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## A Kinetic Study of the Solvolysis of 1-Chloro-1,3,3-Triphenylpropadiene

Sharon Conley Hixon  
*College of William & Mary - Arts & Sciences*

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A KINETIC STUDY OF THE SOLVOLYSIS OF  
1-CHLORO-1,3,3-TRIPHENYLPROPADIENE

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A Thesis

Presented to

The Faculty of the Department of Chemistry  
The College of William and Mary in Virginia

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In Partial Fulfillment

Of the Requirements for the Degree of  
Master of Arts

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By

Sharon C. Hixon

1970

APPROVAL SHEET

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

Sharon C. Hixon

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## ACKNOWLEDGEMENTS

The writer wishes to express appreciation to Professor Melvyn D. Schiavelli for his patient guidance and criticism throughout this investigation. The author is also indebted to Professor Trevor B. Hill and Professor David W. Thompson for their careful reading and criticism of the manuscript. Credit is also due to the author's husband, Edward C. Hixon, for his patience and encouragement during this investigation and for his assistance in preparing the manuscript.

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## ABSTRACT

The object of this research was to investigate the solvolysis of 1-chloro-1,3,3-triphenylpropadiene. Kinetic studies were performed by studying the change in conductivity of acetone-water solutions of the allene with time. The reaction was determined to be first order. Rate constants were measured at different temperatures and different solvent polarities. The product of solvolysis at room temperature was shown to be 1,3,3-triphenyl-2-propyn-1-ol. At elevated temperatures the products of solvolysis were 1,3,3-triphenylprop-2-en-1-one and 1,3,3-triphenyl-2-propyn-1-ol. From the data obtained at different temperatures the activation parameters were calculated and compared with those for similar vinyl systems reported to solvolyze by  $S_N1$  mechanisms. Reaction rates were shown to increase with increasing solvent polarity. The Grunwald-Winstein  $mY$  correlation was compared with data on similar reactions. The mechanism which best explains the data is a classical  $S_N1$  mechanism in which the allene ionizes to chloride ion and a resonance stabilized cation in the rate limiting step. The cation formed at the transition state has two resonance contributing structures, one of which is a vinyl cation. Possible routes which might occur at or after this initial transition state are discussed in order to explain the formation of the  $\alpha,\beta$ -unsaturated ketone as a product at elevated temperatures.



A KINETIC STUDY OF THE SOLVOLYSIS OF  
1-CHLORO-1,3,3-TRIPHENYLPROPADIENE

## I.

### INTRODUCTION

The purpose of this research was to investigate the solvolysis of 1-chloro-1,3,3-triphenylpropadiene and to determine if the mechanism of solvolysis included a vinyl cation intermediate. Vinyl cations formed by a direct solvolysis reaction were first reported by C. A. Grob and G. Cseh<sup>1</sup> in 1964 and these workers investigated the solvolysis of para-substituted  $\alpha$ -bromostyrenes. Prior to this time it had been assumed that all vinyl halides were inert toward solvolysis since they do not form precipitates in ethanolic silver nitrate solution.<sup>2</sup> The bond lengths, bond dissociation energies and ionization potentials of vinyl halides as compared with alkyl halides in Table I demonstrates their inert character toward solvolysis. However, the work performed with  $\alpha$ -bromostyrenes demonstrated that solvolysis does in fact occur if the positively charged intermediate formed can be stabilized by some adjacent system such as an aromatic ring. The marked increase in the rates of solvolysis of the para-substituted bromostyrenes when electron-donating substituents were present, and the converse results for para-substituted electron-withdrawing groups, helped to verify an  $S_N1$  mechanism involving a vinyl cation. In addition, the rates of solvolysis were independent of added nucleophile. See Figure 1.

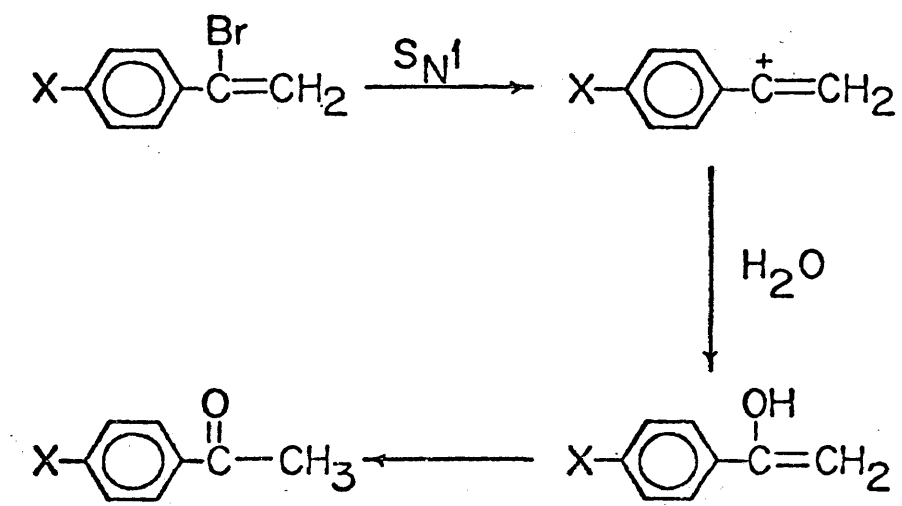
The work on  $\alpha$ -bromostyrenes was expanded by Miller and Kaufman<sup>3</sup> and by Rappoport and Gal.<sup>4</sup> The original halostyrene system was modified by the addition of two more phenyl groups to form a tetrasubstituted

Table I<sup>a</sup>  
Properties of Organic Halides

Compound	Bond Length Å <sup>o</sup>	BDE of RX (Kcal/mole)	IP of R ev
C <sub>2</sub> H <sub>5</sub> Cl	1.77	81.5	8.8
i-C <sub>3</sub> H <sub>7</sub> Cl	1.77	81.0	8.0
CH <sub>2</sub> =CHCl	1.72	84	9.45
C <sub>6</sub> H <sub>5</sub> Cl	1.70	--	9.9
C <sub>2</sub> H <sub>5</sub> I	2.14	53	8.8
t-C <sub>4</sub> H <sub>9</sub> I	2.15	49.5	7.6
CH <sub>2</sub> CHI	2.09	55.5	9.45
C <sub>6</sub> H <sub>5</sub> I	2.08	54	9.9

<sup>a</sup>This table is from Reference 3.

Figure 1  
The Solvolysis of  $\alpha$ -Bromostyrenes



olefin, thus excluding any possible elimination-addition pathway for vinyl substitution. See Figure 2. However, the addition of the phenyl groups in the beta position did not appear to enhance the reaction rate. Any resonance contribution due to delocalization of charge to the beta carbon was thus eliminated. The unimolecular mechanism was substantiated by additional data including ring substituent effects, solvent effects, a comparison of different halogen leaving groups, and common-ion data. Again the positively charged intermediate was stabilized by charge delocalization through the adjacent phenyl ring. The best configuration of the cation for maximum overlap of the empty p orbital with the " $\pi$  cloud" of the benzene ring would be a linear vinyl cation. Rappoport and Apeloig<sup>5</sup> have shown that the product forming intermediate in the solvolysis of 1,2-dianisyl-2-phenylvinyl halide is a linear sp hybridized vinyl cation. The reaction of either the cis or trans vinyl halide with p-toluene-thiolate ion in 80 % ethanol was studied. The final products from each isomer were identical. This study verified a linear cation intermediate because attack at each lobe of the empty p orbital was indicated from the resulting products. A bent cation as an intermediate would have resulted in a retention of configuration for each final product; trans producing a trans product and the cis isomer producing a cis product. See Figure 3.

Reports of the direct generation of vinyl cations in alkyl systems have included the use of the cyclopropane ring, a double bond, or good leaving groups to facilitate solvolysis. Investigations in which ionization occurs in a vinyl halide lacking aromatic substitution at the ionizing center have been reported by Sherrod and Bergman<sup>6</sup> and by Hanack and Bassler.<sup>7</sup> These workers demonstrated that 1-cyclopropyl-1-haloethylenes solvolyzed in aqueous ethanolic silver nitrate at room

Figure 2

## Elimination - Addition Pathway

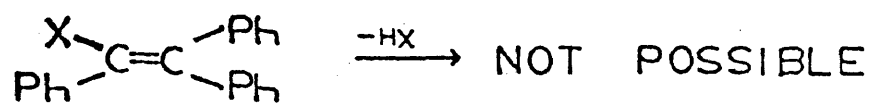
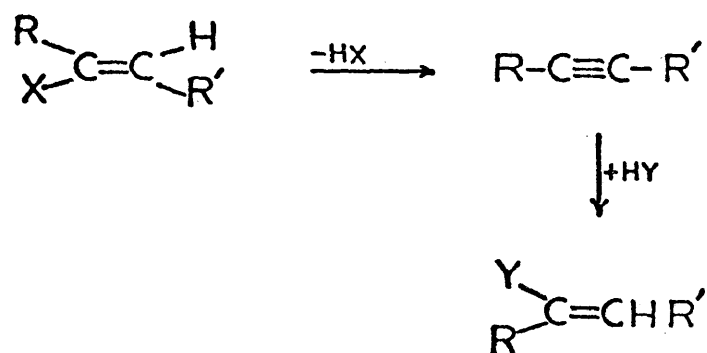
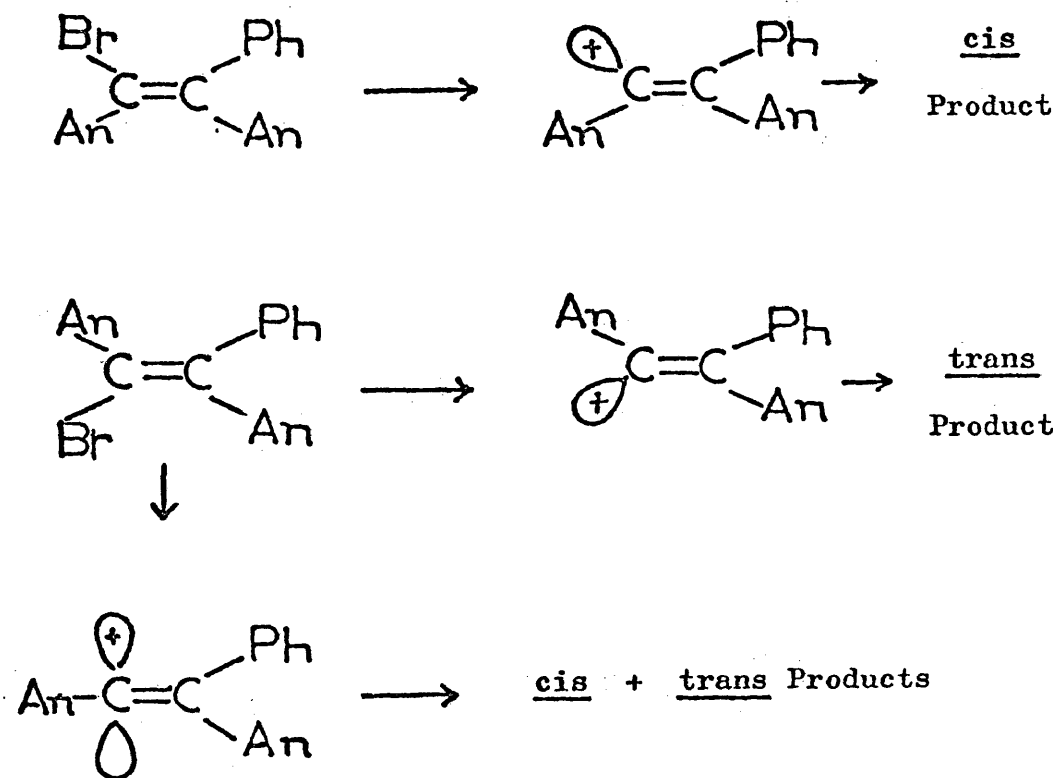


Figure 3

## The Linear vs. The Bent Vinyl Cation



temperature to give cyclopropyl methyl ketone as the prominent product. In contrast to this 2-iodo-3-methyl-1-butene was unreactive toward ethanolic silver nitrate solution at room temperature. See Figure 4. These reactions can only be explained by a special stability imparted to the cation by the presence of the cyclopropane ring. Due to the bond strain in the cyclopropane ring an overlapping involving bent orbitals occurs between the three carbons. This condition permits electron delocalization and results in a type of " $\pi$  cloud" in the plane of the ring.<sup>8</sup> This case is therefore analogous to the stability of those cations discussed in aromatic systems. The vinyl cation is stabilized due to the overlap of the empty p orbital with the cyclopropane ring. The most desirable steric configuration for such an overlap is a linear cation. Kelsey and Bergman<sup>9</sup> have shown by product studies that the intermediate vinyl cation is in fact linear as predicted. The separate ionizations of the cis and trans-1-iodo-1-cyclopropylpropene resulted in essentially identical product distributions. The products formed therefore arose from a common intermediate of a specific steric configuration. The only intermediate from which identical products could be derived from the cis and trans isomers is the linear vinyl cation.

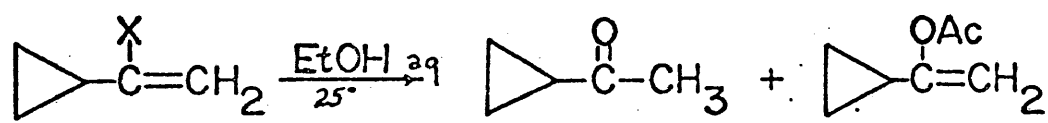
In other attempts to achieve solvolysis via a vinyl cation Stang and Summerville<sup>10</sup> successfully used a simple vinyl ester of trifluoromethanesulfonate. These esters, triflates, are known to be even better leaving groups than the arenesulfonates.<sup>11</sup> The best evidence that cis-2-buten-2-yl triflate proceeds through a vinyl cation is the resulting product. The production of 2-butanone as a principle product of solvolysis can best be explained as coming from an  $S_N1$  mechanism.

Furthermore, it was recently noted by Grob and Spaar<sup>12</sup> that adjacent double bonds will encourage the solvolysis of a vinyl substituted system

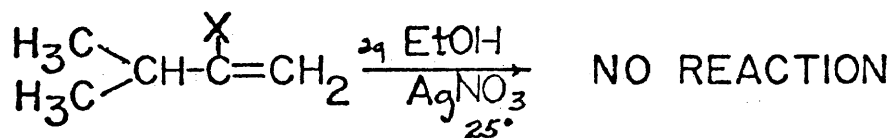


Figure 4

The Effect of the Cyclopropane Ring in the Solvolysis of  
1-Cyclopropyl-1-haloethylenes



X = Br, I

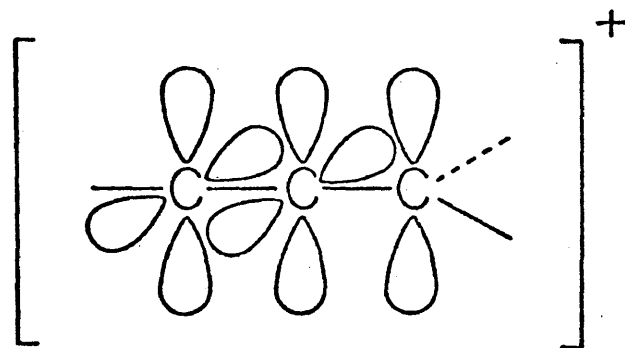
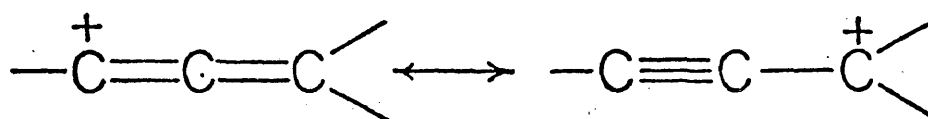


to produce the intermediate cation. Alkyl substituted 2-bromo-1,3-butadienes were shown to undergo facile solvolysis due to the charge stabilization of the cation by the allyl system present. Even more surprising was the fact that 2-bromo-4-methyl-1,3-pentadiene reacted twenty-three times faster than *p*-methoxy- $\alpha$ -bromostyrene. The enhanced ability of the allyl system to undergo solvolysis has been previously pointed out by the work of C. A. Vernon.<sup>13</sup> This work showed that allylic halides undergo solvolytic reactions approximately twenty-five times faster than their saturated analogs due to the resulting charge delocalization through the three carbon  $\pi$  system. Thus it might be interpreted that an allylic system could be used to aid in the stabilization of a vinyl cation.

In 1965 Jacobs and Fenton<sup>14</sup> suggested that haloallenes would undergo hydrolysis to the corresponding propargyl alcohols through a possible  $S_N1$  mechanism. However, not until this time has the solvolysis of such allenes been investigated. This system is of special interest in that the cleavage of the halogen should result in a cation, one of whose resonance contributing structures is a vinyl cation. See Figure 5. The cation produced is unique in that an overlap of p orbitals can result throughout the entire conjugated system. Should an electron-donating substituent be added in the para position of any ring, classical resonance structures could be drawn resulting in a delocalization of the positive charge to that substituent. No other vinyl cation reported to date has such a potential.

Figure 5

The Cation Produced in the Solvolysis of 1-Chloro-1,3,3-triphenylpropadiene



## II.

### EXPERIMENTAL

Routine melting points were determined with a Fisher-Johns melting point apparatus. Melting points and boiling points are uncorrected. Routine infrared spectra were obtained using a Perkin-Elmer Infrared Spectrophotometer Model 700. Accurate determinations of characteristic absorption peaks in the infrared were obtained with a Perkin-Elmer Model 457 Grating Spectrophotometer. Sodium chloride cells were employed in both cases. Spectra of solids were determined using 10 % solutions in carbon tetrachloride. Nmr spectra were obtained using a Perkin-Elmer R-20 Nuclear Magnetic Resonance Spectrometer, 60 Mc/sec.

#### A. Materials

1. Ethynylbenzene obtained from K and K Laboratories was purified by distillation. The fraction boiling between 140 - 143° ( lit.<sup>15</sup> bp 140° at 760 mm ) was collected and stored under refrigeration.
2. n-Butyllithium was obtained from Alpha Inorganics, 22.6 % by weight in hexane. This material was used without further purification.
3. Benzophenone was obtained from J. T. Baker Chemical Co., Reagent Grade. This material was used without further purification.

4. Thionyl chloride was obtained from J. T. Baker Chemical Co., Reagent Grade. This material was used without further purification.

5. Pyridine was obtained from Fisher Scientific Co., Certified A.C.S. This material was used without further purification.

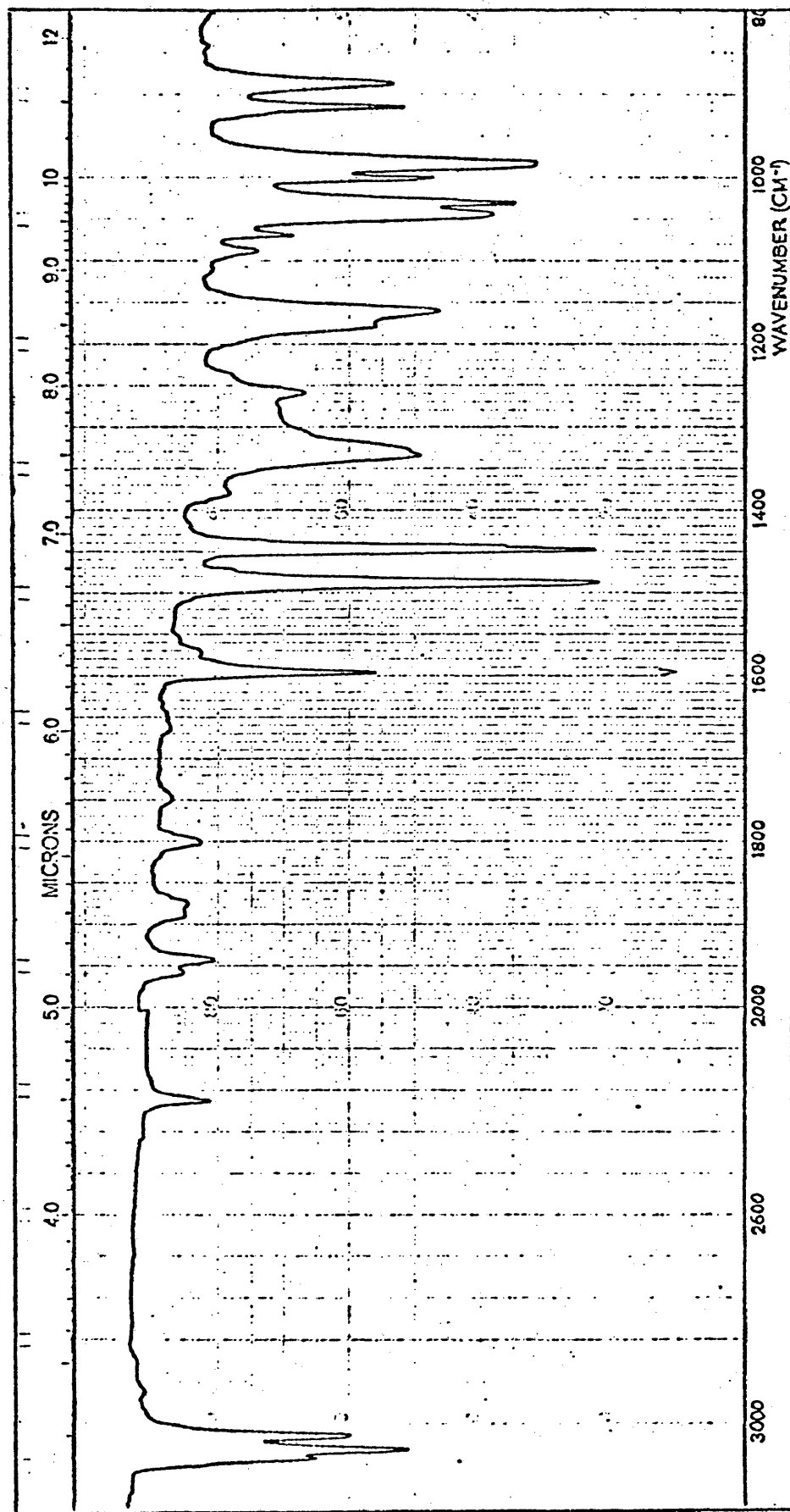
6. Acetone used in kinetic studies was obtained from Fisher Scientific Co., Certified A.C.S. Each 1.5 liters was distilled from 60 g potassium permanganate and approximately 2 g of sodium hydroxide pellets. The fraction collected between 56 - 56.5° was sealed and stored until used. Each volume of distilled acetone was measured for conductance. All acetone used was found to conduct less than 5 micromhos.

7. 1,1,3-Triphenyl-2-propyn-1-ol was synthesized according to the procedure reported by Olah and Pittman.<sup>16</sup> Phenylethynyllithium was prepared by the dropwise addition of 18 g ( 0.18 mole ) ethynylbenzene into a solution of 75 ml n-butyllithium ( 22.6 wt % in hexane ) in 37 ml of hexane, stirring continuously. A nitrogen atmosphere was maintained throughout the preparation. When the addition of ethynylbenzene was complete the solution was diluted with 50 ml anhydrous ether. The reaction vessel was then placed in ice water and 29 g ( 0.16 mole ) of benzophenone in 100 ml of anhydrous ether was added dropwise to the phenylethynyllithium solution. When this addition was complete the solution was refluxed for two hours and then hydrolyzed with 200 - 300 ml of distilled water. The ether layer was separated, washed with water three times and dried over anhydrous magnesium sulfate. The ether was removed by aspiration and the solid alcohol was recrystallized from petroleum ether in a yield of 66 %, mp 80 - 81° ( lit.<sup>17</sup> 82° ). The infrared spectrum of the alcohol

showed a typical O-H stretching vibration at  $3599\text{ cm}^{-1}$  and a C-C triple bond stretching vibration at  $2234\text{ cm}^{-1}$ . The nmr spectrum showed a singlet at  $2.70\ \delta$  for the alcohol proton, and a complex multiplet centered at  $7.40\ \delta$  for the aromatic protons of the three aryl groups present. Integration of the peak areas agrees with this interpretation. See Figures 6 and 7.

8. 1-Chloro-1,3,3-triphenylpropadiene was prepared adapting the procedure reported by Jacobs and Fenton.<sup>14</sup> A mixture of 4 g ( 0.05 mole ) of pyridine and 3 g ( 0.25 mole ) of thionyl chloride in cold ether was added to 7 g ( 0.025 mole ) of 1,3,3-triphenyl-2-propyn-1-ol in 75 ml of ether at  $5^{\circ}$ . The mixture was stirred for one hour. Solid material was then removed from the ether, and the filtrate was washed with 100 ml distilled water, 100 ml 5 % hydrochloric acid, and 100 ml 5 % sodium bicarbonate respectively: and twice again with 100 ml distilled water. The ether layer was dried over anhydrous magnesium sulfate. Upon aspiration of the ether a pale yellow solid remained. The solid was recrystallized from an ether-ethanol solvent pair affording a 55 % yield of colorless crystals, mp  $68 - 69^{\circ}$  ( lit.<sup>18</sup>  $70 - 71^{\circ}$ ). An elemental analysis was done by Schwarzkopf Microanalytical Laboratory, Woodside N. Y. Anal. Calcd. For  $\text{C}_{21}\text{H}_{15}\text{Cl}$ : C, 83.30; H, 4.99; Cl, 11.70. Found: C, 82.63; H, 5.48; Cl, 12.41. The compound was slightly unstable in air decomposing into an orange solid on standing. The infrared spectrum of the allene showed a C-C multiple bond stretching vibration at  $1926\text{ cm}^{-1}$  and  $1964\text{ cm}^{-1}$ . No evidence of an O-H stretching vibration or of a C-C triple bond vibration was observed. The nmr spectrum resulted only in a complex multiplet, centered at  $7.30\ \delta$  for the fifteen aryl protons present. See Figures 8 and 9.

Figure 6  
Infrared Spectrum of 1,3,3-Triphenyl-2-propyn-1-ol



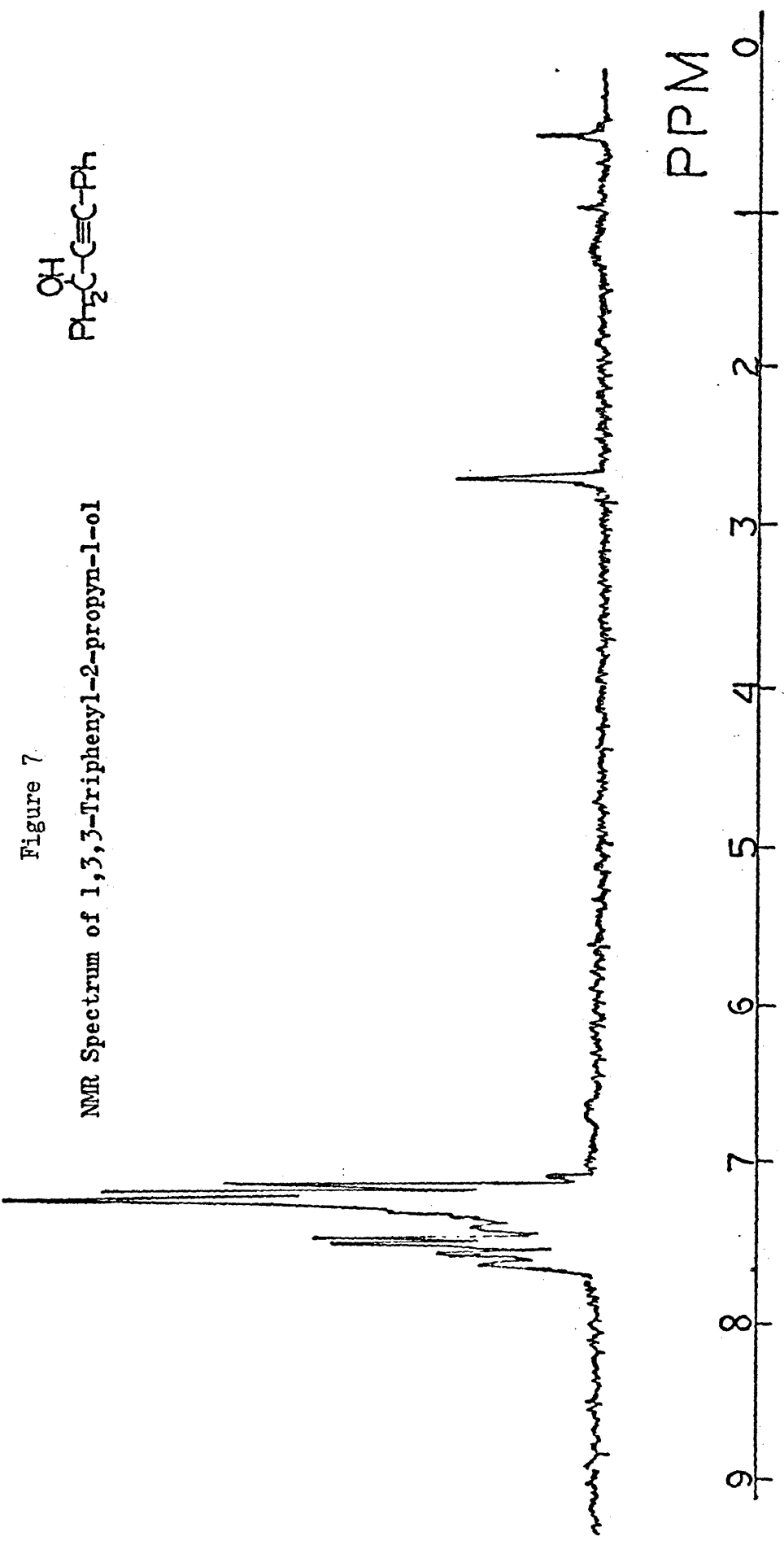




Figure 8

Infrared Spectrum of 1-Chloro-1,3,3-triphenylpropadiene

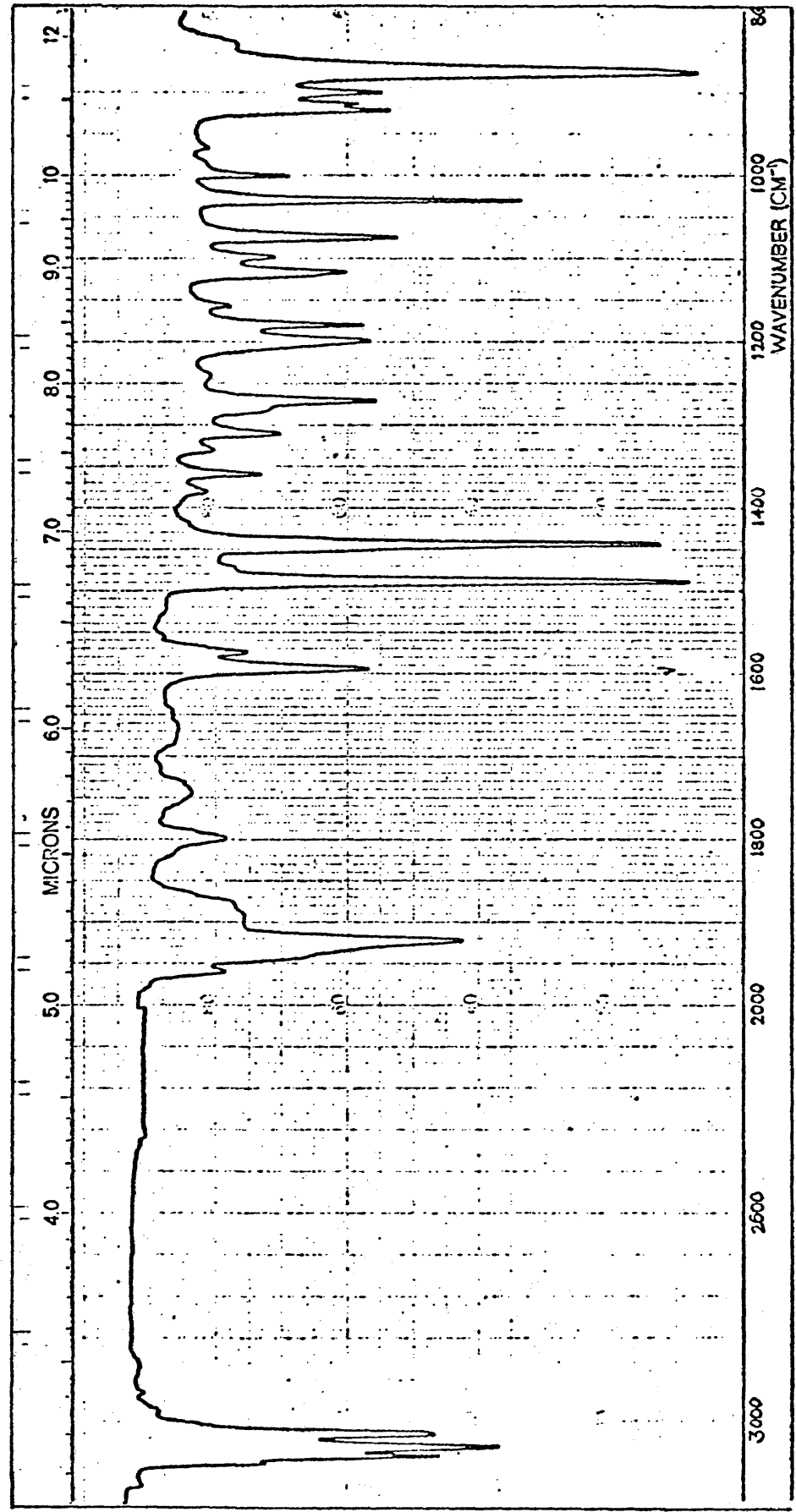
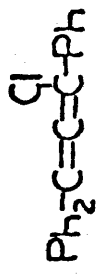
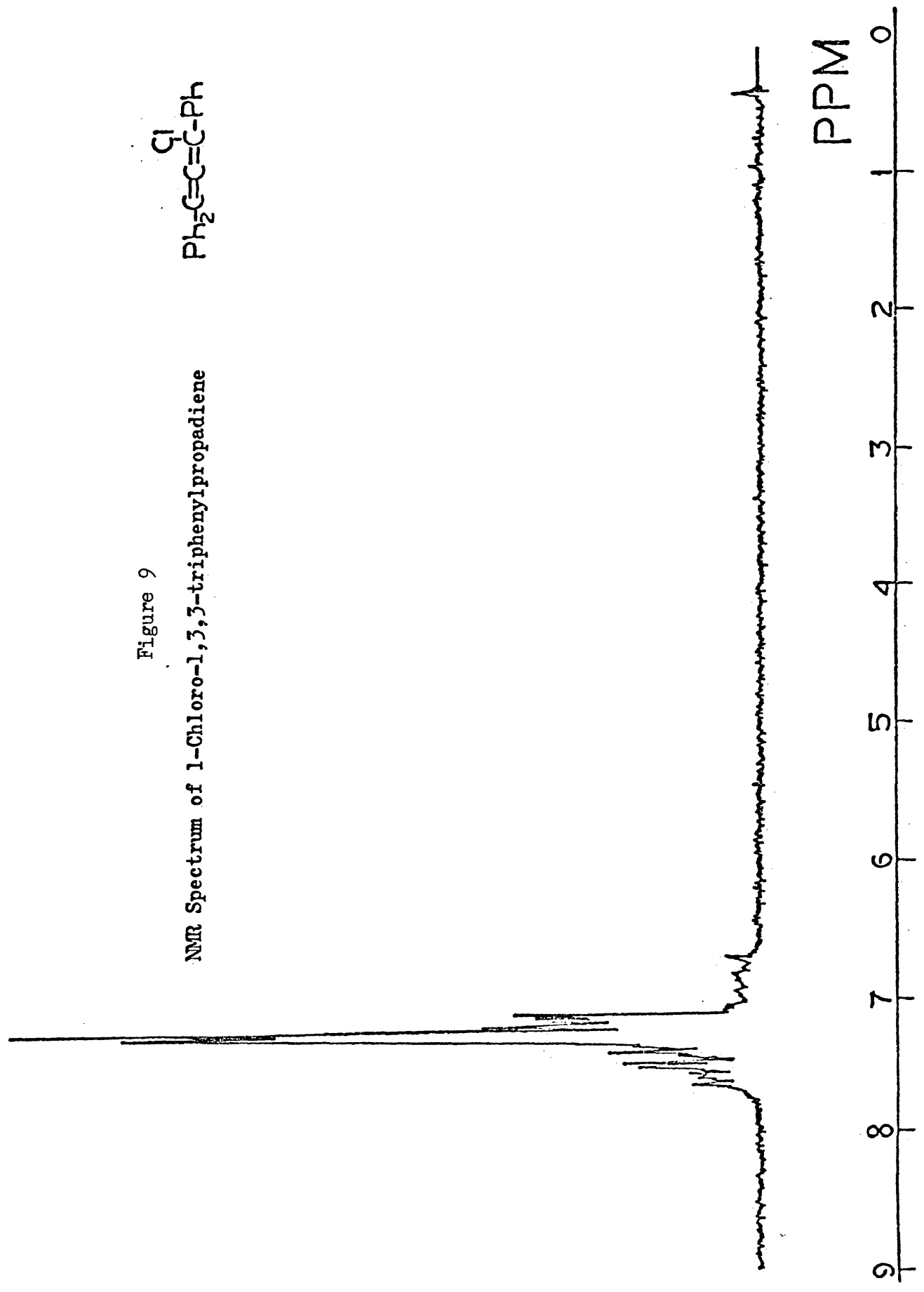
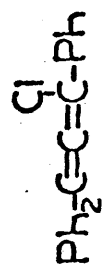


Figure 9

NMR Spectrum of 1-Chloro-1,3,3-triphenylpropadiene



## B. Kinetic Studies

All kinetic studies were performed using an Industrial Instruments Model RC-18 Conductivity Bridge. Conductivity water was prepared from distilled water which had been passed through a mixed bed column of a Bantam Demineralizer Model BD-1. Sample solutions of conductivity water and acetone were checked periodically and found to always conduct less than 10 micromhos. To assure a constant temperature for each kinetic run, water baths were thermostated at known temperatures and monitored by the use of a Beckmann thermometer. The temperature of each water bath was calibrated using a Leeds and Northrup 8160-B Platinum Resistance Thermometer. All volumetric glassware was initially cleaned with sodium dichromate cleaning solution and rinsed with dilute ammonium hydroxide before final rinsings with distilled water and acetone. The conductivity cell used was obtained from Fisher Scientific Co. The cell had an approximate cell constant of  $0.17 \text{ cm}^{-1}$ .

Each experiment was done at a concentration of  $4.0 \times 10^{-4} \pm 0.2 \times 10^{-4}$  mole/liter of the allene. A stock solution of  $1 \times 10^{-2}$  M of the allene was made in distilled acetone. Twenty ml of this stock solution was diluted to 100 ml with acetone in a volumetric flask resulting in a final concentration of  $2 \times 10^{-3}$  M. For a typical kinetic run in which an 80:20 acetone:water solution by volume was desired, 10 ml of the  $2 \times 10^{-3}$  M allene solution was pipetted into a 50 ml volumetric flask. Exactly thirty ml of acetone was then added. When 10 ml of water was added the resulting was an 80:20 acetone:water solution  $4 \times 10^{-4}$  M in allene. The timer was begun as the water was initially introduced into the solution. Each aliquot of water was

always allowed to equilibrate at the desired temperature of the experiment for at least ten minutes before it was added to the allene solution. The flask was then stoppered and inverted several times to assure a uniform mixture. The conductivity cell was rinsed twice with this solution, filled, and placed in a constant temperature bath for measurement of the change in conductivity.

Graphs of the  $\log C_{\infty} - C_t / C_{\infty} - C_0$  (the fraction unreacted) where  $C$  = the conductivity in micromhos, vs. time resulted in good first order plots of the data. See Table II, Figure 10. A computer program LSKINI, written by D. F. Detar and C. E. Detar<sup>19</sup> was used to calculate the rate constant  $k$  ( $\text{sec}^{-1}$ ). The approximate value of  $k$  was submitted to the computer for each reaction. Also an initial and infinite conductivity value were submitted, along with the maximum error allowable or measured for each value. The best values of  $k$ ,  $C_0$  and  $C_{\infty}$  were calculated by the program for the data entered by a curve fitting, least squares calculation. For each data point submitted a theoretical point is calculated and the deviation between the two points reported. Experimental infinity values were within 1 % of the computer-calculated infinity values.

### C. Product Studies

Two product studies were done on like concentrations of allene,  $3.4 \times 10^{-3}M$ , in aqueous acetone under two different conditions. A 1.01 g sample of the chloroallene was transferred to a solution of 700 ml acetone and 300 ml water at  $61.3^{\circ}$  (reflux temperature). This sample was allowed to reflux for 20 hours. For the second product study, 1.03 g of the chloroallene was transferred to a solution of 700 ml acetone and

300 ml water at  $27.8^{\circ}$  and stirred continuously for six hours ( 10 half lives ). At the end of each time period 500 ml of distilled water was added to each sample. Each sample was then transferred to a separatory funnel, and an additional 500 ml of water was added. Each product was then extracted three times with 250 ml aliquots of ether. The ether was dried over anhydrous magnesium sulfate. Upon aspiration of the ether the solid products remained. The sample treated at  $27.8^{\circ}$  was recovered in a yield of 83 %, and the sample treated at  $61.3^{\circ}$  was recovered in a yield of 92 %. The crude products were identified by infrared studies.

Table II

Sample Data of a Kinetic Run - 80:20 DMK<sup>a</sup>: H<sub>2</sub>O - 26.10 °C

Time ( min )	Conductivity ( micromhos )	Fraction Unreacted
10.09	11.78	.9952
31.24	25.89	.9260
37.90	29.90	.9064
43.74	33.10	.8907
52.59	38.60	.8637
61.30	43.30	.8406
74.06	50.40	.8059
81.14	54.10	.7877
101.16	63.90	.7397
112.50	68.20	.7137
124.48	74.60	.6873
132.54	78.10	.6701
140.83	81.60	.6529
149.68	85.20	.6353
161.72	90.00	.6117
171.70	93.80	.5931
184.79	98.60	.5696
196.73	102.80	.5490
207.38	106.40	.5314
252.95	120.50	.4623
262.90	123.30	.4485
275.74	126.80	.4314
287.92	130.00	.4157
302.30	133.60	.3980
317.78	137.30	.3799
331.28	140.40	.3647
353.60	145.20	.3412
368.66	148.30	.3260
389.50	152.30	.3064
405.95	155.30	.2917
422.25	158.10	.2780
436.60	160.50	.2661
458.72	163.90	.2495
478.98	166.90	.2348
492.84	168.80	.2255

<sup>a</sup>DMK is acetone ( dimethyl ketone ).

Table II ( Continued )

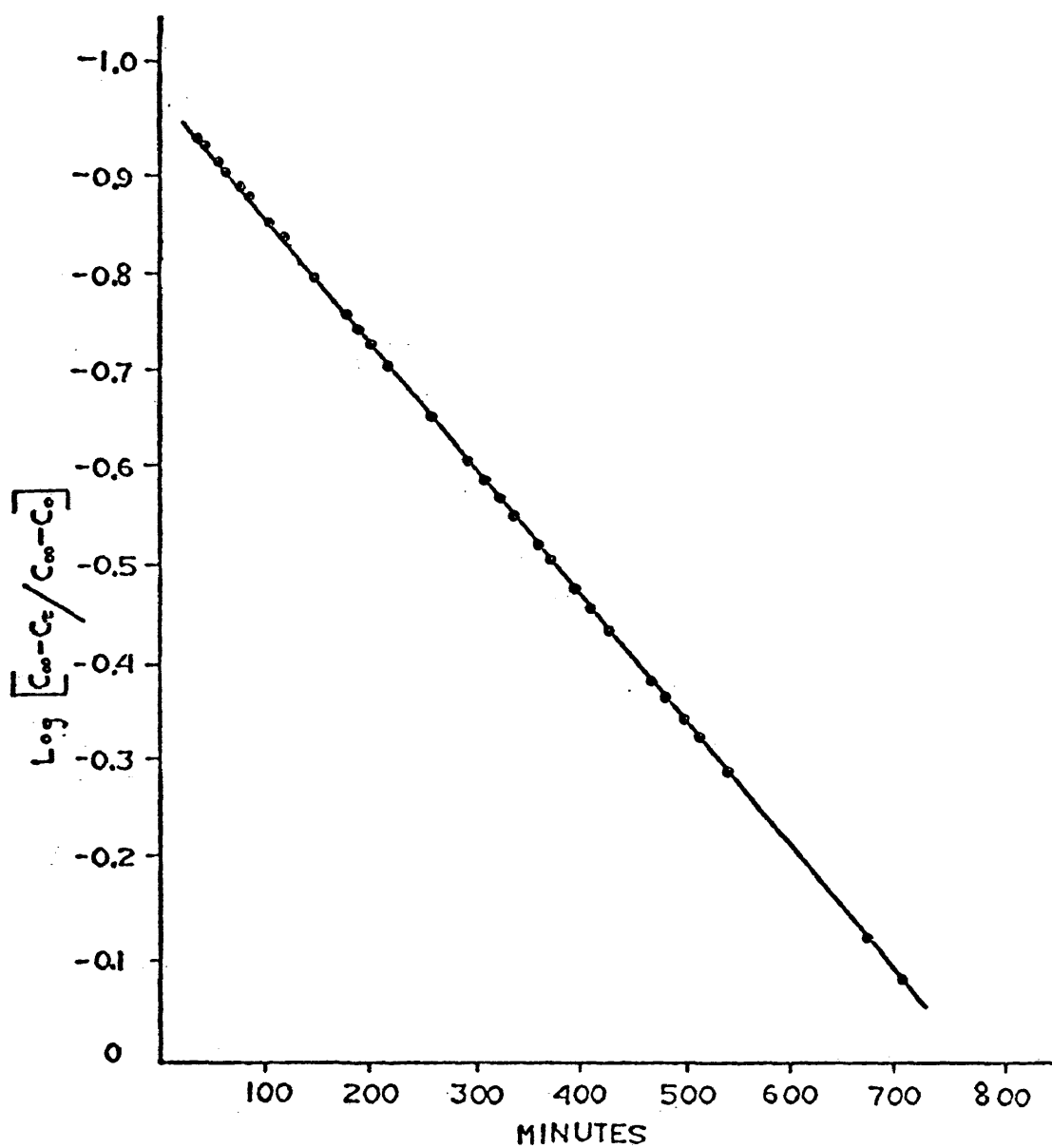
Sample Data of a Kinetic Run - 80:20 DMK : H<sub>2</sub>O - 26.10 °C

---

Time ( min )	Conductivity ( micromhos )	Fraction Unreacted
509.43	171.00	.2147
535.77	174.30	.1985
547.13	175.60	.1921
664.65	187.10	.1357
704.67	190.10	.1217
755.67	193.60	.1039
826.67	197.50	.0848
48 hours	214.80 taken as C <sub>∞</sub>	

---

Figure 10  
Sample First Order Plot of  $\log \frac{C_{\infty} - C_t}{C_{\infty} - C_0}$  vs. Time





### III.

#### RESULTS AND DISCUSSION

Kinetic data was obtained at different temperatures and different solvent polarities as shown in Table III. The solvolysis of 1-chloro-1,3,3-triphenylpropadiene was determined to be a first order reaction as illustrated in Figure 10. From a study of the effect of increasing the solvent polarity the reaction appears to progress via an  $S_N1$  mechanism. Activation parameters were calculated from the rate constants computed at different temperatures and compared with those reported for similar reactions.

##### A. Solvent Effects

A study of the effects of different solvents upon the rate of a vinyl substitution reaction should aid in determining a possible mechanism for the reaction. In an  $S_N1$  mechanism the starting substrate, a neutral compound, ionizes to two ionic species in the rate determining step. In an  $S_N2$  mechanism, the starting reactants consist of a neutral or charged nucleophile which attacks a non-polar substrate in a concerted rate limiting step to produce a polar species with a highly delocalized charge. Thus the  $S_N1$  mechanism proceeds to produce two species at the transition state, each with highly localized charges. The  $S_N2$  mechanism proceeds to the transition state with a species having a highly delocalized charge. A solvent with a high dielectric

Table III

Kinetic Studies of the Solvolysis of 1-Chloro-1,3,3-triphenylpropadiene

Solvent <sup>a</sup> DMK : H <sub>2</sub> O	T <sup>o</sup> C	10 <sup>5</sup> k, sec <sup>-1</sup>	10 <sup>5</sup> average k
80 : 20	26.09 ± .02 <sup>b</sup>	5.46	5.41 ± .05
		5.36	
		5.42	
70 : 30	26.09 ± .02	18.0	18.1 ± 0.2
		18.0	
		18.4	
60 : 40	26.09 ± .02	56.5	56.5 ± 0.3
		56.4	
		56.8	
		54.3 <sup>c</sup>	
		56.1	
80 : 20	24.98 ± .02	4.80	4.80 ± .05
		4.74	
		4.86	
80 : 20	45.00 ± .02	43.3	43.3 ± 0.3
		43.6	
		43.0	
70 : 30	44.99 ± .02	137	138 ± 1.0
		138	
		139	
80 : 20	34.82 ± .02	14.5	14.6 ± 0.1
		14.6	
		14.6	

<sup>a</sup>DMK : H<sub>2</sub>O is Acetone : Water<sup>b</sup>thermometer calibration accurate to ± .02<sup>o</sup><sup>c</sup>not used in calculating the average or the standard deviation

constant should therefore enhance the rate of an  $S_N1$  reaction through the charge stabilization of the transition state species. This same solvent would have either a retarding effect or no effect upon an  $S_N2$  reaction.

An increase in the solvent polarity resulted in marked increases in the rate constants for 1,3,3-triphenylchloroallene as seen in Table IV. For each 10 % increase in the water content of the solvent, the rate constant was increased by a factor of approximately 3.2 .

As the solvent becomes more polar some change results in the activation parameters. At 80:20 acetone:water  $\Delta H_{25}^{\ddagger} = 20.2$  kcal/mole and  $\Delta S_{25}^{\ddagger} = -10.7$  eu and at 70:30 acetone:water  $\Delta H_{25}^{\ddagger} = 19.7$  kcal/mole and  $\Delta S_{25}^{\ddagger} = -9.70$  eu. The greater change was found to occur in the entropy values. This trend appears to occur in those systems which solvolyze through an  $S_N1$  mechanism as can be seen in Table V. The change in  $\Delta S^{\ddagger}$  could be explained by considering the solvent before the reaction occurs. Those solvents with higher dielectric constants will already be highly oriented with regard to the alignment of dipoles before the reaction occurs. Thus at the transition state very little rearrangement should be necessary to align the dipoles about the charged intermediates. This would result in a smaller change in the entropy with those solvents having higher polarities. However, solvents of lower polarities will tend to undergo a greater change in orientation in going to the transition state resulting in larger negative entropy values. An alternative explanation might take into account the amount of charge separation encouraged by each solvent. A highly polar solvent should encourage an increased separation of the charged species at the transition state due to their charge stabilization from the solvent dipoles surrounding them. Hence as the solvent polarity is increased the charged species

Table IV  
Solvent Effects in the Solvolysis of 1-Chloro-1,3,3-triphenylpropadiene

Acetone : Water	T <sup>o</sup> C	10 <sup>5</sup> average k, sec <sup>-1</sup>
80 : 20	26.09	5.41 ± .05
70 : 30	26.09	18.1 ± 0.2
60 : 40	26.09	56.5 ± 0.3
80 : 20	45.00	43.3 ± 0.3
70 : 30	44.99	138 ± 1.0

Table V<sup>a</sup>  
Solvent Effects in S<sub>N</sub>1 Reactions

Compound	Solvent	E <sub>A</sub> kcal/mole	ΔS <sup>‡</sup> at 25° eu
(CH <sub>3</sub> ) <sub>3</sub> CCl	80 % Ethanol	23.1	- 6.2
	50 % Ethanol	22.9	- .67
(CH <sub>3</sub> ) <sub>3</sub> CBr	95 % Acetone	22.7	- 11
	90 % Acetone	20.8	- 8.8
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CHCl	90 % Acetone	19.6	- 19
	80 % Acetone	21.0	- 9.0
(C <sub>6</sub> H <sub>5</sub> )CHClCH <sub>3</sub>	80 % Acetone	21.8	- 14
	60 % Acetone	21.5	- 8.4

<sup>a</sup>E<sub>A</sub> data from Reference 20, ΔS<sup>‡</sup> calculated from data given in the article.

at the transition state are further separated causing an increase in  $\Delta S^\ddagger$  toward a more positive value.

In 1948 Grunwald and Winstein<sup>20</sup> proposed an equation designed to correlate the rates of solvolysis of different compounds with solvent composition. When the values of  $\log k$  for a given compound in a variety of solvents were plotted against the  $\log k$  values of another compound in the same solvents a linear relationship resulted. The linear free energy relationship-

$$\log k = mY + \log k_0$$

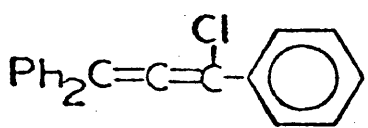
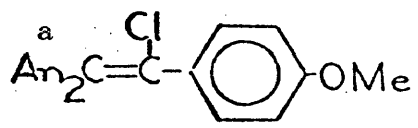
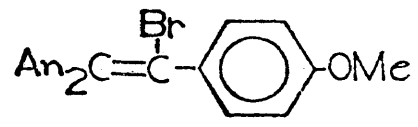
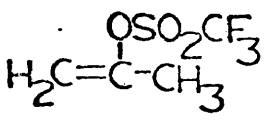
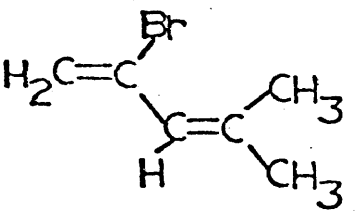
was therefore derived as a result of studies with compounds known to solvolyze through an  $S_N1$  mechanism. In the preceding equation,  $k$  is the rate constant for the solvolysis of a compound in any chosen solvent, whereas  $k_0$  is the rate of solvolysis of a compound in 80 % aqueous ethanol.  $Y$  is an empirical measure of the ionizing power of a solvent.  $Y$  values were determined by assuming the  $m$  value for the solvolysis of *t*-butyl chloride to be unity. All compounds known to solvolyze through a unimolecular mechanism exhibit  $m$  values approaching one as can be seen in Table VI. A plot of  $\log k$  vs.  $Y$  values for the kinetic studies of 1,3,3-triphenylchloroallene resulted in a straight line. The slope,  $m = 0.69$  was computed by a least squares analysis of the data. The linear correlation coefficient was calculated to be 1.00; the standard error of the slope  $\sigma_m = 0.06$ . See Figure 11. This calculated  $m$  value for 1,3,3-triphenylchloroallene appears to be comparable to those obtained in the solvolysis of vinyl systems reported to occur through an  $S_N1$  mechanism, as can be seen in Table VII. The  $m$  value for any reaction tends to distinguish that reaction as being either  $S_N1$  or  $S_N2$ . Studies of reactions known to occur through an  $S_N2$  mechanism have revealed a general range in  $m$  values of  $\sim 0.25 - 0.35$  as shown in Table VI.

Table VI<sup>a</sup>  
 Grunwald - Winstein m Values in Aqueous Ethanol

Compound	T <sup>o</sup> C	m	Mechanism
t-Butyl chloride	25	1.00	S <sub>N</sub> 1
t-Butyl bromide	25	0.917	S <sub>N</sub> 1
α-Methallyl chloride	25	0.894	S <sub>N</sub> 1
α-Phenylethyl chloride	25	1.195	S <sub>N</sub> 1
Benzhydryl chloride	25	0.757	S <sub>N</sub> 1
Methyl bromide	50	0.26	S <sub>N</sub> 2
Methyl tosylate	75	0.23	S <sub>N</sub> 2
Ethyl bromide	55	0.34	S <sub>N</sub> 2
Ethyl tosylate	50	0.26	S <sub>N</sub> 2
n-Propyl chloride	102	0.39	S <sub>N</sub> 2
n-Butyl brosylate	60	0.32	S <sub>N</sub> 2
i-Propyl bromide	50	0.54	S <sub>N</sub> 2
i-Propyl brosylate	70	0.41	S <sub>N</sub> 2

<sup>a</sup>Data in this table is from Reference 20 and 21.

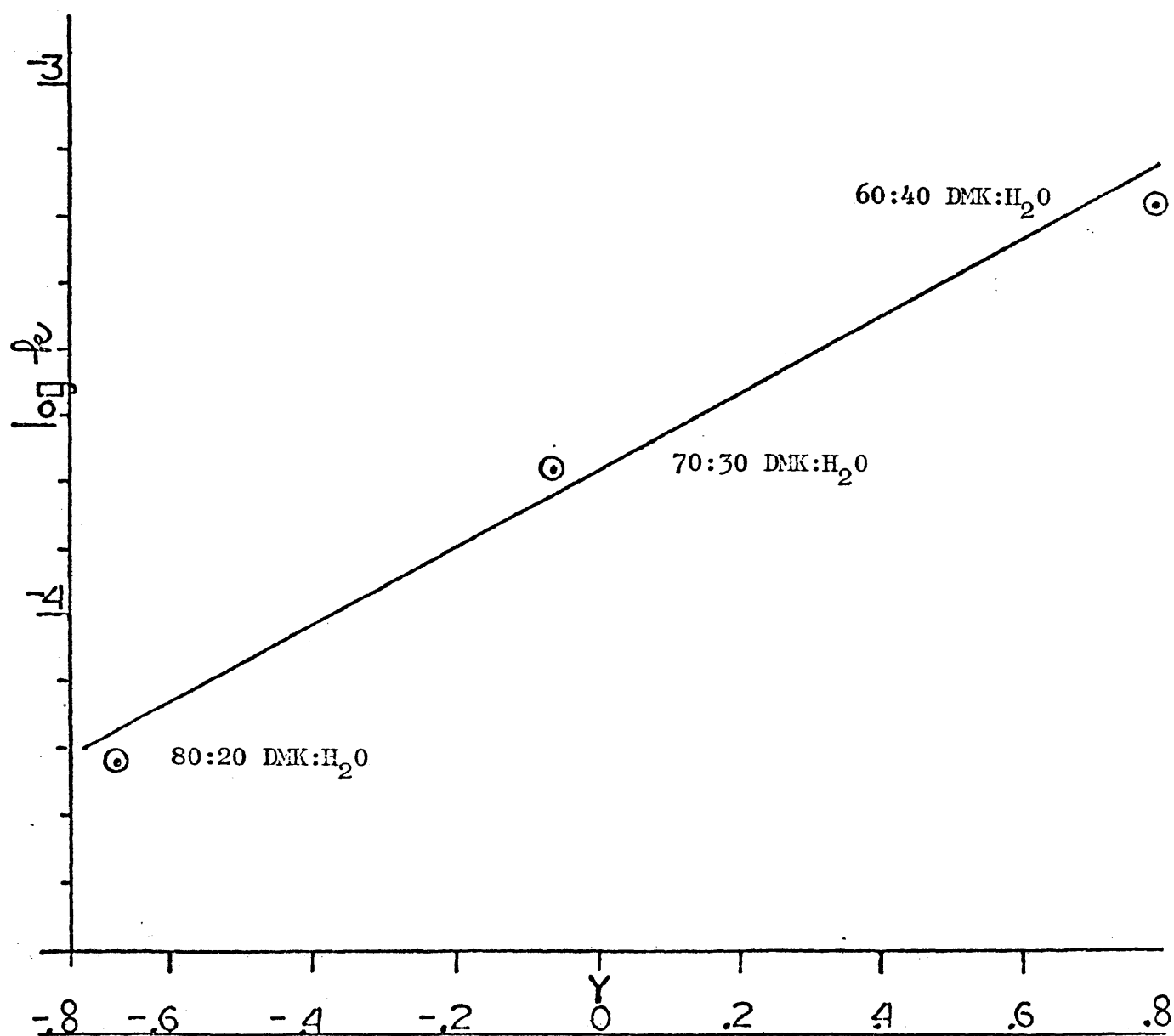
Table VII  
Grunwald-Winstein m Values in Vinyl Systems

Compound	Solvent	m	Reference
	aq Acetone	0.69	This Paper
<sup>a</sup> 	aq Ethanol	0.42 - 0.53	4
	aq Ethanol	0.34	4
	aq Ethanol	0.52	10
	aq Ethanol	0.81	12

<sup>a</sup>An is p-MeO.C<sub>6</sub>H<sub>4</sub>-



Figure 11  
Grunwald-Winstein mY Plot



Ideally the Grunwald-Winstein equation should give the same straight line for different solvents. Such is not always the case. Plots of  $\log k$  for the solvolysis of benzhydryl chloride vs.  $Y$  values in aqueous ethanol, aqueous acetone and aqueous dioxane yield three lines of different slopes.<sup>22</sup> Consequently another characteristic of the solvent should be considered in addition to its ionizing ability. A revised equation was proposed by Grunwald and Winstein<sup>21</sup> in 1951 to include the effect of the nucleophilicity of the solvent.

$$d \ln k = \left( \frac{\partial \ln k}{\partial Y} \right)_N dY + \left( \frac{\partial \ln k}{\partial N} \right)_Y dN$$

In this revised equation  $N$  was assigned as a measure of the nucleophilicity of the solvent. An estimate of this new term  $(\partial \ln k / \partial N)_Y$  can be obtained by comparing the rate of solvolysis of a compound in a solvent of high nucleophilicity to the rate of solvolysis in a solvent of lower nucleophilicity, both solvents having approximately the same  $Y$  value. When 1,3,3-triphenylchloroallene was allowed to solvolyze in aqueous ethanol<sup>23</sup> a rate different from that predicted by the equation  $\log k = mY + \log k_0$  resulted when  $m = 0.69$ . This meant that a plot of  $\log k$  vs.  $Y$  values for the data in acetone and ethanol would result in two straight lines. This situation was therefore analogous to that found in the solvolysis of benzhydryl chloride. Since two straight lines would result in plots of  $\log k$  (acetone) vs.  $Y$  and  $\log k$  (ethanol) vs.  $Y$  some other factor must be considered. Such a factor might be the nucleophilicity term introduced by Grunwald and Winstein. The relative rates at 90 : 10 ethanol and 80 : 20 acetone were compared at a common  $Y$  value. The  $Y$  value used was that of 90 : 10 ethanol, - 0.747. An estimate of the nucleophilicity term was obtained from  $k$  (90 : 10 ethanol) divided by  $k$  (80 : 20 acetone - extrapolated) and found to be 13.9.

The importance of this particular value can only be speculated until further studies are made with other similar  $S_N1$  reactions in these solvents to determine the meaning of this figure. Since the nucleophile in both cases is water, the enhanced rate in ethanol may be due to some more meaningful factor X aside from just the difference in nucleophilicity. The meaning of  $(\partial \ln k / \partial X)_Y$  is yet to be understood.

### B. Temperature Effects

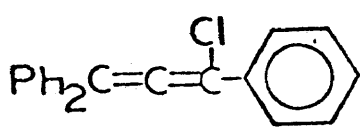
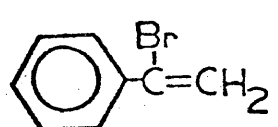
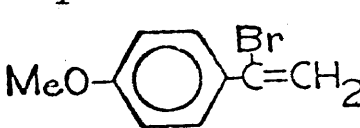
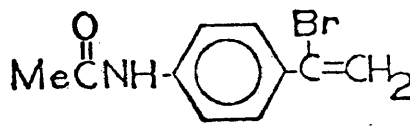
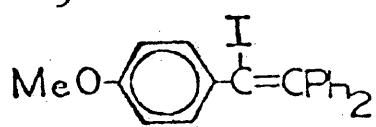
From rate constants determined at different temperatures the activation parameters,  $E_A$ ,  $\Delta H^\ddagger$ , and  $\Delta S^\ddagger$  were determined. With the aid of a computer program, ACTENG, written by D. F. Detar these parameters were calculated by the use of the Arrhenius equation  $k = Ae^{-E_A/RT}$  and the relationship  $A = \frac{ekT}{h} e^{\Delta S^\ddagger/R}$ . A comparison of the activation parameters for 1,3,3-triphenylchloroallene with those of other vinyl systems reported to undergo solvolysis through an  $S_N1$  mechanism can be seen in Table VIII. The parameters for 1,3,3-triphenylchloroallene appear to be consistent with those calculated for other vinyl systems which solvolyze via a vinyl cation. From a comparison of the activation parameters of  $S_N1$  and  $S_N2$  reactions ( Table VIII and Table IX ) certain trends characteristic of each mechanism are seen. The enthalpies of activation are usually larger for those reactions undergoing an  $S_N1$  mechanism. This is probably due to the energy necessary to accomplish the separation of charge when proceeding from a neutral molecule to two charged species in the transition state. An examination of the entropy values for both mechanisms indicates negative values in each case. In the gaseous state one need only to consider the amount of disorder generated at the transition state to determine the entropy of activation. In a typical  $S_N1$  mechanism one particle becomes

two particles in the rate limiting step, while the reverse situation is true for  $S_N2$  reactions. In the gaseous state one would therefore expect a positive  $\Delta S^\ddagger$  for an  $S_N1$  reaction and a negative  $\Delta S^\ddagger$  for an  $S_N2$  reaction. However, as already noted, both entropies are negative when the reaction takes place in solution. The  $S_N1$  reaction has a negative value in solution due to the solvation of the charged species produced at the transition state. Any gain in entropy by the production of two particles from one is offset by the highly ordered system which results as the solvent dipoles align about the charged particles.

Table X lists the rate constants for vinyl systems reported to date which solvolyze through a vinyl cation. Such a comparison emphasizes the unique character of the intermediate cation produced in the hydrolysis of 1,3,3-triphenylchloroallene. This allene appears to solvolyze one-hundred times faster than any other system which is known to proceed through a vinyl cation. This increased rate appears to be due to the special stability imparted to the cation through the resonance stabilization from each phenyl ring present.

Table VIII

Activation Parameters for Reported  $S_N1$  Routes in Vinyl Systems

Substrate	Solvent	$E_A$ kcal/mole	$\Delta H^\ddagger_{25^\circ}$ kcal/mole	$\Delta S^\ddagger_{25^\circ}$ eu
	80 % DMK	$20.8 \pm 0.1$	$20.2 \pm 0.1$	$-10.7 \pm 0.4$
1 <sup>a</sup> 	80 % EtOH	$33.8 \pm 0.3$	$32.9 \pm 0.3$	$-8.9 \pm 0.6$
1 	80 % EtOH	$27.8 \pm 0.2$	$27.1 \pm 0.2$	$-6.8 \pm 0.5$
1 	80 % EtOH	$27.2 \pm 0.2$	$26.4 \pm 0.2$	$-11.3 \pm 0.6$
3 	70 % DMF	$24.9 \pm 0.1$	$24.1 \pm 0.1$	$-15.2 \pm 0.3$

<sup>a</sup>Reference

Table VIII ( Continued )

Activation Parameters for Reported  $S_N1$  Routes in Vinyl Systems

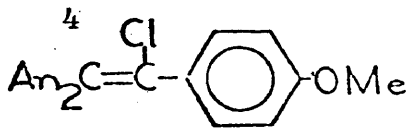
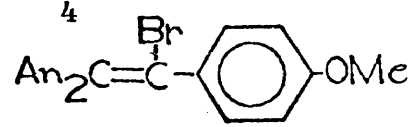
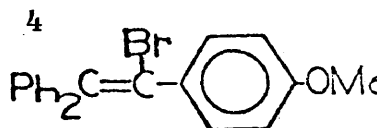
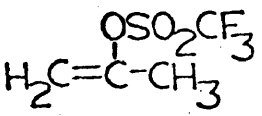
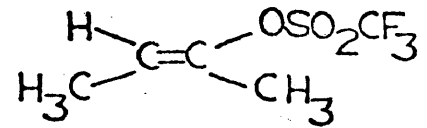
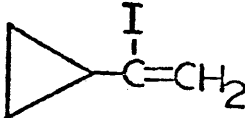
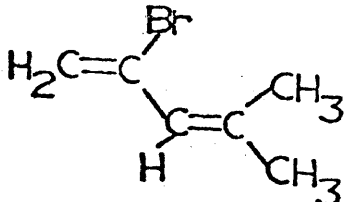
Substrate	Solvent	$E_A$ kcal/mole	$\Delta H^\ddagger$ 25° kcal/mole	$\Delta S^\ddagger$ 25° eu
<sup>4</sup> 	80 % EtOH	27.5 ± 0.2	26.7 ± 0.2	-14.8 ± 0.5
<sup>4</sup> 	80 % EtOH	21.9 ± 0.4	21.2 ± 0.4	-20.8 ± 1.0
<sup>4</sup> 	80 % EtOH	21.8 ± 0.4	21.0 ± 0.4	-22.7 ± 0.9
<sup>10</sup> 	80 % EtOH	25.5 ± 0.2	24.8 ± 0.2	-7.6 ± 0.4
<sup>10</sup> 	80 % EtOH	26.0 ± 0.2	25.3 ± 0.2	-7.7 ± 0.4

Table VIII ( Continued )

Activation Parameters for Reported S<sub>N</sub>1 Routes in Vinyl Systems

Substrate	Solvent	E <sub>A</sub> kcal/mole	ΔH <sup>‡</sup> <sub>25°</sub> kcal/mole	ΔS <sup>‡</sup> <sub>25°</sub> eu
6 	aq MeOH	24.2	23.3 <sup>a</sup>	-21.2
12 	aq EtOH	23.9	23.1 <sup>b</sup>	-10.9

<sup>a</sup>150° No error limits reported<sup>b</sup>100° No error limits reported

Table IX<sup>a</sup>

Activation Parameters for Addition - Elimination Routes

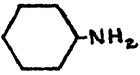
Substrate	Nucleophile & Solvent	$\Delta H^\ddagger_{25^\circ}$		$\Delta S^\ddagger_{25^\circ}$	
		<u>cis</u>	<u>trans</u>	<u>cis</u>	<u>trans</u>
		kcal/mole		eu	
$p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}=\text{CHCl}$	$\text{PhS}^-$ MeOH	17.2	17.0	- 17.8	- 15.2
$p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{CH}=\text{CHBr}$	$\text{PhS}^-$ MeOH	18.3	17.6	- 11.6	- 11.6
$\text{Ph}_2\text{C}=\text{CHCl}$	$p\text{-MeC}_6\text{H}_4\text{S}^-$ DMF	16.2		- 24.0	
$(p\text{-MeC}_6\text{H}_4)_2\text{C}=\text{CHCl}$	$p\text{-MeC}_6\text{H}_4\text{S}^-$ DMF	18.9		- 19.6	
$\text{MeCCl}=\text{CH} \cdot \text{CO}_2\text{Et}$	$\text{EtS}^-$ EtOH	13.5		- 20.5	
$\text{PhCO} \cdot \text{CMe}=\text{CHCl}$	Piperidine EtOH		10.1		- 34.5
$p\text{-MeC}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{CMe}=\text{CHCl}$	$\text{MeO}^-$ MeOH	17.5	14.7	- 16.0	- 25.5
$p\text{-NO}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{SO}_2 \cdot \text{CMe}=\text{CHBr}$	 -NH <sub>2</sub> MeOH	14.1	14.1	- 28.5	-34.5



Table IX ( Continued )

Activation Parameters for Addition - Elimination Routes

Substrate	Nucleophile & Solvent	$\Delta H^\ddagger_{25^\circ}$		$\Delta S^\ddagger_{25^\circ}$	
		<u>cis</u>	<u>trans</u>	<u>cis</u>	<u>trans</u>
		kcal/mole		eu	
MeCCl=CMe.CO <sub>2</sub> Et	EtS <sup>-</sup> EtOH	16.1		- 21.5	
PhCO.CPh=CHCl	Piperidine EtOH		12.6		- 30.0
PhCO.CMe=CHCl	N <sub>3</sub> <sup>-</sup> EtOH		12.3		- 30.6
EtCO.CMe=CHCl	Piperidine EtOH		12.2		- 31.2

<sup>a</sup>This table is from Reference 24.

Table X

Rate Constants Calculated for S<sub>N</sub>1 Routes in Vinyl Systems ( 50° )

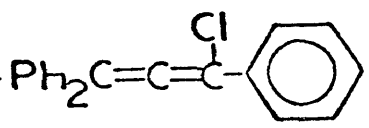
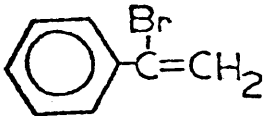
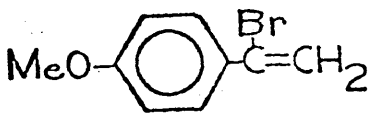
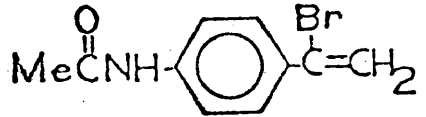
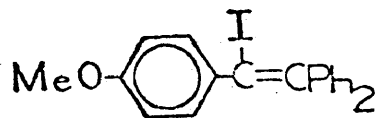
Substrate	Solvent	k ( sec <sup>-1</sup> )	Reference
	80 % DMK	$7.20 \times 10^{-4}$	This Paper
	80 % EtOH	$4.22 \times 10^{-12}$	1
	80 % EtOH	$1.09 \times 10^{-7}$	1
	80 % EtOH	$3.18 \times 10^{-8}$	1
	70 % DMF	$1.57 \times 10^{-7}$	3

Table X ( Continued )

Rate Constants Calculated for S<sub>N</sub>1 Routes in Vinyl Systems ( 50° )

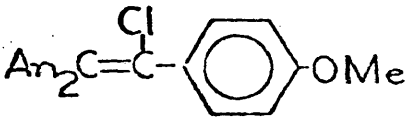
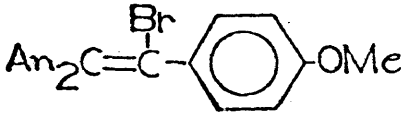
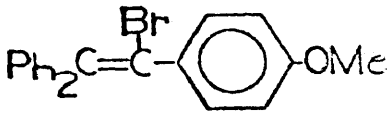
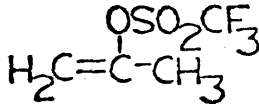
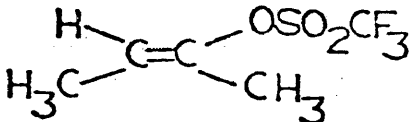
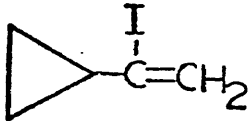
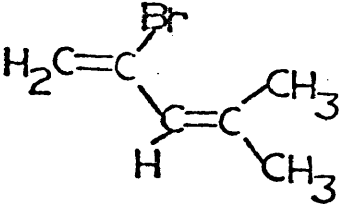
Substrate	Solvent	k ( sec <sup>-1</sup> )	Reference
	80 % EtOH	3.50 x 10 <sup>-9</sup>	4
	80 % EtOH	9.32 x 10 <sup>-7</sup>	4
	80 % EtOH	4.83 x 10 <sup>-7</sup>	4
	80 % EtOH	2.54 x 10 <sup>-6</sup>	10
	80 % EtOH	1.08 x 10 <sup>-6</sup>	10

Table X ( Continued )

Rate Constants Calculated for  $S_N1$  Routes in Vinyl Systems (  $50^\circ$  )

Substrate	Solvent	$k$ ( $\text{sec}^{-1}$ )	Reference
	aq MeOH	$3 \times 10^{-8}$	6
	aq EtOH	$7 \times 10^{-6}$	12

### C. Product Studies

Infrared spectra of the two product studies were compared using the characteristic signals of those compounds of interest. See Table XI. The ir of the sample treated at  $27.8^{\circ}$  showed no evidence of any allene as remaining. A strong peak at  $3599\text{ cm}^{-1}$  and  $2234\text{ cm}^{-1}$  indicated the presence of 1,3,3-triphenyl-2-propyn-1-ol as the only product. The ir of the sample treated at  $61.3^{\circ}$  again showed no evidence of any allene remaining. Strong peaks at  $3599\text{ cm}^{-1}$  and  $2234\text{ cm}^{-1}$  indicated the presence of the propargyl alcohol. In addition, a peak at  $1664\text{ cm}^{-1}$  suggests the production of the ketone, 1,3,3-triphenylprop-2-en-1-one as an additional product of solvolysis.

### D. Possible Mechanisms of Solvolysis

The temperature effects, solvent effects and product studies support a mechanism of solvolysis in which the rate determining step is the loss of the chloride ion from 1,3,3-triphenylchloroallene to form an intermediate cation. However, before any conclusion can be made all possible mechanisms should be examined to verify the  $S_N1$  route as the unique mechanism whereby the predicted product is produced. Any elimination-addition pathway ( Figure 12, # 1. ) is impossible in the allene studied since no hydrogens are present to be eliminated. Feasible addition-elimination mechanisms may be postulated to result in the propargyl alcohol as the product. Several vinyl systems reported to undergo nucleophilic substitution have been shown to proceed through a carbanion intermediate.<sup>25,26</sup> Other compounds undergo this substitution reaction through the concerted addition of the solvent to the double bond. Hence,

Table XI  
Characteristic Infrared Absorptions

Compound	Vibration	cm <sup>-1</sup>
$\text{Ph}_2\text{C}=\overset{\text{Cl}}{\text{C}}=\text{C}-\text{Ph}$	C-C Multiple Bond Stretching	1926
		1964
$\text{Ph}_2\overset{\text{OH}}{\text{C}}-\text{C}\equiv\text{C}-\text{Ph}$	O-H Stretching Vibration	3599
	C-C Multiple Bond Stretching	2234
$\text{Ph}_2\text{C}=\text{CH}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Ph}$	Ketone Stretching Vibration	1664
	C-H Bending ( vinyl hydrogen)	864

Figure 12

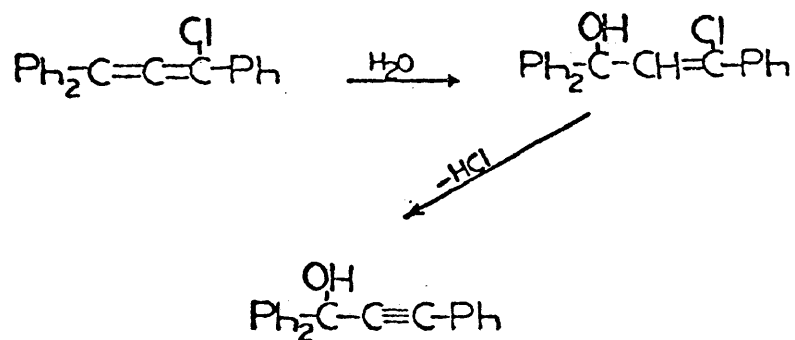
## Possible Mechanisms of the Solvolysis of 1-Chloro-1,3,3-triphenylpropadiene

## 1. Elimination - Addition



## 2. Addition - Elimination

a.



b.

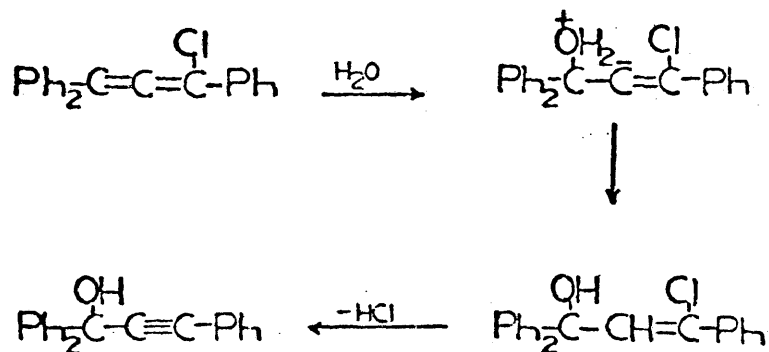
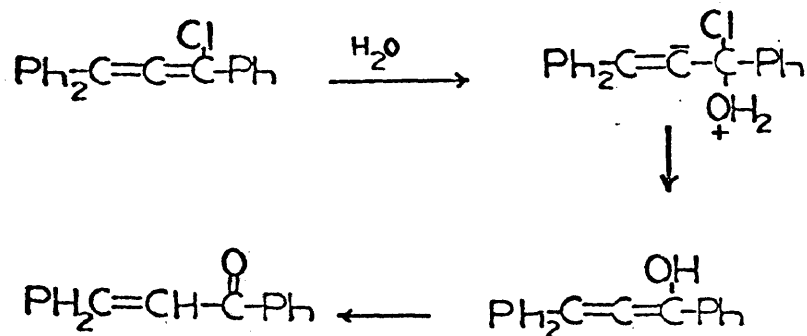


Figure 12 ( Continued )

## Possible Mechanisms of the Solvolysis of 1-Chloro-1,3,3-triphenylpropadiene

## 2. Addition - Elimination

c.



## 3. Protonation

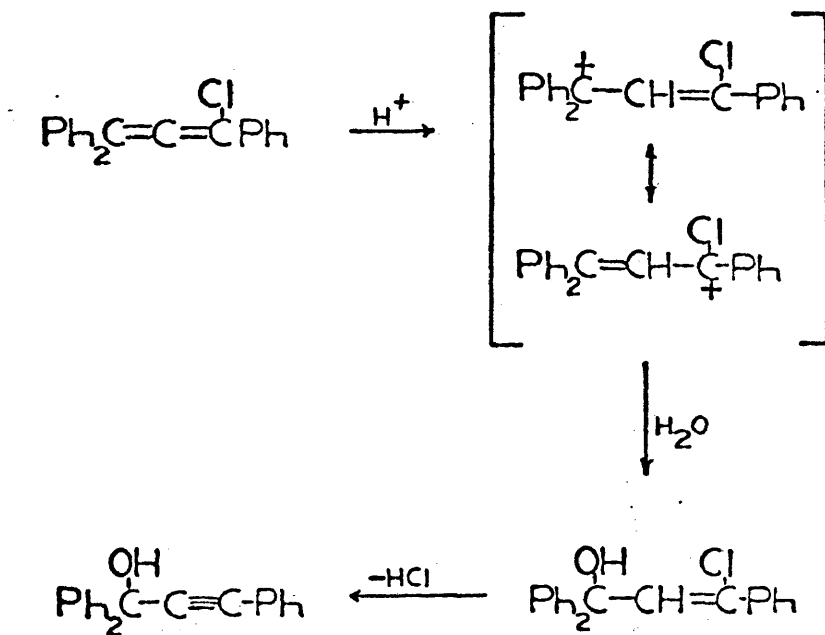
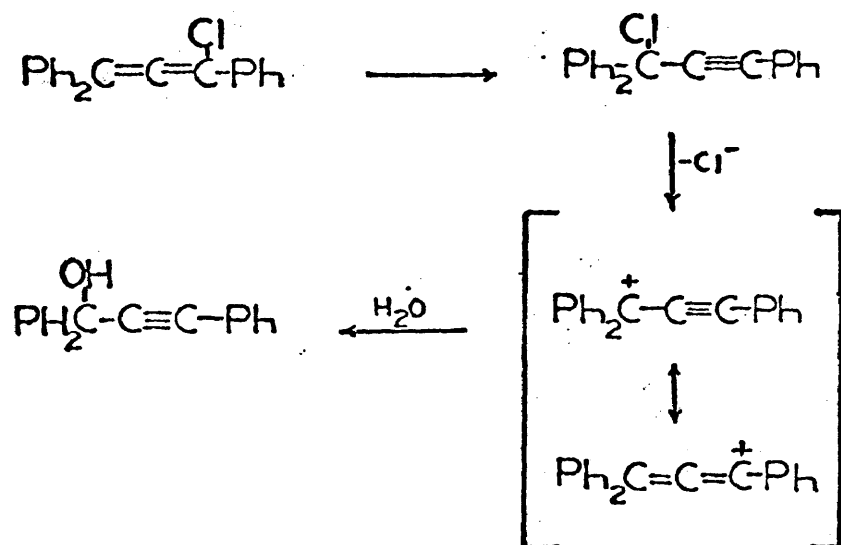
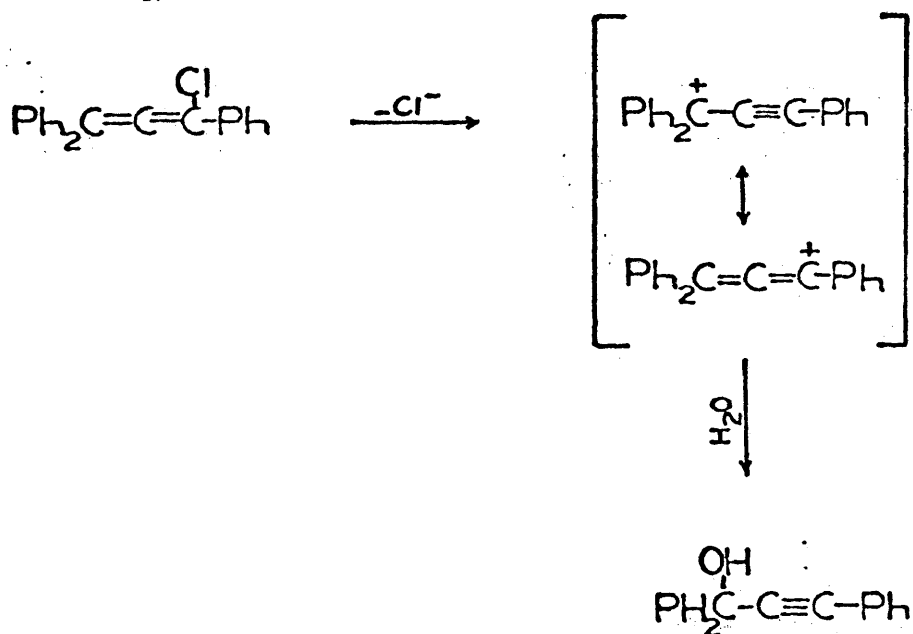




Figure 12 ( Continued )

## Possible Mechanisms of the Solvolysis of 1-Chloro-1,3,3-triphenylpropadiene

## 4. Rearrangement prior to solvolysis

5. Classical  $\text{S}_{\text{N}}1$  Mechanism

the rate limiting step in the addition-elimination process could be either the addition of the nucleophile to form a carbanion intermediate, or the concerted addition of water to the double bond to form an  $\alpha, \beta$ -unsaturated alcohol as the intermediate in the rate determining step. Regardless of which of these routes is postulated, both are bimolecular. It has been shown that the entropy values calculated for 1,3,3-triphenylchloroallene compare favorably with those of other unimolecular reactions rather than with bimolecular reactions. Furthermore, the rate of solvolysis of the allene studied has been shown to be sensitive to increasing polarities of the solvent. This effect would not be present in the concerted addition of water to the allene ( Figure 12, # 2.) since little or no charge is formed at the transition state. In the carbanion formation increased solvent polarities would in fact increase the rate of the reaction. However, note that only the carbanion mechanism # 2.b. is possible to produce the predicted product.

The rho value obtained from the Hammett equation<sup>27</sup>--

$$\frac{\log k_z}{\log k_h} = \sigma \rho$$

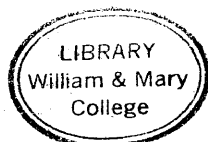
is perhaps the best refutation for the presence of any carbanion intermediate. Moran<sup>31</sup> has reported a rho value vs.  $\sigma^+$  of - 2.0 for the solvolysis of substituted triphenylchloroallenes. Negative rho values are known to be characteristic of positively charged intermediates formed in a reaction, while positive rho values are indicative of processes in which the intermediate is negatively charged. Examples of such rho values which help to characterize a reaction mechanism can be seen in Table XII.

A third mechanism which must be considered is the protonation of the allene ( Figure 12, # 3. ) to produce a cation as the intermediate.

Table XII  
Calculated Rho Values

Substrate	Solvent	$\rho$	Mechanism	Reference
$\text{Ph}_2\text{C}=\text{CHCl}$	EtOH	+ 4.2	$\text{S}_{\text{N}}2$	28
$\text{PhSO}_2\text{CH}=\text{CHCl}$ (trans)	MeOH	+ 1.6	$\text{S}_{\text{N}}2$	29
$\text{PhSO}_2\text{CH}=\text{CHCl}$ (trans)	$\text{N}_3^-$ , MeOH	+ 1.8	$\text{S}_{\text{N}}2$	30
$\text{Ph}_2\text{C}=\text{C}=\text{CClPh}$	aq DMK	- 2.0	$\text{S}_{\text{N}}1$	31
$\text{Ph}_2\text{C}=\text{CIAn}^{\text{a}}$	aq DMK	- 3.6	$\text{S}_{\text{N}}1$	3
$\text{Ph}_2\text{C}=\text{CHBr}$	aq EtOH	- 5.4	$\text{S}_{\text{N}}1$	1
$\text{PhC}\equiv\text{CH}$	$\text{H}_2\text{O}$ (acidic)	- 3.8	$\text{S}_{\text{N}}1$	32
$\text{Ph}(\text{Me})_2\text{CCl}$	aq DMK	- 4.5	$\text{S}_{\text{N}}1$	33

<sup>a</sup> An is  $\text{p-MeO.C}_6\text{H}_4-$



The only possible mechanism which can be postulated for such a route and still produce the expected product is protonation at the central carbon atom of the allene. Addition of the nucleophile would then form the  $\alpha, \beta$ -unsaturated alcohol from which HCl could be eliminated to form the propargyl alcohol. Such a protonation is indeed unlikely in the solvent used in these reported studies, aqueous acetone. All protonation mechanisms in allenes reported to date have been in extremely acidic media often with the addition of catalysts to facilitate reaction. Examples of such reported reactions and the conditions for reaction can be seen in Table XIII. Further proof that a protonation mechanism is unlikely is the prior discussion which tends to show that the solvolysis of 1,3,3-triphenylchloroallene is a first order reaction. Any protonation mechanism in aqueous acetone would of necessity be second order since the protons present are not in excess. Furthermore the loss of HCl from the  $\alpha, \beta$ -unsaturated alcohol to form the propargyl alcohol may be a very slow step or not occur at all.

A fourth mechanism which must be investigated is the possible rearrangement of the allene to the propargyl chloride and its subsequent hydrolysis to form products. To discount this theory an estimate of the rate of solvolysis of the propargyl halide is necessary. No studies of the kinetics of the solvolysis of aryl propargyl halides are reported in the literature. This is due to the difficulty in isolating such halides since they immediately rearrange to the more stable allene in attempted synthesis reactions. One would expect the chloroallene to be more stable than the propargyl chloride since the double bonds of the allene are in conjugation with the three benzene rings present. Furthermore the halide resides in a more stable position in the allene since it is a vinyl halide in the allene, and an alkyl halide in the propargyl chloride.

Table XIII  
Electrophilic Addition to Allenes

Substrate	Solvent	T °C	Maj. Product	Ref.
$\text{CH}_2=\text{C}=\text{CH}_2$	HCl	- 78	$\text{CH}_3\text{ClC}=\text{CH}_2$	34
$\text{CH}_2=\text{C}=\text{CHCH}_3$	HCl	- 78	$\text{CH}_3\text{ClC}=\text{CHCH}_3$	34
$\text{CH}_2=\text{C}=\text{CH}_2$	HBr	- 70	$\text{CH}_3\text{CBr}_2\text{CH}_3$	35
$\text{CH}_2=\text{C}=\text{CHC}_3\text{H}_7$	10 % $\text{H}_2\text{SO}_4$	25	$\text{CH}_3\text{COC}_4\text{H}_9$	36
$\text{MeCH}=\text{C}=\text{CHC}_3\text{H}_7$	80 % $\text{H}_2\text{SO}_4$	25	$\text{C}_2\text{H}_5\text{COC}_4\text{H}_9$	37
$\text{MeCH}=\text{C}=\text{CHCH}_2\text{CH}(\text{CH}_3)_2$	80 % $\text{H}_2\text{SO}_4$	25	$\text{C}_2\text{H}_5\text{COC}_2\text{H}_4\text{CH}(\text{CH}_3)_2$	37

In an attempt to estimate the rate of solvolysis of the propargyl halide an estimate of the influence of the triple bond upon the solvolysis rate was made in a similar propargyl chloride. By comparing the rates of *t*-butyl chloride and 4-chloro-4-methyl-2-pentyne it was found that the propargyl halide reacted 264 times faster than the *t*-butyl chloride. Assuming that this increased rate is due to the insertion of a triple bond into the system one might conclude that the rate should increase approximately the same amount between trityl chloride and 1,3,3-triphenyl-3-chloropropyne. The rate constant of the solvolysis of trityl chloride at 25° is approximately  $8.9 \text{ sec}^{-1}$ . A 264 increase in this value would generate a rate constant of  $2,350 \text{ sec}^{-1}$  for the solvolysis of the propargyl halide in question. The  $k$  ( $\text{sec}^{-1}$ ) of the solvolysis of 1,3,3-triphenylchloroallene under similar conditions is  $4.8 \times 10^{-5} \text{ sec}^{-1}$ . See Table XIV. Thus the rate limiting reaction measured in these kinetic studies cannot be the solvolysis of the propargyl halide.

It has been shown that the rate limiting step in the reaction studied is the formation of two charged species. One might question as to whether this rate determining step leads to an intimate ion pair which undergoes an internal rearrangement to the propargyl chloride which then quickly solvolyzes to products. However, this situation is unlikely since common-ion studies begun by Schiavelli<sup>23</sup> show a definite common-ion rate depression when excess chloride ions are added to the solution of the reacting allene. This effect tends to discount any intimate ion pairs as being present. Thus the rate determining step would probably not involve the rearrangement to the propargyl halide before solvolysis occurs.

Table XIV

## Rates of Solvolysis

Substrate	Solvent ( 25° )	k ( sec <sup>-1</sup> )	Reference
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}-\text{Cl} \\   \\ \text{CH}_3 \end{array}$	80 % Acetone	$1.94 \times 10^{-6}$	20
$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3-\text{C}\equiv\text{C}-\text{C}-\text{Cl} \\   \\ \text{CH}_3 \end{array}$	80 % Acetone	$5.13 \times 10^{-4}$	38
$\begin{array}{c} \text{Ph} \\   \\ \text{Ph}-\text{C}-\text{Cl} \\   \\ \text{Ph} \end{array}$	85 % Acetone	8.9	22,20
$\begin{array}{c} \text{Ph} \\   \\ \text{Ph}-\text{C}\equiv\text{C}-\text{C}-\text{Cl} \\   \\ \text{Ph} \end{array}$	80 % Acetone	$\sim 2,350$	calcd
$\begin{array}{c} \text{Cl} \\   \\ \text{Ph}_2\text{C}=\text{C}=\text{C}-\text{Ph} \end{array}$	80 % Acetone	$4.80 \times 10^{-5}$	This Paper

Having discussed all the alternative mechanisms of solvolysis, the  $S_N1$  mechanism of the solvolysis of 1,3,3-triphenylchloroallene remains as the only route which adequately explains the data presented. Other experiments should confirm this mechanism. One such experiment would be the measurement of an element effect. Since the rate determining step in this study is the cleavage of the halogen bond, different halogens should influence the rates of solvolysis,  $I > Br > Cl > F$ . Such an element effect was reported by Rappoport and Gal<sup>4</sup> in the solvolysis of trianisylvinyl chloride and bromide,  $k_{Br}/k_{Cl} = 58$  at  $120^\circ$ . Bromide is a much better leaving group than the chloride ion due to the increased ability of the bromide ion to accommodate the negative charge. The halogen more easily polarized is therefore the fastest leaving group. The opposite effect is seen in bimolecular reactions. In these reactions the rate determining step is bond formation. Thus the smallest and most electronegative halogen would favor the largest increase in the reaction rate. For example, in the reaction of 1,1-diphenylvinyl halide with sodium ethoxide in ethanol,  $k_{Br}/k_{Cl} = 1.4$ <sup>39</sup> while  $k_F/k_{Cl} = 290$  at  $100^\circ$ .<sup>40</sup> Since Br and Cl tend to be closer in size than Cl and F very little effect is seen in  $k_{Br}/k_{Cl}$  in this  $S_N2$  reaction. However F is much smaller than Cl. This smaller element should sterically favor bond formation. Also F is more electronegative than Cl, meaning that the electron-withdrawing effect of F should favor the attack of a nucleophile. Hence a large element effect seen in bimolecular mechanisms would be the reciprocal effect of that seen in  $S_N1$  mechanisms, i.e.  $k_F/k_{Cl}$  should be large in an  $S_N2$  reaction while  $k_{Cl}/k_F$  should be large in  $S_N1$  reactions.

More supporting evidence for the  $S_N1$  pathway is available through common-ion studies as mentioned previously. Common-ion rate depression indicates that a reversible ionization occurs in the rate determining step.



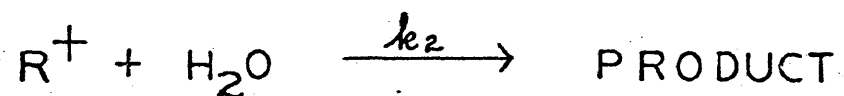
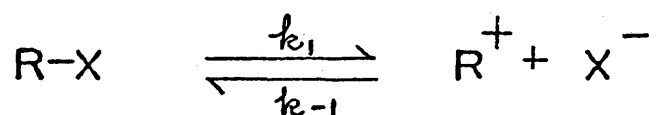
A measure of the stability of the cation formed can be obtained by the amount of rate depression observed when an additional amount of the anion is added to the reaction solution. The ion pair formed in the rate determining step can exist as either a "close knit" ion pair or as free ions in solution. The more stable the cation formed the freer the ion pair is to dissociate into the solvent. Thus a greater influence is seen on the rate depression when the ions are dissociated. If the ions are closely associated, the addition of more anions will have little effect on the reverse reaction. The common-ion rate effect is usually expressed as  $k_{-1}/k_2$ . See Figure 13. A  $k_{-1}/k_2$  value for 1-anisyl-2,2-diphenyliodoethylene was reported by Miller and Kaufman<sup>3</sup> to be approximately 40.

A last study to confirm the  $S_N1$  mechanism should be the effect of added nucleophiles upon the rate of the reaction. Miller and Kaufman<sup>3</sup> demonstrated that the addition of 0.05 M triethylamine to a solution of 1-anisyl-2,2-diphenylethylene in aqueous dimethylformamide showed little effect upon the reaction rate, the rate constant without amine being  $34.4 \times 10^{-5} \text{ sec}^{-1}$ , and with the amine,  $34.3 \times 10^{-5} \text{ sec}^{-1}$ . Grob<sup>1</sup> showed that the rate of solvolysis of *p*-methoxy- $\alpha$ -bromostyrene was not enhanced by the addition of triethylamine. These results relate to the sensitivity of the reaction to the nucleophilicity of the solvent. In any  $S_N1$  mechanism the addition of a strong nucleophile to the solvent should not affect the rate of the reaction since the concentration of the nucleophile is not taken into account in the rate determining step.

The product study at  $61.3^\circ$  revealed the presence of an  $\alpha, \beta$ -unsaturated ketone as a product in addition to the propargyl alcohol formed. The previous discussion has verified that the mechanism of solvolysis is unimolecular producing a cation which has two possible resonance con-

Figure 13

The Common-ion Effect



$$\frac{dP}{dt} = k_2' [R^+] \quad k_2' = k_2 [H_2O]$$

$$\frac{dR^+}{dt} = k_1 [R-X] - k_{-1} [R^+][X^-] - k_2' [R^+] = 0$$

$$\frac{dP}{dt} = \frac{k_1 [R-X]}{\frac{k_{-1}}{k_2'} [X^-] + 1}$$

tributing forms. At 27.8° the exclusive product of solvolysis is the propargyl alcohol 1,3,3-triphenyl-2-propyn-1-ol. This indicates that at room temperature the attack of water occurs exclusively at the propargyl position of the cation. However, at 61.3° the mechanism must be revised to include the possibility of ketone formation. Two routes are available whereby the ketone might be formed. The first possibility is that the attack of water occurs at either the allenyl position or the propargyl position of the cation to produce a mixture of products. See Figure 14. Apparently the higher charge density of the cation occurs at C-1 since the alcohol appears as the exclusive product at room temperature. At higher temperatures attack at C-1 and C-3 becomes more competitive resulting in the formation of some ketone.

The second possibility to explain the product formation at 61.3° is through the rearrangement of the propargyl alcohol initially formed. At 61.3° the alcohol could be formed as the exclusive initial product. However as the solvolysis reaction proceeds the solvent becomes more acidic since HCl is a product. These protons would then protonate the alcohol and rearrangement would result in the  $\alpha, \beta$ -unsaturated ketone, 1,3,3-triphenylprop-2-en-1-one. See Figure 15. However, two possible mechanisms can be written whereby the alcohol is protonated and rearrangement occurs to yield the ketone. See Figure 16. Protonation of the alcohol group to result in the  $\alpha, \beta$ -unsaturated ketone has been called the Meyer-Schuster<sup>41</sup> rearrangement. Protonation of the triple bond could be called a modified Rupe<sup>42</sup> reaction. A clear differentiation of the two mechanisms can be seen by examining Figure 17. The Meyer-Schuster rearrangement involves a 1,3 shift of the hydroxyl group while the classical Rupe reaction involves a 1,2 shift of the hydroxyl group. In an alcohol with no substitution at the triple bond the Meyer-Schuster

rearrangement results in the formation of an aldehyde, while the Rupe rearrangement produced an  $\alpha,\beta$ -unsaturated ketone. However in 1,3,3-triphenyl-2-propyn-1-ol both possible mechanisms involve a 1,3 shift of the hydroxyl group. It is not possible at this point to say which mechanism in fact takes place. Moreau, Dufraisse and Blatt<sup>43</sup> reported in 1924 that 1,3,3-triphenyl-2-propyn-1-ol underwent the Meyer-Schuster rearrangement in acidic ethanol. However, the maximum acidity of the conditions of solvolysis reported here would be a pH of 3.4. One might nevertheless predict that the Meyer-Schuster mechanism would be the most probable since the intermediate cation formed would be more stable than the vinyl cation formed in the protonation of the triple bond. Only by experimentation will one be able to determine which mechanism occurs. In the protonation of the alcohol, the rate limiting step of the mechanism should be the loss of water to form the cation.<sup>44</sup> However, in the modified Rupe reaction the rate determining step would be the protonation of the triple bond.<sup>32</sup> One can only say at this point that the product mixtures resulting in the solvolysis of 1,3,3-triphenylchloroallene at 61.3° can be explained either by the competitive reaction at the propargyl and allenyl position in the cation formed at the transition state, or through the initial formation of the propargyl alcohol and its subsequent rearrangement, or by some combination of both possibilities.

In summary the solvolysis of 1-chloro-1,3,3-triphenylpropadiene is a first order reaction. The kinetic data has been used to confirm that the reaction is a classical  $S_N1$  mechanism in which the allene ionizes to a chloride ion and a resonance stabilized cation at the transition state. The cation is very stable due to the many resonance contributing structures which are available. The product of solvolysis at room temperature is the propargyl alcohol 1,3,3-triphenyl-2-propyn-1-ol. At elevated temperatures

an unsaturated ketone 1,3,3-triphenylprop-2-en-1-one is produced in addition to the propargyl alcohol. Several mechanisms can be employed to explain the formation of the ketone. At this time no definite conclusion may be drawn as to which mechanism applies.

Figure 14

The Attack of Water at the Allenyl and Propargyl Position of the Cation

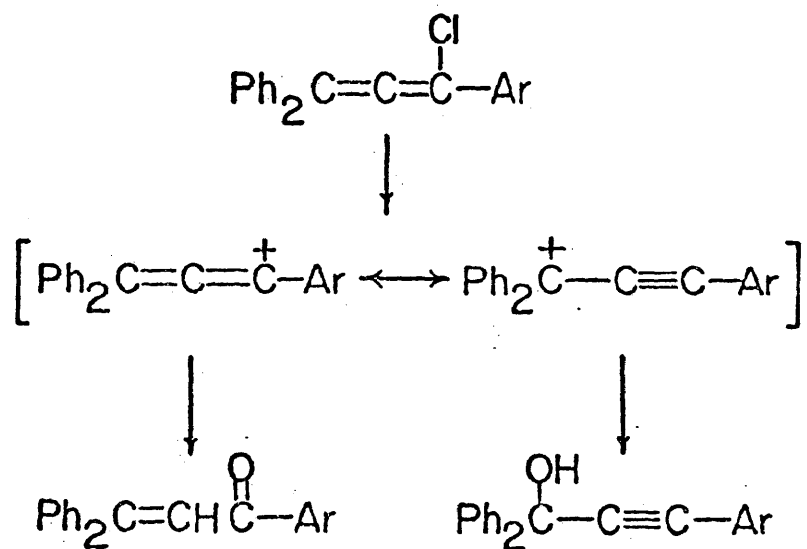


Figure 15  
An Alternate Reaction Pathway

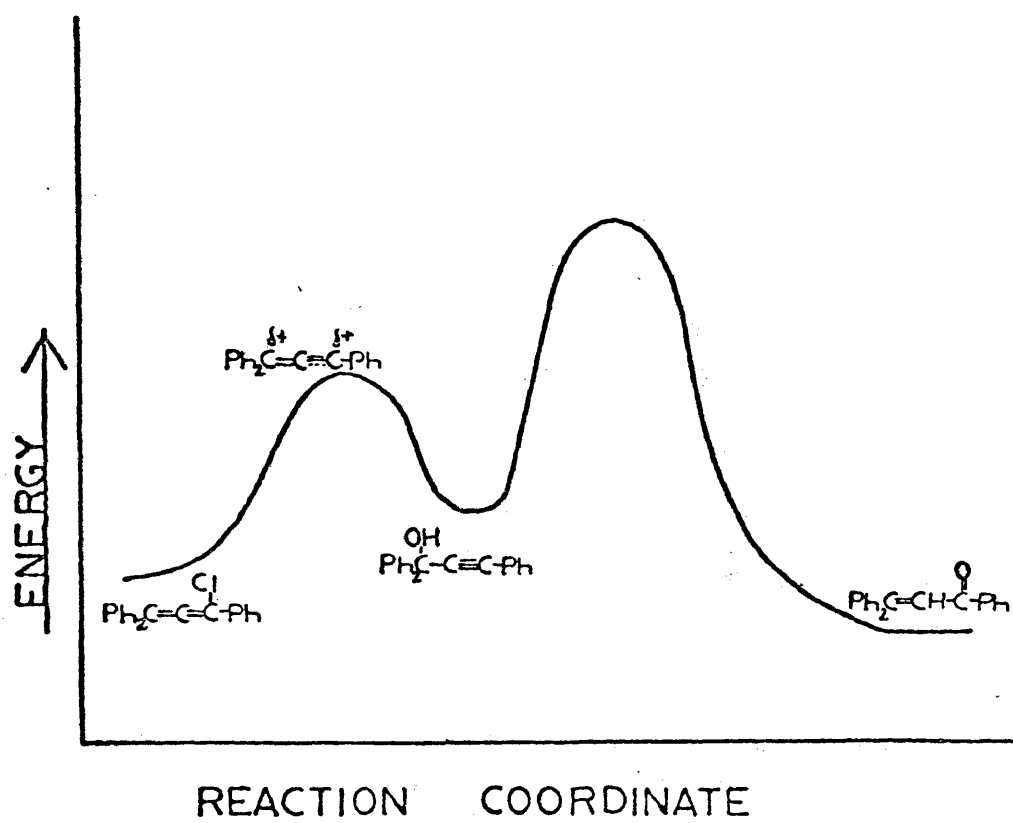


Figure 16

Protonation of 1,1,3-Triphenyl-2-propyn-1-ol

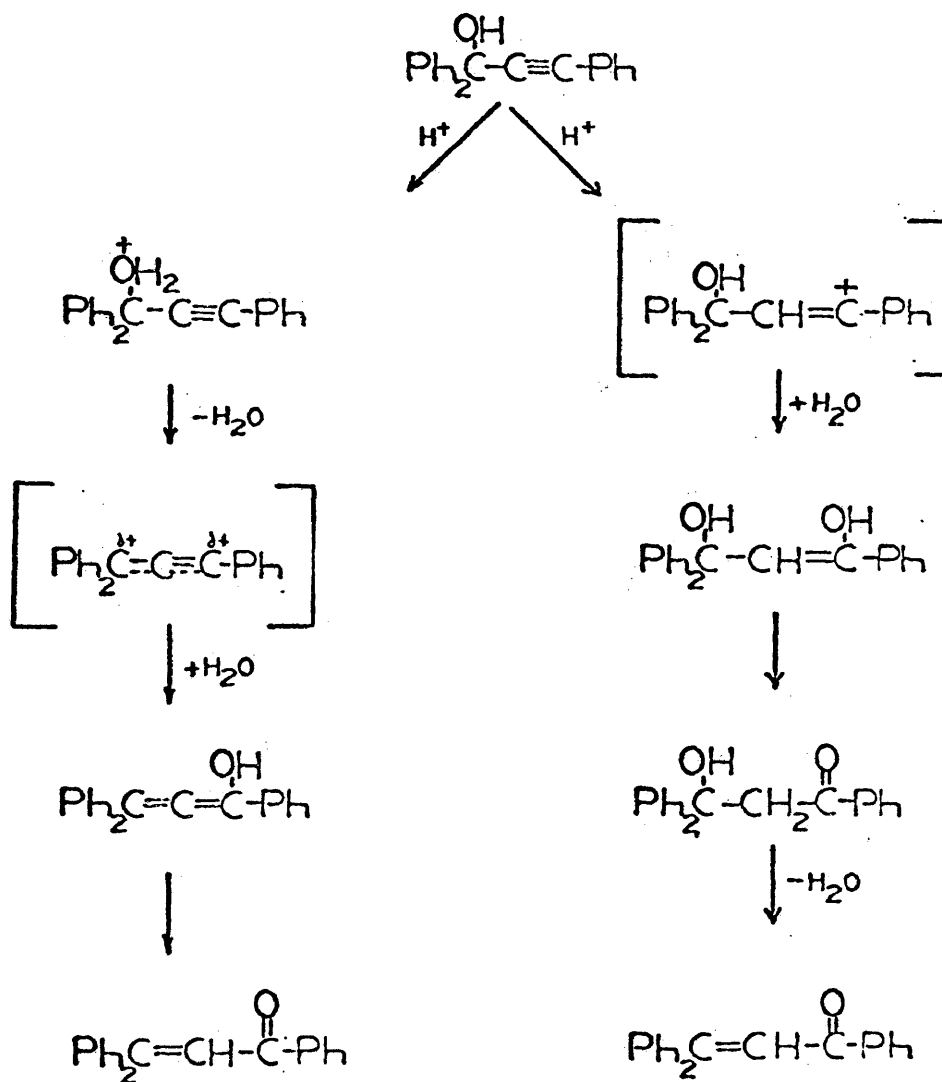
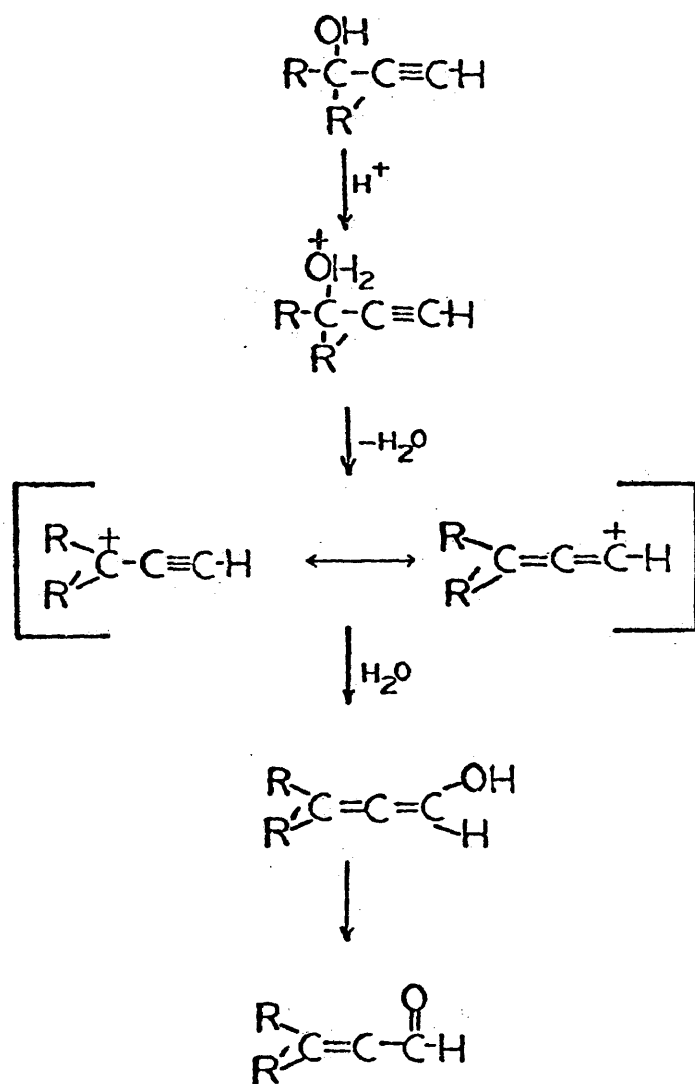




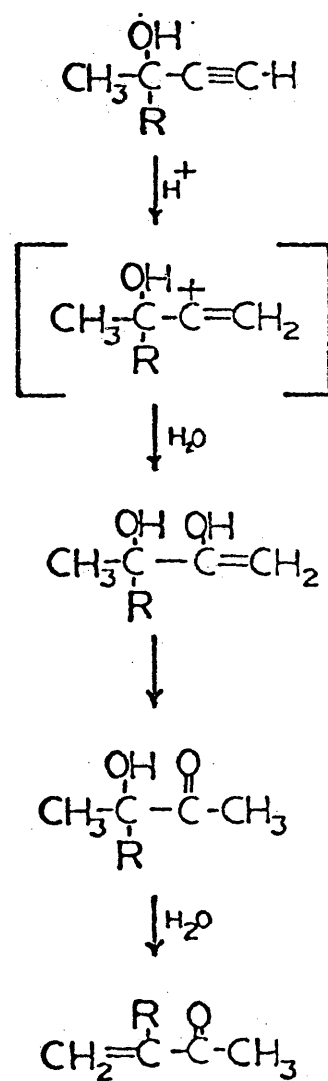
Figure 17

## The Meyer-Schuster Rearrangement and the Rupe Reaction

## Meyer-Schuster



## Rupe



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