THE SOLVOLYSIS OF TRIARYHALOALLENES

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

By

H. Wayne Moran

1971

APPROVAL SHEET

This thesis is submitted in partial fulfillment of

the requirements for the degree of

Master of Arts

N. Wayne Moran

Author

Approved, August 1970

Melvyn D. Schiavelli

Melvyn D. Schiavelli, Ph.D.

Trevor B. Hill

Trevor B. Hill, Ph.D.

Robert Orwoll

Robert Orwoll, Ph.D.

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor Melvyn D. Schiavelli, under whose guidance this investigation was conducted, for his patient guidance and criticism throughout the investigation. The author is also indebted to Professor Robert A. Orwoll and Professor Trevor B. Hill for their careful reading and criticism of the manuscript.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

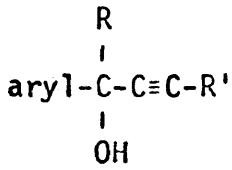
ABSTRACT

The solvolysis of several triarylchloroallenes was investigated to determine the reaction mechanism. In aqueous acetone these allenyl chlorides solvolyze to chloride ion and the substituted propargyl alcohol by an S_N1 type mechanism. Kinetic studies revealed first-order rate behavior, and the rate of product formation was increased by increased solvent polarity, and sensitive to substituents on the α-phenyl group. A $\rho = -2.0$ was computed from the rates of solvolysis of 3,3-diphenyl-1-arylchloroallenes at 25^{o} and Brown's σ^{+} constants. These data are consistent with formation of an intermediate propargyl-allenyl resonance cation. Activation parameters for 1-(4-chlorophenyl)-3,3-diphenylchloroallene were determined.

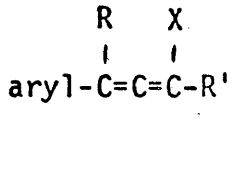
THE SOLVOLYSIS OF TRIARYHALOALLENES

INTRODUCTION

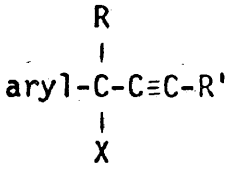
In a series of papers published in the early 1930's Marvel, et al., reported the preparation of a variety of aryl substituted tertiary propargyl alcohols (I) and the conversion of these alcohols to the corresponding halides.[1]



(I)



(II)



(III)

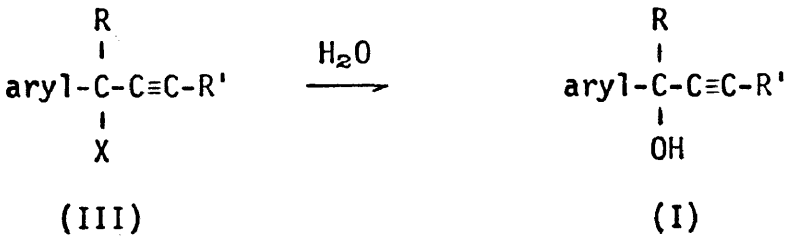
X = halogen

a) R = R' = C_6H_5

b) R = $C(CH_3)_3$; R' = C_6H_5

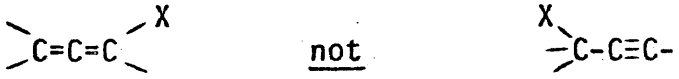
c) R = C_6H_5; R' = $C(CH_3)_3$

Related compounds had been prepared earlier by Moureu and Dufraisse, et al., (Ia)[2], and Willemart (Ib, Ic).[3] At the time of these investigations the possibility of an acetylene-allene rearrangement was recognized because of the frequent low reactivity of the halides to silver ion and the formation of allenyl products during some reactions. However, propargyl structures (III) were assigned the halo derivatives since hydrolysis yielded the original propargyl alcohol.

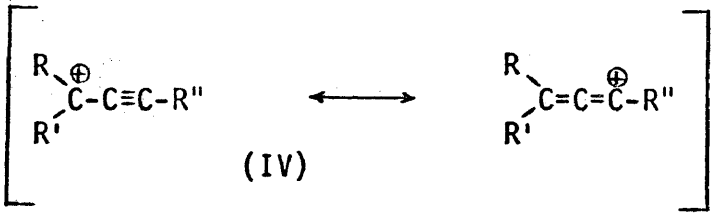


(III) (I)

In 1964 a re-examination of a number of these halides by Jacobs and Fenton[4] established their structures as the allenyl (II) rather than the propargyl configuration



This investigation led to the proposal that the alcohol formed from hydrolysis arose by attack at the propargyl position of a carbonium ion (IV) formed by the initial ionization of the halide.



(IV)

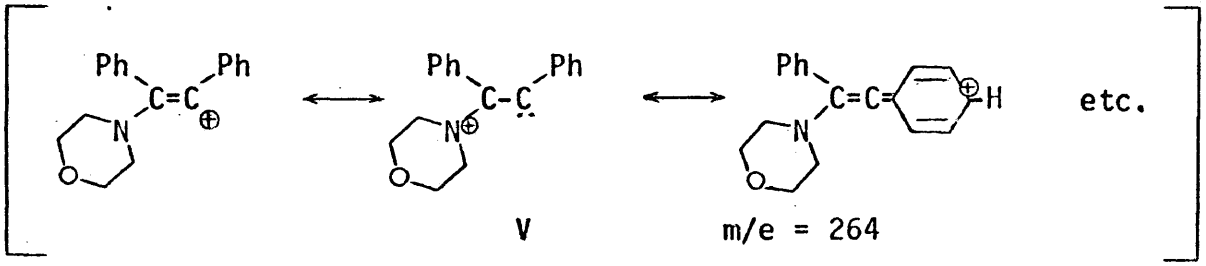
The purpose of the present work was to establish the mechanism for the solvolysis of haloallenes and the validity of the assumptions of earlier workers.

Because of the vinylic nature of the allenyl structure a brief summary of recent work in the area of vinyl cations will now be presented. Early work, showing the inertness of simple vinyl halides toward alcoholic silver nitrate[5] suggested vinyl halides were difficultly solvolyzed. However, in 1964 Grob and Cseh[6] reported the solvolysis

of α-bromostyrenes via an unimolecular mechanism; thus leading to the recognition of vinyl halide solvolysis as a plausible pathway to the study of vinyl cations. Vinyl cations have been postulated as intermediates in other reactions as well.[7] Grob and Cseh made use of the resonance stabilizing ability of the adjacent aryl group to lower the energy of activation for ionization. Solvolysis was reported to exhibit first-order rate constants which increased with increasing electron donating ability of the para-substituent. The rate constants were unchanged by addition of excess base and directly dependent on the solvent composition as demonstrated by the approximate tenfold increase in the reaction rate of α-bromostyrene in going from 80% aqueous ethanol to the more ionizing 50% aqueous ethanol. The para-nitro compound, however, gave results suggesting S_N2 behavior which was ascribed to the destabilization of the cation intermediate by the electron-withdrawing characteristic of the nitro group. The high energy of the transition state requires more extreme conditions to effect reaction, and the competitive bimolecular elimination reaction becomes the preferred pathway.

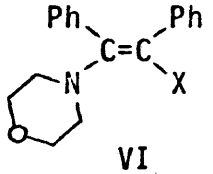
Further work with aryl substituents was performed by Miller and Kaufman[8] who reported an S_N1 mechanism for triaryliodoethylene solvolysis, and by Rappoport and Gal[9] who reported vinyl cations from trianisylvinyl halide solvolysis. An investigation of the solvolysis of 2-bromo-1,3-butadiene by Grob and Spaar[10] utilized a conjugated double bond to stabilize a vinyl cation. The charge delocalizing ability of the cyclopropyl ring was used by Bergman and his co-workers[11] in their investigations of the solvolysis of 1-cyclopropyl-1-iodoethylene

and -propene systems. Hanack and Bassler[12] used similar compounds in their investigation of substituents which encourage ionization by stabilization of the intermediate vinyl cation. Huang and Lessard[13] investigated halo enamines in which the fragmentation patterns of the mass spectra showed the most important fragmented ion to be (V).



V m/e = 264

The ease of formation of this cation suggested to the authors the possibility of such structures (VI) undergoing SN1 reactions.

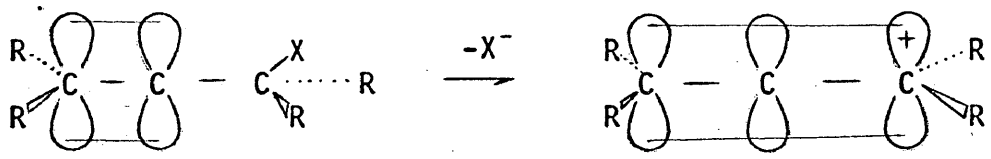


VI X = Cl, Br

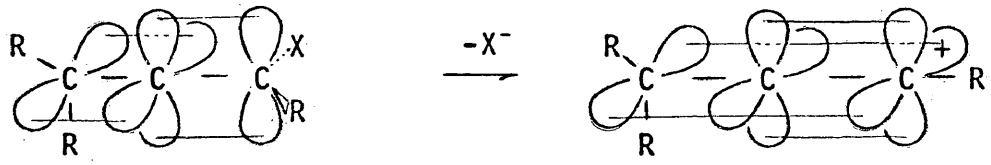
Stang and Summerville[14] reported the first completely alkyl substituted vinyl cation from the solvolysis of the triflate (trifluoromethanesulfonate) esters of cis- and trans-2-buten-ol, although it had earlier been reported by Peterson and Indelicato that the brosylate and tosylate esters of the same compounds failed to react.[15a] More recent work by Peterson, et al., on these compounds would seem to confirm Stang's work, however.[15b]

With the vinyl cation established as a plausible intermediate in a number of solvolysis reactions a study of the effect of the additional double bond in the allenyl system was undertaken. Allylic halides undergo solvolytic reactions at a rate greater than that of their saturated

analogs due to charge delocalization through the three-carbon π-system.[16] Work in these laboratories was undertaken to determine whether allenyl halides, the "unsaturated" analogs of the allyl system, would exhibit similar behavior under solvolytic conditions.[17]



allyl halide (VII)



allenyl halide (VIII)

It can be seen that overlap in both cases is similar and just as in the allyl system (VII) a stabilizing effect should be expected due to the delocalization of charge in the cation through the three-carbon π-system of the allenyl system (VIII). One might expect allenyl halides to solvolyze at a rate faster than their vinyl counterparts.

A kinetic study of the triarylhaloallenyl system was undertaken to achieve the stated purposes of this work. Reaction progress was followed conductometrically with the determination of rate constants performed via a least squares analysis of the experimental data. Reactants and products were subjected to spectral analysis for identification and characterization.

EXPERIMENTAL

Routine melting points reported below were determined with an Arthur H. Thomas capillary melting point apparatus. Melting points and boiling points are uncorrected. Routine infrared spectra were obtained using a Perkin-Elmer Model 700 Infrared Spectrophotometer. 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 on the Model 457 were determined on solutions of carbon tetrachloride.

A. Materials

1. n-Butyllithium, 22.6% by weight in hexane was obtained from Alfa Inorganics. This material was used without further purification.
2. Benzophenone, mp 48-49°, was obtained from J. T. Baker Chemical Co. This material was used without further purification.
3. Thionyl Chloride, Reagent Grade, was obtained from J. T. Baker Chemical Co. This material was used without further purification.
4. Pyridine, Certified A.C.S., was obtained from Fisher Scientific Co. This material was used without further purification.
5. Acetone, Certified A.C.S., used in the kinetic studies, was obtained from Fisher Scientific Co. Each 1.5 liters was distilled

from 60 g of potassium permanganate and approximately two grams of sodium hydroxide pellets. The fraction collected between 56-56.5° was sealed and stored until used. Each newly distilled quantity of acetone was measured for conductance before each kinetic study and found to have a maximum conductance of less than five micromhos at 25° C.

6. 4-Chloroacetophenone, White Label, was obtained from Eastman Organic Chemicals. This material was used without further purification.
7. 4-Methylacetophenone, Yellow Label, was obtained from Eastman Organic Chemicals. This material was used without further purification.
8. Phosphorous Pentachloride, Reagent Grade, was obtained from Allied Chemicals, Baker and Adamson. This material was used without further purification.
9. Anisaldehyde, White Label, was obtained from Eastman Organic Chemicals. This material was used without further purification.
10. Malonic Acid, Reagent Grade, was obtained from Fisher Scientific Co. This material was used without further purification.
11. Bromine, Reagent Grade, was obtained from Allied Chemical, Baker and Adamson. This material was used without further purification.
12. Potassium t-Butoxide was obtained from Alfa Inorganics. This material was used without further purification.
13. 4-Methoxycinnamic acid was prepared by adapting a procedure from Organic Reactions.[18] One mole (136 g) of anisaldehyde and 126 g

(1.2 mole) of malonic acid in 200 ml of absolute ethanol was treated with approximately 210 g of an ammonia solution prepared by adding 65 ml of aqueous ammonia, 15M, to 245 ml of absolute ethanol (one mole NH_3). The addition of the ammonia solution precipitated a white solid. This mixture was then placed in an oil bath at 100° and refluxed for one hour. (The precipitate disappeared after refluxing began). When most of the ethanol had been removed by distillation, a yellow solid separated. The temperature of the oil bath was raised to 110° and maintained until evolution of carbon dioxide ceased. Distillation of the ethanol was continued until the product seemed dry. At this point 700 ml of distilled water and a quantity of sodium carbonate sufficient to dissolve most of the solid was added. Undissolved material was filtered and the filtrate added to a cold sulfuric acid solution (approximately 25% H_2SO_4). A white precipitate formed which was filtered, washed three times with water, and left to dry, mp 167-169° (lit. 166-168°).[18]

14. 4-Methoxyphenylacetylene was prepared by adapting a procedure reported by Allen and Cook.[19] Fifty grams of p-methoxycinnamic acid was placed in a one-liter round bottom flask fitted with reflux condenser, stirrer, and dropping funnel. To this was added 250 ml of chloroform. The flask was then placed in ice water. Forty-eight grams of bromine in 200 ml of chloroform was then added dropwise over a two-hour period with vigorous stirring. The mixture was stirred an additional hour and then cyclohexene added to remove excess bromine. The solvent was

removed by aspiration and the residue washed with carbon tetrachloride. Sixty-eight grams of this product was added to 600 ml of a 10% sodium carbonate solution (foaming) and heated under a gentle reflux for two hours with stirring. The solution turned pale yellow. The reaction mixture was then extracted with three 250-ml portions of ether and the ether layer dried over anhydrous magnesium sulfate.

The solvent was removed from the filtered solution and a crystalline material resulted. This material was refluxed for four hours with 22.4 g of potassium t-butoxide in 280 ml of t-butyl alcohol. Most of the solvent was then removed by distillation and 500 ml of water added forming a dark brown oil. This mixture was extracted with four 200-ml portions of ether and the combined ether layers washed with two 100-ml portions of water and placed over anhydrous magnesium sulfate. Solvent was removed from the filtered solution by aspiration and the residue distilled. The fraction boiling at 85-90° at 8 mm (lit. bp 86° at 9 mm, mp 29°)[19] was collected, mp 29°. The overall yield was 7.5 g or 36% based on p-methoxycinnamic acid.

15. 4-Methylphenylacetylene was prepared adapting the procedure reported by Allen and Cook.[19] One hundred-forty-two grams of phosphorous pentachloride was placed in a 500-ml round bottom flask fitted with reflux condenser and dropping funnel. Eighty-eight grams (0.66 mole) of 4-methylacetophenone was then added dropwise over a period of approximately one hour. The reaction is extremely exothermic and the solution turned yellow-orange

during the addition. After the addition the solution was maintained between 70-80^{o} for one hour. Hydrogen chloride and phosphorous oxychloride formed during the reaction were stripped off under aspiration.

The solution was next vacuum distilled and the fraction boiling between 80 and 95^{o} at 10-15 mm collected. Seventy grams of this material was then placed in a one-liter round bottom flask to which 400 ml of absolute ethanol and 100 g of potassium hydroxide were added. This mixture was refluxed for 20 hours and the resulting red solution poured into one liter of ice water. The organic layer was separated and the water layer extracted with three 300-ml portions of ether. The combined ether layers were washed with 200 ml of a saturated sodium bicarbonate solution and then concentrated to 500 ml. To this ether solution was then added the separated organic material and this solution placed over anhydrous magnesium sulfate. The filtered solution was aspirated and the residue distilled. The fraction boiling between 60 and 65^{o} at 15 mm (lit. 59-60^{o} at 16 mm)[19] was collected. The yield was 28.5 g or 37%, based on p-methylacetophenone.

16. 4-Chlorophenylacetylene was prepared in a manner identical to the preparation of 4-methylphenylacetylene using 102 g of 4-chloroacetophenone (0.66 mole). The product from the reaction with PCl_5 distilled at 65^{o}-70^{o} at .7 mm. Due to clogging of the distillation apparatus an accurate reading of the temperature and pressure of the distilling 4-chloroethynylbenzene could not

be made. However, the melting point was 45-46° (lit. mp 43°, bp 62-63° at 13 mm).[19] The yield was approximately 25 g or 28% based on p-chloroacetaphenone.

17. 1,1-Diphenyl-3-(4-chlorophenyl)-2-propyn-1-ol, was prepared according to the procedure reported by Olah and Pittman[20] for the preparation of 1,1,3-triphenyl-2-propyn-1-ol. After a fifteen minute nitrogen purge of the system a 1.6M solution of n-butyllithium was prepared by injecting 32 ml of a n-butyllithium (.075 mole) solution (22.6 wt% in hexane) into 14.8 ml of hexane. The reaction flask was immersed in an ice bath and 4-chlorophenylethynllithium was then prepared by the dropwise addition of 10.3 g (.075 mole) of 4-chlorophenylacetylene (heated to its mp). The solution turned orange. Following the addition of 25 ml of anhydrous ether, 13.7 g (.075 mole) of benzophenone dissolved in 50 ml of anhydrous ether was added dropwise. The solution turned green and then pale orange. Following this addition the ice bath was removed, the reaction mixture was refluxed for two hours and then hydrolyzed with approximately 65 ml of distilled water. A nitrogen atmosphere had been maintained until the beginning of the reflux period. A white precipitate formed on first addition of the water, but redissolved on further addition. The water layer was separated and the ether layer washed with three 35-ml portions of water and placed over anhydrous magnesium sulfate to dry. After filtration the ether was removed by aspiration and an oil remained (22.5 g, crude yield 94%).

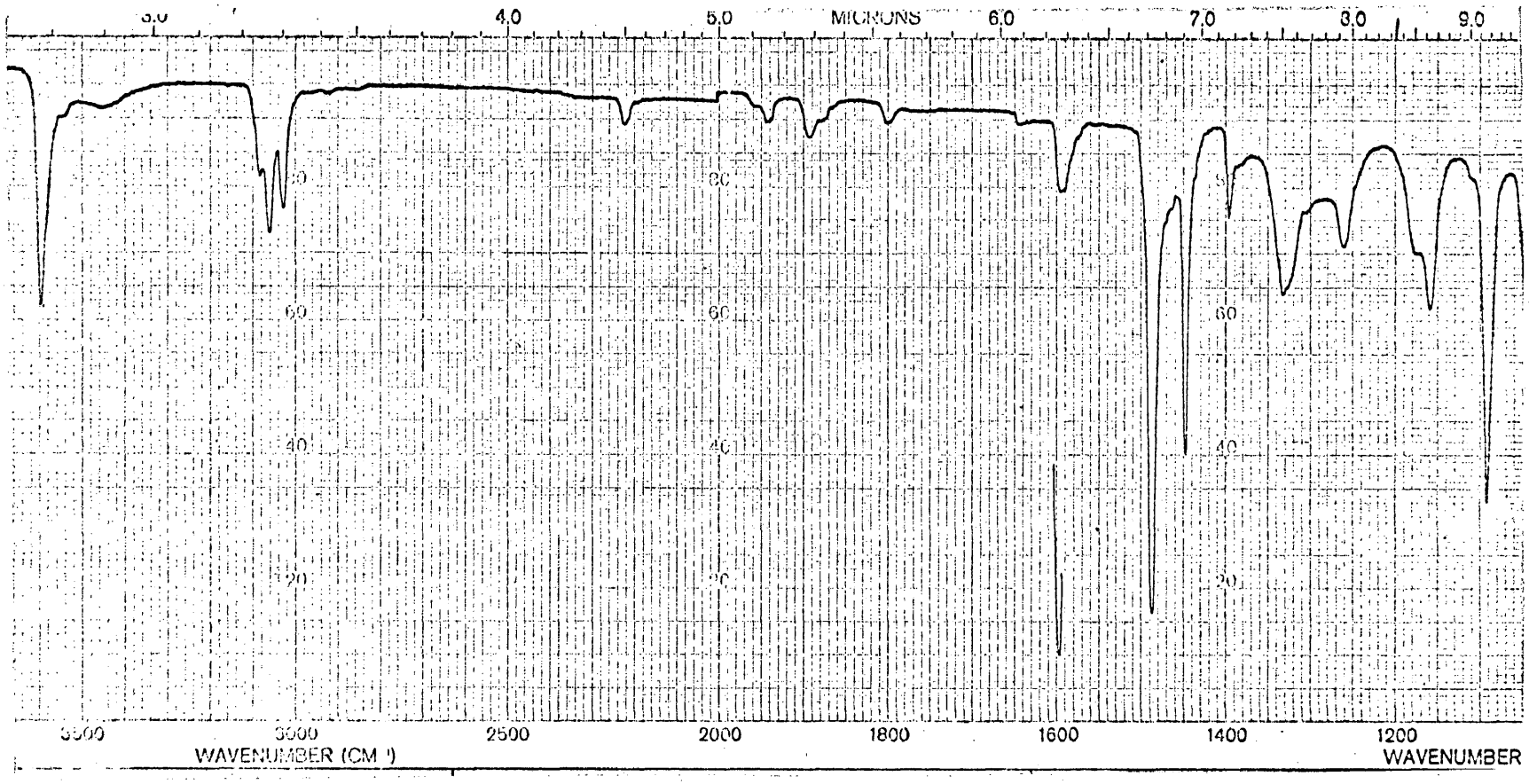
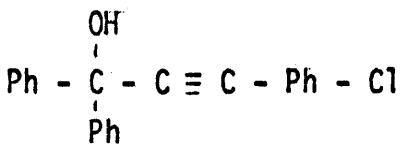


Figure 1.

Ir spectrum of 1,1-Diphenyl-3-(4-chlorophenyl)-2-propyn-1-ol.



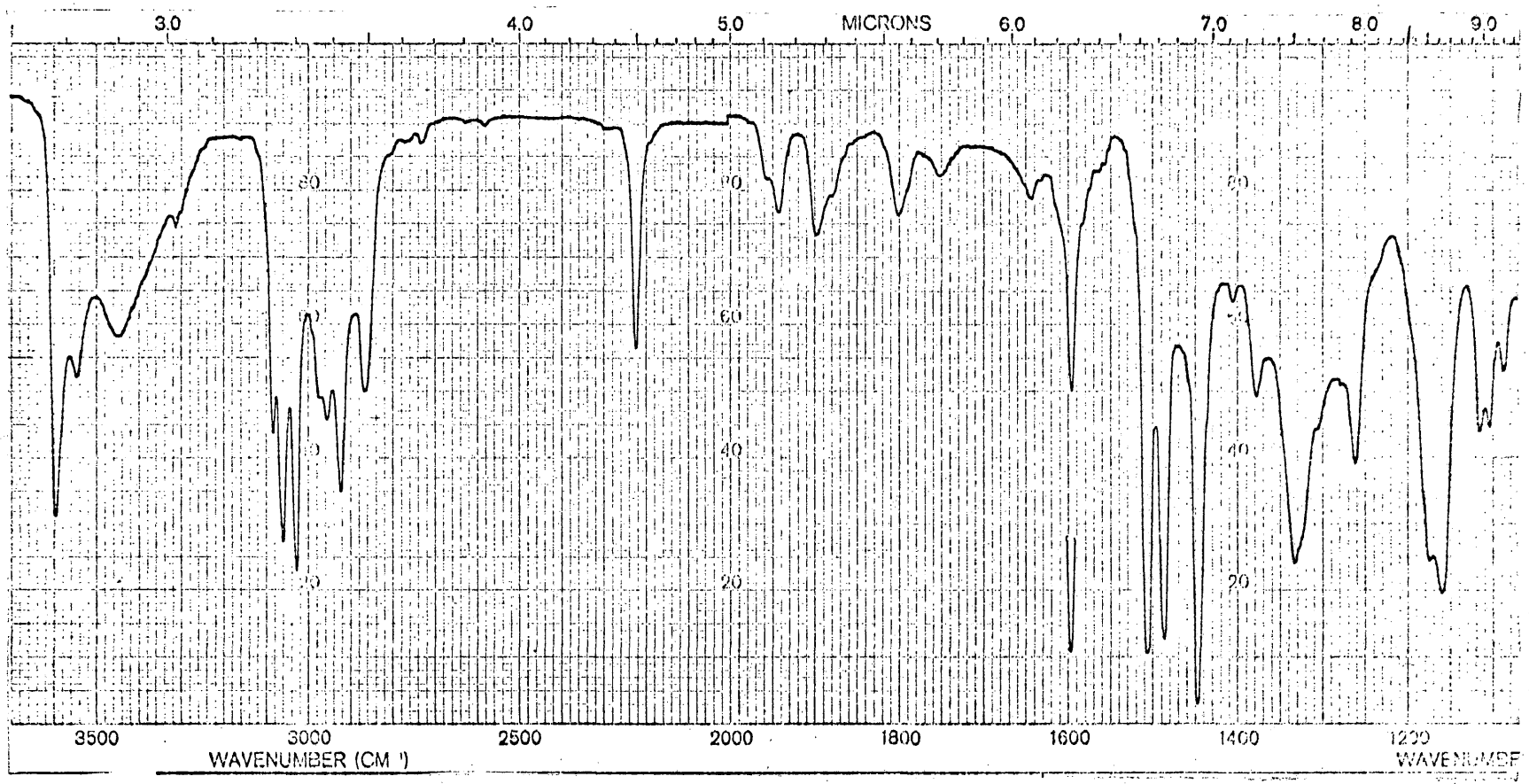
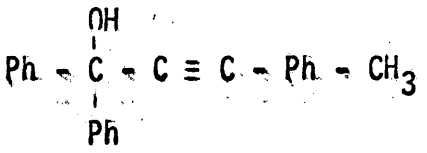


Figure 2.

Ir spectrum of 1,1-Diphenyl-3-(4-methylphenyl)-2-propyn-1-ol.



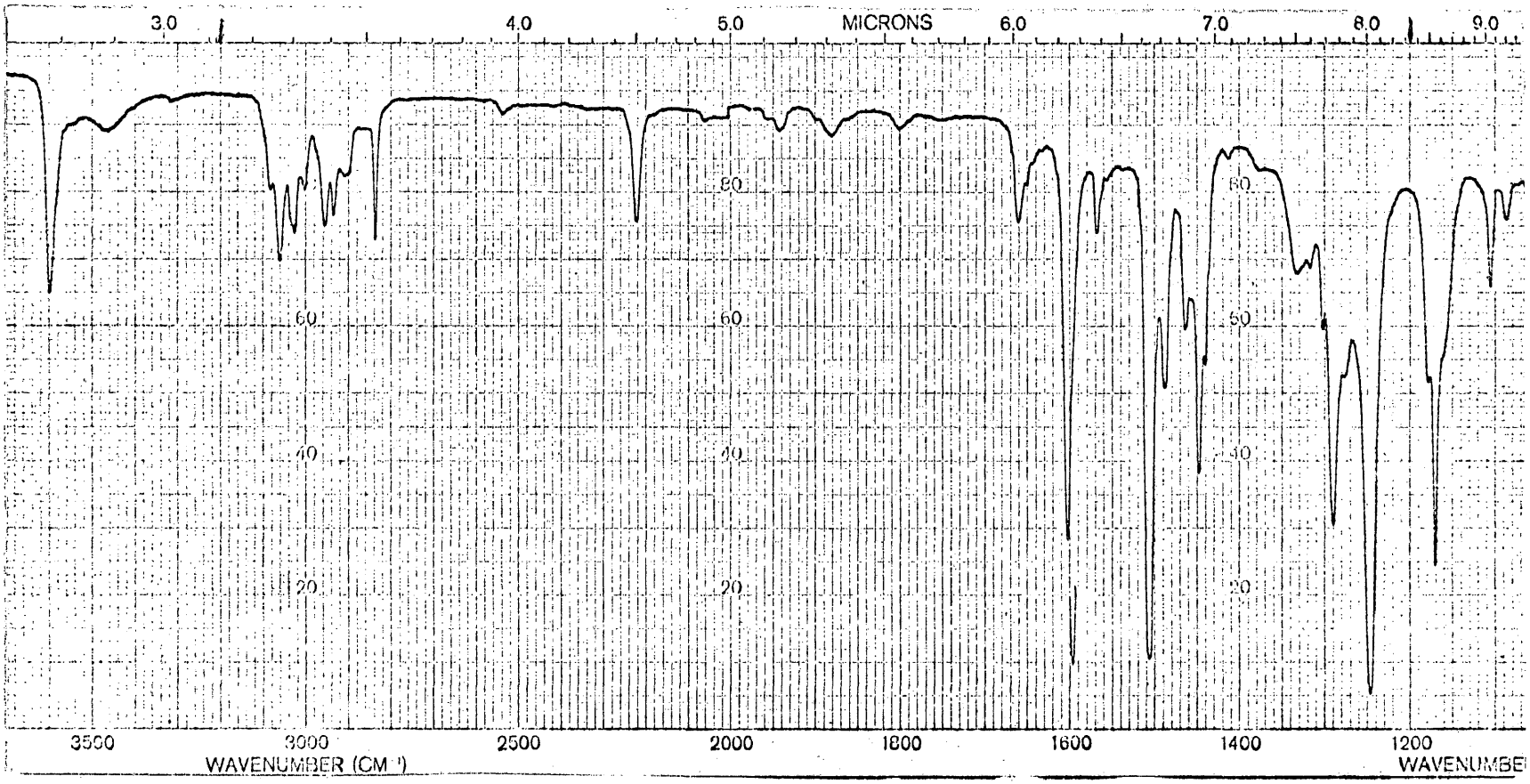
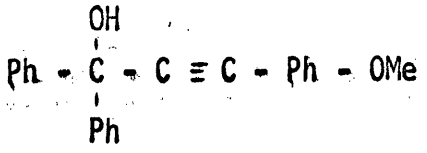


Figure 3.

Ir spectrum of 1,1-Diphenyl-3-(4-methoxyphenyl)-2-propyn-1-ol.



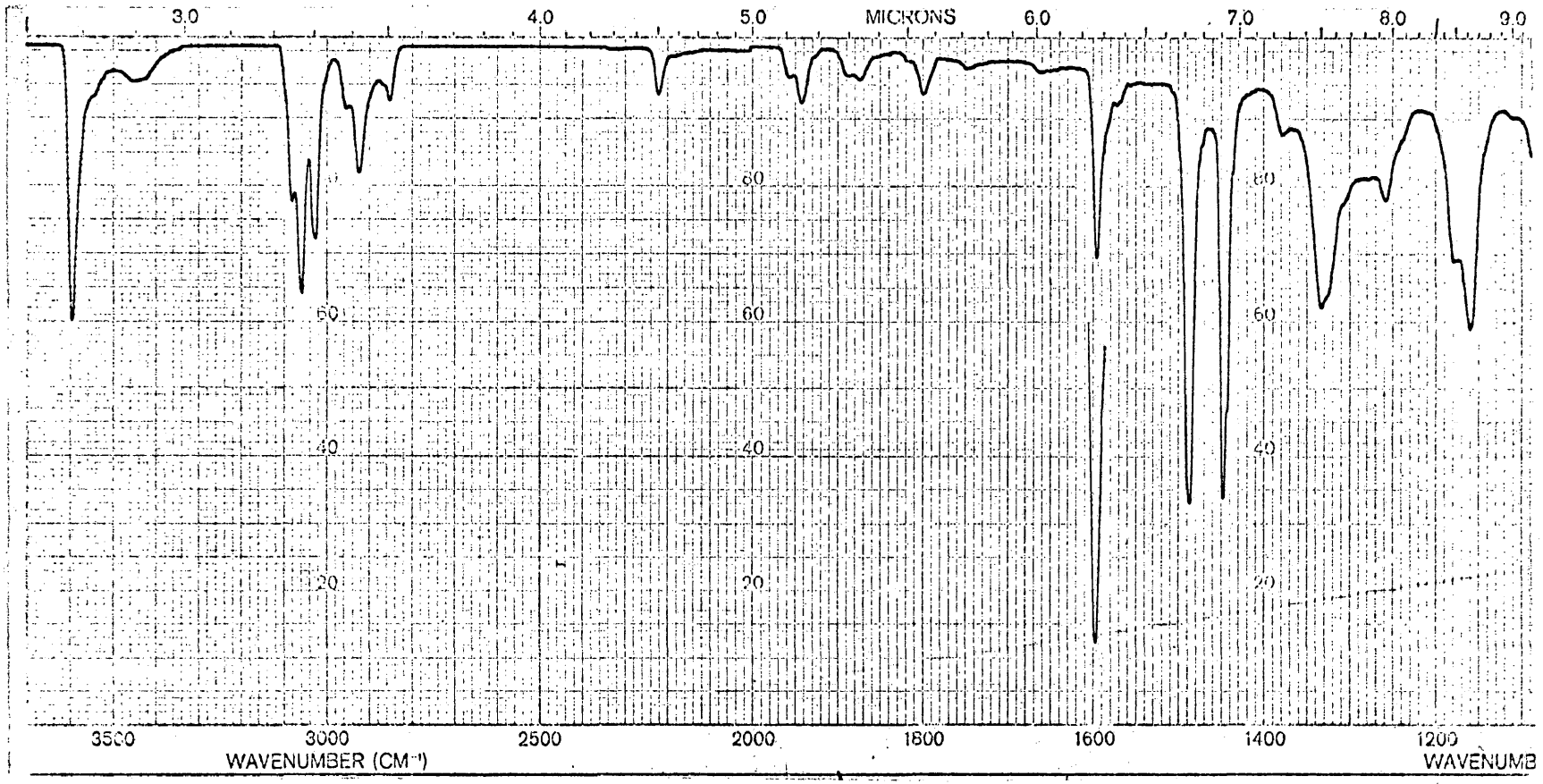
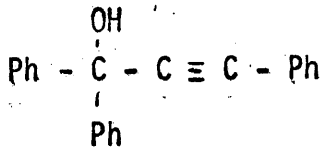


Figure 4.

Ir spectrum of 1,1,3-Triphenyl-2-propyn-1-ol.



The oil was recrystallized from an ethanol-water mixture, mp 74-75°. Ir; OH stretch 3600 cm^{-1}, C≡C stretch 2225 cm^{-1} (see Fig. 1).

18. 1,1-Diphenyl-3-(4-methylphenyl)-2-propyn-1-ol was prepared by a method identical to that for the preparation of the "p-Cl" propargyl alcohol above using 4-methylphenylacetylene. The recrystallized product gave a mp 64-66°; crude yield 94% (see Fig. 2).

19. 1,1-Diphenyl-3-(4-methoxyphenyl)-2-propyn-1-ol was prepared by a method identical to that for the preparation of the "p-Cl" propargyl alcohol above using 4-methoxyphenylacetylene. The recrystallized product gave a mp 65-66°. Ir; OH stretch 3600 cm^{-1}, C≡C stretch 2225 cm^{-1} (see Fig. 3).

20. 1,1,3-Triphenyl-2-propyn-1-ol. The author is indebted to Miss Cora J. Boswell for providing this material. Prepared using the procedure of Olah and Pittman,[20] the material had a mp 80-81° (lit. mp 81-81.5°).[20] Ir; OH stretch 3600 cm^{-1}, C≡C stretch 2225 cm^{-1}(see Fig. 4).

21. 1-Chloro-1-(4-chlorophenyl)-3,3-diphenylpropadiene was prepared by adopting the procedure reported by Jacobs and Fenton[4] for 1-chloro-1,3,3-triphenyl-propadiene. A mixture of 7.1 g of pyridene (0.09 mole) and 5.4 g of thionyl chloride (.045 mole) in 75 ml of anhydrous ether was added slowly to 14.4 g (.045 mole) of the above "p-Cl" propargyl alcohol dissolved in 75 ml of anhydrous ether. This solution was contained in a 500-ml round bottom flask immersed in an ice bath. The reaction mixture was then diluted to a total volume of 250 ml with anhydrous ether and the ice bath removed. The mixture was stirred throughout this preparation. After standing for one hour at room temperature,

the mixture was brought to reflux for five minutes and again allowed to come to room temperature for one hour. The reaction mixture was then filtered and the filtrate washed with 100 ml distilled water, 100 ml 5% hydrochloric acid, 100 ml 5% sodium bicarbonate, and twice again with 100 ml distilled water. The ether solution was dried over anhydrous magnesium sulfate. The ether was removed by aspiration from the filtered solution, leaving yellow-orange crystals (crude yield, 80%). Recrystallization from an ether-ethanol mixture yielded pale orange crystals. A second recrystallization yielded faintly pink crystals, mp 84-85°. Ir; C=C=C stretch 1926 cm^{-1} (see Fig. 5).

22. 1-Chloro-1-(4-methylphenyl)-3,3-diphenylpropadiene was prepared by a method identical to that for "p-Cl" chloroallene and yielded a white crystalline product, mp 127-128°, which turned pink at 115°. Ir; C=C=C stretch 1926 cm^{-1} (see Fig. 6).

23. 1-Chloro-1-(4-methoxyphenyl)-3,3-diphenylpropadiene was prepared by a method identical to that for "p-Cl" chloroallene and yielded a white crystalline product, mp 131-132°, which turned pink at 128°. Ir; C=C=C stretch 1926 cm^{-1} (see Fig. 7).

24. 1-Chloro-1,3,3-triphenylpropadiene. The author is indebted to Mrs. Sharon C. Hixon for providing this material. Prepared by the procedure of Jacobs and Fenton[4] the compound melted at 68-69° (lit. mp 68-69°). Ir; C=C=C stretch 1926 cm^{-1} (see Fig. 8).

B. Product Studies

About one gram of reactant (see column 1 of Table I), dissolved in a small amount of acetone, was added to the reaction flask containing

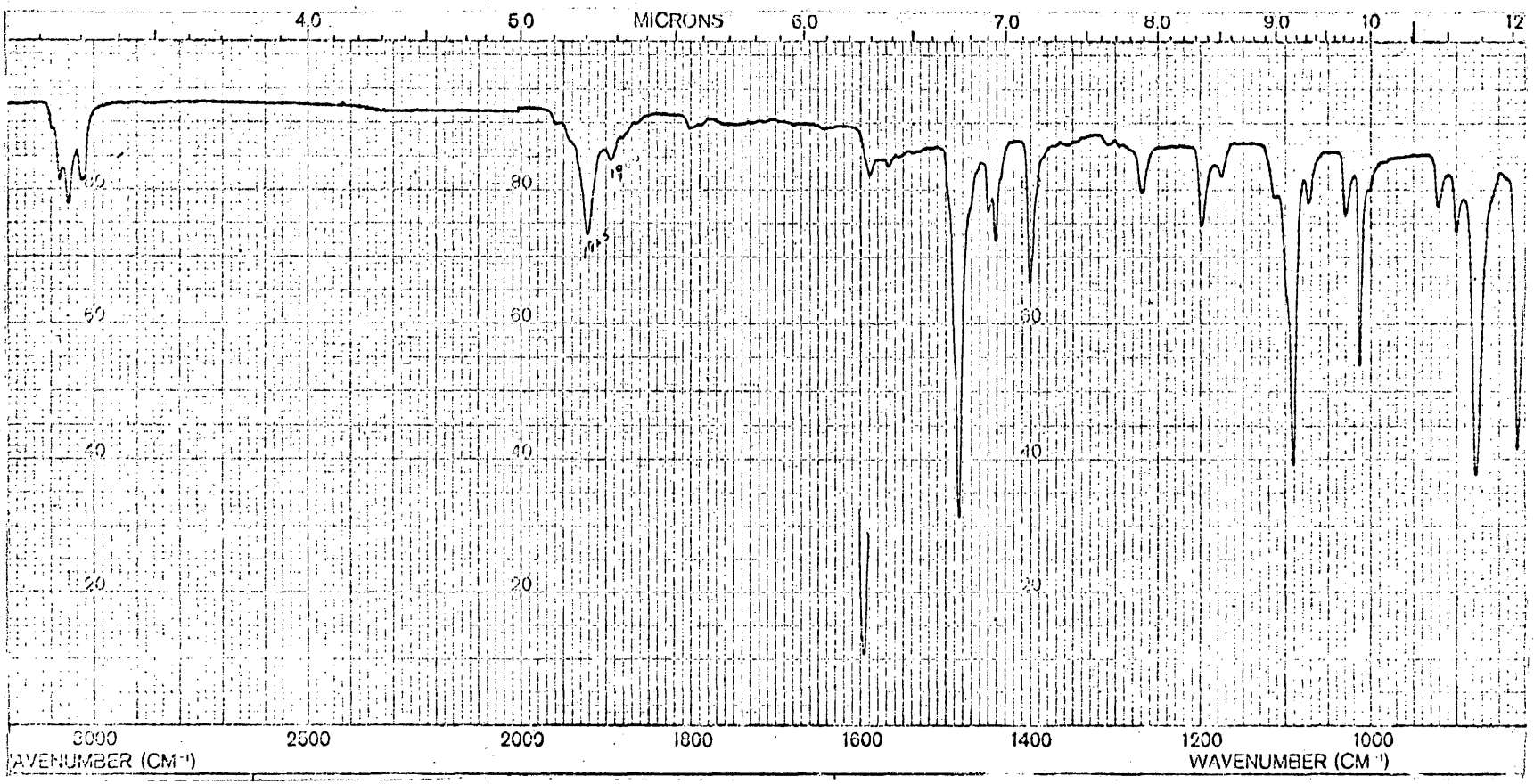
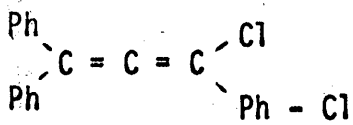


Figure 5.

Ir spectrum of 1-Chloro-1-(4-chlorophenyl)-3,3-diphenylpropadiene.



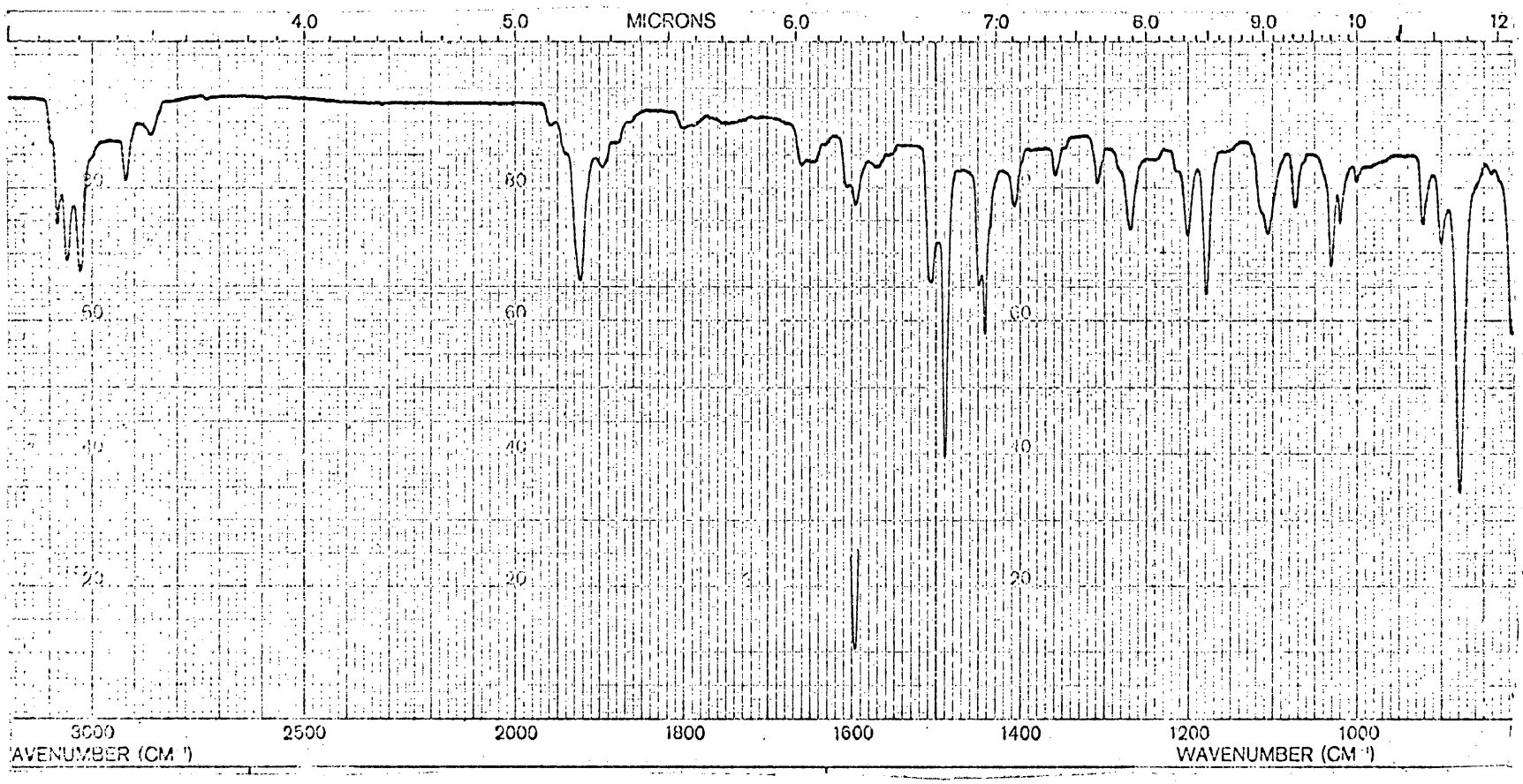
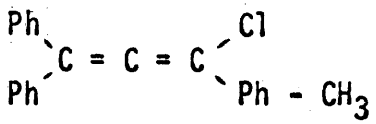


Figure 6.

Ir spectrum of 1-Chloro-1-(4-methylphenyl)-3,3-diphenylpropadiene.



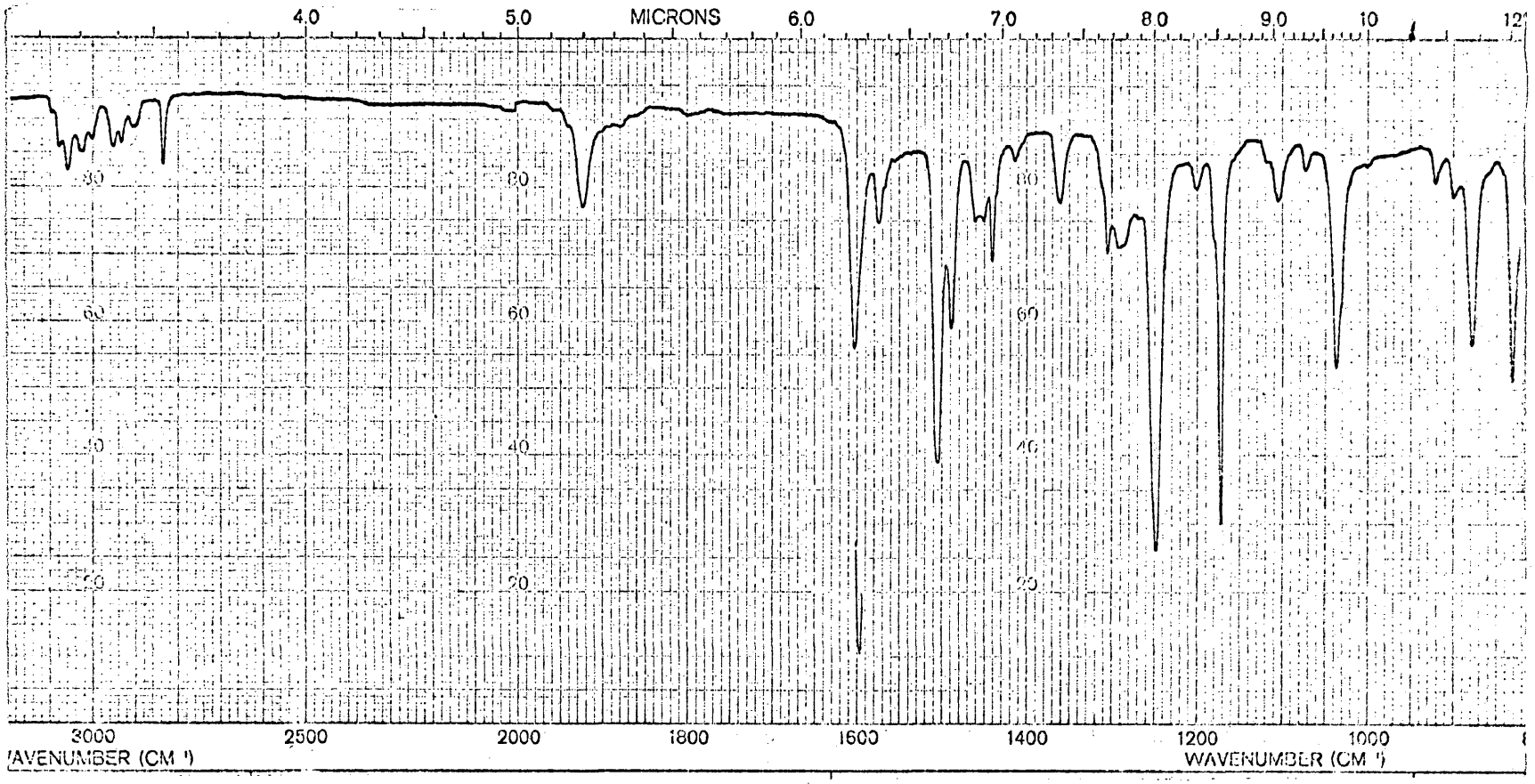
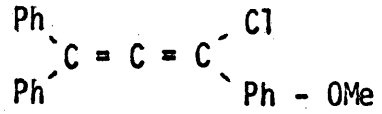


Figure 7.

Ir spectrum of 1-Chloro-1-(4-methoxyphenyl)-3,3-diphenylpropadiene.



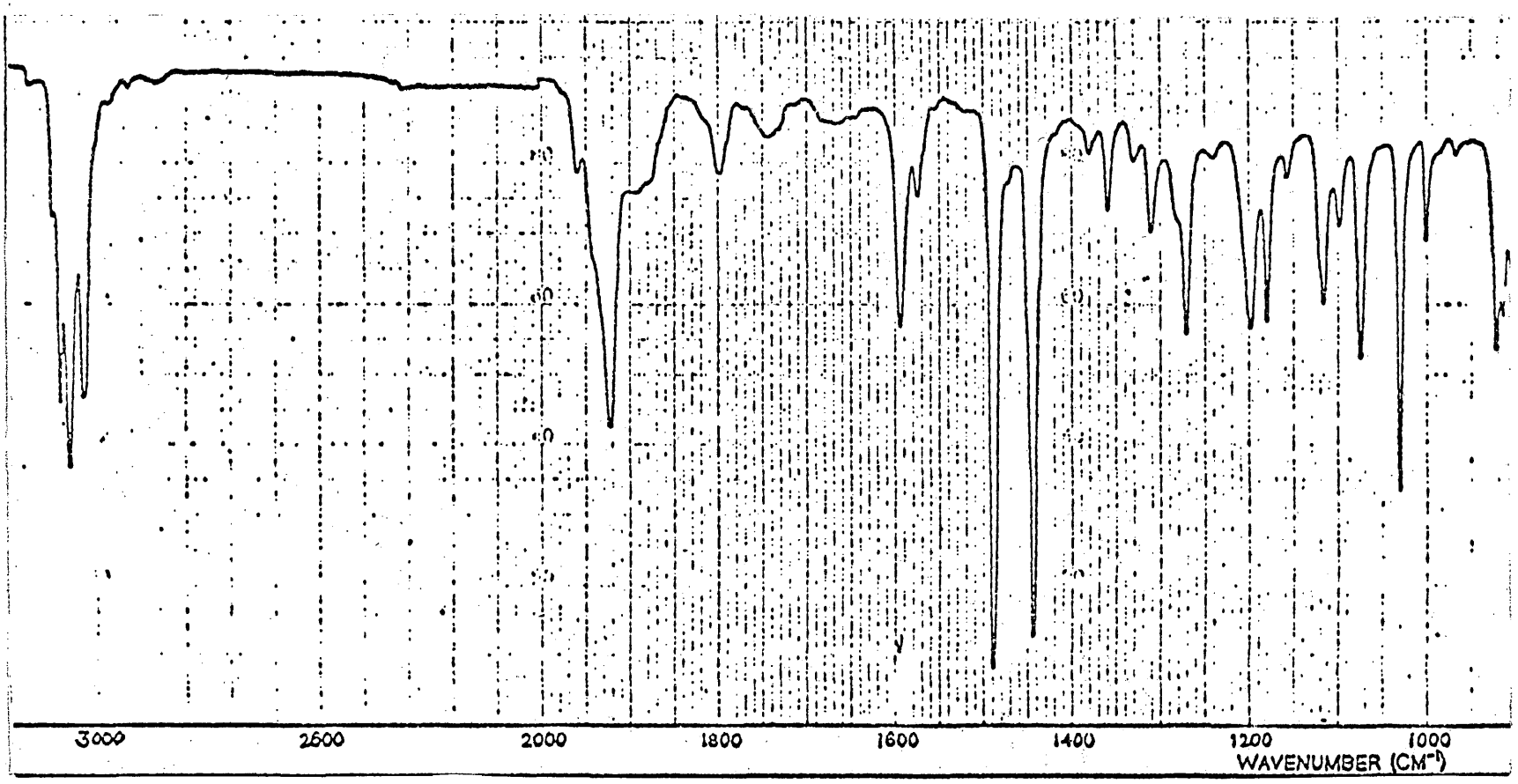
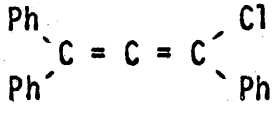


Figure 8.

Ir spectrum of 1-Chloro-1,3,3-triphenylpropadiene.



the specified amount of water and acetone (all volumes were transferred by pipet or buret). The reaction was then allowed to proceed at the specified temperature for the alotted time interval.

One liter of water was then added to the reaction mixture and a faint cloudiness appeared. This solution was then extracted with four 250-ml portions of ether and the combined solutions placed over anhydrous magnesium sulfate to dry. The ether was then removed by aspiration and an infrared spectrum made of the residue. Data from these experiments are compiled in Table I.

C. Kinetic Measurements

1. Procedure

All kinetic studies were performed using an Industrial Instruments' Conductivity Bridge, Model RC-18. Conductivity water (conductance, <1 umho) was prepared from distilled water which had been passed through a mixed bed column of a Bantam Demineralizer, Model BD-1. The temperature of each water bath was calibrated using a Leeds and Northrup B160-B Platinum Resistance Thermometer in conjunction with a Mueller Resistance Bridge from Rubican Instruments and monitored by use of a Beckmann thermometer.

These experiments were performed at a concentration of approximately 4×10^{-4}M (allene in aqueous acetone). Stock solutions of 1×10^{-2}M and 2×10^{-3}M were made by placing $5.0 \pm .07 \times 10^{-4}$ mole of the respective allene in a 50-ml volumetric flask, diluting up to the mark with acetone (1×10^{-2}M), pipetting 20 ml of this solution into

Table I

Data From Product Studies

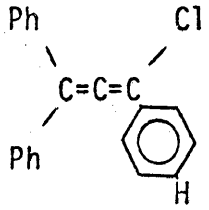
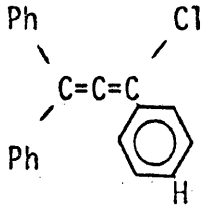
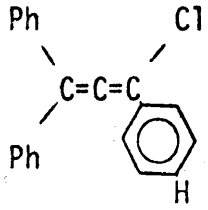
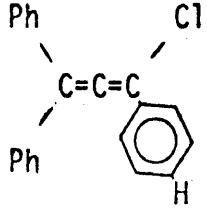
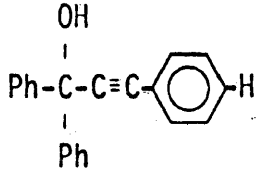
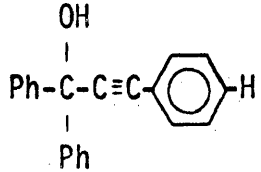
	Reactant Material	Solvent Composition H_2O (ml)	Acetone (ml)	Additional Reactants	Temperature	Time	Ir Figure No.	Results and Comments[b]
1.		300	700		61°C.	20 hrs.	9	A considerable amount of α,β-unsaturated ketone present[d]
2.		300	700		room temp.	6 hrs. (10 half-lives)	10	Only trace amounts of α,β-saturated ketone present (if present at all)[d]
3.		200	800		61°C.	45 min.	11	A considerable amount of the α,β-unsaturated ketone present.
4.		200	800		room temp.	75 min. (10 half-lives)	12	Only trace amounts of the α,β-unsaturated ketone present (if present at al

Table I

Data From Product Studies (continued)

	Reactant Material	Solvent Composition H_2O(ml)	Acetone(ml)	Additional Reactants	Temperature	Time	Ir Figure No.	Results and Comments[b]
5.		300	700	HCl	61°C.	20 hrs.	13	Only trace amounts of the α,β-unsaturated ketone present (if present at all)
6.		200	800	HCl	61°C.	45 min.	14	An amount of α,β-unsaturated ketone was present and although no quantitative means were available, the amount of this compound seemed to b less here than in case 3.

a Volumes quoted represent total amount of each solvent present, including any used in preparing reactants.

b Amounts of ketone present are in addition to the respective propargyl alcohols which are responsible for the greater parts of the spectrum.

c A titrated amount of standardized HCl was used to give a final solution with equal molar amount of alcohol and acid.

d This work was performed by Mrs. S. C. Hixon.

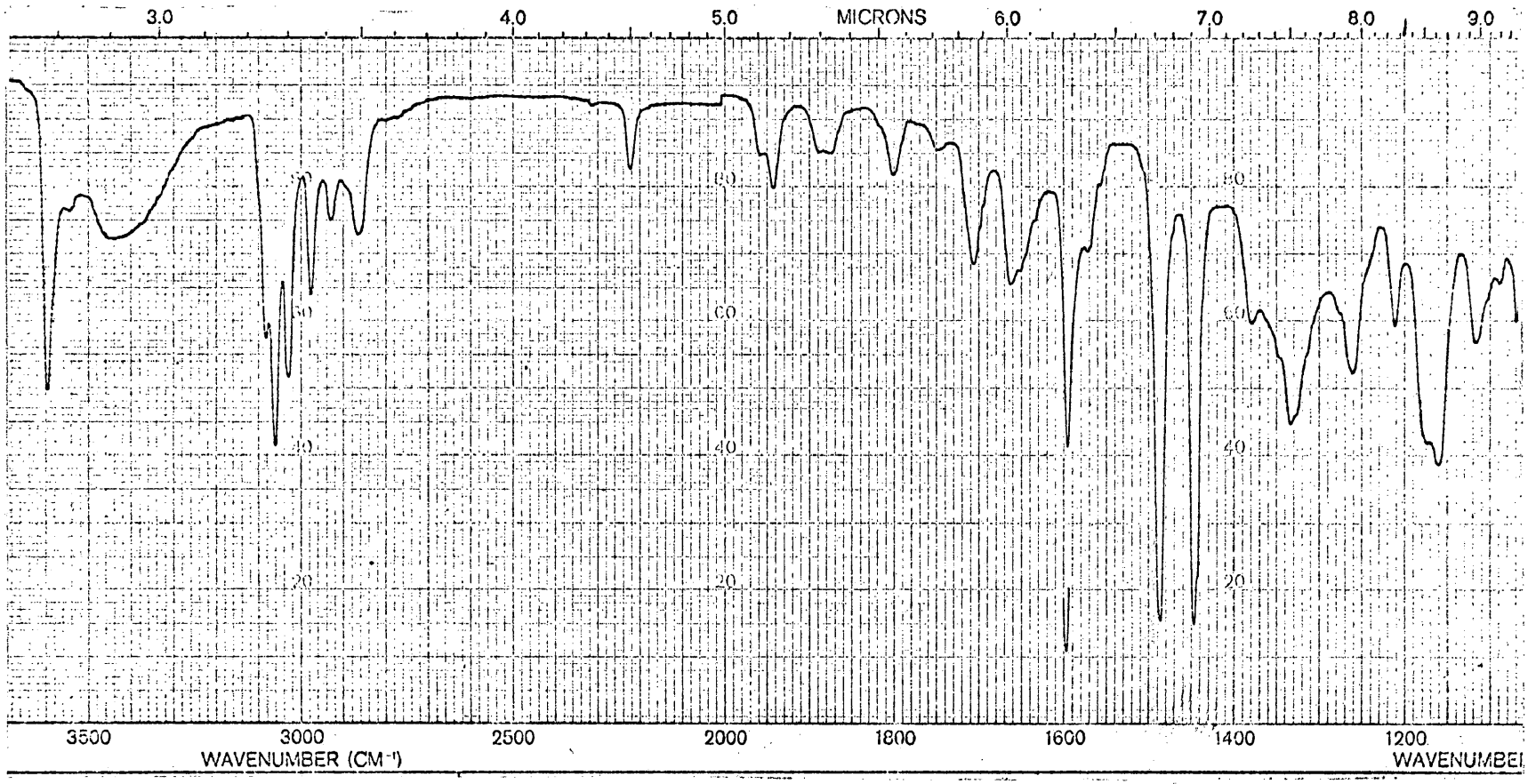


Figure 9.

Ir spectrum of product from Experiment #1, Table I.

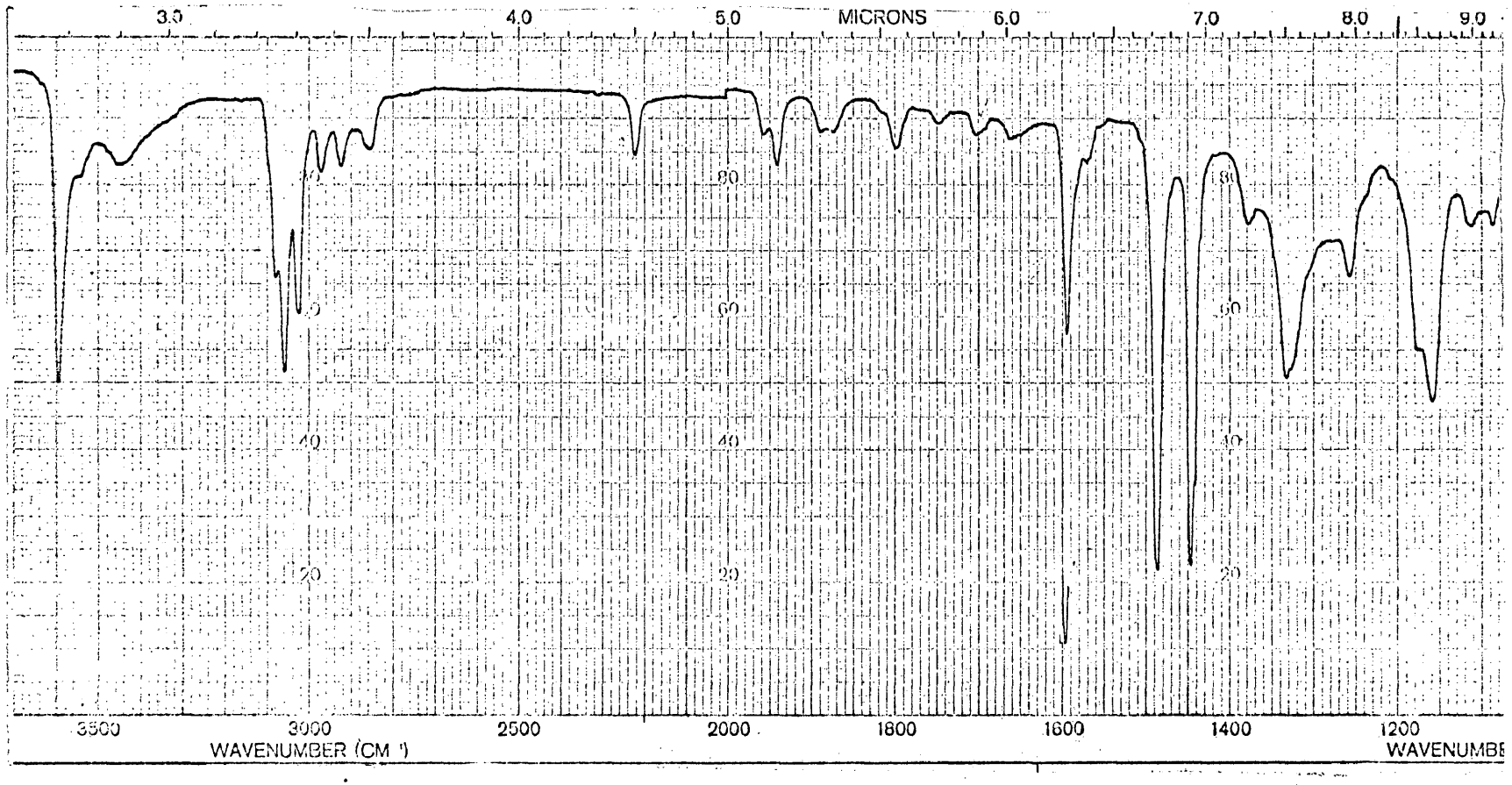


Figure 10.

Ir spectrum of product from Experiment #2, Table I.

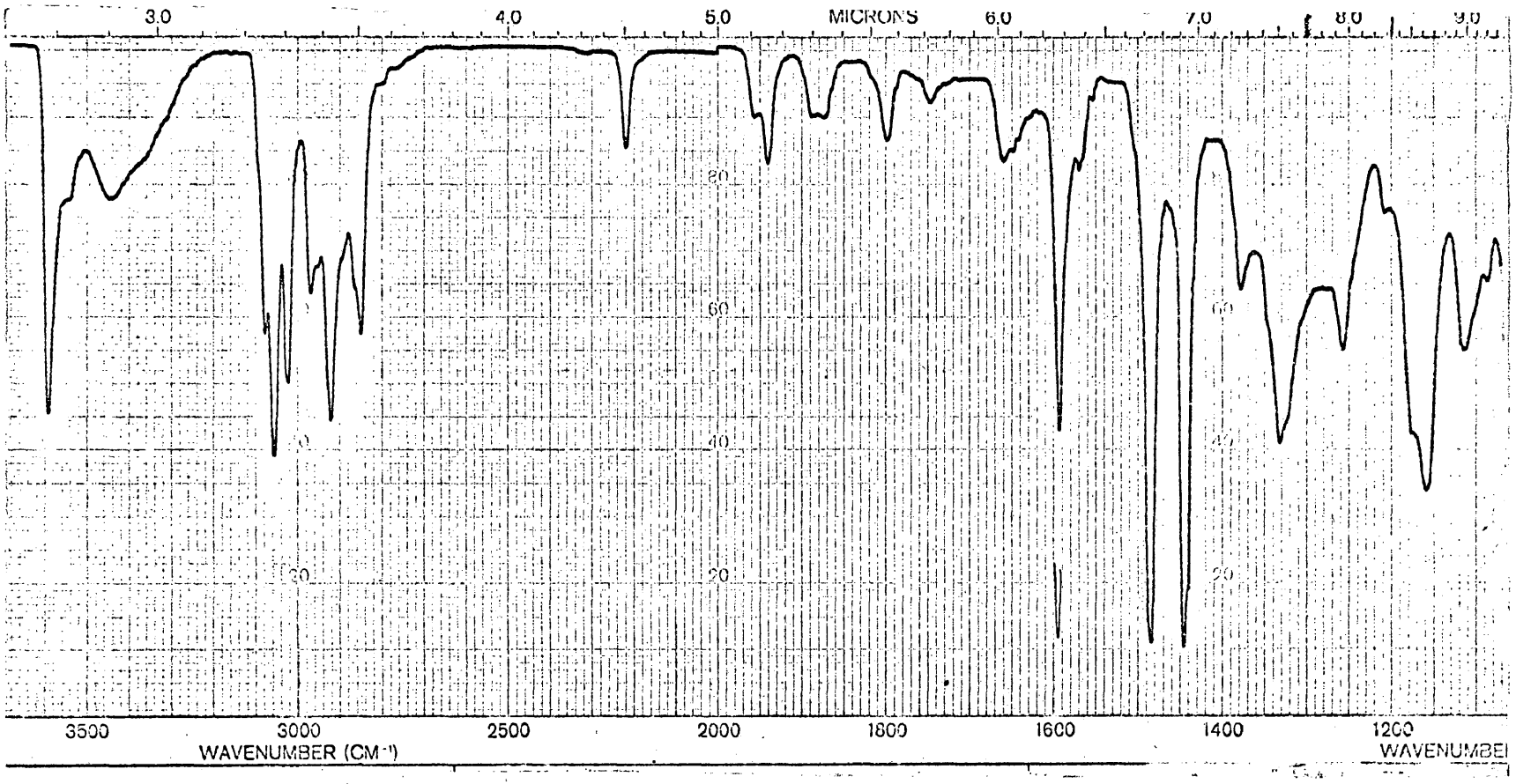


Figure 11.

Ir spectrum of product from Experiment #3, Table I.

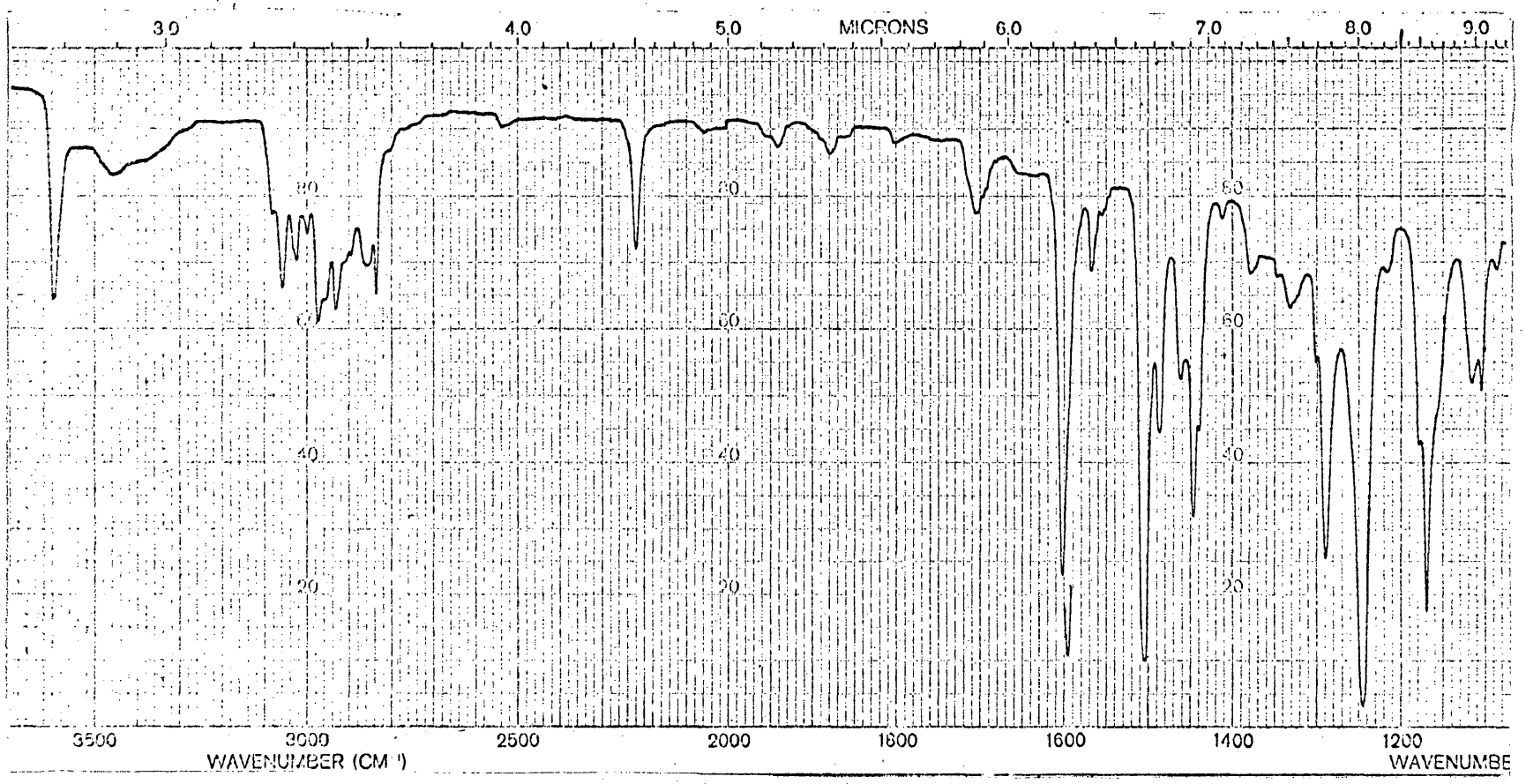


Figure 12.

Ir spectrum of product from Experiment #4, Table I.

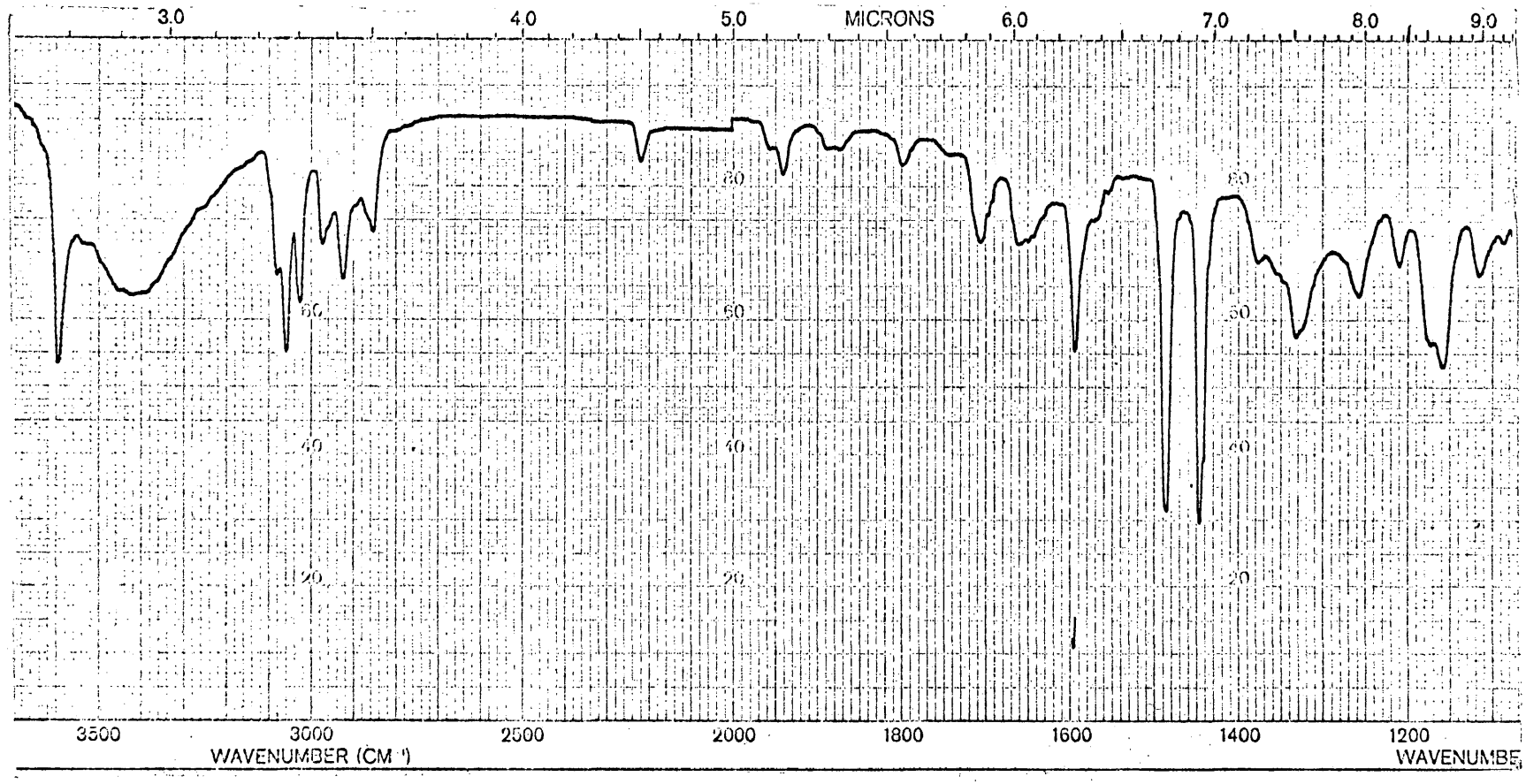


Figure 13.

Ir spectrum of product from Experiment #5, Table I.

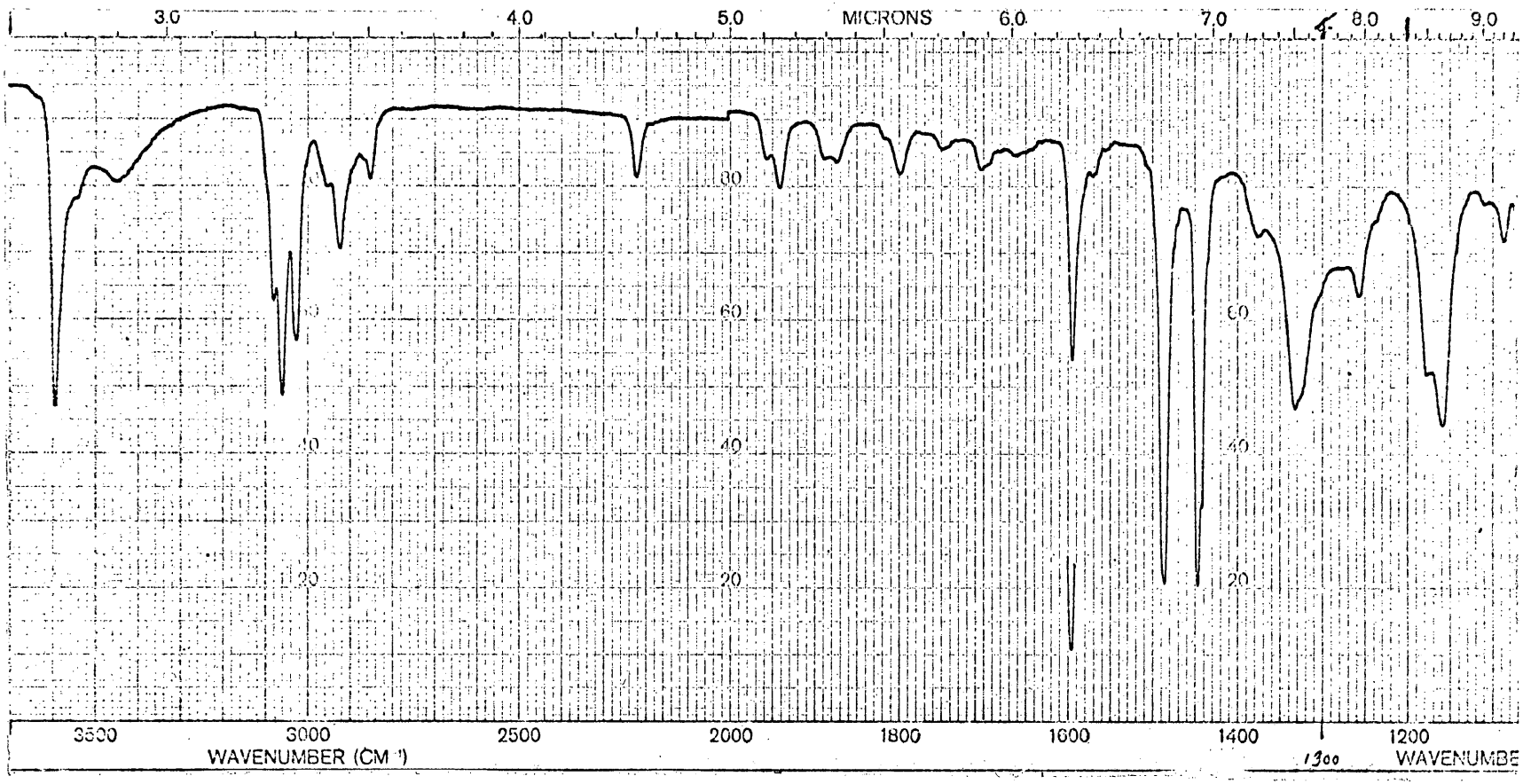


Figure 14.

Ir spectrum of product from Experiment #6, Table I.

a 100-ml volumetric flask, and filling it to the mark with acetone (2×10^{-3}M). A portion of the crude allene sufficient to give the desired amount for each new stock solution was recrystallized just prior to preparation.

Preparation of a typical kinetic run:

For a desired final solution of 80:20 acetone:water, 10 ml of the stock solution (2×10^{-3}M) was pipetted into a 50-ml volumetric flask. Exactly 30 ml of acetone was then added. This solution and a quantity of conductivity water were then equilibrated at the reaction temperature for fifteen minutes. When 10.0 ml of this water was then added to the allene solution, an 80:20 acetone:water solution, approximately 4×10^{-4}M in allene, was obtained. The flask was then stoppered and inverted several times to insure a uniform solution. Timing was begun with the addition of the water. The conductivity cell, a borosilicate glass cell with platinum electrodes and a cell constant of approximately 0.17 cm^{-1}, was rinsed twice with this solution, filled, and placed in the constant temperature bath. Measurements were then made of the changing conductivity.

2. Calculations

Graphs of log (C_∞ - Ct/C_∞ - C_o) - the logarithm of the fraction unreacted - versus time resulted in good first-order plots of the data. The fraction unreacted (in this case where the concentrations of HCl are small) is represented by the difference in conductivities

at infinity, C_∞, and time t, C_t, divided by the difference in conductivities at infinity and time zero, C_o. A computer program, LSG, written by D. F. Detar and C. E. Detar[21] was used to calculate the best value of the rate constant by a least squares fit of the data. This program is abstracted from a larger and more sophisticated program, LSKIN1. Both programs, however, perform nearly the same function except that the LSG does not have general plotting options. A typical plot of the data and a computer printout can be seen in Figures 15 and 16 respectively.

Experimental infinity values were within 1% of the computed value. These values were also, within experimental deviations, equivalent to the conductance of prepared infinity concentrations of HCl. These were determined during an examination to assure the linearity of the conductance-concentration relationship (see Section II D, p. 33).

D. A Test of the Linearity of the Conductance-Concentration Relationship

This experiment involved the preparation of a series of solutions resembling the experimental conditions of the kinetic studies. Four solutions of concentrations equaling 2 X 10^{-4}M, 4 X 10^{-4}M, 6 X 10^{-4}M, and 8 X 10^{-4}M in HCl and 1-(4-chlorophenyl)-3,3-diphenylchloroallene were prepared. Each solution was brought to equilibrium at 35° in the conductivity cell and conductance reading made. The respective conductances were plotted against concentration (see Fig. 17) and the results verified the expected linearity.

Figure 15

First-order Plot of Typical Kinetic Run

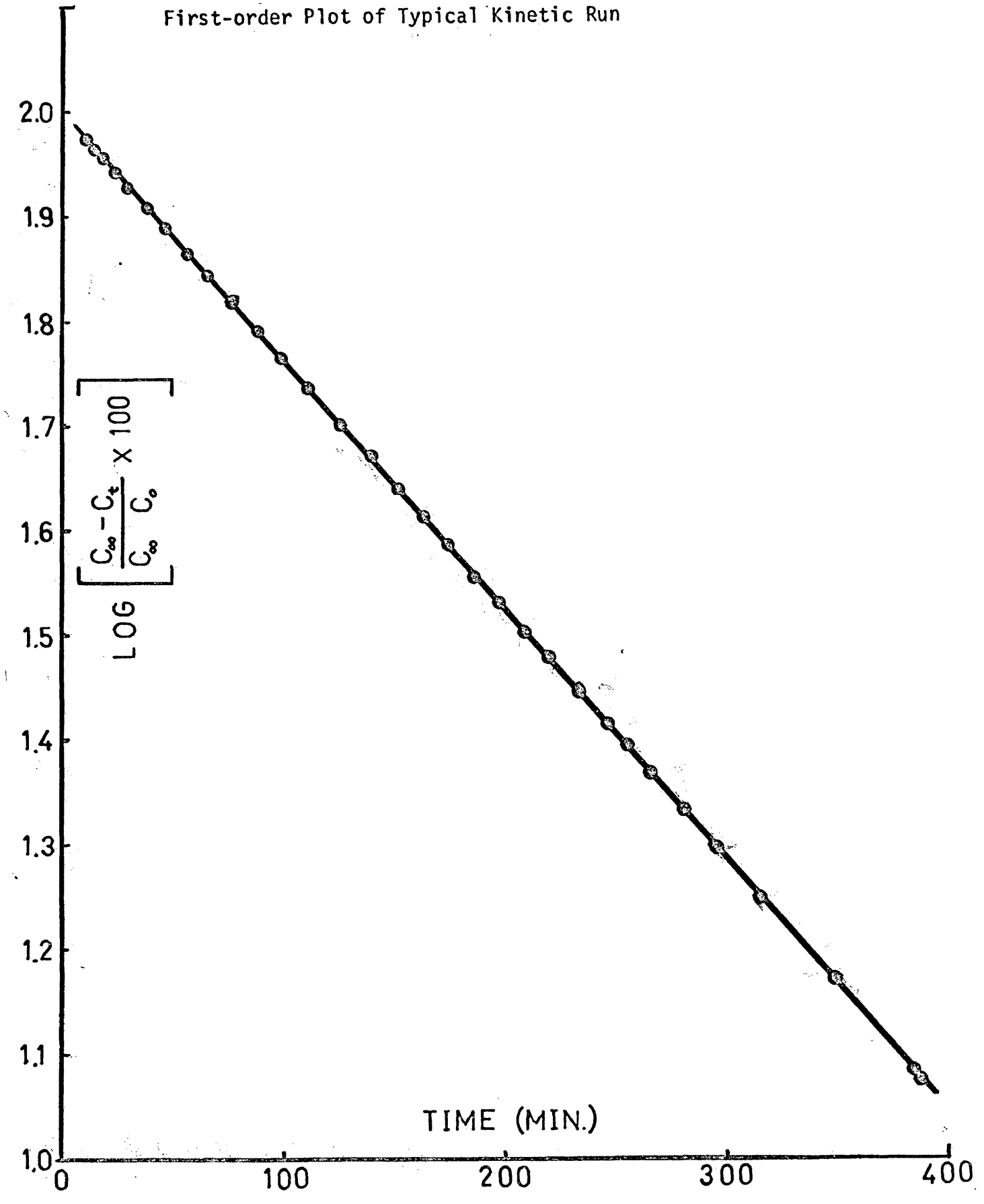


Figure 16

Computer Printout of Typical Kinetic Run

LEAST SQUARES CALCULATION FOR FIRST ORDER RATE DATA
RUN 12 "P-CL" TRIPHENYLCHLOROALLENE 80:20 DMK:H2O 35 DEG.

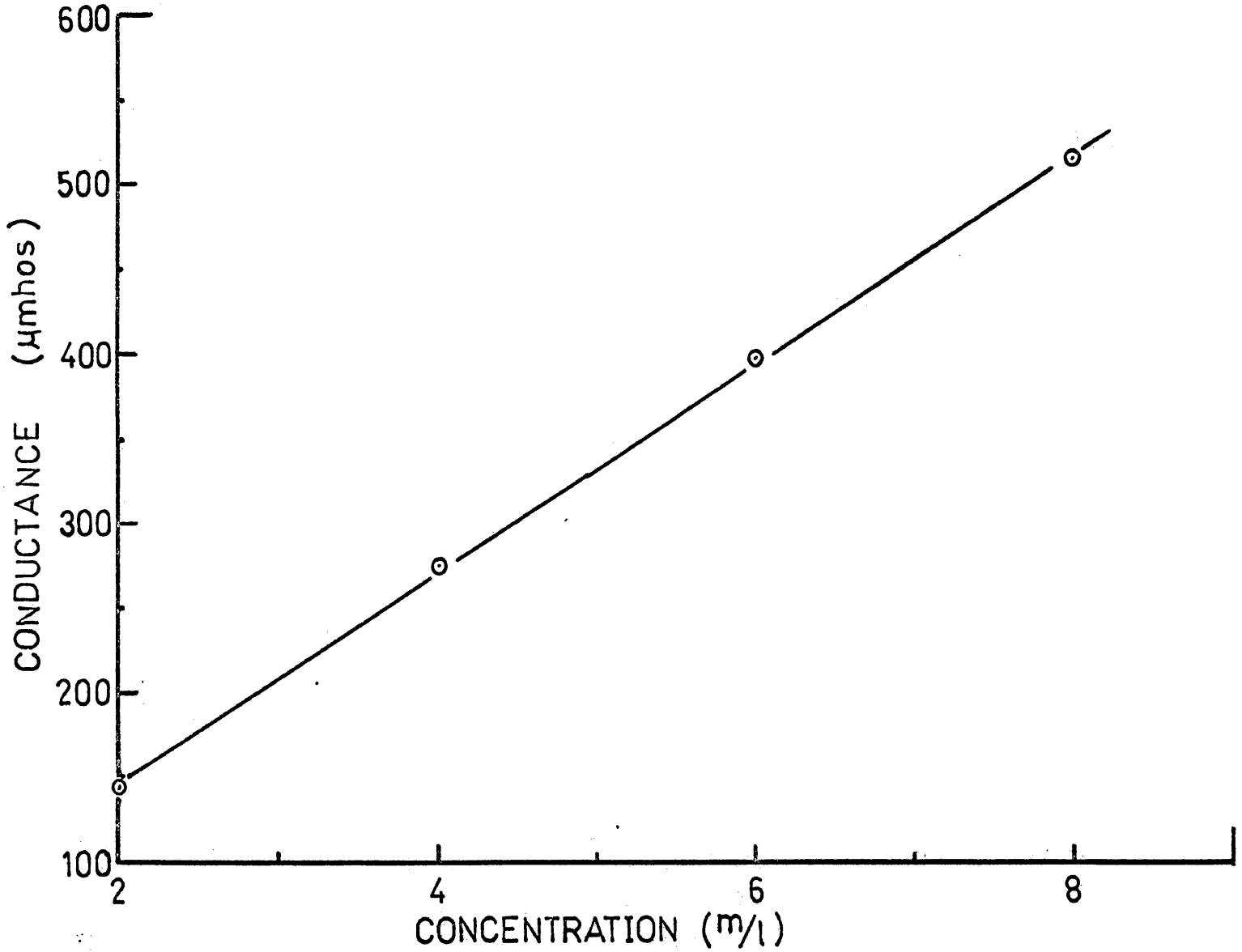
ERROR MINIMIZED - SCALAR IN INPUT VARIABLE	TIME - MIN.		
NO. OF ITERATIONS	K	G(0)	G(INF)
0	7.9000E-05	5.0000E 00	2.7350E 02
1	9.1465E-05	5.5380E 00	2.6494E 02
2	9.1575E-05	5.3334E 00	2.6723E 02
3	9.1575E-05	5.3331E 00	2.6723E 02
STANDARD DEVIATION	1.0E-08	5.6E-03	1.3E-02

STD. DEV. OF ABOVE PARAMETERS BASED ON STD. DEV. OF 1.00E-02
(VALUE FOR THIS RUN 4.38E-01)

TIME	PC.REACT.	G OBSD.	G CALC.	DELTA
0.1105E 02	5.89	0.2000E 02	0.2076E 02	-0.76E 00
0.1462E 02	7.72	0.2500E 02	0.2555E 02	-0.55E 00
0.1829E 02	9.56	0.3000E 02	0.3037E 02	-0.37E 00
0.2435E 02	12.52	0.3800E 02	0.3813E 02	-0.13E 00
0.2985E 02	15.13	0.4500E 02	0.4495E 02	0.51E-01
0.3805E 02	18.87	0.5500E 02	0.5474E 02	0.26E 00
0.4669E 02	22.63	0.6500E 02	0.6459E 02	0.41E 00
0.5676E 02	26.79	0.7600E 02	0.7550E 02	0.50E 00
0.6546E 02	30.21	0.8500E 02	0.8445E 02	0.55E 00
0.7571E 02	34.03	0.9500E 02	0.9446E 02	0.54E 00
0.8774E 02	38.25	0.1060E 03	0.1055E 03	0.49E 00
0.9824E 02	41.71	0.1150E 03	0.1146E 03	0.43E 00
0.1107E 03	45.57	0.1250E 03	0.1247E 03	0.33E 00
0.1255E 03	49.82	0.1360E 03	0.1358E 03	0.20E 00
0.1386E 03	53.29	0.1450E 03	0.1449E 03	0.91E-01
0.1510E 03	56.38	0.1530E 03	0.1530E 03	0.39E-02
0.1627E 03	59.09	0.1600E 03	0.1601E 03	-0.97E-01
0.1733E 03	61.41	0.1660E 03	0.1662E 03	-0.16E 00
0.1855E 03	63.92	0.1725E 03	0.1727E 03	-0.23E 00
0.1965E 03	66.04	0.1780E 03	0.1783E 03	-0.28E 00
0.2082E 03	68.15	0.1830E 03	0.1838E 03	-0.81E 00
0.2184E 03	69.89	0.1880E 03	0.1883E 03	-0.34E 00
0.2329E 03	72.18	0.1940E 03	0.1944E 03	-0.36E 00
0.2458E 03	74.09	0.1990E 03	0.1994E 03	-0.37E 00
0.2539E 03	75.22	0.2020E 03	0.2023E 03	-0.33E 00
0.2655E 03	76.74	0.2060E 03	0.2063E 03	-0.32E 00
0.2800E 03	78.53	0.2107E 03	0.2110E 03	-0.30E 00
0.2952E 03	80.25	0.2153E 03	0.2155E 03	-0.21E 00
0.3148E 03	82.27	0.2207E 03	0.2208E 03	-0.83E-01
0.3480E 03	85.22	0.2288E 03	0.2285E 03	0.27E 00
0.3836E 03	87.85	0.2362E 03	0.2354E 03	0.80E 00
0.3872E 03	88.09	0.2368E 03	0.2360E 03	0.77E 00

Figure 17

Conductance vs Concentration Plot



Stock solutions were prepared in the following manner:

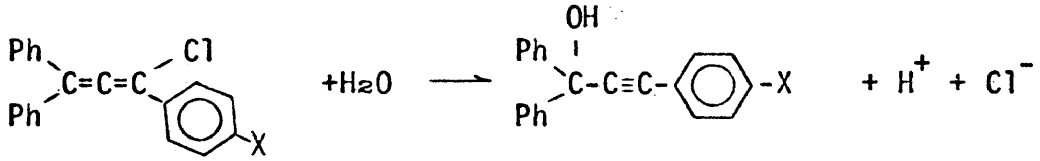
1. prepared and standardized .1N aqueous HCl solution
2. prepared stock HCl solutions (in water)
   4 ml .1N HCL diluted to 100 ml with H_2O $4 \times 10^{-3}M$
3. prepared stock propargyl alcohol solutions (in acetone)
   .12 g of propargyl alcohol in 100 ml of acetone solution
   $4 \times 10^{-3}M$
4. prepared stock 80:20 acetone:water solution
   80 ml of water plus 20 ml of acetone
5. prepared series of equimolar HCl and propargyl alcohol solutions in 80:20 acetone:water

   a) $8 \times 10^{-4}M$
      20 ml of $4 \times 10^{-3}M$ HCl
      20 ml of $4 \times 10^{-3}M$ propargyl alcohol
      60 ml of acetone
      made to 100 ml in volumetric flask with a stock 80:20 acetone:water solution
   b) $6 \times 10^{-4}M$
      30 ml of $8 \times 10^{-4}M$ solution (a)
      10 ml of 80:20 acetone:water solution
   c) $4 \times 10^{-4}M$
      25 ml of 8×10^{-4} solution (a)
      25 ml of 80:20 acetone:water solution
   d) $2 \times 10^{-4}M$
      25 ml of $4 \times 10^{-4}M$ solution (c)
      25 ml of 80:20 acetone:water solution

RESULTS AND DISCUSSION

A. Introduction

Rate studies have been made on a series of p-substituted 1-aryl-3,3-diphenylchloroallenes by following the production of ion products conductometrically.



X = H , Cl , CH_3 , and CH_3O

Good first-order plots were obtained from the data but the solvolytic nature of the reaction creates the possibility of pseudo-first-order reactions. Table II summarizes the pertinent data concerning studies on these compounds.

The reaction investigated was the solvolysis of these haloallenes in aqueous acetone (generally 80:20 acetone:water) at varying temperatures. The only products, observed by infrared analysis, from the reaction under conditions similar to those of the kinetic studies were the corresponding propargy alcohols.

B. Substituent Effects

Considerable information about the mechanism of reaction in

Table II

Pertinent Kinetic Data for Triarylchloroallenes Investigated

Substituent	Solvent Acetone:Water	T°C	10^5k, sec^{-1}	10^5 average k	Std. Dev.
CH_3O	80:20	26.096	194		
		26.091	194	194	0.6
		26.086	195		
		26.09 ± .02[a]			
	90:10	26.081	23.9		
		26.084	23.1	23.7	.42
		26.087	23.9		
		26.096	24.0		
		26.09 ± .02[a]			
	80:20	24.984	179		
		24.986	180	180	.58
		24.988	180		
		24.99 ± .02[a]			
CH_3	80:20	24.984	17.3		
		24.988	17.8	17.6	.34
		24.984	17.9		
		24.99 ± .02[a]			

Table II (continued)

Pertinent Kinetic Data for Triarylchloroallenes Investigated

Substituent	Solvent Acetone:Water	T°C	10^5k, sec^{-1}	10^5 average k	Std. Dev.
Cl	80:20	25.007	2.72		
		24.993	2.77	2.76	.036
		24.994	2.79		
		25.00 ± .02[a]			
	80:20	34.784	8.95[b]		
		34.822	8.81[b]		
		34.835	9.16	9.16	.09
		34.833	9.23		
		34.834	9.10		
		34.83 ± .02[a]			
	80:20	45.075	27.3		
		45.074	27.7	27.7	.35
		45.075	28.0		
		45.07 ± .02[a]			

a The error limits given for the temperature are those reported for the accuracy of the PRT used. The temperature was stable to ±.01 as evidenced by Beckmann thermometer.

b Values not used in calculating average or Standard deviation.

solution can be provided by studies of a given type of reaction in which a number of different substituents have been introduced into the reactant molecule. The effects of such substituents on the rate can lead to an increased understanding of the detailed mechanism.

The influence of substituents on the rate of chemical reactions may be exerted in part by bringing about a displacement of electron density. Certain types of reactions, for example, are favored by an increase of electron density at the reaction center, and substituents that bring about such an increase will cause an increase in the rate. Among the several important generalizations developed in connection with the quanititative effects of substituents, the best known extrathermodynamic linear free energy relationship is the Hammett equation,

$$\log k = \sigma\rho + \log k_0 \quad .$$

So defined, a rate or equilibrium constant, k, associated with the reaction of any one of the substituted derivations may be determined from the value, k_0, for the parent, i.e., unsubstituted, compound if the two parameters σ and ρ are known. The reaction constant, ρ, is a proportionality constant, dependent upon the nature of the reaction and the conditions, and measures the sensitivity of a given reaction series to ring substitution. The substituent constant σ, however, is dependent only on the substituent and its mode of electronic interaction.

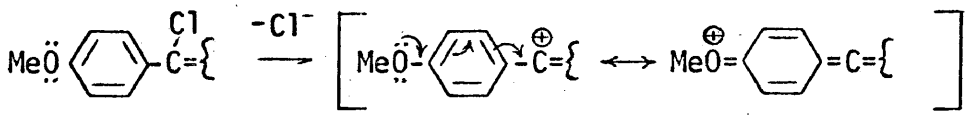
The Hammett equation has been found to be applicable to the correlation of a large number of rate and equilibrium constants[22]

and thus proves valuable in predicting such constants from a small number of σ and ρ values. Originally a value of unity was arbitrarily chosen for ρ for the ionization equilibrium of substituted benzoic acids in aqueous solution at 25°[23]. Using values of σ defined in this manner the values of ρ for the other reactions may then be determined. The sign and magnitude of these ρ values may then be used as an important tool in the study of reaction mechanisms. As originally defined, groups which are electron withdrawing with respect to hydrogen would have a positive σ value. Therefore, a reaction series in which rate or equilibria are enhanced by electron withdrawal will have a positive ρ value. A negative value, consequently, indicates enhancement by electron-donating substituents. Values of ρ are usually obtained by plotting log k − log k_o *versus* σ. The slope of the resulting line is ρ. The sensitivity to substitution is directly proportional to this value.

Although useful in a number of systems, it became obvious after a time that Hammett's original σ constants were limited in their ability to correlate reactions in which resonance interaction of the substituent with charge developed at the reaction center played any noticeable part. That is, a set of substituent constants is limited to use in reactions where the substituent interacts in essentially the same manner as it does in the reaction chosen to define those constants.

In 1958 Brown and Okamoto[24] devised a scheme for defining a new substituent constant, σ^+. Utilizing the solvolysis of 2-phenyl-2-chloropropane in 90% acetone-water at 25° as the standard reaction,

they derived a reaction constant (ρ value) from a study of the meta-substituted chlorides. They felt that resonance contribution from the m-substituent should be negligible and therefore the σ_m-constants defined by Hammett would be used for correlation of the rate constants. The reaction constant thus obtained was used to evaluate the new substituent constants for p-substituents where resonance should be the major interaction at the reaction center,



It should be noted that σ^+ values could be useful in any reaction system where positive charge is generated in conjugation with the para position of an aromatic ring. Selected examples of reactions correlating with σ^+ may be seen in Table III.

The relative rates of four p-substituted triarylchloroallenes were measured at 25°. A plot of the logarithm of the relative rates of solvolysis versus σ^+ is shown in Figure 18 and the data are summarized in Table IV. Unlike the linearity of this plot (correlation coef. = .999) a plot of the relative rates versus Hammett's σ was highly curved as also seen in Figure 18.

The rho obtained, -2.02 ± .03, is consistent with a mechanism in which some degree of positive charge is developed at the reaction center - a mechanism such as that proposed by Jacobs and Fenton[4].

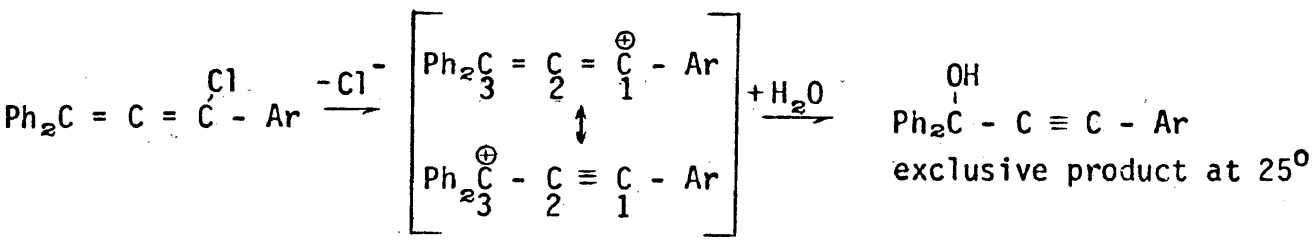


Table III

Selected Examples of Reactions Correlated with σ^+

Substrates	ρ	Solvent	T	Reaction
t-Cumylchlorides	-4.54	90% aq. acetone	25°	solvolysis
	-4.67	EtOH	25°	solvolysis
Benzhydrole	-6.67	aq. H_2SO_4		ionization equilibrium
p-alkylbenzhydrylchloride	-4.63	EtOH	25°	solvolysis
p-halobenzhydrylchloride	-4.11	70% aq. acetone	25°	solvolysis
benzydydrylchloride	-4.06	2-propanol	25°	solvolysis
	-4.05	EtOH	25°	solvolysis
triphenylcarbinols	-3.64	aq. H_2SO_4	25°	ionization equilibrium
triphenylcarbinylchlorides	-2.34	{40% EtOH}	25°	solvolysis
	-2.57	{60% Et_2O}	60°	solvolysis
α-phenylethylchlorocarbonate	-2.87	Toluene	80°	thermal rearrangement
t-Cumylhydroperoxide	-4.57	50% aq. EtOH	50°	acid-catalyzed decomposition
$\overline{X}$-$C_6H_4CH(OH)CH{=}CHCH_3$	-2.97	60% aq. dioxane	30°	acid-catalyzed rearrangement
Phenylacetylenes[b]	-3.84	5% aq. EtOH	25°	hydration
α-bromostyrenes[c]	-5.4	80% aq. EtOH	120°	solvolysis
2,2-diphenyl-1-aryliodoethylenes[d]	-3.6	70.4% DMF	189.5°	solvolysis
α-aryldiphenylchloroallenes[e]	-2.02	80% aq. acetone	25°	solvolysis

a Data taken from ref. 25 unless otherwise referenced.

b Ref. 26.

c Calculated from data in ref. 6.

d Ref. 8.

e This work.

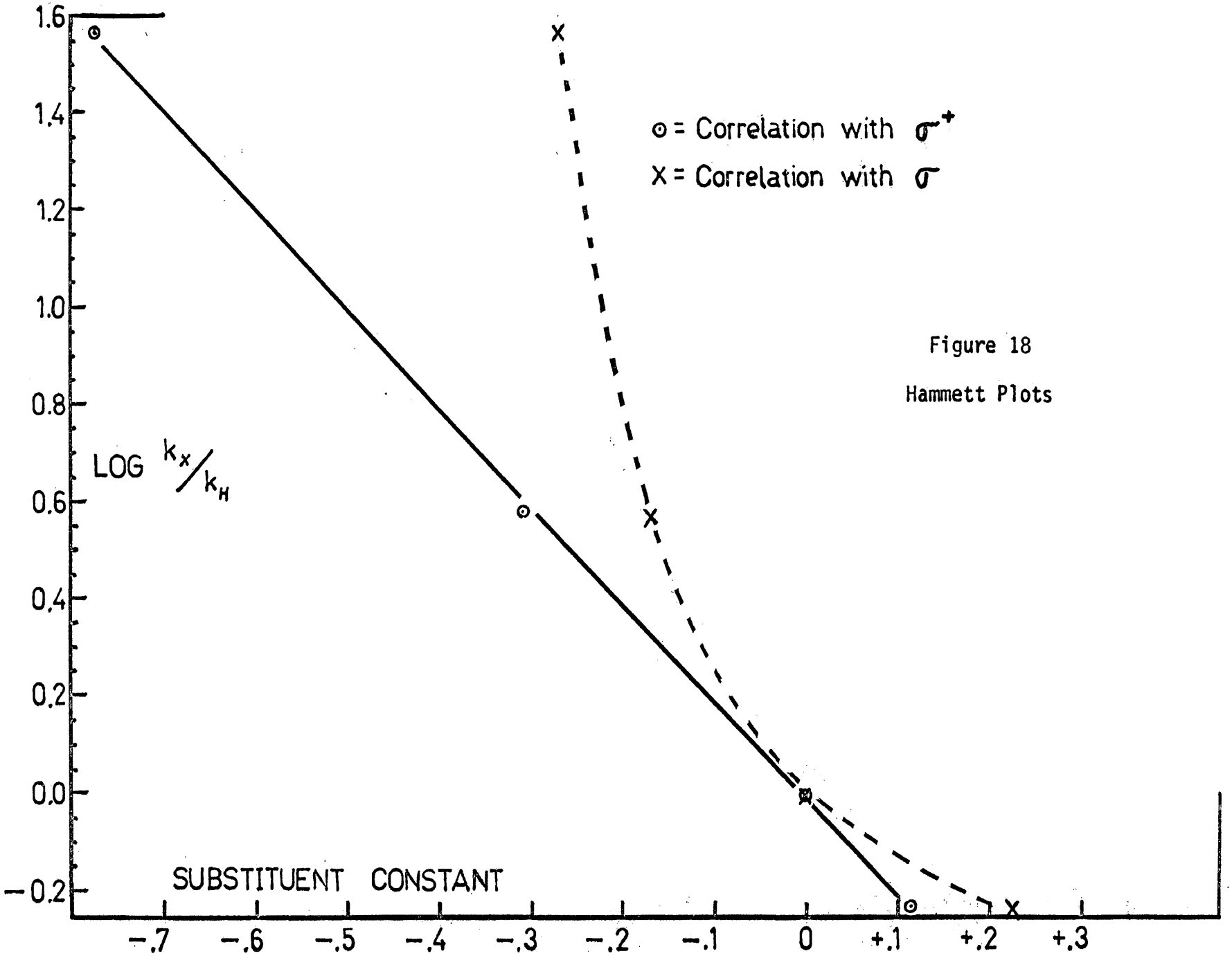
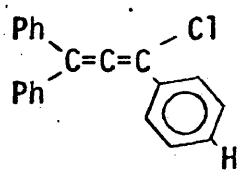
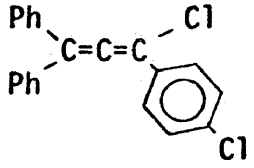
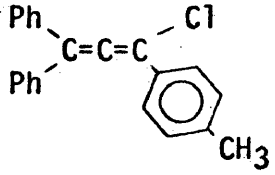
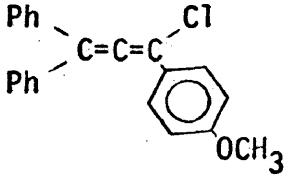


Figure 18

Hammett Plots

Table IV

Summary of Data Used for Calculation of Rho[a]

Compound	k_{rel} (k_x/k_H)	log $k_{rel.}$	σ^+
	1.00	0.000	0.00
	.58	-0.240	+0.114
	3.67	0.565	-0.311
	37.50	1.574	-0.778

[a] 25°, 80:20 acetone:water

It should be noted that this mechanism involves a resonance stabilized intermediate carbonium ion in which some of the positive charge originally at C-1 due to the initial ionization, has been delocalized to C-3, thereby possibly accounting for the relatively small absolute value of ρ observed, due to substituent effects at C-1. It can be seen by comparing similar systems (Table III) that increases in charge stabilizing groups (such as in the case of going from benzhydryl to triphenylcarbinyl system) causes a decrease in the absolute value of ρ. The additional resonance stabilizing ability of the aryl substituted three carbon allenyl system would be expected to show similar results, and this seemingly is borne out by the observed ρ. It seems reasonable to assume that the high reactivity of this allenyl system in comparison to other vinyl systems (see Table XIII) is derived from the described delocalization to C-3, thereby allowing further delocalization into the two aromatic rings at the propargyl position. It may be argued that this delocalization is substantially due to the relative stabilizing ability of those two phenyl rings compared to the one at C-1. This argument would seem to be borne out by the preferential attack of solvent at that position. The comparative degree of delocalization, however, is still unknown. Olah and co-workers[20] and Richey and co-workers[27] have reported a substantial contribution of the allenyl cation form in their nmr studies of various alkynylcarbonium ions. As pointed out by Richey, et al., these carbonium ions may well be regarded as allenyl carbonium ions depending on the importance of the allenyl resonance structure. Further work involving para-substitution in C-3 aryl rings should shed more light into this area.

C. Solvent Effects

Further evidence of some form of charge development in the transition state can be seen from the effect of increasing the polarity of the medium. In 1948 Grunwald and Winstein postulated the relationship between rate constant and solvent polarity as a linear free energy relationship,

$$\log k = \log k_o + mY \qquad (1)$$

where k and k_o were originally defined as the rate constants at 25^o for t-butyl chloride in any solvent and in 80% aqueous ethanol respectively, and Y was a measure of the ionizing ability of the solvent.[28] The term m in this defining case was taken as unity. When the relationship is used for other systems m becomes a measure of the susceptibility of the substrate to the solvent ionizing power relative to t-butyl chloride, and k_o becomes the solvolytic rate at Y = 0.0.

A study of the rate constant for the solvolysis of 1-anisyl-3,3-diphenylchloroallene revealed that a change in the solvent composition from 90:10 to 80:20 acetone:water caused an 8.2 fold rate increase. This increase is reflected in a value of m = 0.77 in equation 1. Such a value, demonstrating considerable substrate sensitivity to medium changes, is comparable to reactions involving S_N1 mechanisms. Table V lists a number of reaction systems and

Table V

Grunwald-Winstein m Values in Aqueous Ethanol[a]

Substrate	T	m	Mechanistic Designation
t-Butylchloride	25	(1.00)	S_N1
t-Butylbromide	25	0.940	S_N1
t-Amylbromide	25	0.90	S_N1
α-Phenylethylchloride	50	1.195	S_N1
α-Methylallylchloride	25	0.894	S_N1
Benzhydrylchloride	25	0.757	S_N1
Methylbromide	50	0.26	S_N2
Methyltosylate	75	0.23	S_N2
Ethylbromide	55	0.34	S_N2
Ethyltosylate	50	0.26	S_N2
n-Propylbromide	95	0.34	S_N2

Table V (continued)

Grunwald-Winstein m Values in Aqueous Ethanol[a]

Substrate	T	m	Mechanistic Designation
n-Butylbrosylate	60	0.32	S_N2
Vinyl Systems			
$H_2C=CBrCH=C(CH_3)_2$	100	0.81[b]	S_N1
$H_2C=C(CH_3)T$[h]	76.1	0.52[c]	E_2
$(An)_2C=CAnCl$[i]	120	0.42-0.53[d]	S_N1
$(An)_2C=CAnBr$	120	0.34[d]	S_N1
$(Ph)_2C=C=CPhCl$	25	0.69[e,f]	S_N1
$(Ph)_2C=C=CAnCl$	25	0.77[f,g]	S_N1

a Data taken from ref. 29 and 30 unless otherwise referenced.
b ref. 10
c ref. 14
d ref. 9
e ref. 31
f aqueous acetone
g This work
h T=triflate
i An=Anisyl

their respective m values. It should be noticed that values close to unity are observed for substrate undergoing S_N1 mechanisms of solvolysis, whereas S_N2 mechanisms usually exhibit values for m between 0.25 and 0.35. For example, the solvolysis of t-butyl bromide (m = .940) and ethyl bromide (m = .34) proceed by S_N1 and S_N2 mechanisms respectively. The greater susceptibility of S_N1 processes toward the ionizing power of the solvent is suspected to be due to the fact that although the amount of charge developed may be the same

S_N1 $\quad (CH_3)_3C\text{-}Br \longrightarrow \left[(CH_3)_3\overset{\delta+}{C}\text{-----}\overset{\delta-}{Br}\right]^{\ddagger} \longrightarrow (CH_3)_3C^+ + Br^-$

S_N2 $\quad CH_3CH_2Br + HOH \left[\begin{matrix} H & \delta+ & H & H & \\ & O\text{-----} & C & \text{-----} & \overset{\delta-}{Br} \\ H & & CH_3 & & \end{matrix}\right]^{\ddagger} \longrightarrow CH_3CH_2OH + H^+ + Br^-$

in both cases, localized charge intensity should be greater in the case of unimolecular ionization. This greater intensity is caused by the smaller charge radius in S_N1 processes. Charge dilution, therefore, resulting from spreading charge over a specific area, does not occur to the extent to which it occurs in the bimolecular case.[32] Solvent dependence for reactions of vinyl systems reported to proceed via unimolecular mechanisms are also given in Table V and these values too are consistent with the observed value in this investigation. A more thorough study of solvent effects on the triaryl substituted chloroallene system was performed by Hixon[31] using 1,3,3-triphenyl-

chloroallene (the parent compound for substitution studies reported in this paper). In this case m = 0.69(± .06) was calculated from a logarithmic plot of $k_{rel.}$ *versus* Y. Hixon concluded that this value was consistent with a S_N1 process. The higher value for the "*p*-MeO" compound is consistent with the larger charge separation expected in the transition state for this substrate because of the greater degree of bond breaking in the transition state made possible by the electron donating ability of the methoxy group.

With these and other data to be presented as needed, a number of pathways for allenic substitution will now be examined using various criteria to differentiate and select the most detailed and accurate representation for the present system.

D. Possible Pathways for Triarylchloroallene Solvolysis

1. The "Elimination-Addition" Route (Fig. 19)

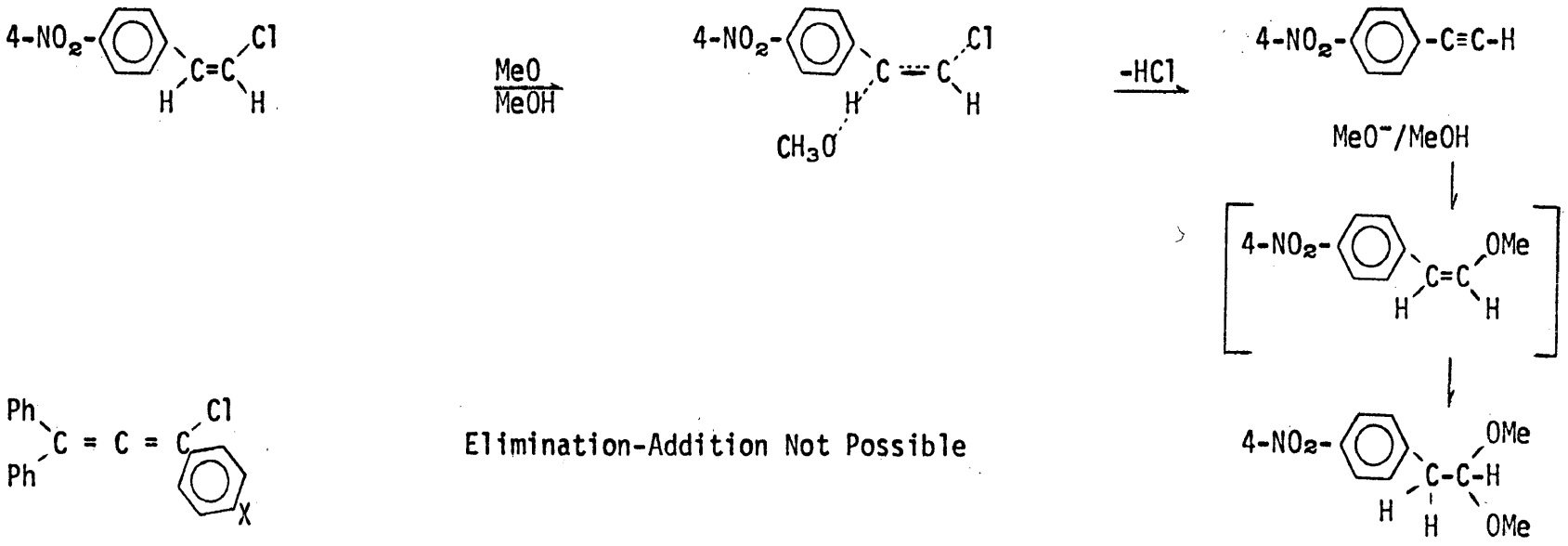
This mechanism is impossible as there are no protons available for elimination. It is, however, theoretically a route by which vinyl halides could undergo substitution. An example of a system where this mechanism is thought to take place is in the reaction of *cis* *p*-nitro-β-chlorostyrene with methoxide ion in methanol.[33]

2. The "Addition-Elimination" Route (Fig. 20)

Addition of water across one of the double bonds via a concerted mechanism may lead to a number of products (as do many of these mechanisms) but only that mechanism producing the propargyl alcohol

Figure 19

An Example of a Possible Elimination-Addition Mechanism in Vinyl Systems

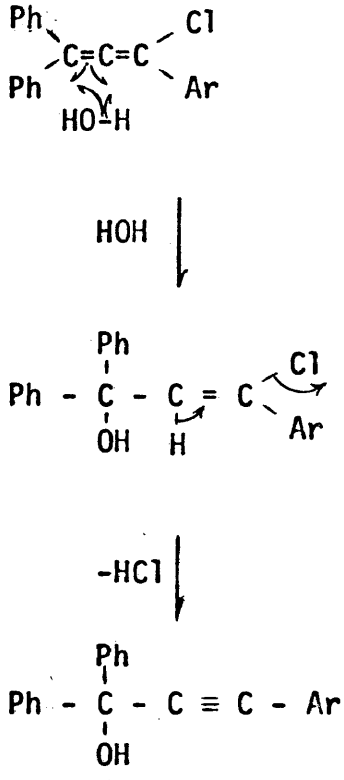


Elimination-Addition Not Possible

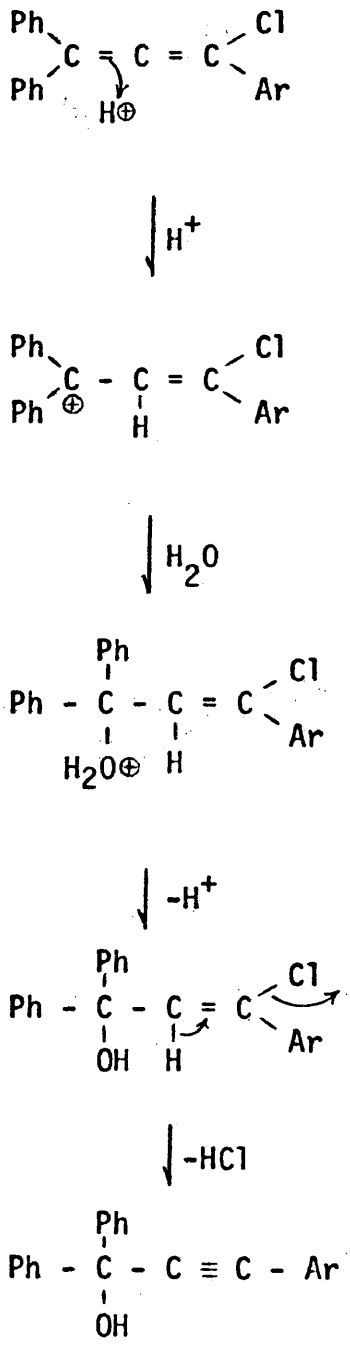
Figure 20

The Addition-Elimination Route

a) via Concerted Addition of Water



b) via Protonation



will be discussed since this alcohol is the only product isolated under conditions approximating the kinetic runs. Inability of the author to find examples of the concerted addition of HX to olefins suggests it is an uncommon if not unknown mechanism. Furthermore, since no charge is developed the mechanism would not conform to the negative rho observed from the substituent study. The uncharged character of the mechanism also does not fit the degree of solvent dependence discussed earlier.

Protonation of the double bond with subsequent attack by water is a more commonly observed pathway for the addition of water but this mechanism too is highly unlikely. Although the solvent effect may be consistent with such a mechanism, reactions of this type usually involve higher acid concentration (see Table VI) than are present in our studies (max. pH, 3.4).

It is also logical to assume that the high point of the energy diagram in this mechanism would be the elimination of HCl due to the vinyl character of those substituents. A summary of the reasons for this logic are listed in Table VII. Furthermore, this is a procedure which normally requires use of a strong base.[30] The neutral to acidic conditions of the overall reaction are thus inconsistent with this pathway. The hydrated allene would be expected as an isolable intermediate in such a reaction. This latter reasoning could apply equally well to either addition-elimination mechanism discussed since both involve the loss of HCl in the final step.

A third argument against protonation is the size of the rho value. The overall effect of substituents on the rate would be a

Table VI

Selected Reactions Involving Protonation of Allenes

Substrate	Solvent	T, °c	Major Product	Ref.
$H_2C=C=CH_2$	HX (X=I,Br,Cl)	-70 to 20°	$(CH_3)_2CX_2$ [a]	34
$H_2C=C=CH_2$	HF	-76 to 69°	$(CH_3)_2CF_2$	35
		Hydration		
$CH_2=C=CHC_3H_7$	8% H_2SO_4 [b]	25°	$CH_3COC_4H_9$	36
$CH_3CH=C=CHC_3H_7$	80% H_2SO_4	25°	$C_2H_5COC_4H_9$	37
$CH_3CH=C=CHCH-(CH_3)_2$	80% H_2SO_4	25°	$C_2H_5COC_2H_4(CH_3)_2$	37

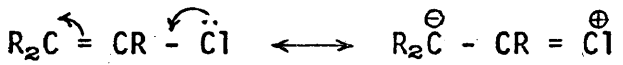
[a]Cyclobutane products thought to arise from an intermediate vinyl cations were also observed.

[b]The use of a mercuric salt catalyst was needed in this reaction.

Table VII[a]

Explanations for Lethargic Nature of Vinyl Halide Solvolysis

1. Partial π character of the vinyl carbon-halogen bond



2. A stronger vinyl carbon-halogen σ bond due to the different hybridization of the vinyl carbon.

Properties of Organic Halides

Compound (RX)	Bond Length, A°	BDE of RX, kcal/mol	IP of R·, eV
C_2H_5Cl	1.77	81.5	8.8
i-C_3H_7Cl	1.77	81.0	8.0
CH_2=CHCl	1.72	84	9.45
C_6H_5Cl	1.70		9.9
C_2H_5I	2.14	53	8.8
t-C_4H_9I	2.15	49.5	7.6
CH_2=CHI	2.09	55.5	9.45
C_6H_5I	2.08	54	9.9

[a] Taken from ref. 8.

composite of the individual effects in each step prior to the high point on the energy diagram. Since positive charge resides at the carbon bearing the substituted phenyl group in only one such step, it should be expected that rho would have a value closer to zero, that is, less negative than is observed. Similar reasoning may be used as well to argue that a lower m value than is observed should accompany this mechanism.

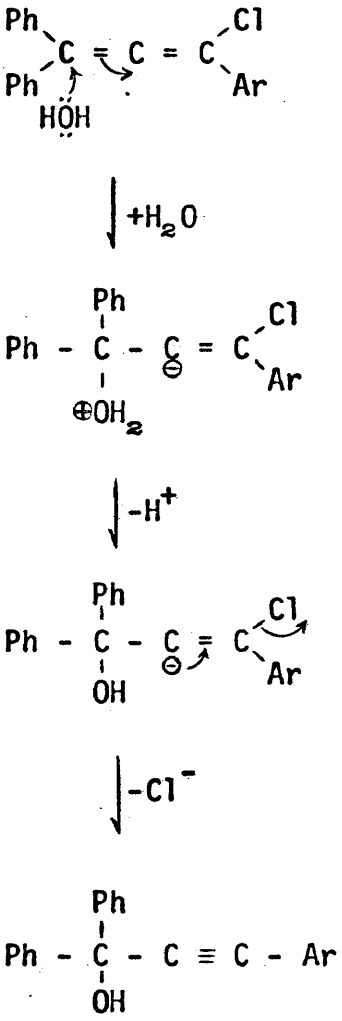
3. Nucleophilic Attack (S_N2') (Fig. 21)

Both mechanisms 3a and 3b yield the propargyl alcohol through nucleophilic attack by water at the diaryl substituted carbon atom, that is, an S_N2' reaction. Mechanism 3a involves the preliminary formation of a carbanion with subsequent loss of a proton and a chloride ion to form the product. Mechanism 3b involves a concerted route. Both mechanisms can be eliminated on a basis of the substituent study. The electron rich nature of the incoming nucleophile would suggest that the reaction should be facilitated by substituents which would diminish the electron density at the double bond. The opposite effect, however, was observed in this work. In the series $-Cl<H<CH_3<CH_3O-$ where electron donating ability increases as shown, corresponding rate increases were observed. The observed negative value of rho indicates development of positive charge on the aryl substituted carbon. Although the solvent effects witnessed in this work might be expected for a carbanion mechanism the negative charge of the species certainly is not consistent with a negative rho. In a concerted mechanism no charge is developed at all.

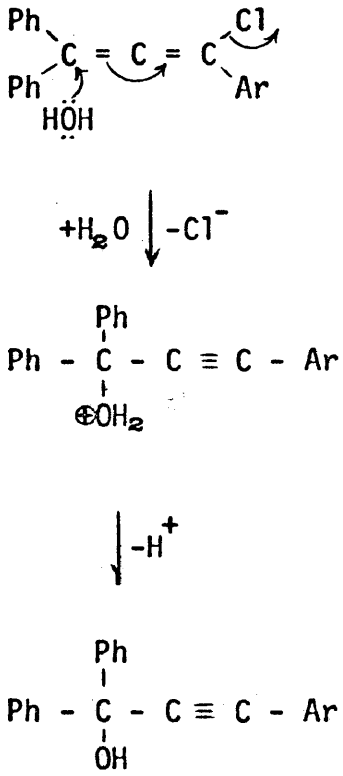
Figure 21

Nucleophilic Attack (S_N2')

a) via Carbanion Formation



b) via a Concerted Mechanism



In the case of the carbanion mechanism it would be expected that a positive rho value of approximately 2.2 would be observed.[32] This value is consistent with negative charge developed one carbon away from the substituted ring. A very small or zero value of ρ should be observed in the concerted mechanism since no formal charge is developed in the activated complex. A comparison of rho values for various degrees of charge development may be seen in Table VIII. S_N2 reactions are generally characterized by small negative or positive rho values.

Another indication as to whether or not solvolysis proceeds via a S_N2 mechanism is the sensitivity of the reaction to the nucleophilic strength of the solvent. In a bimolecular reaction the nucleophile participates in the rate determining step and therefore rate constants should be highly dependent on its characteristics. A unimolecular mechanism, however, involving the breaking of a bond in the rate determining step, should be little affected by changes in the nucleophilicity of the solvent as attack occurs after the bond breakage. In 1951 Grunwald, Winstein, and Jones revised the free energy relationship involving solvent effects to include a term representing the nucleophilicity of the solvent.[29] By comparing rate constants in solvents of similar ionizing abilities (that is, similar Y values) the effect of changes in nucleophilicity can be studied.

$$d \ln k = \left(\frac{\partial \ln k}{\partial Y}\right)_N dY + \left(\frac{\partial \ln k}{\partial N}\right)_Y dN \qquad \text{G.W.J. eq.}$$

effect of solvent ionizing power

effect of solvent nucleophilicity

Table VIII

Some Typical Reaction Constants[a]

Reaction	Solvent	T	ρ
1. $Ar(C_6H_5)\cdot CHCl + C_2H_5OH \longrightarrow Ar(C_6H_5)\cdot CHO\cdot C_2H_5$	C_2H_5OH	25	-5.09
2. $ArCHOHCH{=}CHCH_3 + H^+ \longrightarrow ArCH{=}CHCHOHCH_3$	40% dioxane	30	-4.67
3. $ArNH_2 + 2,4\text{-}(NO_2)_2C_6H_3Cl \longrightarrow 2,4\text{-}(NO_2)_2C_6H_3CHAr$	C_2H_5OH	25	-3.98
4. $ArN(CH_3)_2 + CH_3I \longrightarrow ArN(CH_3)_3^+I^-$	90% acetone	35	-3.30
5. $ArCH_2Cl + H_2O \longrightarrow ArCH_2OH$	48% C_2H_5OH	30	-2.18
6. $ArOH + CH_3COBr \longrightarrow ArOCOCH_3$	$CH_3CO_2C_2H_5$	0	-1.45
7. $ArO^- + C_2H_5I \longrightarrow ArOC_2H_5$	C_2H_5OH	43	-0.99
8. $ArCH_3 + (CH_2CO)_2NBr \longrightarrow ArCH_2Br$	CCl_4	80	-1.46
9. $ArCH_3 + Br_2 \longrightarrow ArCH_2Br$	CCl_4	80	-1.37

Table VIII (continued)

Some Typical Reaction Constants[a]

Reaction	Solvent	T	ρ
10. $ArCH_3 + Cl_2 \longrightarrow ArCH_2Cl$	CCl_4		-1.25
11. $ArCHO + C_6H_5CO_3\cdot \longrightarrow ArCO\cdot$	Ac_2O	30	-0.50
12. $ArSH + R\cdot \longrightarrow ArS\cdot$	$C_6H_5CH_3$		-0.4
13. $(ArCO_2)_2 \longrightarrow ArCO_2\cdot$	$CH_3COC_6H_5$	80	-0.20
14. $ArOCOC_6H_5 + HO^- \longrightarrow ArO^-$	60% acetone	0	0.98
15. $ArCN + HS^- \longrightarrow ArC(SH)=NH$	C_2H_5OH	61	2.15
16. $ArNHCOCH_3 + CH_3O^- \longrightarrow ArNH_2$	CH_3OH		2.15
17. $ArCO_2CH_3 + HO^- \longrightarrow ArCO_2^-$	60% acetone	25	2.23
18. $ArCHO + HCN \longrightarrow ArCHOH\cdot CN$	95% C_2H_5OH	20	2.33
19. $BrCH_2ONO + OEt^- \longrightarrow ArCHO$	C_2H_5OH	30	3.4

eq. 1 - 7: processes in which the electron density at reaction center is decreased during the reaction.

eq. 8 - 13: processes leading to no formal change in charge.

eq. 13 - 19: processes leading to an increase in electron density.

---

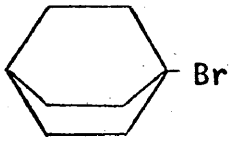
[a] Taken from ref. 32.

In their work Grunwald, Winstein, and Jones chose to compare the reactions of various compounds in a highly nucleophilic ethanol-water solvent with those in the much less nucleophilic formic and acetic acids. The data collected in these studies may be seen in Table IX. It should be noticed that reactions which are characterized by a large m value have a low sensitivity toward solvent nucleophilicity, while those having small m values have a high sensitivity toward this fact The relative sensitivities in these studies showed that S_N1 processes typically give values near unity whereas S_N2 reactions have values ranging between 20 and 200. The relative sensitivities, however, are a function of the solvent systems under investigation. Therefore typical data for S_N1 and S_N2 reactions must be collected in any two solvent systems chosen for such a nucleophilicity comparison, before the effect of changing from one to the other system can be used to distinguish between the two mechanisms.

A comparison of the rate constants for 1,3,3-triphenylchloroallene in 90:10 ethanol:water[39] (Y = -.727) and an aqueous acetone solution[40] having an equal Y value gave a $k_{ethanol\text{-}water}/k_{aq.\ acetone}$ = 13.9. Any value for this ratio other than unity implies that the rate constant in 90:10 ethanol:water would not fit on the original mY plot by Hixon for triphenylchloroallene. The necessity of explaining such descrepancies originally led Grunwald, Winstein, and Jones to propose the new relationship including the nucleophilicity term. The importance of the above value for the sensitivity of triphenylchloroallene in distinguishing possible solvolytic mechanisms is small at the present time as data concerning the sensitivity of

Table IX

The Effect of Solvent Nucleophilicity Changes[a]

Compound	T,C	m(aq. EtOH)	k_{EtOH}/k_{HCO_2H}
CH_3Br	50	0.26	200
CH_3OTs	75	0.23[b]	55
EtBr	55	0.34	80
EtOTs	50	0.26	18
n-PrBr	95	(0.34)[c]	68
iso-PrBr	50	0.54	20
tert-BuBr	25	1.00	1
$C_6H_5CH_2Cl$	50	0.43	4
	100	0.88	0.5

a From ref. 30.

b value for $MeOSO_2C_6H_5$ at 50°C.

c assumed value.

S_N1 and S_N2 processes in the respective solvents (that is, acetone: H_2O vs EtOH:H_2O) has not been compiled.

4. Unimolecular Substitution (S_N1')

It can be seen that a unimolecular mechanism is most compatible with the data obtained in our investigation. A summary of the evidence and its implications is collected in Table X. It should be noted that no evidence has yet been found to conflict with the unimolecular process.

5. Rearrangement

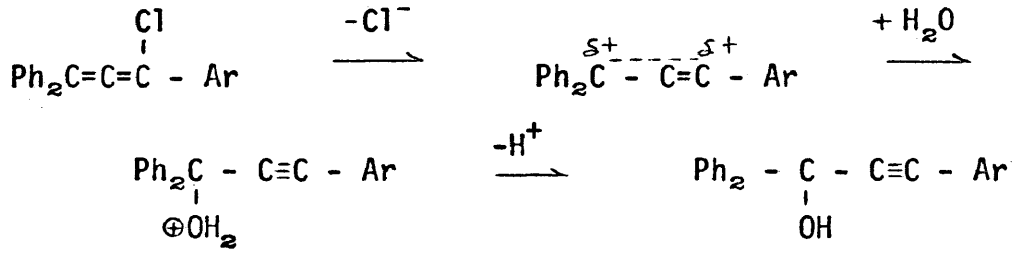
One final mechanism which must be considered is the rearrangement of the allenyl chloride to the propargyl chloride before solvolysis. Jacobs and Fenton[4] have suggested that the allene would be expected to be the more stable of the two compounds from both steric and resonance considerations. The C-Cl bond of the propargyl chloride, in which the halogen atom is bonded to a sp^3 orbital of carbon and is surrounded by two bulky phenyl rings, should be considerably more sterically strained than that of the allenyl chloride where the halogen resides in a planar sp^2 configuration. Also the more extensive configuration of the allenyl system should lower its ground state energy compared to that of the propargyl chloride.

Since a search of the literature revealed no reported studies involving 1-chloro-1,1,3-triphenyl-2-propyne (XII), the propargyl counterpart of the triphenylchloroallene (XIII) it was necessary to estimate its rate of solvolysis. The effect of the acetylenic bond on the rate of solvolysis was first estimated. The rate constant for

Table X

A Summary of Evidence Favoring a S_N1' Mechanism

Mechanism



evidence	inference
p = -2.02 ± .03	positive charge developed in transition state
increase in k, with increase in solvent polarity	charged species in transition state
common ion rate depression[a]	free carbonium ion production

[a] This work was performed by M. D. Schiavelli.

the solvolysis of t-butyl chloride (IX) may be compared with that for 3-chloro-3-methyl-1-butyne (X). The interposition of the triple bond has the effect of increasing the value of the rate constant by a factor of 264. Assuming a similar effect by the triple bond in 1-chloro-1,1,3-triphenyl-2-propyne (XII) the rate constant for solvolysis of this compound would be estimated from the rate constant of triphenylmethylchloride (XI) by multiplying its rate constant by the same factor of 264. Doing this, a figure of approximately 2350 sec^{-1} was derived for the rate constant of the triphenyl propargyl chloride structure (XII) in 85% acetone. The 5% difference in solvent composition is a relatively small factor and the fact that the figure of 2350 sec^{-1} is 10^8 times greater than the observed rate constant in these studies would seem to eliminate a rearrangement mechanism beyond any doubt. The data used in the estimation of the above rate constant is collected in Table XI.

E. Product Studies

Since it has been demonstrated that the S_N1 mechanism is the most probable mechanism involved in the solvolysis of triarylchloroallenes, it must be asked why the propargyl alcohol is the exclusive product produced in this reaction (see Table I). It should be remembered that the intermediate carbonium ion is a resonance stabilized structure in which positive charge is developed at both ends of the original allenyl structure.

$$-\overset{\delta+}{C}\cdots\equiv C-\overset{\delta+}{C}\Big\rangle \equiv \left[\begin{array}{ccccccc} -C & \equiv & C & - & \overset{\oplus}{C}\Big\rangle & \longleftrightarrow & -\overset{\oplus}{C} = C = C\Big\rangle \\ 1 & & 2 & & 3 & & 1 \quad 2 \quad 3 \end{array}\right]$$

TABLE XI

Data For Estimation of Triphenylpropargylchloride Rate Constant

Compound	Solvent Acetone:Water	T, °C	10 k, sec^{-1}[a]	Ref.
$H_3C - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - Cl$ (IX) t-butyl chloride	80:20	25°	1.94×10^{-6} (1)	28
$HC \equiv C - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}} - Cl$ (X) 3-chloro-3-methyl-1-butyne	80:20	25°	5.13×10^{-2} (264)	41
$Ph - \underset{\displaystyle Ph}{\overset{\displaystyle Ph}{\overset{|}{\underset{|}{C}}}} - Cl$ (XI)	85:15	25°	8.9	28
$Ph - C \equiv C - \underset{\displaystyle Ph}{\overset{\displaystyle Ph}{\overset{|}{\underset{|}{C}}}} - Cl$ (XII)		25°	2.35×10^{3} (10^{8})[b]	calculated
$\begin{matrix} Ph & & Ph \\ \diagdown & & \diagup \\ & C = C = C & \\ \diagup & & \diagdown \\ Ph & & Cl \end{matrix}$ (XIII)	85:15	25°	4.8×10^{-5}	31

[a] Values in parenthesis indicate relative k.

[b] relative to (XIII)

The question then arises as to why no product from attack at the allenyl position was isolated under conditions approximating those of the kinetic studies.

Because of the fully overlapped nature of the p orbital system (see Fig. 22), π electron delocalization between C-3 and C-1 must result from differences in stability. Molecular orbital calculations involving the ethyl and vinyl cations suggest that the saturated ion is of a lower energy than its unsaturated counterpart. It could be inferred from these data that, given a choice, positive charge would prefer to reside at the propargyl rather than the vinyl position. Such inferences, however, may be unwarranted in this more complex system. A simpler explanation, involving the stabilizing effect of two phenyl rings at the propargyl position as opposed to only one at the allenyl position may be sufficient. Regardless of the reasoning as to why charge density should be greater at C-3, such an excess should lead to increased possibility of solvent attack at that position. Indeed, at room temperature attack at the propargyl carbon is the only route taken by the nucleophile. At elevated temperature (reflux, 67.3°), however, a new product was found. This product, based on analysis of ir spectra, was felt to be the α,β-unsaturated ketone, 1,3,3-triphenylpropen-1-one, which is the expected product from attack at the allenyl carbon,

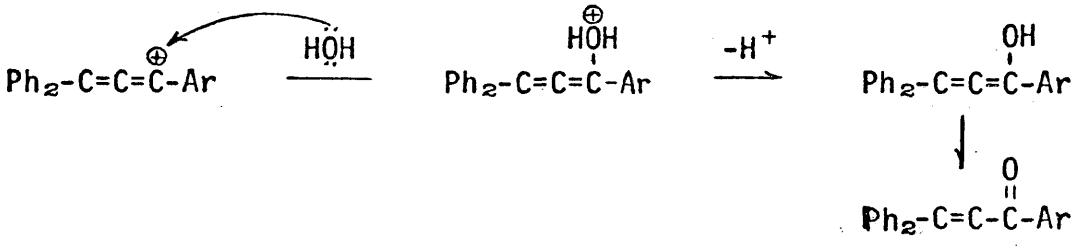
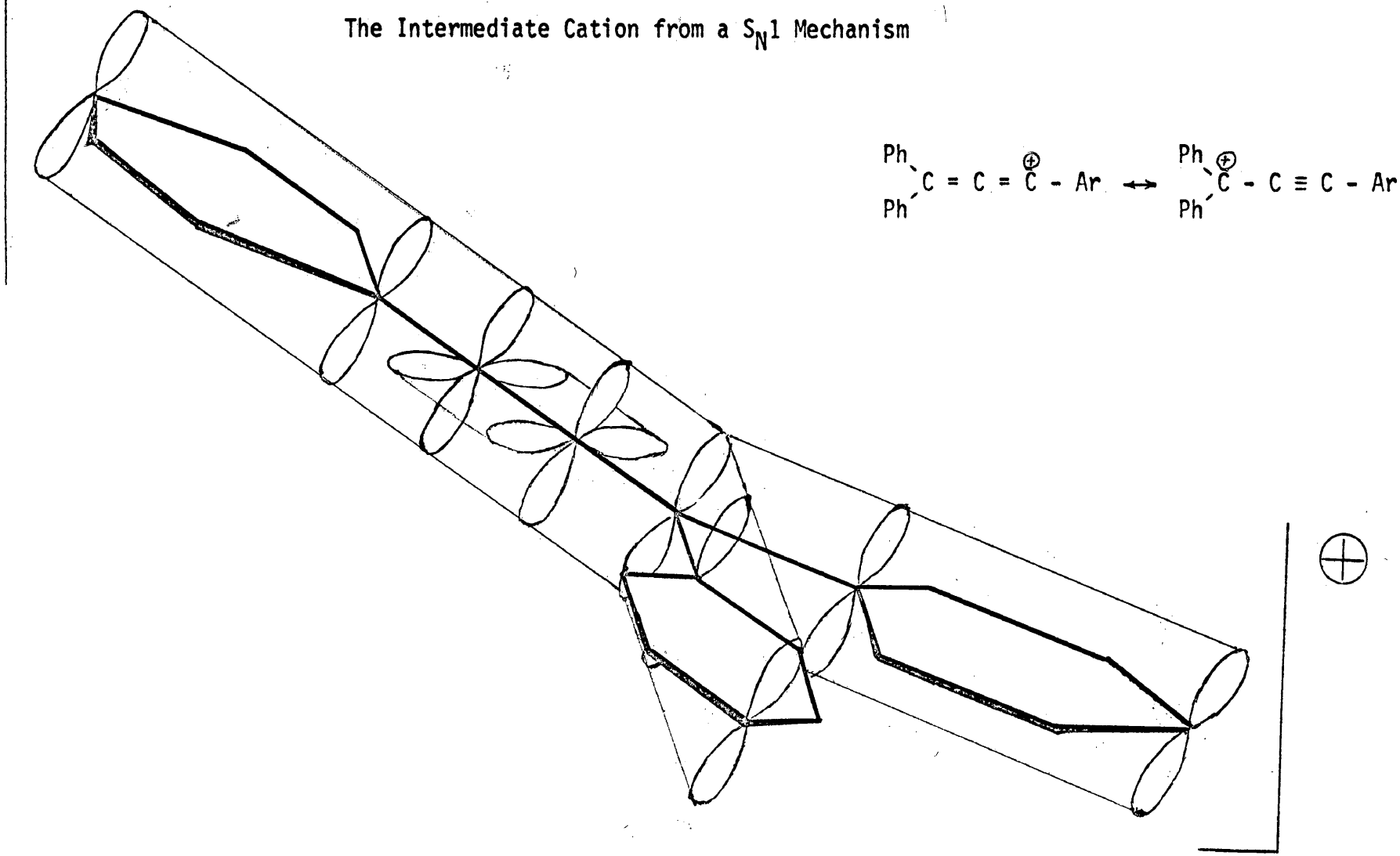


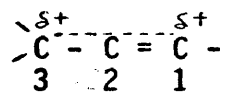
Figure 22

The Intermediate Cation from a S_N1 Mechanism



This ketone, as suggested by Jacobs and Fenton,[4] should be a much more stable product than the propargyl alcohol based on both steric and resonance considerations.

An additional explanation as to why attack might be hampered at the allenyl position may be that there is extra electron density at that position,



Comparing carbons 1 and 3 we see that in the resonance structures a constant excess of electron density is maintained in the overlapped p orbital of C-1 and C-2. This π cloud of extra electrons may comparatively hinder the entrance of the electron rich nucleophile by electrostatic repulsion, thereby adding to the additional energy already needed to cause bonding at the C-1 position. This effect would be expected to be of only slight importance in comparison with the attractive strength of a formal charge, however. The needed energies mentioned above may be gained from the higher temperature of reflux, and thereby account for the production of the α,β-unsaturated ketone.

A second method for the production of this ketone should be considered as well. In 1922 Meyer and Schuster[42] reported the rearrangement of 1,1,3-triphenylpropargyl alcohol to 1,3,3-triphenylpropen-1-one, the α,β-unsaturated ketone which has been reported here as a minor product of solvolysis at elevated temperatures. The rearrangement, an apparent 1,3 hydroxyl shift, normally occurs in

highly acidic media (original work - 10 g propargyl alc., 50 cc. AcOH, 2cc conc. H_2SO_4). The ketone was properly identified and exhibits a melting point of 86-87°, In 1923 Moureau, Dufraisse and Mackall[2b] reported that the same carbinol yielded a yellow material, mp 87-87.5 , when heated with alcoholic H_2SO_4 or HCl. Presumably this product was also the α,β-unsaturated ketone.

Since the early discoveries of rearrangements involving propargyl alcohols a number of mechanisms have been proposed [43] (see Fig. 23). Some degree of confusion still remains as to the exact mechanisms of the Meyer-Schuster rearrangement and of a specialized case known as the Rupe rearrangement. The initial step is generally considered to be either protonation of the hydroxyl group or the acetylenic bond. In the first case the loss of water should form a cation identical to that postulated in the present work. This cation can then lose a proton to form an ene-yne structure, which on subsequent hydration of the acetylenic bond forms an enol. Tautomerization then yields a carbonyl product. A second possible reaction of the resonance cation is attack by water at the allenyl position to yield a second carbonyl product.

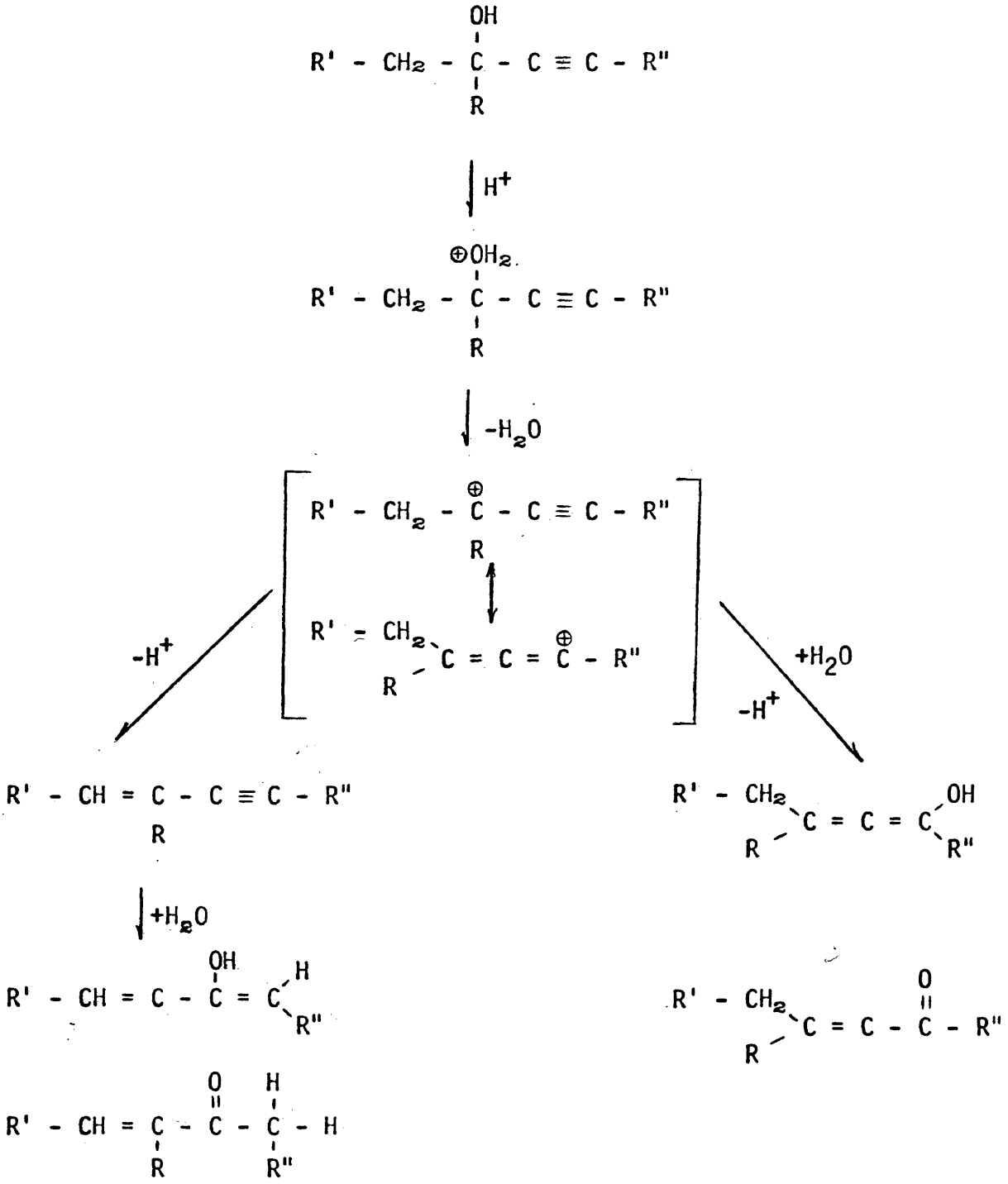
The alternative initial step mentioned, protonation of the acetylenic bond, can also lead to formation of a rearranged ketone by a number of pathways. These involve direct hydroxyl shifts, epoxide oxonium salt formation, and hydration-dehydration mechanisms.

Further studies must be made before the exact mechanism involving the rearrangement of the triphenyl propargyl alcohol can be formulated. However, the most reasonable pathway (see Fig. 24) would seem to

Figure 23

Proposed Mechanism Involved in Meyer-Schuster Rearrangements

a) Protonation of Hydroxyl Group



"apparent" 1,2 hydroxy shift generally referred to as the Rupe Rearrangement.

Figure 23 (continued)

b) Protonation of Acetylenic Bond

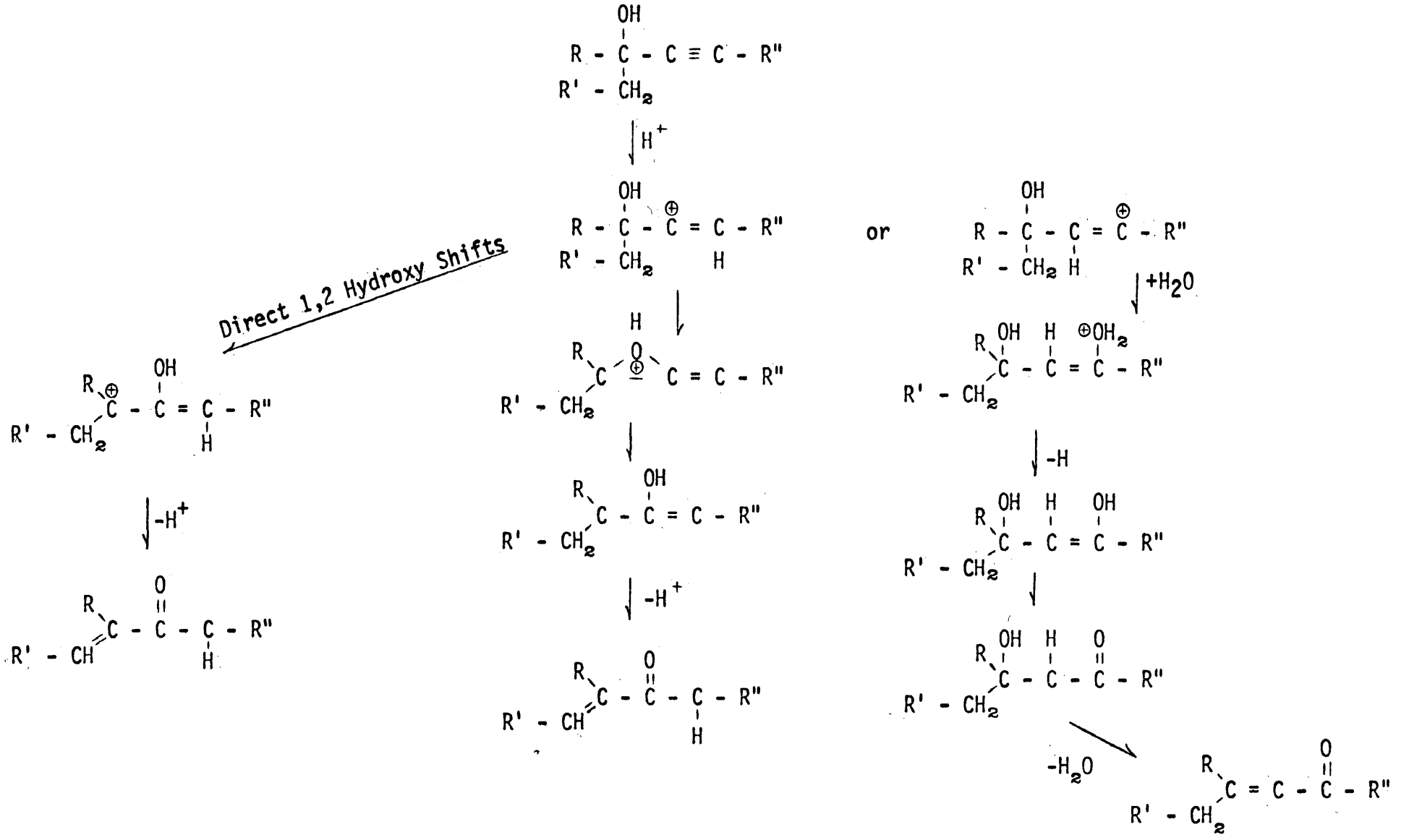
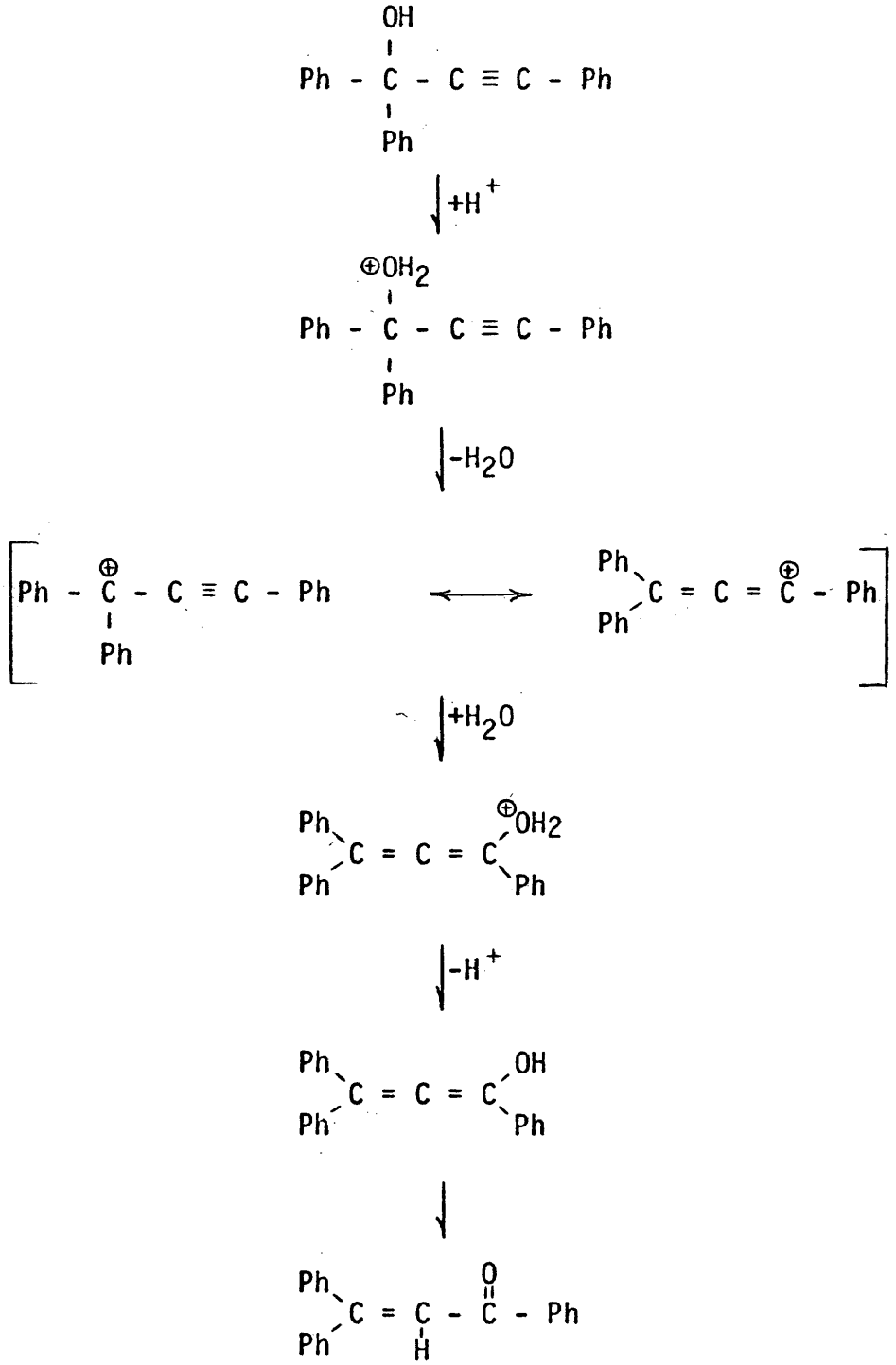


Figure 24

Most Reasonable Pathway for Meyer-Schuster Rearrangement in Triphenylpropargyl Alcohol



involve a facile protonation of the hydroxyl group leading to the formation of a highly stabilized propargyl-allenyl cation by loss of water which is then attacked at the allenyl carbon. Any pathway resulting in an apparent 1,2 shift can automatically be eliminated, as can the loss of a proton from the cation intermediate in general mechanism (A). Formation of the carbonium ion should be an important step in both cases. However, protonation of the triple bond does not yield a cation with the stability of the cation formed in mechanism (A).

Evidence favoring the carbonium ion pathway to the α,β-unsaturated ketone over rearrangement of the carbinol would lend additional proof for the specific carbonium ion intermediate postulated in the solvolysis of the triarylchloroallenes. Table I shows the results of studies undertaken in an attempt to find such evidence. A comparison of experiments 3 and 6 are of the greatest assistance in shedding light on the dilemma. Experiment 3 involved refluxing 1,3,3-triphenylchloroallene in an 80:20 acetone:water solution for 45 minutes. In experiment 6 equimolar amounts of 1,1,3-triphenyl-2-propyn-1-ol and HCl were placed in a 80:20 acetone:water solution, and it too was refluxed for 45 minutes. Approximately equal amounts of the allene and the carbinol were used in the two experiments.

Although no quantitative measurements were made to determine the relative amounts of products present, a qualitative examination of the carbonyl and vinyl hydrogen absorptions in the ir spectra would seem to indicate that a substantially greater amount of ketone was produced from the allene than from the carbinol solution. In

fact, no characteristic absorptions of the ketone are evident in the carbinol-acid experiment. If rearrangement of the carbinol were the only mechanism involved, one could logically expect no more ketone from the allene than an amount equal to that from the carbinol. The excess ketone must have been produced via the second mechanism -- namely nucleophilic attack of water on the allenyl cation and subsequent tautomerism to the α,β-unsaturated ketone. These data would seem to add to the evidence for the resonance stabilized intermediate carbonium ion postulated earlier. The qualitative nature of the conclusions from ir spectra, however, make further studies in this area of ketone production desirable. Figure 25 shows a postulated energy diagram for the solvolysis reaction of this chloroallene.

F. Activation Parameters of 1-(4-chlorophenyl)-3,3-diphenylchloroallene.

Rates of solvolysis for 1-(4-chlorophenyl)-3,3-diphenylchloroallenes were determined in 80:20 acetone:water at 25°, 35°, and 45°. The data were used to compute the activation parameters of the compound by using a computer program by D. F. Detar and C. E. Detar[44].

Table XII

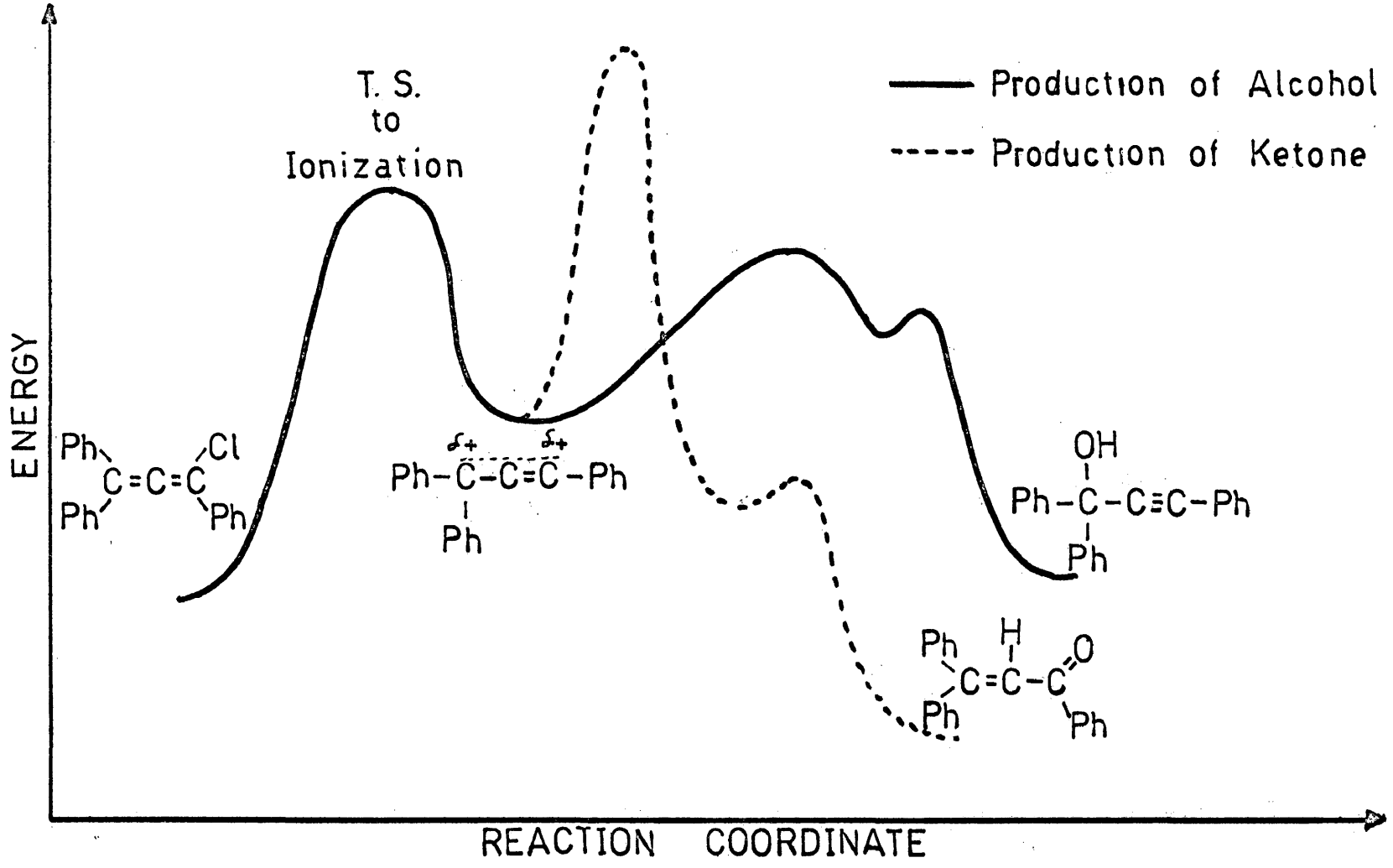
Data for Calculation of Activation Parameters of 1-(4-chlorophenyl)-3,3-diphenylchloroallene

$10^5 k$, sec^{-1}	T°C	ln k	$10^3 \frac{1}{T}$
27.7 ± .10	25.00 ± .02	-10.50	3.35
9.16 ± .10	34.83 ± .02	- 9.30	3.25
2.76 ± .10	45.08 ± .02	- 8.19	3.14

Figure 25

Possible Energy Diagram for Solvolysis

of Triphenylchloroallene



The calculated values at 25° were Ea = 21.7 ± .13 kcal/mole, $\Delta S^{\ddagger}$= -8.80 ± .43 e.u., $\Delta H^{\ddagger}$= 21.1 ± .13 kcal/mole, and $\Delta G^{\ddagger}$= 23.7 kcal/mole. Table XII shows the data collected.

A comparison of these results and those of earlier vinyl systems thought to involve a S_N1 mechanism may be seen in Table XIII. The data for this chloroallene seem compatible with such systems. The lower energy of activation, $Ea^{\ddagger}$, and the enthalpy of activation, $\Delta H^{\ddagger}$, values for the two allenyl compounds investigated in this study, would be expected due to the large amount of charge delocalization affording stabilization of the transition state. The slightly higher values of these two parameters for the p-chloro substituted allenyl compound compared to those for the unsubstituted triphenylchloroallene are also expected since the electron withdrawing chlorine atom would tend to have a destabilizing effect on the carbonium ion intermediate. The slightly less negative $\Delta S^{\ddagger}$ for the p-chloro substituted compound can be interpreted as resulting from the decreased solvent alignment around the activated complex as compared to that of the parent compound. This decrease in solvent alignment, resulting in an increase in $\Delta S^{\ddagger}$, is due to the smaller degree of positive charge developed at the reaction center. This smaller degree of bond breaking is caused by the destabilizing effect of the p-chloro substituent, which does not allow bond breaking to occur to the same extent as the relative neutral effect of hydrogen. Added to this is the fact that the charge which is developed would be spread over a larger area thereby decreasing the intensity of such charge. It is well to note that

the isolated incident of decreased bond breaking should, however, result in a decrease in the entropy. It would seem, then, from the observed increase in $\Delta S^{\ddagger}$, that solvent orientation is the more important effect in this case.

A comparison of activation parameters for unimolecular and bimolecular reactions involving the vinyl system may be established by examining Tables XIII and XIV respectively. In solution unimolecular reactions of these systems exhibit higher activation parameters than do their bimolecular reactions. The higher values for $Ea^{\ddagger}$ and $\Delta H^{\ddagger}$ can be explained in light of the fact that more energy is needed to break the bond between leaving group and substrate when there is no assistance due to bond formation as in the case of bimolecular reactions. Both of these reactions usually exhibit negative values of $\Delta S^{\ddagger}$ in solution. In the gas phase, a unimolecular reaction involving the production of two species from one, would be expected to have a positive $\Delta S^{\ddagger}$ since the system becomes more disordered in the transition state. The opposite is expected for bimolecular reactions in the gas phase. Two species joining to form one in the transition state cause an increase in the ordering of the system and therefore a negative $\Delta S^{\ddagger}$ is expected. In solution, however, the entropy of the entire system must be considered since the solvent has an effect on the overall entropy change. In solvolytic reactions charge development may be involved to some extent in both mechanisms. In particular the bimolecular reaction of solvent with substrate has been compared with the simple unimolecular solvolysis reaction

Table XIII

Activation Parameters for Vinyl Systems Reported to Solvolyze by S_N1 Mechanisms

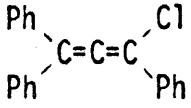
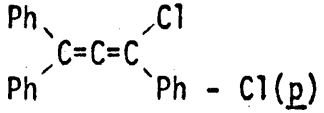
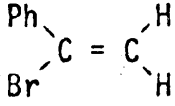
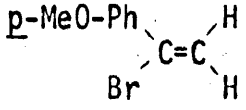
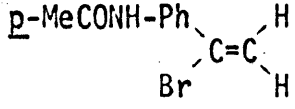
Substrate	Solvent	k(sec^{-1}) 50°	$E_a^{\ddagger}$	$\Delta H^{\ddagger}25°$	$\Delta S^{\ddagger}25°$	Ref.
	80% aq. acetone	7.20×10^{-4}	20.8	20.2	-10.7	31
	80% aq. acetone	4.72×10^{-4}	21.7	21.1	-8.80	This work
	80% aq. EtOH	4.22×10^{-12}	33.8	32.9	-8.94	6
	80% aq. EtOH	1.09×10^{-7}	27.8	27.1	-6.79	6
	80% aq. EtOH	3.18×10^{-8}	27.2	26.4	-11.3	6

Table XIII (continued)

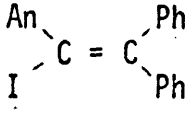
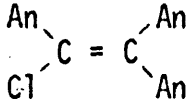
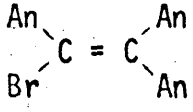
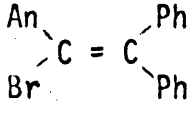
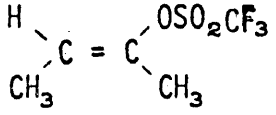
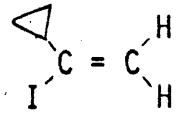
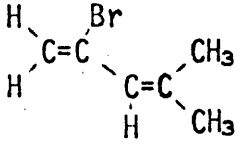
Substrate	Solvent	$k(sec^{-1})$ 50°	$E_a^{\ddagger}$	$\Delta H^{\ddagger}25°$	$\Delta S^{\ddagger}25°$	Ref.
	70% aq. DMF	1.57×10^{-7}	24.9	24.1	-15.2	8
	80% aq. EtOH	3.50×10^{-9}	27.5	26.7	-14.8	9
	80% aq. EtOH	9.32×10^{-7}	21.9	21.2	-20.8	9
	80% aq. EtOH	4.83×10^{-7}	21.8	21.0	-22.7	9
	80% aq. EtOH	1.08×10^{-6}	26.0	25.3	-7.69	14
	aq. Methanol	3×10^{-8}	24.2	23.3[a]	-21.1[a]	11a

Table XIII (continued)

Substrate	Solvent	k(sec^{-1}) 50°	$E_a^{\ddagger}$	$\Delta H^{\ddagger}25°$	$\Delta S^{\ddagger}25°$	Ref.
	aq. Methanol	7 X 10^{-6}	23.9	23.1[b]	-10.9[b]	10

[a] at 150°

[b] at 100°

Table XIV

Activation Parameters for Selected Bimolecular Reactions Involving the Vinyl System[a]

Substrate	Nucleophile	Solvent	cis $\Delta H^{\ddagger}$	cis $\Delta S^{\ddagger}$	trans $\Delta H^{\ddagger}$	trans $\Delta S^{\ddagger}$
p-$NO_2C_6H_4$=CHCl	PhS	MeOH	17.2	-17.8	17.0	-15.2
PhCO·CMe=CHCl	piperidine	EtOH			10.1	-34.2
PhCO·CPh=CHCl	N_3^-	98% EtOH			16.8	-23
	piperidine	EtOH			12.6	-30
MeCCl=CH·CO_2Et	PhS^-	EtOH	14.7	-23.5	15.4	-17.5
p-MeC_6H_4·SO_2·CH=CHCl	n-Bu_2NH	MeOH	11.6	-27.5	12.1	-25.5
	cyclohexylamine	MeOH	12.9	-26.0	12.6	-28.5
	EtO^-[b]	EtOH	26.6	+19		
EtCO·CMe=CHCl	piperidine	EtOH			12.2	-31.2

a Taken from ref. 45 and involving add.-elim. mechanism unless otherwise stated.

b Reacts probably via elim.-add.

in Section C (p. 51). Therefore solvent dipoles align themselves to stabilize such charges, causing a decrease in $\Delta S^{\ddagger}$. Depending on the nature of the solvent and the charged species, this effect may be of greater importance than the bond breaking and bond making considerations to the sign of the overall $\Delta S^{\ddagger}$. Since the two effects oppose one another in the case of the unimolecular mechanism, the relative $\Delta S^{\ddagger}$ would tend to be higher, that is, less negative, than in bimolecular mechanisms where the two effects work in the same direction.

PROPOSAL FOR FUTURE STUDIES

A number of studies could be undertaken to further understand the mechanism involved in these solvolysis studies.

A. Further Investigation of S_N1 vs S_N2 mechanism:

1. The effect of changing the leaving group: Element Effects

A comparison of the rates of compounds differing only in the leaving group can yield valuable information as to whether such leaving groups participate in the rate-determining step of the reaction. This comparison usually involves halide ions as the leaving groups. Mechanisms which require a considerable degree of bond breaking between the substrate and the leaving group in the transition state, that is S_N1 mechanisms, should undergo a rate increase following the order I>Br>Cl>>F. This series represents the order for increased ease of carbon halogen bond breaking. On the other hand, if bond making, that is an S_N2 mechanism, is involved in the rate-determining process, the more polarizable and less hindered system will be the more reactive. The rate series then would be represented as I>F>>Br>Cl. Table XV lists a number of reactions and the calculated element effects. An example of the use of such data can be taken from the work of Rappoport and Gal[9] involving the solvolysis of the 1-anisyl-2,2-diphenylethenyl halides (Hal. = Br, Cl). In this work

Table XV

Typical Data for Element Effect Studies[a]

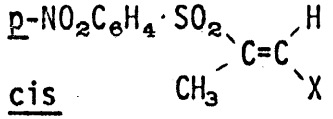
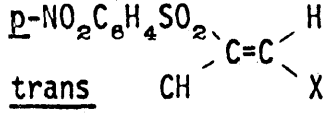
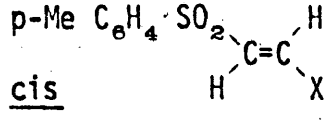
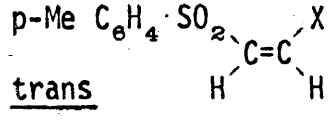
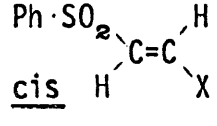
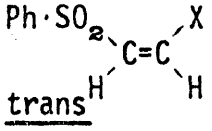
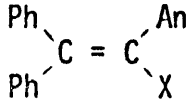
Substrate	Relative Reactivity k_{Br}/k_{Cl}	Mechanism Inferred
 cis	.93	unimolecular
 trans	.85	unimolecular
 cis	185	bimolecular
 trans	.84	unimolecular
 cis	144	bimolecular

Table XV (continued)

Typical Data for Element Effect Studies

Substrate	Relative Reactivity k_{Br}/k_{Cl}	Mechanism Inferred
 trans	.84	unimolecular
cis $4\text{-}NO_2C_6H_4 \cdot CH{=}CHX$	108	bimolecular
trans $4\text{-}NO_2C_6H_4 \cdot CH{=}CHX$	.88	unimolecular
	57.6[b]	unimolecular

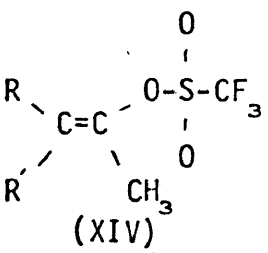
a Taken from ref. 45 unless otherwise referenced.

b ref. 8.

a bromide/chloride rate ratio of 57.6 at 120° was taken as evidence for a unimolecular mechanism. Since the bromide compound solvolyzed at a rate greater than that for the chloride compound, the influence of bond breaking must have been more important in the rate-determining step. For this and other reasons, the reaction was discussed in terms of an intermediate vinyl cation formed by a S_N1 mechanism.

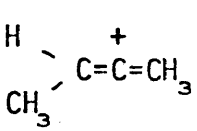
2. The effect of a changing substituting agent: Added Nucleophile

The effect of a change in the nucleophile involved in the substitution reaction can be of great importance in distinguishing mechanistic characteristics. If the addition of a powerful nucleophile (compound to the solvent, e.g., OH^-, or Et_3N:) does not show an appreciable influence on the reaction rate, it is inconceivable that the solvent should function as a reagent in the rate-determining step. If, on the other hand, such reagents do affect the rate, it must mean their participation in the incursion of a bimolecular reaction. It requires further consideration to determine whether or not the same is true of the reaction with solvent, however. Such studies would only serve to suggest the likelihood of a S_N2 solvolysis and the degree of consideration warranted. A summary of added nucleophile studies performed on alkyl bromides and the inferences made from them is to be found in Table XVI. One example of their use was in the study of vinyl triflates made by Stang and Summerville.[14] The mechanism for solvolysis of these compounds (XIV)



(XIV)

a) R=R'=H
b) R=CH_3, R'=H
c) R=H, R'=CH_3



(XV)

Table XVI

Typical Data From Added Nucleophile Studies[a,b]

Substrate	10 k , (obs.) (First order Solvolytic reaction)	10 k (obs.) (Second order Reaction with NaOH)	10 k (calc.) (Total reaction [NaOH] = 1)	Mechanism
MeBr	0.349	2140	2140	S 2
EtBr	0.139	171	171	S 2
iso-PrBr	0.237	4.75	4.99	S 2 - S 1
tert-BuBr	1010	----	1010	S 1

a
ref. 46
b
80% aq. EtOH as solvent at 55°
c
k = first order constant in sec
d
k = second order constant in sec g - mol 1.

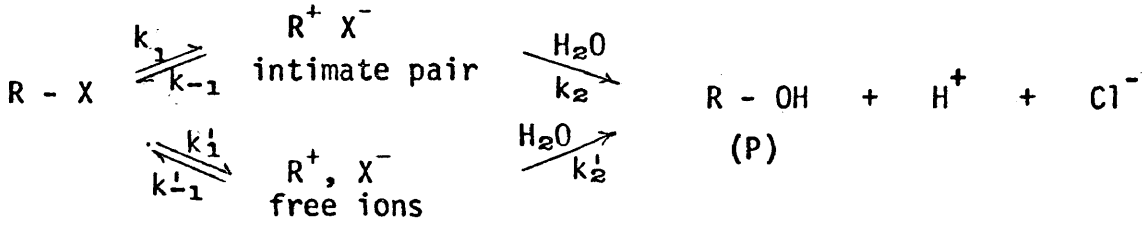
was seen as a balance between concerted elimination and a unimolecular ionization, the importance of each changing with changes in R and R'. On the basis of a 37-fold increase in reaction rate with added NaOH the concerted elimination was favored in the case of isopropenyl triflate (XIVa). In the cis and trans 2-buten-2-yl triflates the trans configuration lends itself readily to the elimination mechanism. The cis isomer, however, is in a geometrically unfavorable configuration. If competition between the two possible mechanisms were involved, a rate enhancement should occur in the bimolecular elimination reaction with the addition of a base such as pyridine to the system. This would lead to an increase in the relative portions of the elimination products (dimethylacetylene, 58% of total product; methylallene, 9% of total product) in comparison to the unimolecular ionization product (2-butanone, 33% of total product). No such change in the observed product ratio was noted and in combination with other data this evidence was used to postulate a unimolecular ionization mechanism for the solvolysis of cis-2-buten-2-yl triflate via the vinyl cation (XV).

B. Characterization of the intermediate:

1. Changes in rate due to added ions: Salt Effects

Assuming an S_N1 mechanism to be correct, the specific nature of the intermediate ion pair can sometimes be characterized through the effect of added common ions on the reaction rate. The ion pair

formed by bond cleavage can exist in one of two states, either as an intimate pair or as essentially free ions. The unimolecular solvolytic reaction can be represented as,



Systems best represented by a free ion pair show a definite rate decrease on adding a common ion salt to the reaction mixture. This decrease is caused by competition of the added and original anions for the carbonium ion versus the solvent. The rate of return to starting material should be increased due to the mass law effect, thereby weighting the competition in favor of such return. In systems where the ion exists as an intimate ion pair, the rate shows no dependence on added common ion. In this case, the original anion collapses with the carbonium ion preferentially to attack by external ions. The concentration of such added ions is thus irrelevant and there should be no effect on the rate of return to starting material. Consequently no effect on the overall rate of solvolysis is observed.

A somewhat more sophisticated manner of explaining the common ion effect may be by examining the differential rate equations for the two possibilities. Parallel development of the respective equations from the general reaction is shown in Figure 26. It should

Figure 26

Parallel Development of Differential Rate Equations

for Intimate and Free Ions

Free Ions

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

since H_2O is in large excess $k_2 = k'[H_2O]$ = constant

$$\frac{dRt}{dt} = k_1[RX]-k_{-1}[R^+][Cl^-]-k_2[R^+] = 0$$

making the steady state approximation

$$[R\ ] = \frac{k_1[RX]}{k_{-1}[Cl^-] + k_2}$$

$$\frac{dP}{dt} = k_2\left[\frac{k_1[RX]}{k\ [Cl\ ] + k_2}\right]$$

$$= \frac{k_1[RX]}{k_{-1}/k_2[Cl\ ] + 1}$$

Intimate Pair

$$\frac{dP}{dt} = k_2'[R^+Cl^-]$$

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

$$[R\ Cl\ ] = \frac{k_1[RX]}{k_{-1}' + k_2'}$$

$$\frac{dP}{dt} = k_2'\left[\frac{k_1[RX]}{k_{-1}' + k_2}\right]$$

$$= \frac{k_1[RX]}{k_{-1}'/k_2' + 1}$$

be noted that only in the case of free ions does the chloride ion concentration play a role in the rate determination and that increasing the chloride in concentration in that system decreases the expected rate of product formation. The ratio k_{-1}/k_2, the selectivity of the carbonium ion, is generally used as a measure of common ion effect. Preliminary work by Schiavelli involving the effects of added rates on the solvolysis of 1,3,3-triphenylchloroallene at 25° in 90:10 ethanol:water has shown a definite common ion rate depression with added chloride ions in the form of LiCl. Added LiBr showed no depression, but rather a small rate enhancement. These results tend to discount an intimate ion pair as the intermediate in the solvolysis of that compound. The rate increase upon addition of LiBr was seen as the result of increased polarity of the solvent due to excess ions present. Some typical data for common ion depression studies are compiled in Table XVII. It may be seen from this table that both 1-anisyl-2,2-diphenylbromo and iodoethylene exhibit solvolytic rate depressions on addition of common ion. The value for its bromo compound, however, is somewhat smaller, which is expected and supports the hypothesis that selectivity results from the relative stability of the intermediate cation. The energy barrier to the reversal of the ionization process for the iodo compound should be lower than that for the bromo compound as iodide ion is the better nucleophile. The lower energy would raise the value of k_{-1}, and therefore the value of the selectivity term-k_{-1}/k_2 (k_2 is the same in both systems). The observance of no common ion depression in the case of triphenyliodoethylene can be interpreted

Table XVII

Typical Data From Common Ion Depression Studies
Selectivities of Carbonium Ions[a]

Halide	k_{-1}/k_2
Triphenylmethyl chloride	400
Benhydryl chloride	10-16
Benhydryl bromide	50-70
t-Butyl bromide	1-2
2,2-diphenyl-1-anisyliodoethylene	30-50
1,2,2-triphenyliodoethylene	0
2,2-diphenyl-1-anisylbromoethylene	10
1,3,3-triphenylchloroallene	5-13[b]

a
Table taken from ref. 8 unless otherwise specified.
b
Private communication from M. D. Schiavelli.

as being due to the higher energy of the cation since no stabilizing substituent is available to delocalize the charge developed. This fact may decrease the selectivity to such a point that reversal to starting material is impossible. A possible relative energy diagram for these systems may be seen in Figure 27.

It should be recognized from this discussion that rate depressions, due to common ions, demand a reversable intermediate, involving essentially free ions, whereas, no effect due to common ions makes no definite argument favoring either an intimate pair or free ions. It is worth noting here that when speaking in terms of the rate, what is meant is the overall rate of solvolysis. In the studies of this laboratory, however, rates of product formation have been used as those of the overall rate. An investigation involving the rate of disappearance of allene would be advisable. If these rates were identical to those determined by following product formation, long lived or intimate ion pairs would be impossible.

It should be obvious that the salt effects discussed above do not apply to the one-step non-reversible bimolecular mechanism,

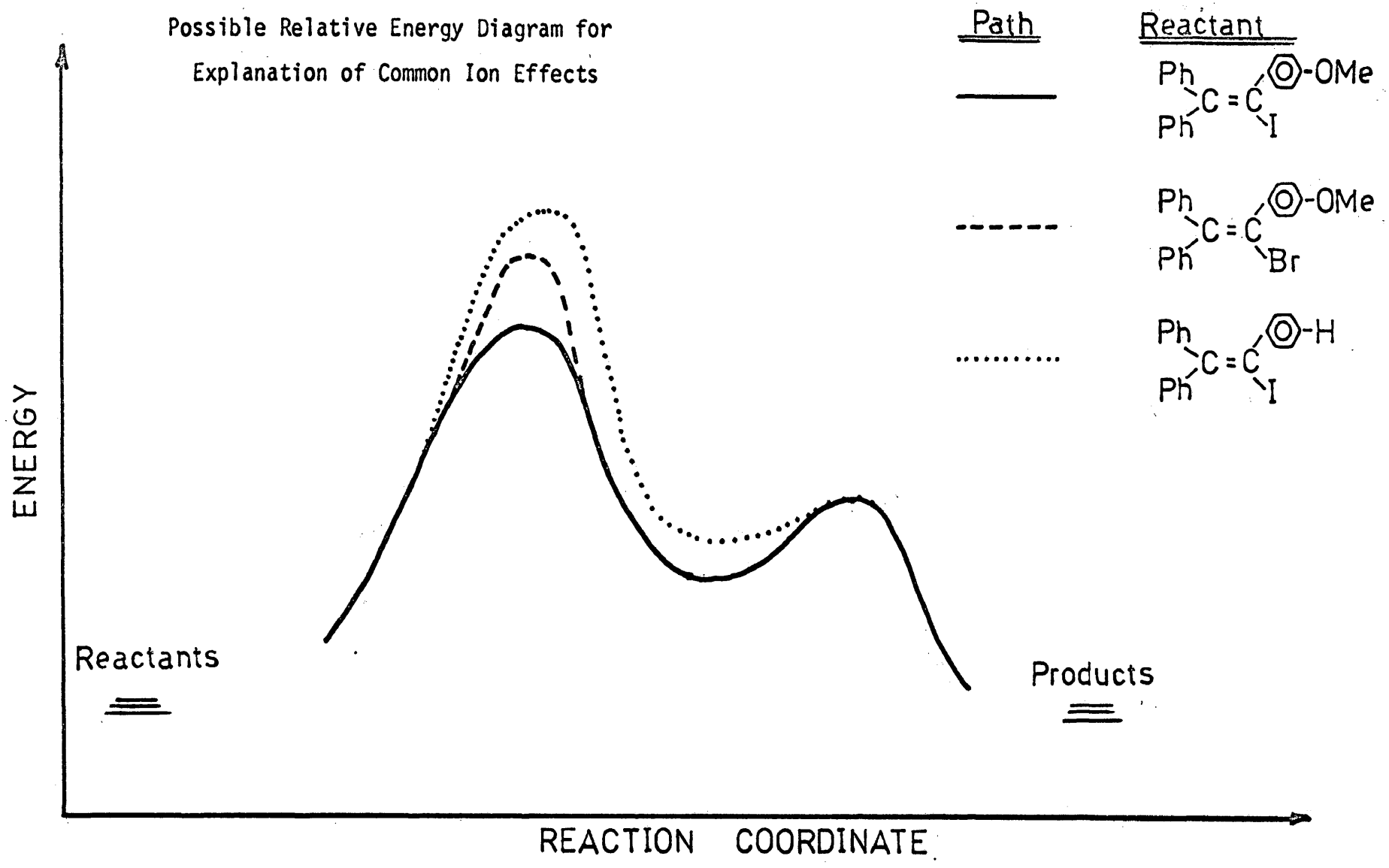
$$R\text{-}X \xrightarrow{H_2O} R\text{-}OH + H^+ + Cl^-$$

No such depression of the rate should be observed from added common ion and the only direct effect of added noncommon ions would be a possible rate increase in the loss of reactant, depending on the extent to which the added ions might attack the substrate.

Figure 27

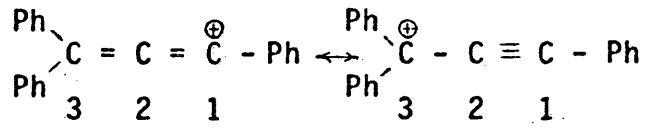
Possible Relative Energy Diagram for

Explanation of Common Ion Effects



2. The effect of changes in the structure of the substrate: Substituent and Structural Effects

Changing the p-substituents in the phenyl ring at C-1 of the triarylchloroallene resulted in the detection of positive charge at that carbon atom. The solvolysis of these compounds has been discussed in terms of the resonance-stabilized cation,



This cation was postulated to have a greater charge density at C-3 due to increased delocalization by the additional phenyl ring there. Substituent effect studies involving the two aromatic rings at that position should yield information concerning the degree of charge at that carbon.

More drastic substituent changes on the basic allene system itself should give further insight into the mechanism of haloallene solvolysis in general. Systematic substitution of allyl or other groups for the phenyl rings followed by investigations of any corresponding changes in characteristics of the reactions (rate, products, solvent dependence, etc.) could lead to a greater understanding of the intermediate cation. By increasing or decreasing electron density around particular carbon atoms, changes in the degree to which the allenyl or propargyl forms contribute to the configuration of the cation can be affected. On such study is now in process involving the substitution of t-butyl groups at C-3 for the two phenyl rings, that is 1-phenyl-3,3-di-t-butylchloroallene.[47] This substitution should substantially decrease the stabilization of

charge at C-3, thereby increasing the amount of charge at C-1 and the likelihood of solvent attack at that position. No data are yet available from that work.

C. To Round Out the Examination:

Although there can be little doubt of the mechanism involved in the solvolysis of triarylhaloallenes after the above studies, a number of loose ends should be tied. First, a determination of the activation parameters for all the substituted allenes should be determined if only for informational purposes. Secondly, a product study should be performed in ethanol-water solutions to establish that the same products are obtained in them as in acetone-water solutions. This is necessary to assure that the data obtained in the former system are comparable to that of the latter (salt effects and nucleophilicity comparisons). Moureau, Dufraisse and Mackall[2b] reported earlier that the product (now known to be the respective chloroallene) from the reaction of 1,1,3-triphenylpropyn-1-ol with PCl_3 was hydrolyzed in alcohol to give what is now felt to be the α,β-unsaturated ketone, 1,3,3-triphenyl-propen-1-one. However, recent investigations as part of this work disclosed that 1,3,3-triphenylchloroallene, on standing at room temperature for three days in 90:10 ethanol:water, gave a uv spectrum identical to the propargyl alcohol, 1,1,3-triphenylpropyn-1-ol.

Finally, the true identification of the minor product from the product studies, taken to be the α,β-unsaturated ketone,

1,3,3-triphenylpropen-1-one (or diphenylacrylophenone), should be made. The uv characteristic absorption for this compound can be found in non-related work by Black and Lutz.[48]

REFERENCES

1

a) P. L. Salzberg and C. S. Marvel, J. Am. Chem. Soc., 50, 2840 (1928).
b) I. L. Ozanne and C. S. Marvel, J. Am. Chem. Soc., 52, 5267 (1930).
c) J. G. Stampfli and C. S. Marvel, J. Am. Chem. Soc., 53, 4057 (1931).
d) R. S. Sweet and C. S. Marvel, J. Am. Chem. Soc., 54, 1184, (1932).
e) J. C. Tsao and C. S. Marvel, J. Am. Chem. Soc., 55, 4709 (1933).
f) J. H. Ford, C. D. Thompson, and C. S. Marvel, J. Am. Chem. Soc., 57, 2619 (1935).

2

a) C. Moureu, C. Dufraisse, and A. S. Houghton, Bull. soc. chim. France, [4] 41, 53 (1927).
b) C. Moureu, C. D. Dufraisse, and C. Mackall, Bull. soc. chim. France, [4] 33, 934 (1923).
c) C. Moureu, C. Dufraisse, and H. Blatt, Bull. soc. chim. France, [4] 35, 1412 (1924).

3

A. Willemart, Compt. rend., 200, 561, 755, (1935); Bull. soc. chim. France, [5] 2, 867 (1935).

4

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

5

R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 5th ed., John Wiley & Sons, Inc., New York, N. Y., 1967, p. 157.

6

C. A. Grob and G. Cseh, Helv. Chim. Acta., 47, 194 (1964).

7

Other reaction types involving vinyl cations included:
1) electrophilic addition to acetylenic or allenic bonds; e.g., A. S. Noyce and M. D. Schiavelli, J. Am. Chem. Soc., 90, 1020, 1023 (1968), and references cited therein.
2) vinyl cations via vinyl diazonium ion; e.g., A. C. Day and M. D. Whiting, J. Chem. Soc., B , 991 (1967).
3) solvolytic reactions where triple bond participation may be involved; e.g., P. E. Peterson and R. J. Kamat, J. Am. Chem. Soc., 88, 3152 (1966).

8

L. L. Miller and D. A. Kaufman, J. Am. Chem. Soc., 90, 7282 (1968).

9
Z. Rappoport and A. Gal, J. Am. Chem. Soc., 91, 5246 (1969).

10
C. A. Grob and R. Spaar, Tetrahedron Letters, 1439 (1969).

11
a) S. A. Sherrod and R. G. Bergman, J. Am. Chem. Soc., 91, 2115 (1969).
b) D. R. Kelsey and R. G. Bergman, J. Am. Chem. Soc., 92, 228 (1970).

12
M. Hanack and T. Bassler, J. Am. Chem. Soc., 91, 2117 (1969).

13
S. J. Huang and M. V. Lessard, J. Am. Chem. Soc., 90, 2432 (1968).

14
P. J. Stang and R. Summerville, J. Am. Chem. Soc., 91, 4600 (1969).

15
a) P. E. Peterson and J. E. Indelicato, J. Am. Chem. Soc., 90, 6515 (1968);
b) J. Am. Chem. Soc., 91, 6194 (1969).

16
C. A. Vernon, J. Chem. Soc., 423 (1954).

17
M. D. Schiavelli, S. C. Hixon, and H. W. Moran, J. Am. Chem. Soc., 92, 1082 (1970).

18
J. R. Johnson, "Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., vol. I, p. 249 (1942).

19
A. D. Allen and C. D. Cook, Can. J. Chem., 41, 1084 (1963).

20
C. U. Pittman, Jr., and G. A. Olah, J. Am. Chem. Soc., 87, 5632 (1965).

21
D. F. Detar and C. E. Detar, "Computer Programs for Chemistry," vol. I, W. A. Benjamin Inc., 1968, Chapter 6.

22
H. H. Jaffe, Chem. Revs., 53, 191 (1953).

23
a) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, 1940, pp. 184-199.
b) L. P. Hammett, J. Am. Chem. Soc., 59, 96 (1937).
c) L. P. Hammett, Trans. Faraday Soc., 34, 156 (1938).

24
H. C. Brown and Y. Ohamoto, J. Am. Chem. Soc., 80, 4979 (1958).

25
J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, New York, p. 208 (1963).

26
D. S. Noyce and M. D. Schiavelli, J. Am. Chem. Soc., 90, 1020 (1968).

27
a) H. G. Richey, Jr., J. C. Philips, and L. E. Rennick, J. Am. Chem. Soc., 87, 1381 (1965).
b) H. G. Richey, Jr., L. E. Rennick, A. S. Kushner, J. M. Richey, and J. C. Philips, J. Am. Chem. Soc., 87, 4017 (1965).

28
E. Grunwald and S. Winstein, J. Am. Chem. Soc., 70, 846 (1948).

29
S. Winstein, E. Grunwald, and H. W. Jones, J. Am. Chem. Soc., 73, 2700 (1951).

30
A. Streitwiser, Jr., Chem. Revs., 56, 57 (1956).

31
S. C. Hixon, M. A. Thesis, College of William & Mary, 1970.

32
K. B. Wiberg, "Physical Organic Chemistry," John Wiley & Sons, Inc., New York, 1964, pp. 403-423.

33
G. Marchese, G. Modena, and F. Naso, J. Chem. Soc., B, 958 (1968).

34
K. Grieshaum, W. Naegele, and K. Wanks, J. Am. Chem. Soc., 87, 3151 (1965).

35
Chem. Abstr., 46, 3799 (1952).

36
G. F. Hennion and J. J. Sheehan, J. Am. Chem. Soc., 71, 1964 (1949).

37
A. V. Federova and A. A. Petrov, J. Gen. Chem. USSR., 32, 1740, (1962).

38
R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed., Allyn and Bacon, Inc., Boston, Mass., 1966, p. 484.

39
private communication, M. D. Schiavelli.

40
extrapolated from work in reference 31.

41
A. Buraway and E. Spinner, J. Chem. Soc., 3752 (1954).

42
K. H. Meyer and K. Schuster, Ber., 55B, 819 (1922).

43
a) W. S. MacGregor, J. Am. Chem. Soc., 70, 3953 (1948).
b) G. F. Nenion, R. B. Davis, D. E. Maloney, J. Am. Chem. Soc., 71, 2813 (1949).
c) C. W. Shoppee, J. C. Craig, and R. E. Lach, J. Chem. Soc., 1311 (1961), and references cited therein.

44
unpublished work, D. F. Detar and C. E. Detar.

45
Z. Rappoport, Advances in Physical Organic Chemistry, 7, 1 (1969).

46
L. C. Bateman, K. A. Cooper, E. D. Hughes, C. H. Ingold, J. Chem. Soc., 925 (1940).

47
Conrad D. Tomea, Jr., unpublished work, undergraduate research program, College of William & Mary, 1970.

48
W. B. Black and R. E. Lutz, J. Am. Chem. Soc., 77, 5134 (1955).

VITA

Henry Wayne Moran

Born in Richmond, Virginia, April 17, 1946. Graduated from Highland Springs High School in Highland Springs, Virginia, June 1964. B.S., University of Richmond, 1968.

In September 1968, the author entered the College of William and Mary as a graduate assistant in the Department of Chemistry.