crowding pentavalent transition state. The most direct comparison of isotope effects may be made by calculating $\Delta\Delta F = RT\ln k_H/k_D$, as was done for each compound in Table X. For the trialkylhaloallene, Ia, under study here, $\Delta\Delta F = 39.2$ cal/D, is a value fairly typical of a β-secondary deuterium isotope effect in S_N1 solvolysis. It is smaller than that observed for 3-bromo-3-methyl-1-butyne[19] (Table X). This is consistent with increased charge delocalization to the allenic resonance form over the primary allenyl cation generated in the latter situation. In 2-bromo-3-pentyne[22] more charge delocalization of this type would be expected to occur and the isotope effects are, indeed, very nearly equivalent.

Structural Effects

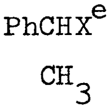
Two types of structural effects will be discussed here, leaving group changes, and replacement of alkyl groups in the allenyl halide. An element effect, k_{Br}/k_{Cl}, representing a structural alteration of the former type, was measured in aqueous ethanol for Ib, tri-*t*-butylbromoallene. Large values for this ratio indicate R-X bond breaking at or before the transition state (Table XI). The observed value of 14.6 is the lowest to date for an S_N1 reaction. In aqueous acetone k_{Br}/k_{Cl} was 19.9 for the same compound.[44] Values close to these have been found for 3-halo-3-methyl-1-butyne and 1-phenylethyl halide (Table XI) in aqueous ethanol solutions.

Low values for k_{Br}/k_{Cl} introduce the possibility that some rate determining addition of water across a double bond is occurring. The tremendous rate enhancement (800-1000) observed in the transition from aqueous ethanol to an aqueous TFE solution (with much less water present) renders this unlikely here. Also, the magnitude of this element effect for 1-phenylethyl halide, where the above reaction is not structurally feasible, somewhat diminishes the importance of such an alternative.

The second structural alteration studied was replacement of the 3-*t*-butyl group with a 3-methyl. This resulted in an 18-fold rate increase. There have been many instances in which such effects have been observed, originally by Nathan and Baker in 1935.[50] Burawoy and Spinner[16] studied one system designed to eliminate steric effects, a p-alkyl substituted series which showed a rate enhancement of 1.96 ($k_{Me}/k_{t\text{-}Bu}$), thus following the Nathan-Baker order of substituent effects. This was very close to the value[16] observed for the more structurally similar 2-chloro-2-methyl-3-pentyne, IVb, and 2-chloro-2,5,5-trimethyl-3-hexyne, IVe ($k_{Me}/k_{t\text{-}Bu} = 1.8$, Figure 1). The remainder of the rather large value observed here is undoubtedly due to increased solvation upon substitution for the bulky

Table XI

Element Effects in S_N1 and S_N2 Solvolysis Reactions

COMPOUND	REACTION[a] CONDITIONS	MECHANISM	k_{Br}/k_{Cl}
CH_3CH_2X[b]	ETO^-, ETOH, 40°	S_N2	42
$CH_3CH_2CH_2X$[c]	ETO^-, ETOH, 30°	S_N2	62.5
$CH_2 = CH - CH_2X$[a]	ETO^-, ETOH, 40°	S_N2	52.6
$PhCH_2X$[d]	pyridine, 90% ETOH, 30.5°	S_N2	50
 $\underset{CH_3}{\mathrm{PhCHX}}$[e]	80% ETOH, 25°	S_N1	20.2
t-BuX[f]	80% ETOH, 25°	S_N1	39.3
$HC \equiv C - C(CH_3)_2X$[g]	80% ETOH, 25°	S_N1	19.5
$(t\text{-Bu})(Ph)C = C = C(t\text{-Bu})$[h]	50% DMK, 35°	S_N1	56

[a] Aqueous solutions, volume percent.

[b] C.H. Grant and C.N. Hinshelwood, J. Chem. Soc., 258 (1933).

[c] A. Streitwieser, Jr., "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N.Y. (1962) p.30.

[d] J.W. Baker, J. Chem. Soc., 2631 (1932).

[e] Reference 25.

[f] Reference 7.

[g] References 16 and 18.

[h] Reference 5. DMK is acetone(dimethylketone).

t-butyl group. The inverse effect found when relief of backstrain is important ($k_{Me}/k_{t\text{-}Bu} = 0.829$ for $RC(CH_3)_2Cl$) is not expected to contribute significantly.

Solvolysis Reactivity

A final look at the relative rates of alkyl, aryl, vinyl, and allenyl halides may prove enlightening. It may be seen in Table XII that the allenyl halides are more reactive than is generally appreciated, especially in comparison to vinyl halides. 1,3-Di-*t*-butyl-3-methylbromoallene, for example, is intermediate in reactivity to 1-phenylethyl chloride and bromide[25], faster than *t*-butyl chloride[51] and much faster than the triarylvinyl halides.[42] It shows the expected slower rate in comparison to similar propargyl derivatives.[20,22]

Table XII

Relative Rates of Halide Solvolysis[a]

COMPOUND	RELATIVE RATE
$PhC(CH_3)_2Cl$[b]	2030.
$CH_2 = CHC(CH_3)_2Cl$[c]	53.
$(Ph)_2CHCl$[d]	46.
$CH_3C \equiv CC(CH_3)_2Cl$[e]	14.6
$(CH_3)_2CClC \equiv CCH_3$[f]	14.4
$CH_3CH_2C \equiv CC(CH_3)_2Cl$[e]	13.0
$(CH_3)_3CBr$[d]	9.7
$(CH_3)_2CHC \equiv CC(CH_3)_2Cl$[e]	9.1
$(CH_3)_3CC{\equiv}CC(CH_3)_2Cl$[e]	7.4
$PhCH(CH_3)Br$[g]	5.4
$(t\text{-}Bu)(CH_3)C = C = C(t\text{-}Bu)Br$[h]	1.0
$CH_3CH_2C(CH_3)_2Cl$[i]	0.42
$(CH_3)_3CC(CH_3)_2Cl$[e]	0.31
$PhCH(CH_3)Cl$[g]	0.29
$(CH_3)_2CHC(CH_3)_2Cl$[d]	0.24
$(CH_3)_3CCl$[j]	0.24
$HC \equiv CC(CH_3)_2Br$[k,p]	0.12
$CH_2 = CHCH(CH_3)Cl$[d]	0.01
$HC \equiv CC(CH_3)_2Cl$[e,l]	0.006
$(CH_3)_2CHBr$[m]	0.002
$CH_2 = C(An)Br$[n,q]	0.00008
$(CH_3)_2CHCl$[c]	0.00005

Table XII (cont'd)

COMPOUND	RELATIVE RATE
2-adamantyl Br^{m}	0.000003
$(An)_2C = C\ (An)Br^{n,q}$	0.000003
$CH_2 = C = CHBr^{o,p}$	o.0000001

[a] 80:20 ethanol:water (v/v) at 25°.

[b] C.G. Swain and E.R. Thornton, J. Am. Chem. Soc., 84, 817 (1962).

[c] H.G. Richey, Jr., and J.M. Richey, "Carbonium Ions," G.A. Olah and P.V.R. Schleyer, Eds., Wiley-Interscience, New York, N.Y., 1970, Vol. II., pp. 931-949.

[d] Reference 7.

[e] Reference 16.

[f] Reference 20.

[g] Reference 25.

[h] This work.

[i] V.J. Shiner, Jr., J. Am. Chem. Soc., 75, 2925 (1953).

[j] Reference 51.

[k] Reference 18.

[l] Reference 14.

[m] J.L. Fry, J.M. Harris, R.C. Bingham, and P.V.R. Schleyer, J. Am. Chem. Soc., 92, 2540 (1970).

[n] Reference 42.

[o] Reference 15.

[p] Extrapolated using Grunwald-Winstein equation.

[q] Extrapolated using Arrhenius equation.

BIBLIOGRAPHY

1. P.J. Stang, *Adv. Phys. Org. Chem.*, *10*, 000 (1972). (In press).
2. M. Hanack, *Acc. Chem. Res.*, *3*, 209 (1970).
3. G. Modena and U. Tonellato, *Adv. Phys. Org. Chem.*, *9*, 185 (1971).
4. Z. Rappaport, *Adv. Phys. Org. Chem.*, *7*, 98 (1969).
5. (a) M.D. Schiavelli, S.C. Hixon, and H.W. Moran, *J. Am. Chem. Soc.*, *92*, 1082 (1970); (b) M.S. Schiavelli, S.C. Hixon, H.W. Moran, and C.J. Boswell, *J. Am. Chem. Soc.*, *93*, 6989 (1971).
6. M.D. Schiavelli, R.P. Gilbert, W.A. Boynton, and C.J. Boswell, *J. Am. Chem. Soc.*, *94*, 5061 (1972).
7. E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, *70*, 846 (1948).
8. L.C. Bateman, M.G. Church, E.D. Douglas, C.K. Ingold, and N. Taher, *J. Chem.Soc.*, 979 (1940).
9. L.L. Miller and D.A. Kaufman, *J. Am. Chem. Soc.*, *90*, 7282 (1968).
10. R. Sustmann, J. E. Williams, M.J.S. Dewar, L.C. Allen, and P.V.R. Schleyer, *J. Am. Chem. Soc.*, *91*, 5350 (1969).
11. C.U. Pittman, Jr., and G.A. Olah, *J. Am. Chem. Soc.*, *87*, 5632 (1965).
12. H.G. Richey, Jr., L.E. Rennick, A.S. Kushner, J.M. Richey, and J.C. Philips, *J. Am. Chem. Soc.*, *37*, 4017 (1965).
13. H.G. Richey, Jr., J.C. Philips, and L.E. Rennick, *J. Am. Chem. Soc.*, *87*, 1381 (1965).
14. G.F. Hennion and D.E. Maloney, *J. Am. Chem. Soc.*, *73*, 4735 (1951).
15. C.V. Lee, R.J. Hargrove, T.E. Dueber, and P.J. Stang, *Tetrahedron Letters*, 2519 (1971).
16. A. Burawoy and E. Spinner, *J. Chem. Soc.*, 3752 (1954).
17. R.S. Macomber, *Tetrahedron Letters*, 4639 (1970).
18. V.J. Shiner, Jr. and J.W. Wilson, *J. Am. Chem. Soc.*, *84*, 2402 (1962).

19. V.J. Shiner, Jr., J.W. Wilson, G. Heinemann, and N. Solliday, *J. Am. Chem. Soc.*, 2408 (1962).

20. V.J. Shiner, Jr., and G.S. Kriz, Jr., *J. Am. Chem. Soc.*, *86*, 2643 (1964).

21. V.J. Shiner, Jr., and J.S. Humphrey, Jr., *J. Am. Chem. Soc.*, *89* , 622 (1967).

22. V.J. Shiner, Jr., and W. Dowd, *J. Am. Chem. Soc.*, *93*, 1029 (1971).

23. A. Streitwieser, Jr., R.H. Jagow, R.C. Fahey, and S. Suzuki, *J. Am. Chem. Soc.*, *80*, 2326 (1958).

24. A.F. Thomas, "Deuterium Labeling in Organic Chemistry," Appleton-Century-Crofts, New York, N.Y., 1971, p.401.

25. V.J. Shiner, Jr., W.E. Buddenbaum, B.L. Murr, and G. Lamaty, *J. Am. Chem. Soc.*, *9D*, 418 (1968).

26. G.J. Karabatsos, G.C. Sonnichsen, G.G. Papaioannou, S.E. Scheppele, and R.L. Shone, *J. Am. Chem. Soc.*, *89*, 463 (1967).

27. E.L. Allred, D.M. Grant, and W. Goodlett, *J. Am. Chem. Soc.*, *87*, 673 (1965).

28. V.J. Shiner, Jr., and J.S. Humphrey, Jr., *J. Am. Chem. Soc.*, *85*, 2416 (1963).

29. D.S. Noy e and M.D. Schiavelli, *J. Am. Chem. Soc.*, *90*, 1023 (1968).

30. L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis," John Wiley and Sons, Inc., New York, N.Y.(1967) p.1158.

31. F.L. Griffith, Undergraduate Research, College of William and Mary, Williamsburg, Virginia, 23185, 1971-1972.

32. M.D. Schiavelli, Professor, College of William and Mary, Williamsburg, Virginia, 23185.

33. C.U. Pittman, Jr., and G.A. Olah, *J. Am. Chem. Soc.*, *87*, 5632 (1965).

34. J.H. Ford, C.D. Thompson, and C.S. Marvel, *J. Am. Chem. Soc.*, *57*, 2619 (1935).

35. D.H. Hunt, Professor, University of Virginia, Charlottesville, Virginia 22904.

36. T.L. Jacobs and D.M. Fenten, *J. Org. Chem.*, *30*, 1808 (1965).

37. D.F. Detar, "Computer Programs for Chemistry," W.A. Benjamin, Inc., New York, N.Y., 1968, Vol. I.

38. W.J. LeNoble, V. Tatsukami, and H.F. Morris, *J. Am. Chem. Soc.*, *92*, 5681 (1970).

39. W.A. Boynton, M.A. Thesis, College of William and Mary, Williamsburg, Virginia, 23185, 1971.

40. W. Jones, and D.D. Maness, *J. Am. Chem. Soc.*, *92*, 5457 (1970).

41. Z. Rappaport and J. Kaspi, *J. Am. Chem. Soc.*, *92*, 3220 (1970).

42. Z. Rappaport and A. Gal, *J. Am. Chem. Soc.*, *91*, 5246 (1969).

43. V.J. Shiner, Jr., W. Dowd, R.D. Fisher, S.R. Hartshorn, M.A. Kessick, L.M. Milakotsky, and M.W. Rapp, *J. Am. Chem. Soc.*,*91*, 4838 (1969) and references therein.

44. M.D. Schiavelli, Professor, College of William and Mary, Williamsburg, Virginia, 23185, unpublished observation.

45. V.J. Shiner, Jr., B.L. Murr, and G. Heinemann, *J. Am. Chem. Soc.*, *85*, 2413 (1963).

46. L. Hakka, A. Queen, and R.E. Robertson, *J. Am. Chem. Soc.*,*87*, 161 (1965).

47. S.H. Liggero, J.J. Harper, P.V.R. Schleyer, A.P. Krapcho, and D.E. Horm, *J. Am. Chem. Soc.*, *92*, 3789 (1970).

48. A. Streitwieser, Jr., C.L. Wilkins, and E. Kiehlmann, *J. Am. Chem. Soc.*, *90*, 1598 (1968).

49. 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*, 2538 (1970).

50. J.W. Baker and W.S. Nathan, *J. Chem. Soc.*, 1844 (1935).

51. V.J. Shiner, Jr., *J. Am. Chem. Soc.*, *76*, 1603 (1954).

VITA

Dwight Ellen Foster Ellis

Born in Clinton, Oklahoma, March 18, 1949. Graduated from Muskogee Central High School, Muskogee, Oklahoma in May, 1967. B.S. with a major in Chemistry, Oklahoma State University, May, 1971. Entered College of William and Mary January, 1972, after one semester of graduate work at Oklahoma State. With course requirements completed, became M.A. candidate January, 1973.