

THE MECHANISM OF THE MEYER-SCHUSTER  
REARRANGEMENT

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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

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by

Carol Virginia Roane

1976

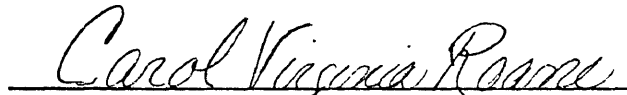
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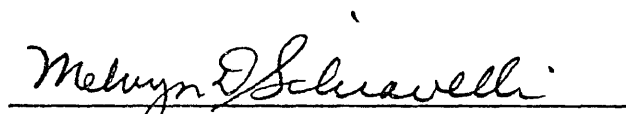
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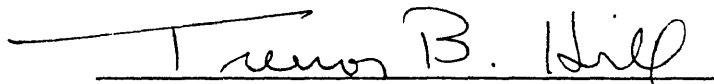
APPROVAL SHEET

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

  
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Approved, August 1976

  
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## ABSTRACT

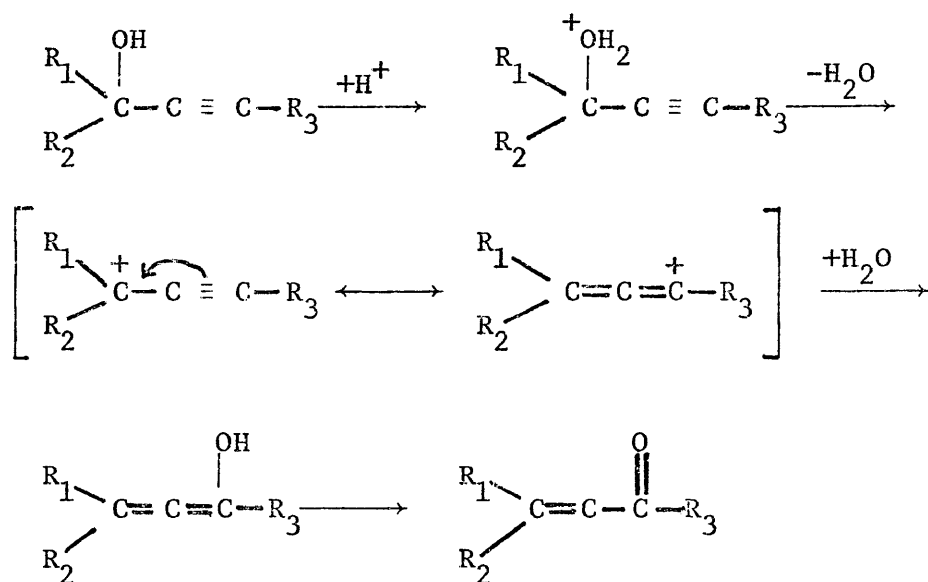
The Meyer-Schuster rearrangement of 1,1-diphenyl-2-propyn-1-ol, in moderately concentrated sulfuric acid, to 3,3-diphenyl-2-propen-1-al was investigated to determine the reaction mechanism. Kinetic studies revealed first-order rate behavior and linearity related to the acidity function,  $H_0$ . Activation parameters ( $\Delta S^\ddagger = -27.4$  e.u. at  $H_0 = 0$ ), solvent isotope effect ( $k_{H_2O}/k_{D_2O} = 0.52$ ) and predicted substituent effects ( $\rho =$  at least  $-1.8$ ) are consistent only with a mechanism which involves a rapid pre-equilibrium formation of the conjugate acid of the alcohol followed by unimolecular or pseudo-unimolecular rearrangement to the product. Theoretical treatment of the solvent isotope effect limits the transition state to one with only electrostatic interaction.

THE MECHANISM OF THE MEYER-SCHUSTER  
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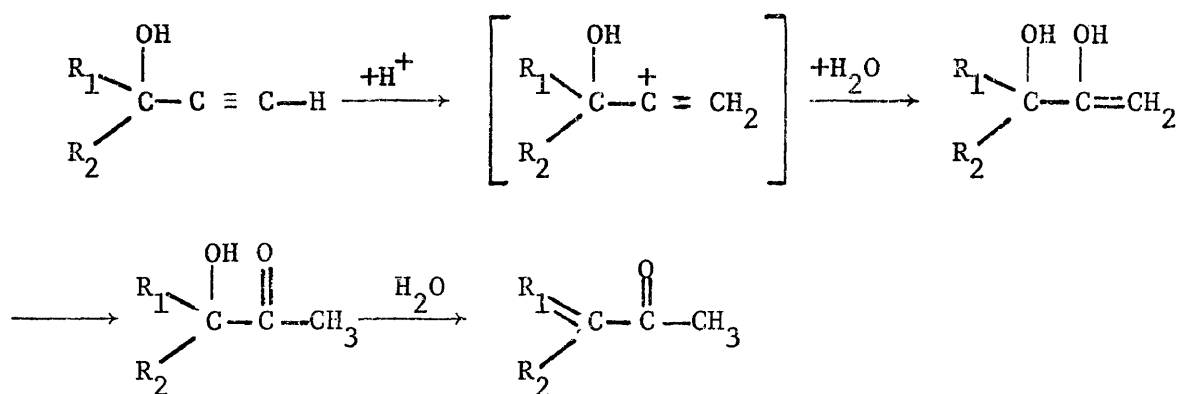
## CHAPTER I

### INTRODUCTION

The Meyer-Schuster rearrangement is the isomerization by a 1,3 shift, of secondary and tertiary  $\alpha$ -acetylenic alcohols to  $\alpha,\beta$ -unsaturated carbonyl products. When the acetylenic group is terminal, the products are aldehydes; otherwise, they are ketones.<sup>1</sup>



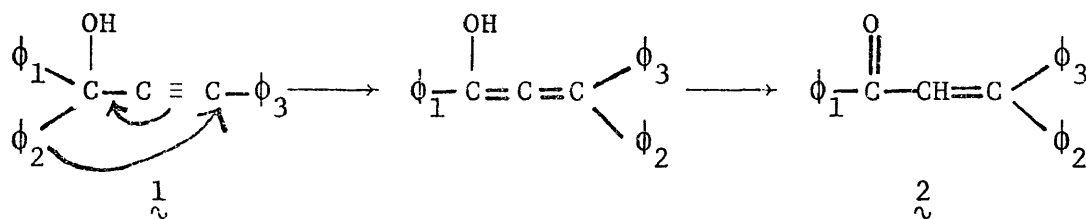
The Rupe rearrangement has been defined as the acid-catalyzed rearrangement of tertiary  $\alpha$ -acetylenic alcohols leading to the formation, predominantly of  $\alpha,\beta$ -unsaturated ketones.<sup>1</sup>



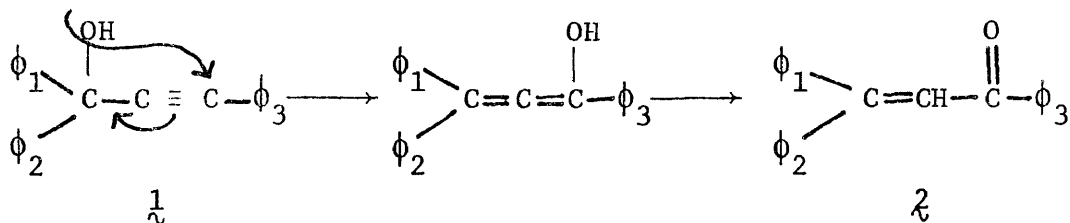
In 1922, Kurt H. Meyer and Kurt Schuster reported the first example of a Meyer-Schuster rearrangement when they converted 1,1,3-triphenylprop-2-yn-1-ol, 1, to the corresponding ketone,  $\beta$ -phenyl-chalcone, 2, in acetyl chloride. When they repeated the experiment in a variety of acidic catalysts---acetic anhydride, thionyl chloride, hydrogen chloride, sulfuric acid---they found that the ketone was still the only product.<sup>2</sup>

They proposed two schemes for this rearrangement.

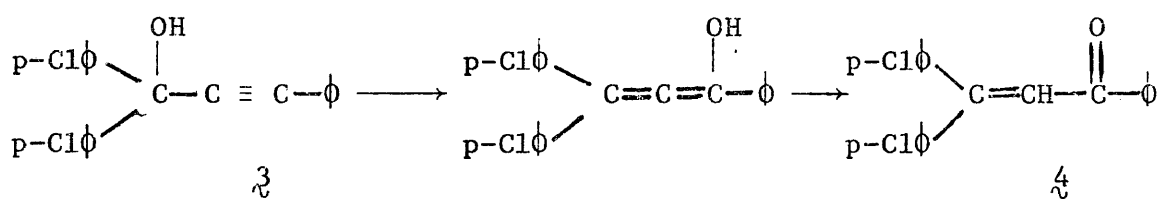
Scheme 1:



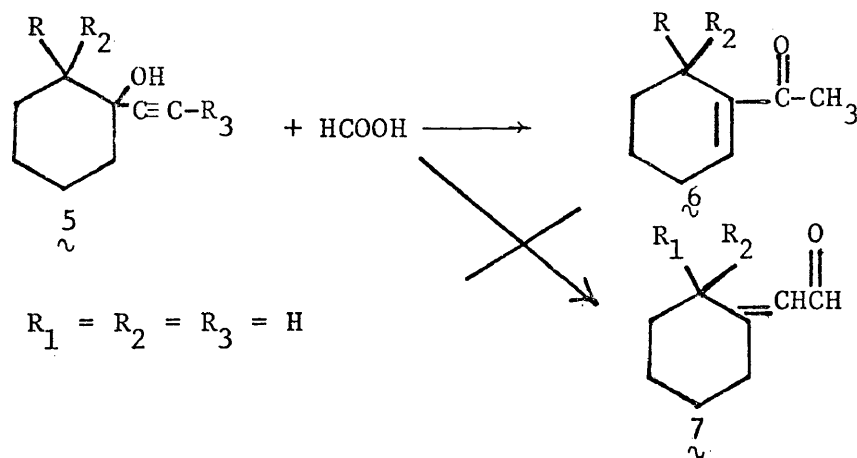
Scheme 2:



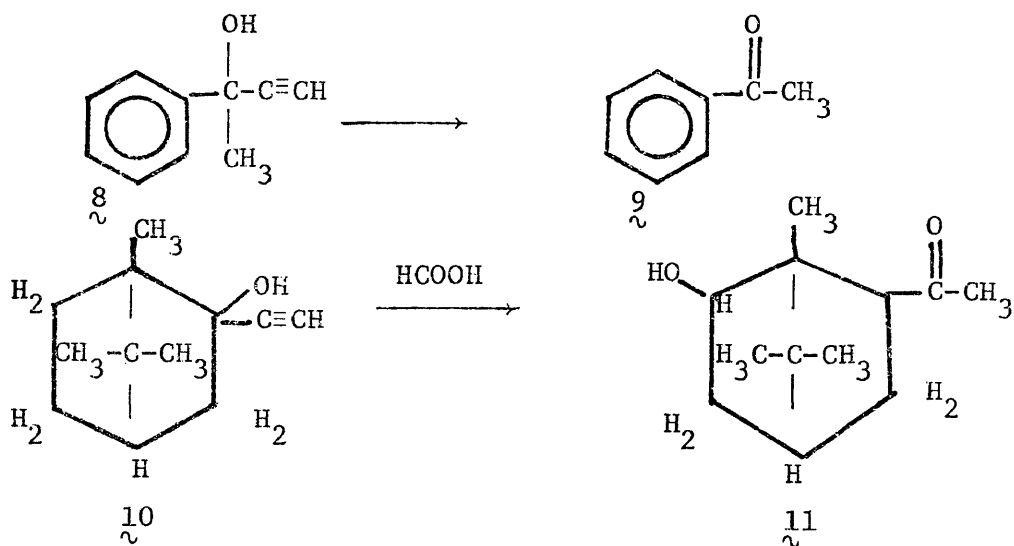
In Scheme 1, the aromatic radical is migrating by a 1,3 shift and in Scheme 2, the hydroxyl group is migrating by a 1,3 shift. In order to determine which reaction scheme was taking place, they performed the reaction on **3**. If it were the hydroxyl group, migrating the rearrangement would yield a ketone with a structure like **4**, and this is what they found.<sup>2</sup> After this information had been obtained, various other acetylenic alcohols were investigated in a



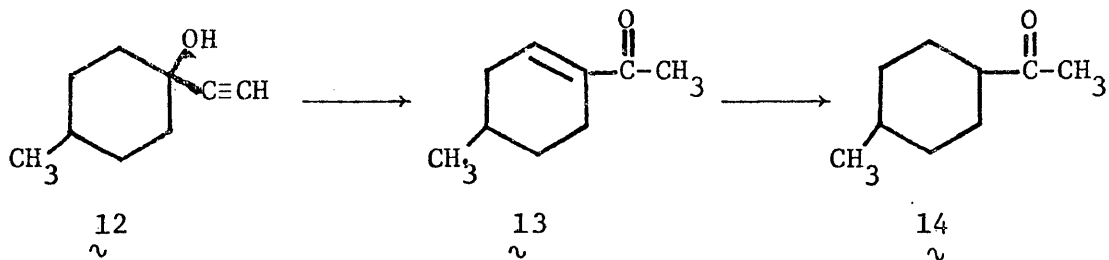
variety of different acid agents.<sup>3</sup> It has been found that a great variety of compounds undergo this rearrangement.<sup>3c</sup> Rupe and co-workers then investigated the acid-catalyzed isomerization of a large number of  $\alpha$ -acetylenic alcohols with active acetylenic hydrogens in formic acid and reported that they yielded the corresponding aldehydes.<sup>4</sup> Subsequent studies on these compounds did not confirm the results of Rupe and his colleagues. Fischer and Lowenbey<sup>5</sup> showed that when heated in formic acid **5** yielded an isomeric ketone, **6**, and not an aldehyde, **7**, as Rupe had stated.

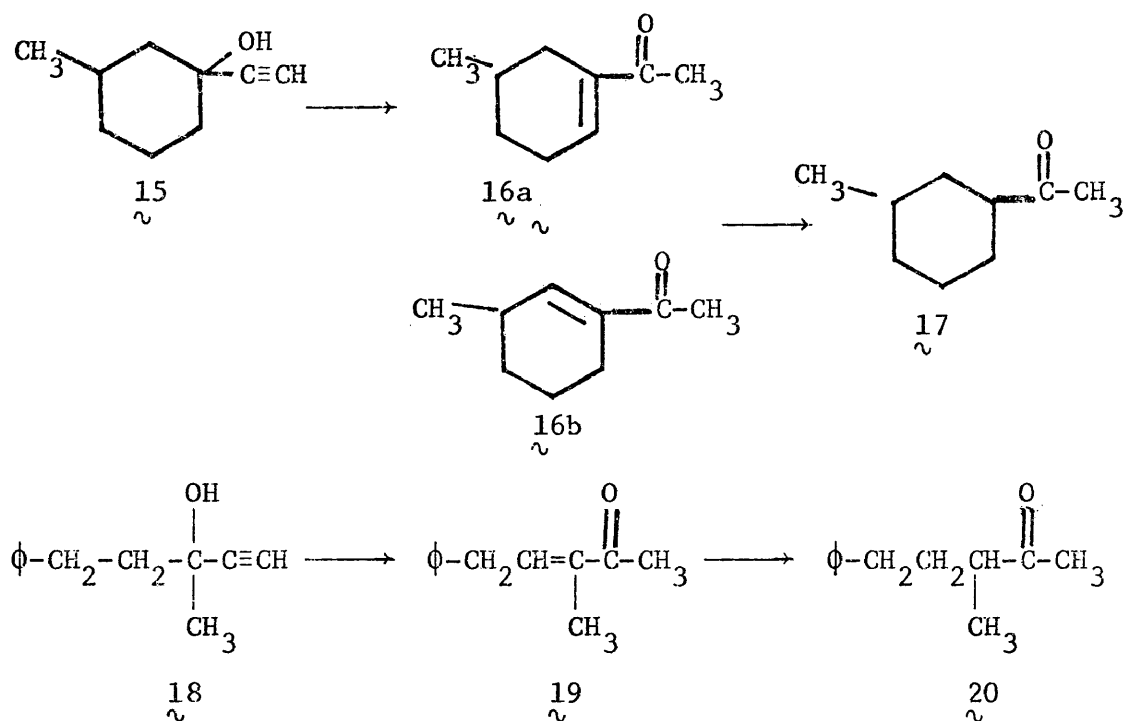


These workers suggested that ketones were the main products of the rearrangement and that aldehydes were formed only in very small quantities. Hurd and Christ<sup>6</sup> repeated some of Rupe's work on ethynylcarbinols,  $\underset{\sim}{10}$ ,  $\underset{\sim}{8}$  and studied an additional compound  $\underset{\sim}{10}$ . His investigation was prompted by the following inconsistency:

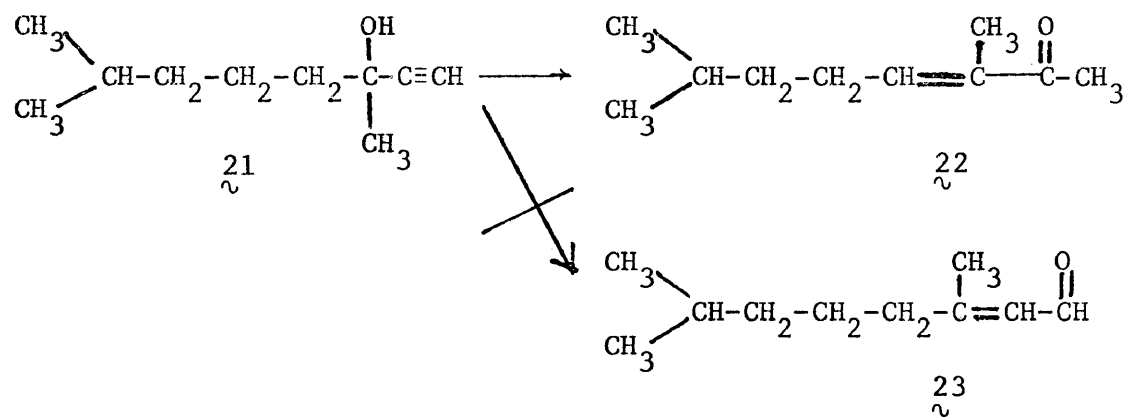


Rupe had reported that in the rearrangement of  $\underset{\sim}{12}$ ,<sup>4f</sup>  $\underset{\sim}{15}$ ,<sup>4h</sup> and  $\underset{\sim}{18}$ ,<sup>4e</sup> that the  $\alpha,\beta$ -unsaturated ketones,  $\underset{\sim}{13}$ ,  $\underset{\sim}{16ab}$ , and  $\underset{\sim}{19}$ , were formed while in the majority of the other compounds he studied<sup>4a-m</sup> only the unsaturated aldehydes were obtained. No explanation as to why aldehydes were formed in some cases and ketones in other cases had been given.

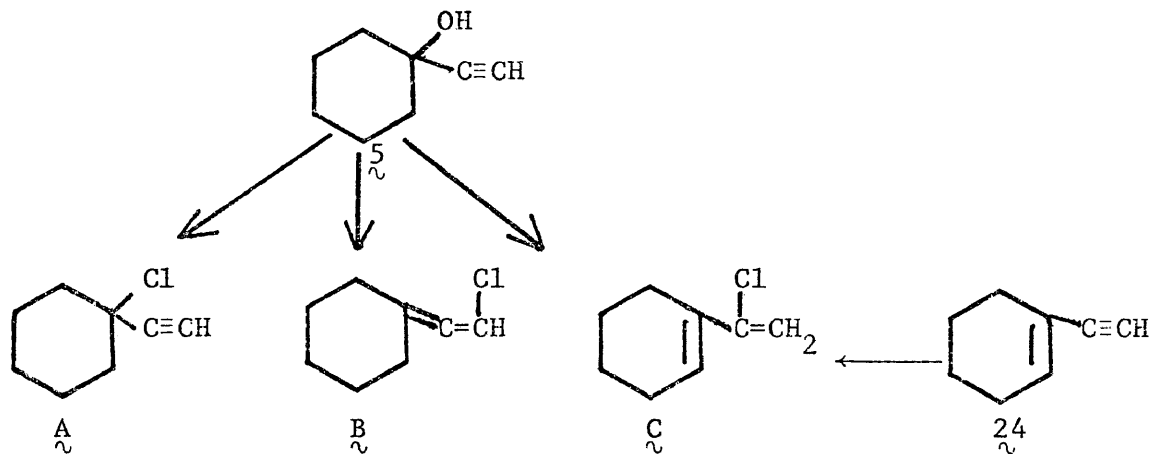




Hurd found that in all the cases he studied, ketones  $\underset{\sim}{6}$ ,  $\underset{\sim}{9}$ , and  $\underset{\sim}{11}$  were formed and that there was no indication of any aldehydic products.<sup>6</sup> Price and Meisel<sup>7</sup> repeated work on  $\underset{\sim}{21}$  and reported that they obtained the ketone,  $\underset{\sim}{22}$ , instead of the aldehyde,  $\underset{\sim}{23}$ . They postulated that the most likely path for this rearrangement to take would be the initial dehydration of the carbinol to a vinylacetylenic homolog since vinylacetylenes are readily hydrated to  $\alpha,\beta$ -unsaturated ketones (vinylacetylene, itself, is hydrated to methyl vinyl ketone).

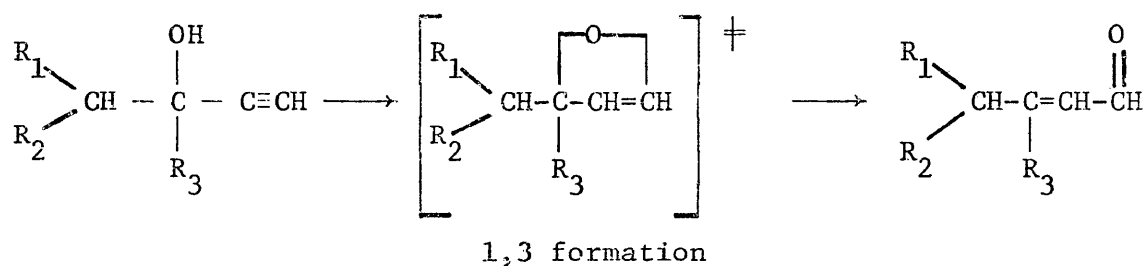
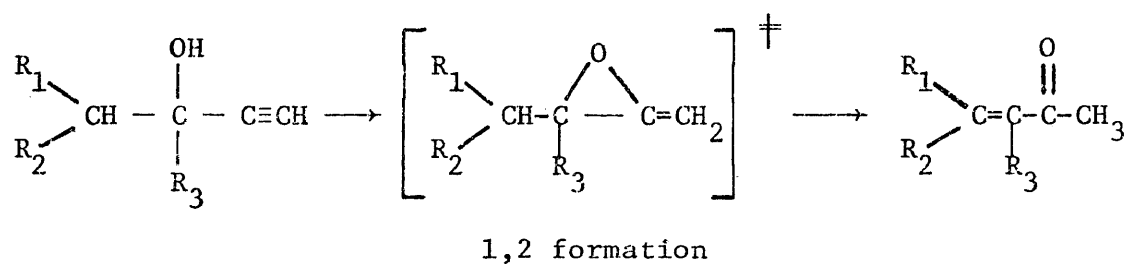


Hurd and Jones<sup>8</sup> postulated that 1-ethynylcyclohexanols rearranged to their corresponding unsaturated ketones through an "enyne" intermediate. On treating  $\underline{5}$  with chlorinating agents, they did tests to see which of the following three products were formed:

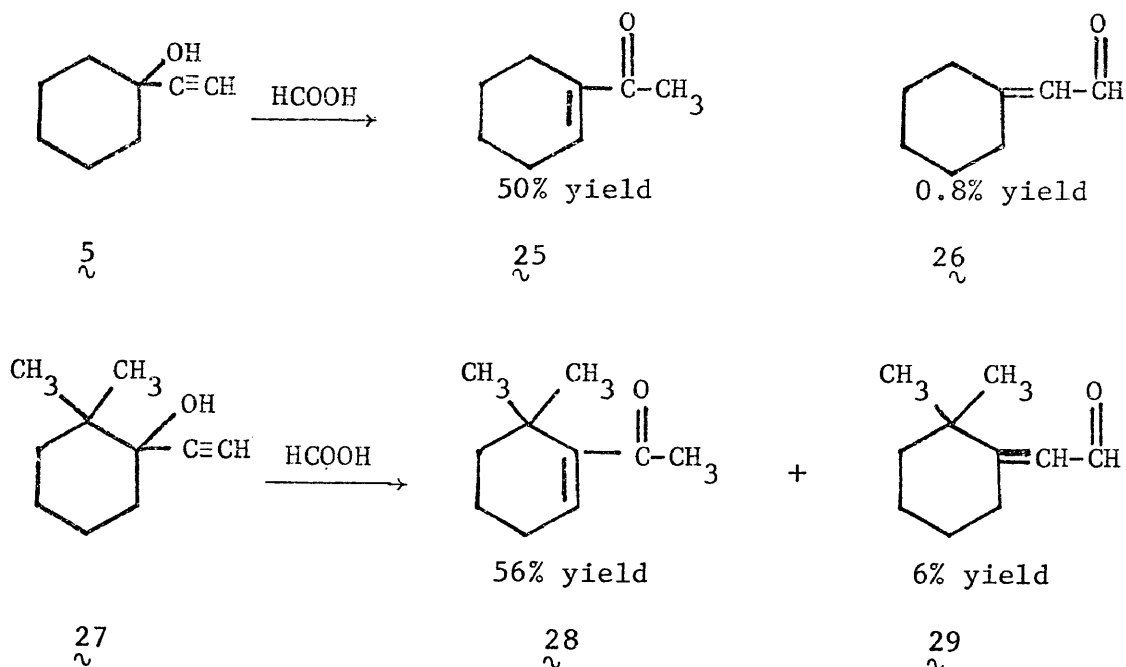


Structure  $\underline{A}$  was eliminated because the product did not display acetylenic reactions and did not possess a reactive chlorine atom. Structure  $\underline{B}$  was eliminated because upon ozonolysis it should have yielded cyclohexanone which it did not. Compound  $\underline{C}$  was prepared by Carothus and Coffman<sup>9</sup> by the addition of hydrochloric acid to  $\underline{24}$  in the presence of cuprous and ammonium chlorides. Their product proved to be identical to Hurd's structure  $\underline{C}$  through boiling point, refractive index and the melting point of the naphthoquinone derivative. Therefore, Hurd presumed  $\underline{24}$  to be an intermediate in the transformation of  $\underline{5}$  into  $\underline{C}$ .<sup>8</sup>

Rupe<sup>4j</sup> explained the formation of both aldehydes and ketones by proposing a mechanism for the rearrangement with the intermediate formation of "expoxide" compounds.

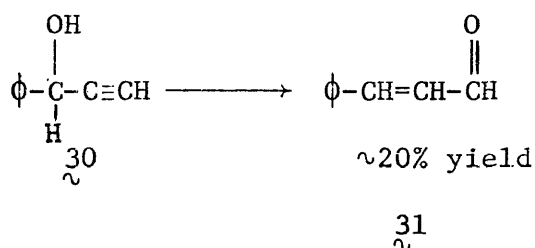


Chanely<sup>10</sup> supported this proposal with the convincing evidence that in the rearrangement of  $\underset{\sim}{5}$  and its derivatives, in addition to ketones, the corresponding  $\alpha,\beta$ -unsaturated aldehydes are formed.

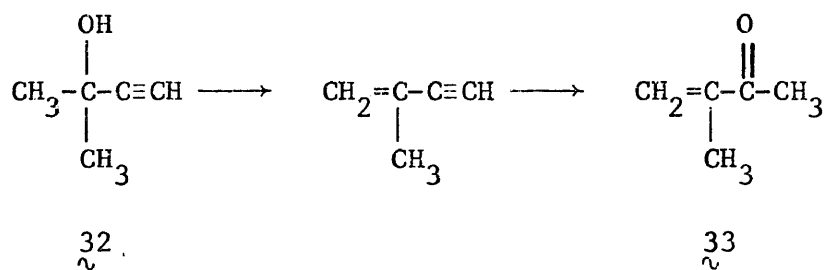


Despite this, several authors stated, in their papers, that only the  $\alpha,\beta$ -unsaturated ketones were obtained,<sup>11,16,7,17,24</sup> while others stated that both the unsaturated ketones and aldehydes were found.<sup>12,15</sup>

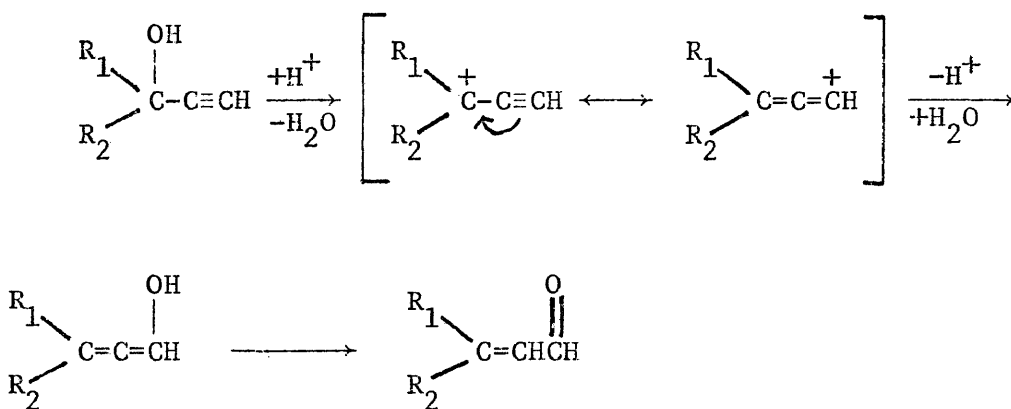
In contrast to the above results, the rearrangement of aromatic acetylenic alcohols with an active acetylenic hydrogen led to the formation mainly of the expected aldehydes.<sup>13,14</sup> One particular example was given by MacGregor.<sup>14</sup> He postulated that the rearrangement of ethynylcarbinols probably proceeded by initial elimination of the hydroxyl group to form a carbonium ion. The loss of a proton from an adjacent carbon followed by hydration of the triple bonds and ketonization would yield the observed unsaturated ketones. Shifting the carbonium ion to the allenic structure followed by reaction with water at the positive terminal carbon would yield the enolic form of the unsaturated aldehyde which is in equilibrium with the aldehyde. With phenylethynylcarbinol,  $\underset{\sim}{30}$ , he found that indeed the unsaturated aldehyde,  $\underset{\sim}{31}$ , was formed. This is because the carbonium ion formed cannot eliminate a proton from the adjacent carbon.<sup>14</sup>



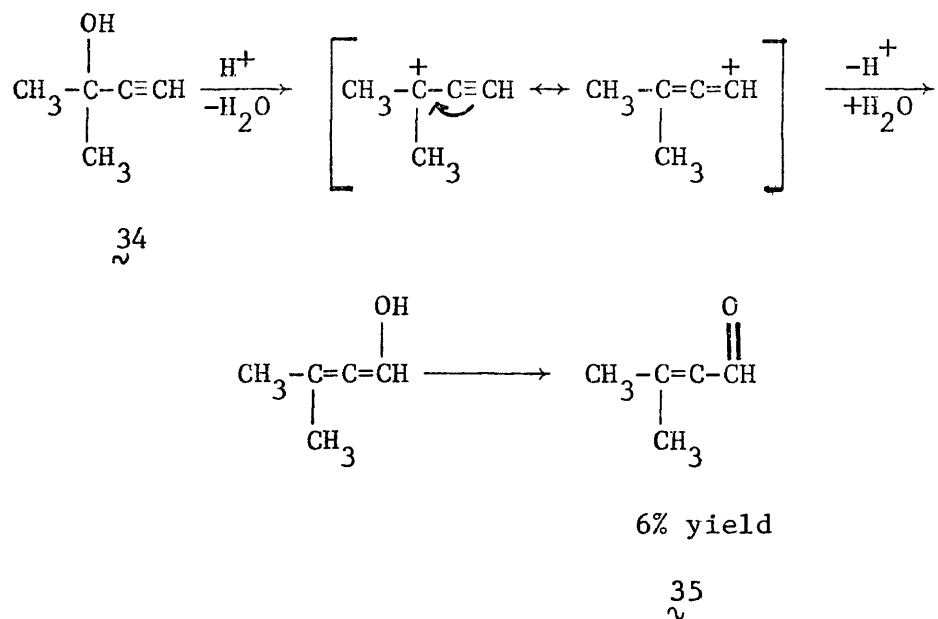
Bergmann,<sup>15</sup> in his study of  $\underset{\sim}{32}$ , said that the ketones appeared to be forming almost exclusively by the dehydration of the tertiary carbinol group followed by hydration at the triple bond.



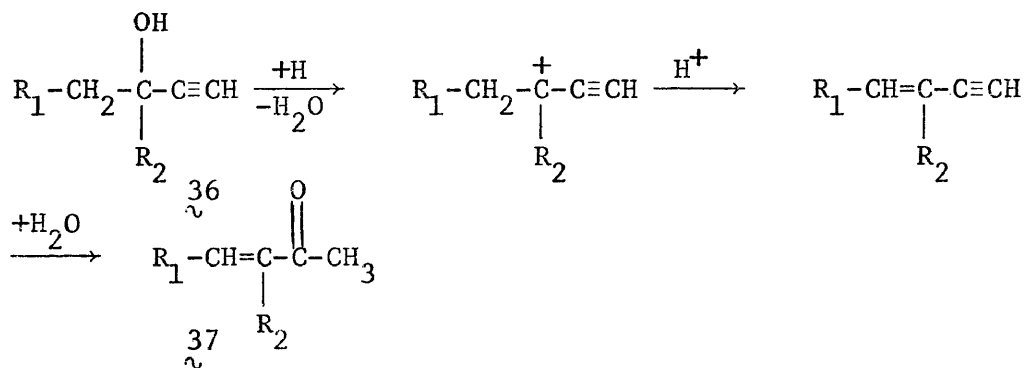
Hennion, Davis, and Maloney<sup>16</sup> represented the mechanism of the ethynylcarbinol rearrangement as an allyl rearrangement.



This is supported by Chanely,<sup>10</sup> who found that the dehydration and isomerization of  $\underset{\sim}{34}$  formed  $\underset{\sim}{35}$ --an allylic shift.

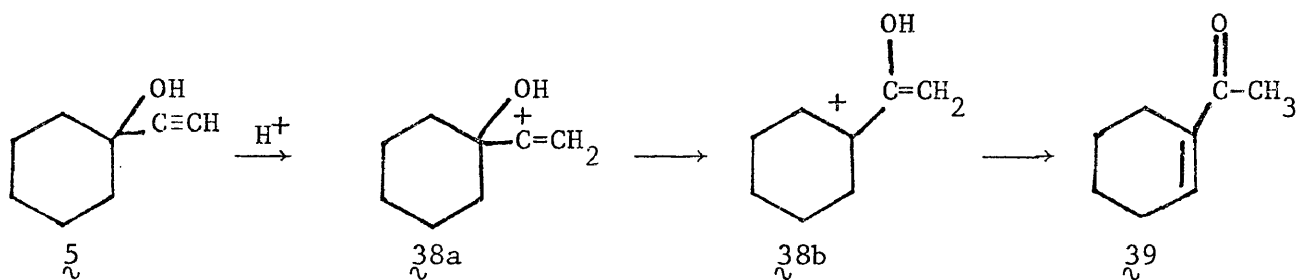


Another example is methylethylethynylcarbinol,  $\underline{36}$ . Rupe<sup>4a</sup> originally thought that the product was the aldehyde but it was repeatedly shown to be the unsaturated ketone,  $\underline{37}$ .<sup>5,7,8</sup>



Therefore, the Rupe rearrangement reaction was proposed to occur by an apparent 1,2 shift of the hydroxyl group while the Meyer-Schuster rearrangement was a 1,3--or allylic shift.<sup>16</sup>

Newman<sup>17</sup> suggested a carbocation mechanism for the rearrangement of ethynylcarbinols into  $\alpha,\beta$ -unsaturated ketones.

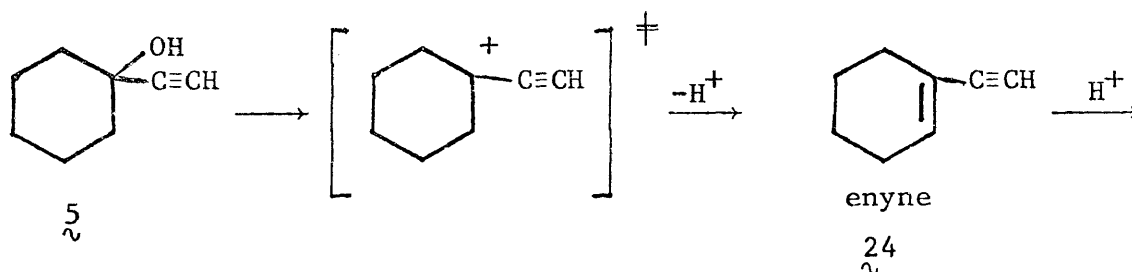


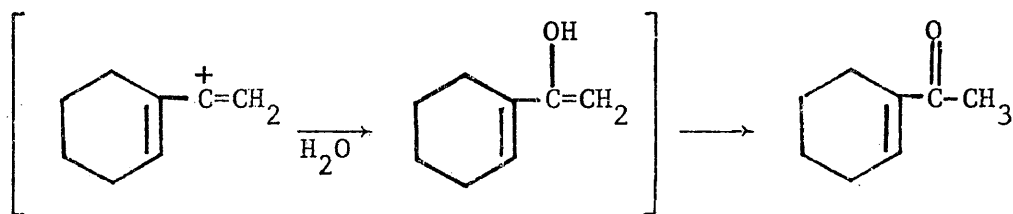
He observed that ethynylcyclohexene,  $\underline{24}$ , was transformed much slower than ethynylcyclohexanol,  $\underline{5}$ , rearranged to  $\underline{39}$  by the acid form of Dowex 50 in acetic acid. Therefore, he said a mechanism with an enyne as an intermediate (as was proposed in Reference 8) was not likely. Thus, there must be molecular rearrangement taking place

rather than hydroxyl migration through 38a. He found that a number of compounds were smoothly hydrated to corresponding carbonyl compounds in 70 to 80 percent yields by this mechanism.

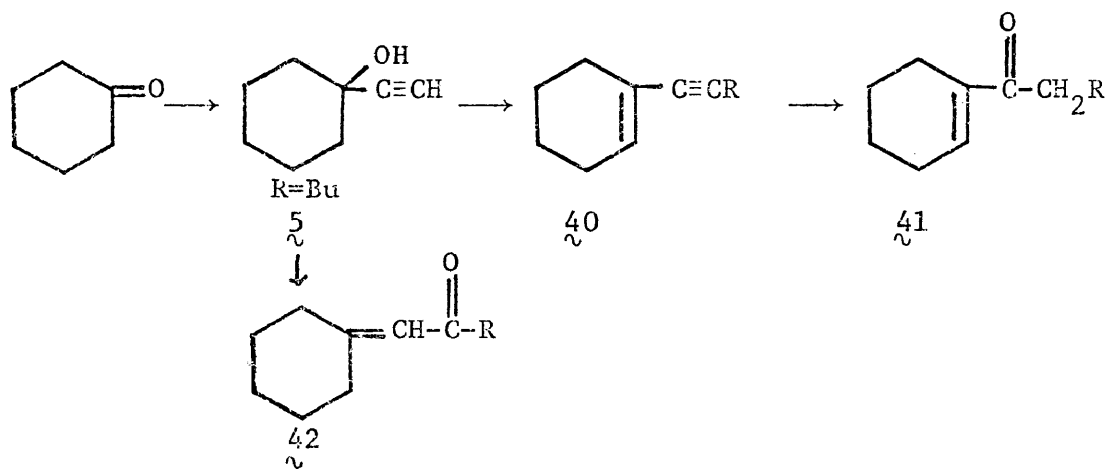
Ansell, Hancock, and Hickinbottom<sup>18</sup> accepted this mechanism in their study of the hydration of terminal vinylacetylenes with formic acid in benzene. However, this mechanism was refuted by Apparau and Glenat<sup>19</sup> who observed enynes as well as ketonic products during the isomerization of some ethynylcarbinols with Dowex 50 in acetic acid. Contrary to both of the above reports,<sup>17,18</sup> they were able to get quick and complete hydration of vinylacetylenes with Dowex 50 in acetic acid. While they, too, observed that enynes with terminal vinyl groups were hydrated much slower than ethynylcarbinols, they were able to bring about rapid isomerization by using sulfuric acid in acetic acid.

Hurd and Christ,<sup>6</sup> Hennion, Davis, and Maloney,<sup>16</sup> and Hamlet, Henbest and Jones,<sup>20</sup> all agree that acetylenic alcohols are dehydrated into enynes and their subsequent hydration leads to the formation of ketones. This is the generally accepted mechanism for the Rupe rearrangement.



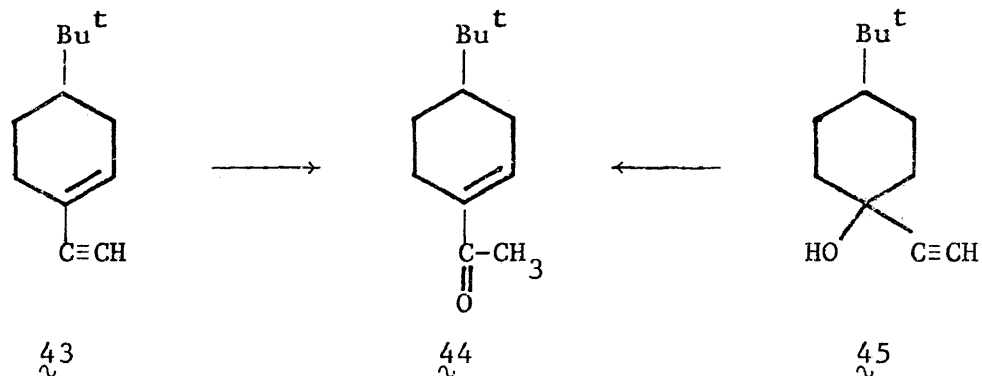


Hamlet, Henbest and Jones<sup>20</sup> reported that after ten minutes of heating  $\underline{5}$  in formic acid, a mixture of  $\underline{40}$  and  $\underline{41}$  was found. After

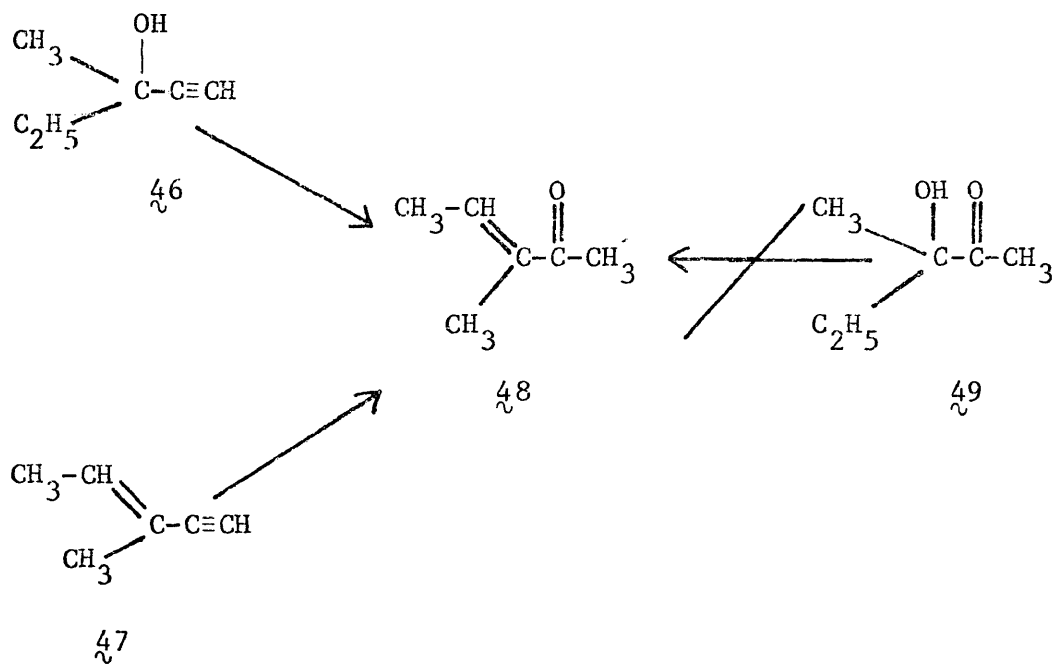


45 minutes of heating the same mixture was obtained but with a greater proportion of  $\underline{41}$ . Only one ketone was formed,  $\underline{41}$ , therefore, the dehydration must be more rapid than the alternative 1,3 shift of the hydroxyl group leading to  $\underline{42}$ .

This dehydration-hydration mechanism is further supported by the spectroscopic detection of the enyne intermediate<sup>21</sup> and the isolation of enynes.<sup>8,18,20,22,23</sup> Newman and Golbe<sup>24</sup> afford even greater evidence when they observed that  $\underline{43}$  was converted to  $\underline{44}$  quicker than  $\underline{45}$ .

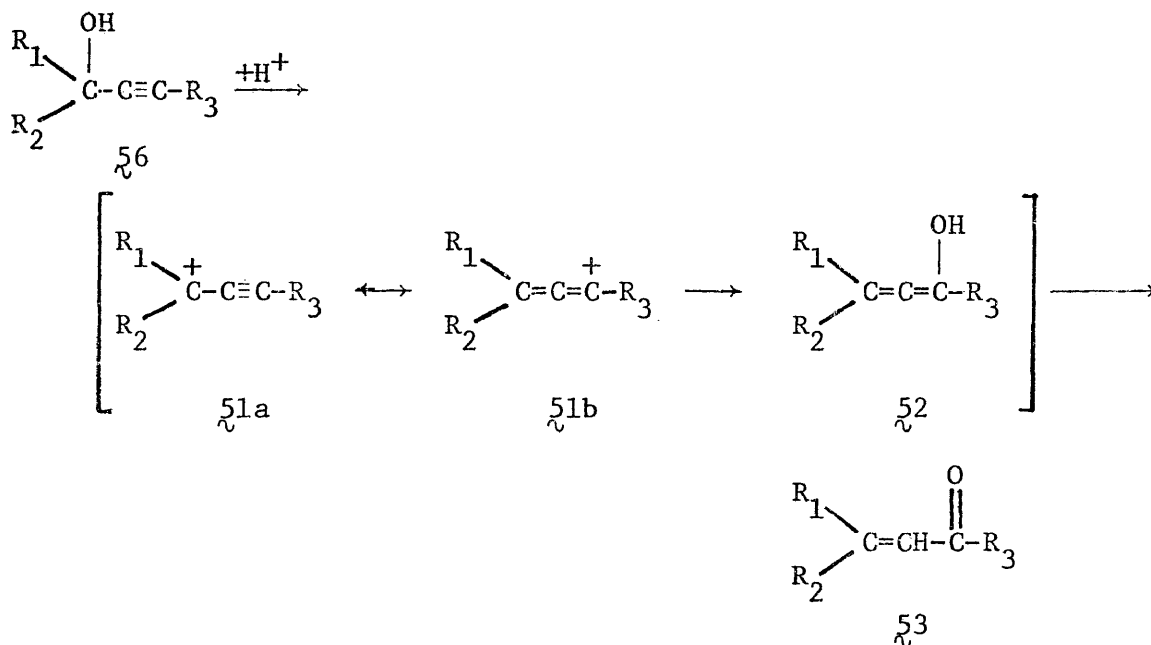


This favors the intermediacy of  $\underset{\sim}{43}$  in the rearrangement of  $\underset{\sim}{45}$  to  $\underset{\sim}{44}$ . Hennion, Davis, and Maloney,<sup>16</sup> ruled out the possibility of a hydration-dehydration sequence when they observed that  $\underset{\sim}{46}$  and  $\underset{\sim}{47}$  are converted by formic acid to  $\underset{\sim}{48}$  but  $\underset{\sim}{49}$  was found to be inactive.



Dornow and Ische<sup>25</sup> suggested a reaction mechanism for the Meyer-Schuster rearrangement involving a carbonium ion followed by an intermediate vinyl alcohol and subsequent isomerization into a

vinyl ketone.



Alkynyl cations like  $\text{51a}$  have been spectroscopically detected by both NMR and UV.<sup>26</sup> Appara and Glenat<sup>19</sup> found that when some ethynylcarbinols were reacted in acetic acid, allenyl acetates were formed. This was considered to be good evidence for the transient existence of an allenyl cation like  $\text{51b}$ . These cations have also been shown to be intermediate in the solvolysis of haloallenes.<sup>27</sup> Meyer and Schuster<sup>2</sup> were able to isolate 4,4'-dichlorobenzophenone from the acid-catalyzed isomerization of  $\text{3}$  and oxidative degradation. This is additional good supportive evidence. Woitz<sup>28</sup> also supports this 1,3 propargyl shift.

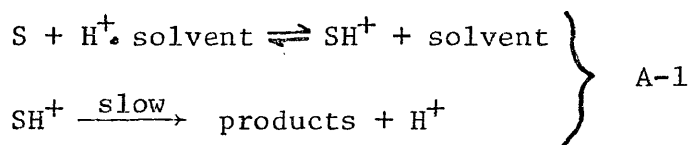
While the Meyer-Schuster rearrangement has been shown to occur by a formal 1,3-propargyl shift of hydroxyl, the details of the mechanism have not been determined.

## CHAPTER II

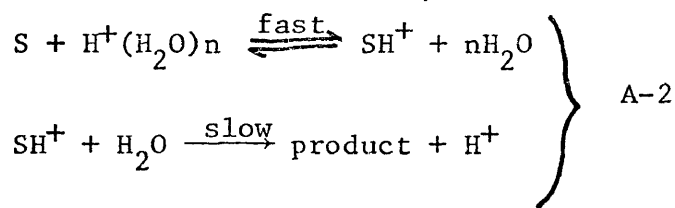
### MECHANISMS

The hydroxyl groups in alcohols are not good leaving groups until they are protonated to  $\text{ROH}_2^+$ . Reactions in which the leaving group does not come off until it is protonated are called  $\text{S}_{\text{N}}1\text{cA}$  and  $\text{S}_{\text{N}}2\text{cA}$  (depending on whether the reaction after the protonation is an  $\text{S}_{\text{N}}1$  or an  $\text{S}_{\text{N}}2$  process). This is often shorted to A-1 and A-2.<sup>29a</sup>

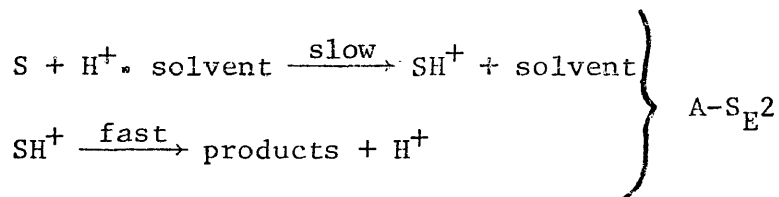
In an A-1 reaction, the protonation of the substrate occurs quickly. The first step is the rapid formation of the conjugate acid of the substrate--a pre-equilibrium step. In the second step, the conjugate acid then undergoes a slow unimolecular transformation into reaction products.



In an A-2 reaction, the first step is the same as in the A-1 reaction. In the second step, the conjugate acid may undergo a slow dissociation before reacting with water in a third faster step or water as a nucleophile may attack the conjugate acid of the substrate.

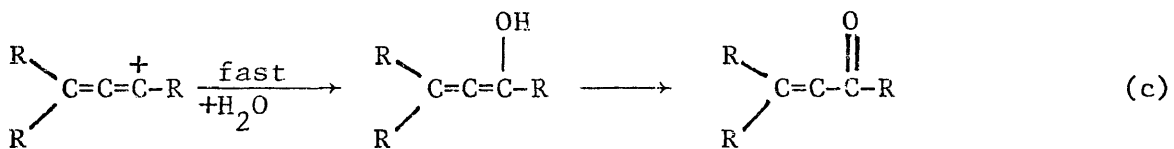
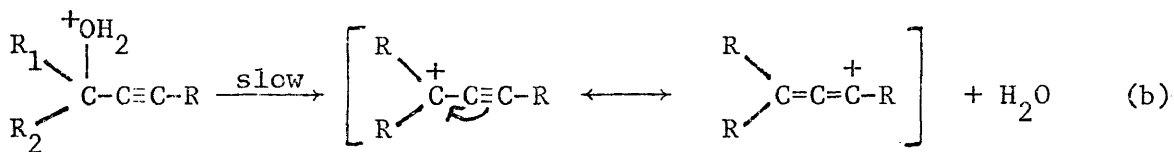


A special type of A-2 reaction is the A-S<sub>E</sub>2. It is, in fact, an electrophilic substitution which involves the substrate and the proton in the rate determining step. It involves a slow proton transfer from an acidic species to the substrate, followed by a rapid further reaction of the conjugate acid.<sup>29b</sup>

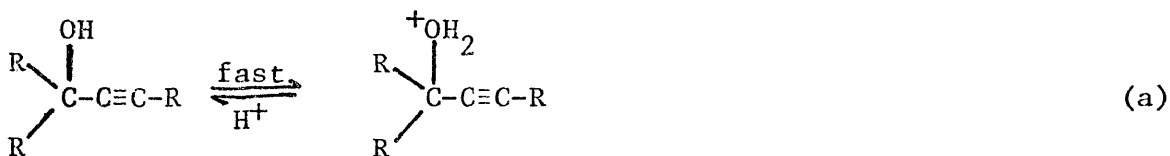


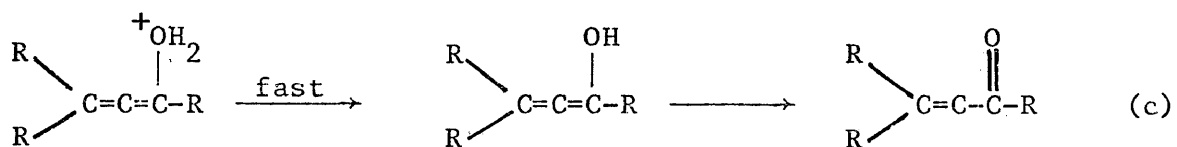
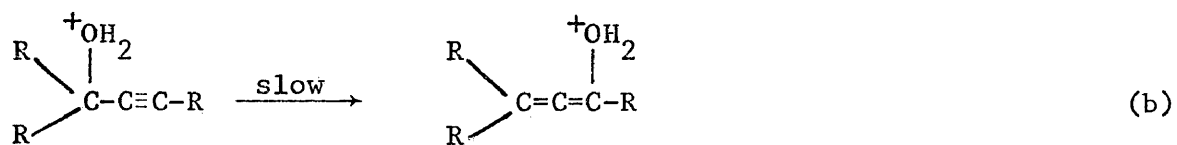
The following are possible mechanisms for the Meyer-Schuster rearrangement in sulfuric acid.

1. Equilibrium protonation of the alcohol with water elimination rate-limiting.

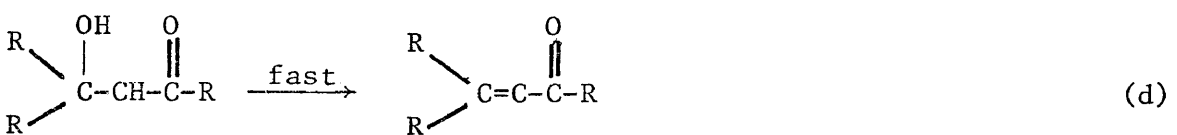
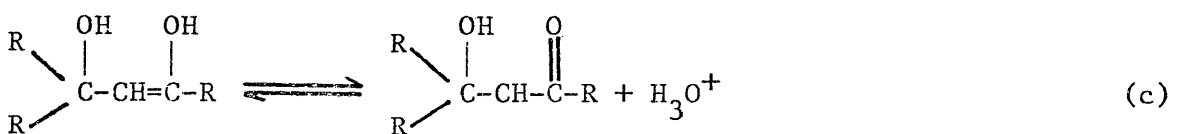
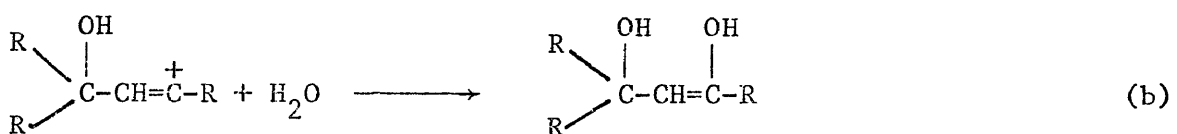
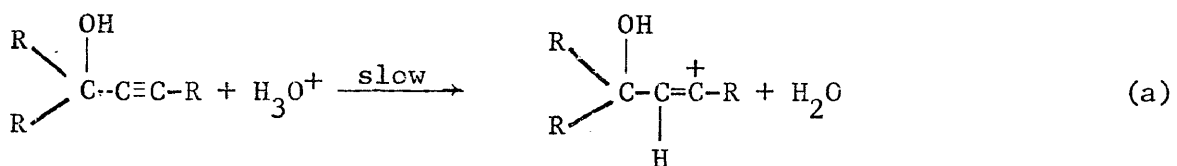


2. Equilibrium protonation of alcohol with addition of water rate-limiting.





### 3. Rate-limiting proton transfer.



## CHAPTER III

### EXPERIMENTAL

#### Materials

Ultraviolet spectra were recorded using a Beckman DK-2 ratio recording spectrophotometer. Routine infrared spectra were obtained using a Perkins-Elmer Model 337 spectrophotometer.

1. 1,1-Diphenyl-2-propyn-1-ol. The writer is indebted to Whitney A. Boynton for this sample.<sup>30</sup> It was used without further purification.

2. Deuterium oxide was obtained from Bio-Rad Laboratories and was 99.88% deuterated.

3. Deuteriosulfuric acid was obtained from Mallinckrodt Chemical Works and had an isotopic purity of 99.5%.

4. Other materials. Reagent grade sulfuric acid and certified ACS grade dioxane were obtained from Fisher Scientific Company and were used without further purification.

#### Kinetic Studies

##### 1. Procedure and Calculations

All kinetic studies were performed on a Gilford Instruments Model 240 spectrophotometer. The cell compartment was thermostated at known temperatures to assure a constant temperature.

for each kinetic run. A matched set of 1 cm cells from Luminon, Inc., were used.

A stock solution of  $5 \times 10^{-3} \text{M}$  of the alcohol was prepared in dioxane. Appropriate dilutions of this stock solution were made to achieve a final concentration of  $1.25 \times 10^{-4} \text{M}$  which was to be used in the kinetic work. For a typical kinetic run in which a 40:60 dioxane:sulfuric acid solution by volume was desired, 10 ml of the  $1.25 \times 10^{-4} \text{M}$  alcohol solution was pipeted into a 25-ml volumetric flask. Exactly 15 ml of aqueous sulfuric acid of the desired concentration was added by pipet resulting in a solution of final concentration of  $5.0 \times 10^{-5} \text{M}$  in the alcohol. The flask was inverted twice and the UV cell quickly rinsed twice with the kinetic solution. The cell was then filled, stoppered, placed in the cell compartment, and allowed to equilibrate. The appearance of the product absorbance,  $n \rightarrow \pi^*$ , 304  $\mu\text{m}$ , was recorded versus time by first zeroing the instrument on a blank identical to the sample except for the presence of the alcohol. At the end of each kinetic run, the absorbances were read off of the graph by subtracting out the absorbance of the blank.

A volumetrically measured and weighed portion of the kinetic solution was titrated against standardized sodium hydroxide. The weight percent and molarity were calculated. The Hammett acidity function was then determined by reference to the  $H_0$  scale of Torck, Hellen, and Coussemant for aqueous sulfuric acid in 40:60 dioxane: water solution at 25°C.<sup>31</sup> A computer program was used to do a least

squares treatment of the data to obtain the rate constants.

## 2. Solvent Deuterium Isotope Effect Measurement

A stock solution of the alcohol was prepared by diluting 5 ml of the  $5 \times 10^{-4}$  M alcohol solution with 5 ml of pure dioxane and 15 ml of  $D_2O$ . A 40:60 dioxane: $D_2O$  solution was prepared by diluting 20 ml of pure dioxane with 30 ml of  $D_2O$ . An approximately 1.5 M  $D_2SO_4$  stock solution was prepared by diluting 2 ml  $D_2SO_4$  with 25 ml of the above 40:60 dioxane: $D_2O$  solution.

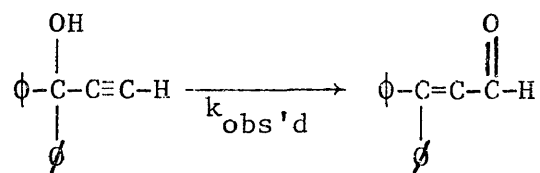
For each kinetic study, 4 ml of the  $1.25 \times 10^{-4}$  M alcohol solution was pipeted into a 25-ml volumetric flask. Appropriate volumes of the 40:60 dioxane: $D_2O$  solution and the  $D_2SO_4$  stock solution were added by pipet so as to achieve the various molarities desired. The kinetic study was then conducted as previously described.

## Results

Tables I and II present the data collected in this work. Figure 1 presents the acidity profile of the compound studied. The data from this graph is summarized in Table III.

TABLE I

1,1-DIPHENYL-2-PROPYN-1-OL REARRANGEMENT  
IN  $\text{H}_2\text{SO}_4$



Run	Weight Percent $\text{H}_2\text{SO}_4$	M	$10^{-5} k_{\text{obs'd}}, \text{sec}^{-1}{}^a$	$\text{H}_2\text{O}^b$	$-\log k_{\text{obs'd}}$	$T^\circ\text{C}$
1	10.279	1.150	0.794	0.53	5.100	24.65
2	11.429	1.304	1.114	0.43	4.955	24.65
3	13.523	1.534	2.022	0.28	4.694	24.65
4	14.447	1.647	2.826	0.22	4.548	24.65
6	15.609	1.792	4.341	0.11	4.362	24.65
5	16.006	1.856	5.010	0.07	4.300	24.65
10	8.751	0.968	1.656	0.66	4.779	35.00
7	10.202	1.129	2.368	0.55	4.625	35.00
8	11.379	1.275	3.156	0.45	4.500	35.00
9	13.523	1.542	5.425	0.28	4.265	35.00
11	14.553	1.663	6.758	0.21	4.170	35.00
12	16.039	1.854	9.729	0.07	4.012	35.00
16	4.789	0.519	1.593	1.06	4.798	44.10
17	5.321	0.576	2.047	0.99	4.688	44.10

TABLE I (continued)

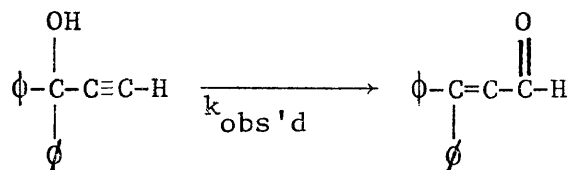
Run	Weight Percent H <sub>2</sub> SO <sub>4</sub>	M	10 <sup>-5</sup> k <sub>obs'd</sub> sec <sup>-1</sup> <sup>a</sup>	H <sub>o</sub> <sup>b</sup>	-log k <sub>obs'd</sub>	T°C
18	7.164	0.783	3.366	0.80	4.472	44.10
13	9.100	1.005	5.370	0.63	4.270	44.10
14	10.513	1.169	7.326	0.53	4.135	44.10
15	11.766	1.315	9.759	0.43	4.010	44.10
19	13.546	1.536	15.26	0.29	3.815	44.10

<sup>a</sup>In 40:60 (v/v) dioxane:water

<sup>b</sup>from Ref. 31

TABLE II

1,1-DIPHENYL-2-PROPYN-1-OL REARRANGEMENT  
IN  $D_2SO_4$  AT  $24.65^\circ$



Run	Weight Percent $D_2SO_4$	M	$10^{-5} k_{\text{obs'd}}$ sec <sup>-1</sup> <sup>a</sup>	$D_o$ <sup>b</sup>	$-\log k_{\text{obs'd}}$
A	3.656	0.408	0.316	1.18	5.50
B	12.067	0.667	0.592	0.91	5.22
D	14.135	0.788	0.772	0.80	5.05
C	14.395	0.808	0.889	0.78	5.14
E	17.174	0.966	1.176	0.65	4.92
F	20.586	1.177	1.887	0.53	4.72

<sup>a</sup>In 40:60 (v/v) dioxane:water

<sup>b</sup> $D_o = H_o$  at the same M  $L_2SO_4$ , Ref. 32

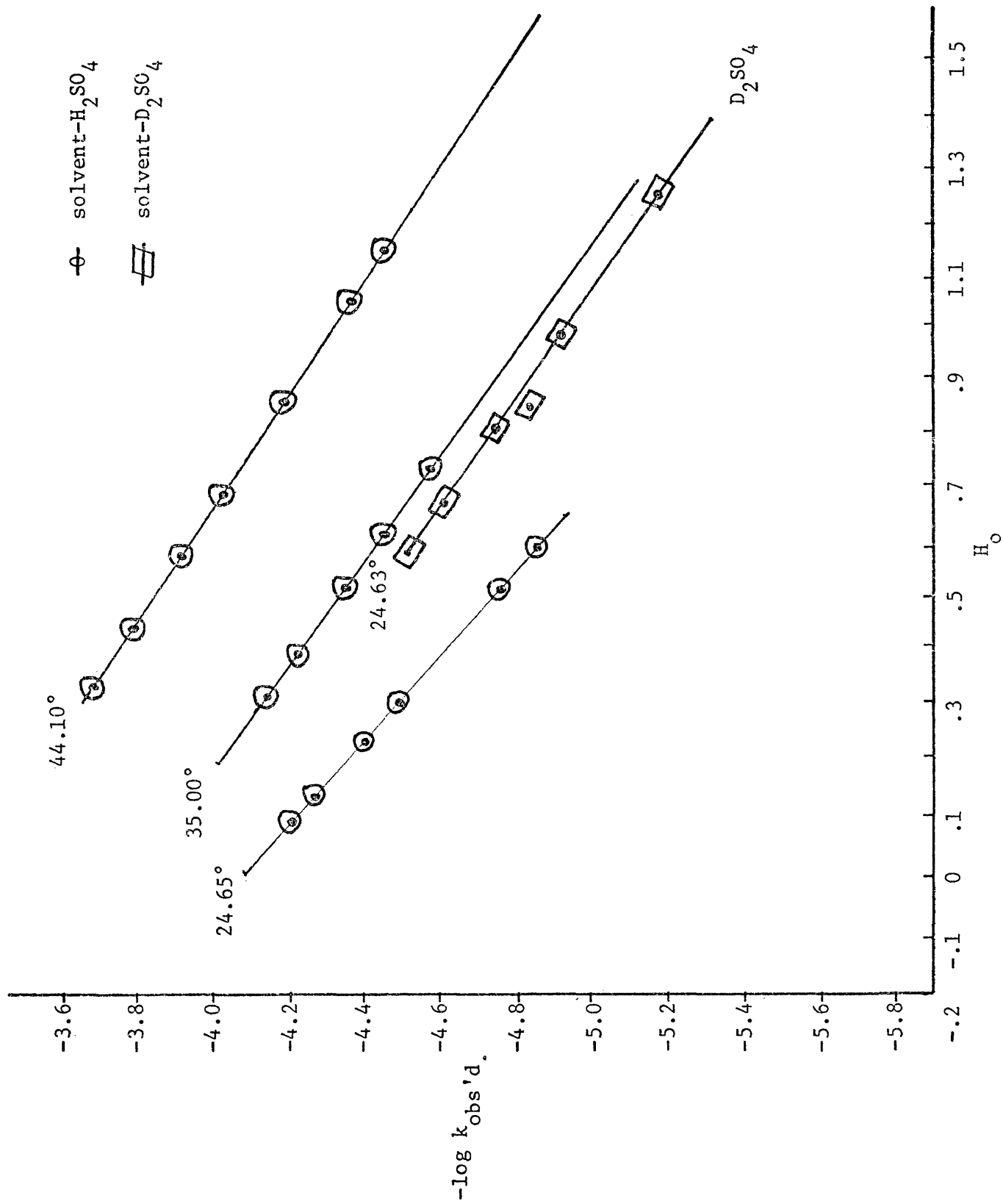
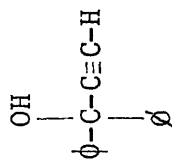


Fig. 1. Acidity Dependence of the Rearrangement Reaction of 1,1-Diphenyl-2-propyn-1-ol

TABLE III  
 LEAST SQUARES TREATMENT OF ACIDITY DEPENDENCE DATA FOR  
 1,1-DIPHENYL-2-PROPYN-1-OL



T	Acidity Range <sup>a</sup>	-d log k <sub>o</sub> /dH <sub>o</sub> <sup>b</sup>	-log k <sub>o</sub> <sup>d</sup>	-log k <sub>o.5</sub> <sup>e</sup>	r <sup>f</sup>	Solvent
24.65	10.279-16.006	1.681	4.176	5.016	0.9971	H <sub>2</sub> SO <sub>4</sub>
35.00	8.789-16.039	1.318	3.904	4.562	0.9993	H <sub>2</sub> SO <sub>4</sub>
44.10	4.789-13.546	1.251	3.467	4.093	0.9994	H <sub>2</sub> SO <sub>4</sub>
24.65	3.656-20.586	1.170 <sup>c</sup>	4.149	4.734	0.9903	D <sub>2</sub> SO <sub>4</sub>

<sup>a</sup>Weight percent sulfuric acid.

<sup>b</sup>Slope of log k<sub>obs</sub>'d versus H<sub>o</sub> plot as determined by least squares treatment.

<sup>c</sup>D<sub>o</sub> = H<sub>o</sub> at the same M L<sub>2</sub>SO<sub>4</sub>, Ref. 32.

<sup>d</sup>Extrapolated rate at H<sub>o</sub> = 0.0, i.e., intercept of log k<sub>obs</sub>'d versus H<sub>o</sub> plot.

<sup>e</sup>Extrapolated rate at H<sub>o</sub> = 0.5.

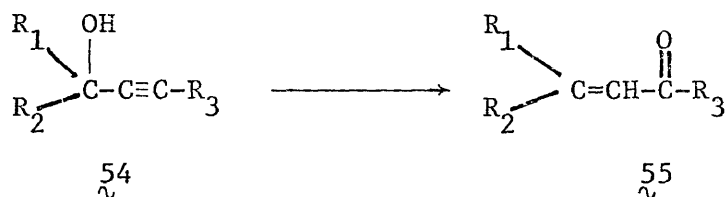
<sup>f</sup>Correlation coefficient.

CHAPTER IV

DISCUSSION

The Rate of Rearrangement of  
1,1-Diphenyl-2-propyn-1-ol

Tertiary propargyl alcohols, 54, undergo rearrangement readily in aqueous acid solutions to  $\alpha,\beta$ -unsaturated ketones, 55.<sup>2</sup> For

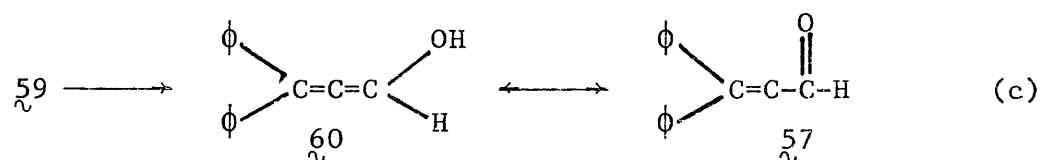
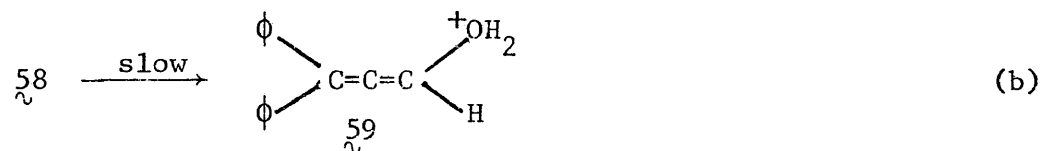
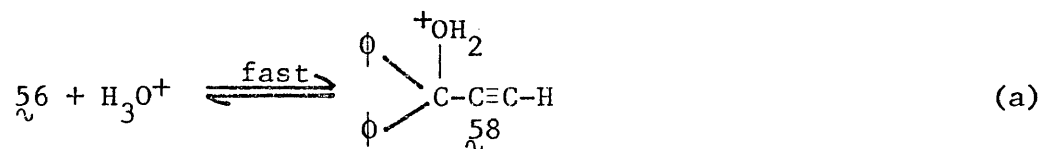


example, 1,1-diphenyl-2-propyn-1-ol, 56, rearranges to 3,3-diphenyl-2-propen-1-al, 57 (cf. Tables I and II). When  $R_1$  and  $R_2$  are groups which contain hydrogens  $\alpha$  to the alcohol group, elimination is a

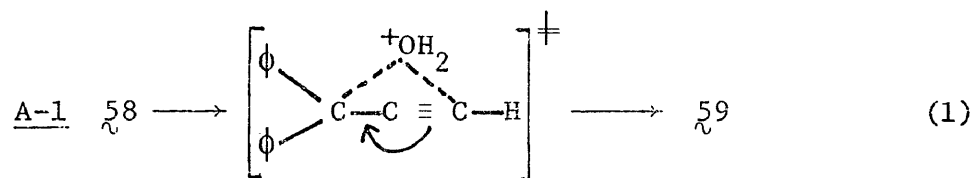


competing reaction yielding an ene-yne.

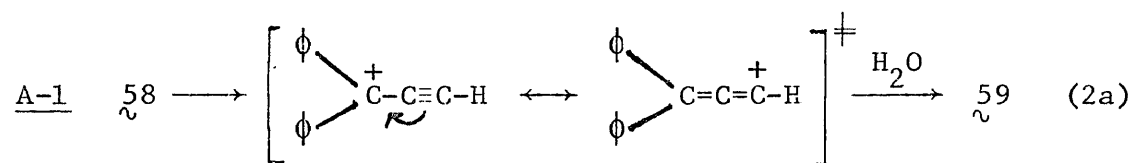
The two mechanisms which are proposed for this particular rearrangement reaction are as follows: In Scheme A, fast protonation of the alcohol at oxygen, 56, is followed by formation of the protonated allenol, 59. The allenol loses a proton and keto-enol tautomerization results in the formation of the aldehyde, 57.

Scheme A:

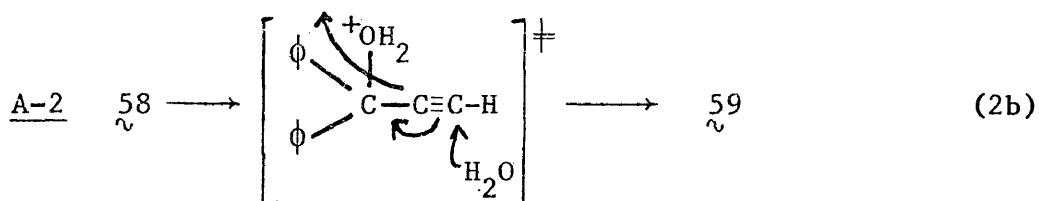
The rearrangement step, (b), may proceed by two different routes. First, it may be intramolecular.



Second, it may be intermolecular. The intermolecular reaction may take place by an  $\text{S}_{\text{N}}1$ -like reaction, (2a), or by an  $\text{S}_{\text{N}}2'$ -like reaction, (2b). The carbonium ion undoubtedly exists as a heavily solvated ion rather than as a free ion. Since water is present in excess, it could



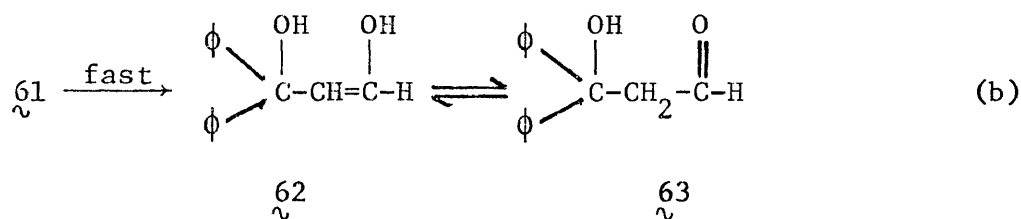
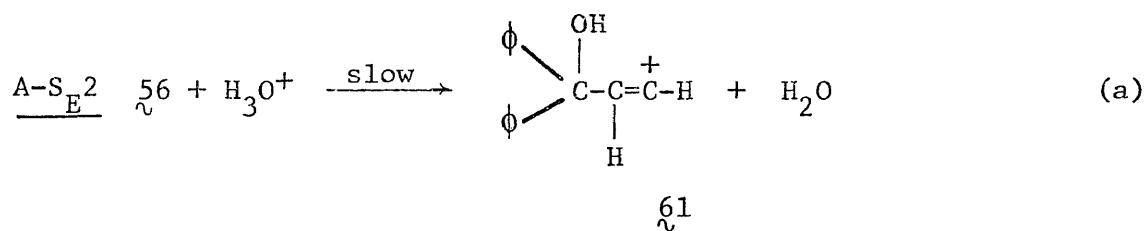
involve attack by water at the allenic position and still obey the same rate law as the above two.



This question has been considered in several reports on acid-catalyzed rearrangements of alcohols.<sup>33,34</sup> Goering and Dilgren, in the acid-catalyzed rearrangement of  $\alpha$ -phenylallyl alcohol to cinnamyl alcohol investigated this question by doing oxygen exchange experiments with  $\text{O}^{18}$ . They favor an intermolecular rearrangement involving the 1-phenylallyl cation. Stiles and Longray investigated the question in the rearrangement of  $\beta$ -alkoxyallyl alcohols. They detected no intramolecular contribution.

In Scheme B, slow protonation of the alcohol at carbon-2 results first in the hydration of the triple bond to an aldol,  $\underset{\sim}{63}$ , which is then dehydrated rapidly to the aldehyde.

Scheme B:



Since A-1 reactions undergo a slow unimolecular transformation into reaction products they would be expected to exhibit first-order kinetics. A-2 reactions, on the other hand, involve the attack of a nucleophile on the substrate. Therefore, the rate of the reaction will be a function of the concentration of both the substrate and the nucleophile and, hence, exhibit second-order kinetics. When the nucleophile is present in excess, i.e., when it is the solvent, then, the rate will be dependent only on the concentration of the substrate since any change in nucleophile concentration will be negligible. In these cases, the rate of A-2 reactions will be expected to exhibit first-order kinetics and are thus indistinguishable from A-1 reactions on kinetic data alone. A-S<sub>E</sub>2 reactions, a special type of A-2 reaction, when in moderately concentration acid, exhibits first-order kinetics. This is because the hydrogen ion concentration is high and remains constant since these ions are regenerated in the second step of the reaction.<sup>29b</sup>

The appearance of 3,3-diphenyl-2-propen-1-al follows first-order kinetics. This is consistent with both the mechanism schemes proposed above.

#### The Acidity Dependence of the Rearrangement Reaction

The rate of rearrangement of 1,1-diphenyl-2-propyn-1-ol to its corresponding aldehyde exhibits linearity with the acidity function, H<sub>0</sub>. This indicates that an acid-catalyzed reaction is taking place.

Therefore, only these types of reaction schemes need be considered. The slope of the  $-\log k$  versus  $H_0$  plots ranged from +1.17 to +1.68. A-1 reactions, being first-order reactions, are expected to show a linear correlation between  $-\log k$  and  $H_0$ . The acid-catalyzed isomerization of cis-4-methoxychalcone which is known to proceed by an A-1 mechanism and has been shown to exhibit a slope of 1.14 supports this expectation.<sup>35</sup> Likewise, A-2 reactions, in which the concentration of the water present is high (moderately concentrated acid), show this same linear correlation. Supporting evidence is the acid-catalyzed hydration of ethylene oxide which exhibits a slope of 1.06 and is known to react through an A-2 mechanism.<sup>36</sup> On the other hand, the hydration of cis-chalcone is found to exhibit a slope of 0.45 and also proceeds by an A-2 mechanism. This curvature in its  $H_0$  profile is due to the high acid concentrations that are needed in order to get a measurable reaction rate.<sup>35,37</sup> At high acid concentrations, the activity of water falls sharply, thus, the retardation of the reaction rate.<sup>29b</sup>

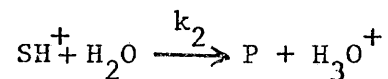
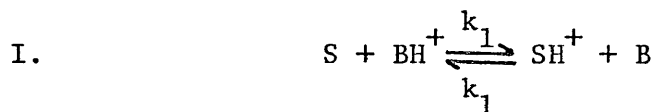
Therefore, while this does not provide a means of differentiating between Schemes A and B, it does allow one to predict from the plot of  $-\log k_0$  versus  $H_0$ , the behavior of the reaction at acidities that cannot actually be studied. If the rate of reaction could be studied in an aqueous acid buffer solution, a study of general acid catalysis could be made. If the results from such a study implied specific acid catalysis, it would give convincing

evidence for a reaction Scheme A with the rate-determining step proceeding by mechanism (2b) (cf. p. 29 ). This is because only one of the four rate expressions that can be written for the mechanisms under consideration indicates specific acid catalysis.<sup>38</sup> The other three indicate general acid catalysis (cf. Fig. 2). Unfortunately, the reaction rate of this system makes this study impossible.

#### The Effect of Temperature on the Rate of Rearrangement

The effect of temperature on the reaction rate was measured so that the activation parameters for the rearrangement of the 1,1-diphenyl-2-propyn-1-ol could be calculated. The energy of activation ( $E_a$ ), entropy of activation ( $\Delta S^\ddagger$ ), enthalpy of activation ( $\Delta H^\ddagger$ ), and free energy of activation ( $\Delta G^\ddagger$ ) are tabulated in Table IV.

Activation parameters must be used with care when trying to determine mechanism.<sup>39,36b,40</sup> While some distinctions are evident in the relative magnitudes of the entropy of activation for A-1, A-2, and A-S<sub>E</sub>2 reactions, to argue in favor of one solely because the entropy of activation is large or small is difficult. In the A-1 mechanism positive values for the entropy of activation would be expected since the reaction proceeds from a more ordered state (protonated substrate) to a less ordered state (usually H<sub>2</sub>O and R<sup>+</sup>). A-2 mechanisms would be expected to exhibit negative  $\Delta S^\ddagger$  values since in these reactions two species [ nucleophile (in this case, the solvent) and substrate ] are combining to form one specie. Contrary to these expectations, the literature shows that a number of reactions



Writing steady-state for  $[SH^+]$ ; with  $[H_2O]$  incorporated into  $k_2$ .

$$k_1[S][BH^+] - k_{-1}[SH^+][B] - k_2[SH^+] = 0$$

$$\therefore \frac{dP}{dt} = k_2[SH^+] = \frac{k_1 k_2 [S][BH^+]}{k_{-1}[B] + k_2}$$

A.  $k_{-1}[B] \gg k_2$ , i.e., second step is rate-determining.

Remember,  $BH^+ + H_2O \xrightleftharpoons{K} B + H_3O^+$  and

$$K = \frac{[B][H_3O^+]}{[BH^+]}$$

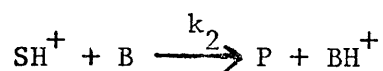
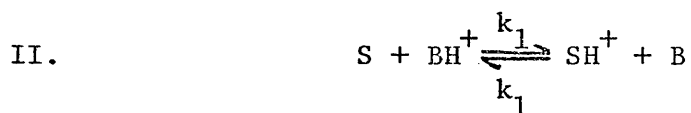
$$\therefore \frac{dP}{dt} = \frac{k_1 k_2}{k_{-1} K} [S][H_3O^+]$$

Specific Acid-catalysis (pseudo A-2)

B.  $k_2 \gg k_{-1}[B]$ , i.e., first step is rate-determining

$$\frac{dP}{dt} = k_1[S][BH^+]$$

General Acid-catalysis (A-S<sub>E</sub>2)



Writing steady-state for  $[SH^+]$ ;

$$k_1[S][BH^+] - k_{-1}[SH^+][B] - k_2[SH^+][B] = 0$$

$$\therefore \frac{dP}{dt} = k_2[SH^+][B] = \frac{k_1 k_2 [S][BH^+]}{k_{-1} + k_2}$$

A.  $k_{-1} \gg k_2$ , second step rate-determining

$$\frac{dP}{dt} = \frac{k_1 k_2}{k_{-1}} [S][BH^+]$$

General Acid-catalysis (A-1)

B.  $k_2 \gg k_{-1}$ , first step rate-determining

$$\frac{dP}{dt} = k_1 [S][BH^+]$$

General Acid-catalysis (A-S<sub>E</sub>2)

Fig. 2. Four Mechanisms Exhibiting  
Acid-Catalysis in Aqueous Solution<sup>38</sup>

TABLE IV  
ACTIVATION PARAMETERS FOR THE REARRANGEMENT  
OF 1,1-DIPHENYL-2-PROPYN-1-OL AT 25°

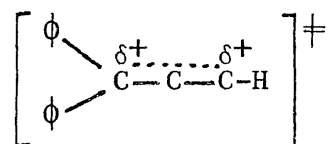
	$E_a$	$\Delta H^\ddagger$ (kcal/mole)	$\Delta S^\ddagger$ (e.u.)	$\Delta G^\ddagger$ (kcal/mole)
a	+15.6	+15.0	-27.4	+23.2
b	+20.4	+19.9	-14.9	+24.3

<sup>a</sup>At  $H_o = 0.0$

<sup>b</sup>At  $H_o = 0.5$

known to proceed by an A-1 mechanism exhibit negative  $\Delta S^\ddagger$  values. Table V contains the entropy of activation values for some known reactions and amply illustrates this phenomenon.

If one examines the reaction paths of both the A-1 and A-2 mechanisms (Scheme A (2a) and (2b) above), it can be seen that this is not unreasonable. In each mechanism the first step is fast protonation. Thus, the substrate and solvent form one specie. This increase in order would give rise to an entropy of activation with a negative value. In the second step of the A-1 mechanism, the protonated specie loses water and forms a carbonium ion. The loss



of water from the protonated specie causes an increase in disorder and, therefore, an entropy of activation greater than zero. The magnitude of the positive  $\Delta S^\ddagger$  value depends on how far apart the water molecule and the substrate travel. It is the contributions from these two steps that yield the small negative entropy of activation values exhibited for A-1 type mechanisms.

If one considers the second step in the A-2 type mechanism, it is seen that the protonated specie is reacting with the solvent (water in this case) to form a transition state complex that has at least one solvent molecule bound to it. It is in a sense "frozen"

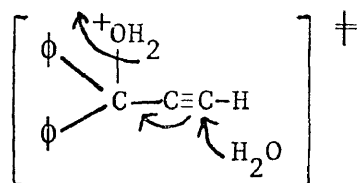


TABLE V

## ENTROPY OF ACTIVATION VALUES FOR SELECTED ACID-CATALYZED REACTIONS

Compound	Reaction	$\Delta S^\ddagger$ e.u. <sup>a</sup>	Mechanism	Solvent	Ref
t-Butyl acetate	Hydrolysis	+9.9	A-1	H <sub>2</sub> O	48
p-Methoxydiphenyl methylbenzoate	Hydrolysis	+11.9	A-1	60% aqueous dioxane	49
2,2-Dimethyl- ethylenimine	Acid Hydrolysis	-1.9	A-1	H <sub>2</sub> O	52
p-Methoxydiphenyl methyl acetate	Hydrolysis	-1.9	A-1	H <sub>2</sub> O	50
Methyl acetate	Hydrolysis	-21.3	A-2	H <sub>2</sub> O	51
Ethyl acetate	Hydrolysis	-23.0	A-2	H <sub>2</sub> O	51
Ethylene oxide	Acid-catalyzed Hydrolysis	-6.1	A-2	H <sub>2</sub> O	36b
Propylene oxide	Acid-catalyzed Hydrolysis	-4.3	?	H <sub>2</sub> O	36b
Isobutylene oxide	Acid-catalyzed Hydrolysis	-4.0	?	H <sub>2</sub> O	36b
Ethylene imine	Acid-catalyzed Hydrolysis	-9.4	A-2	H <sub>2</sub> O	52

TABLE V (continued)

Compound	Reaction	$\Delta S^\ddagger$ e.u. <sup>a</sup>	Mechanism	Solvent	Ref
<u>cis</u> -p-Methoxychalcone	Hydration-isomerization	-10.0	A-1	5% aqueous dioxane	35a
<u>cis</u> -Chalcone	Hydration-isomerization	-24.0	A-2	5% aqueous dioxane	35a
Propyl ethynyl ether	Hydration	-1.0	A-S <sub>E</sub> 2		53
Azulene	Hydration	-7.0	A-S <sub>E</sub> 2	HClO <sub>4</sub>	54
2-Methylphenyl-acetylene	Hydration	-10.4	A-S <sub>E</sub> 2	H <sub>2</sub> SO <sub>4</sub>	44
2-Ethoxy-1-cyclopentene-1-carboxylic acid	Hydration	-15.0	A-S <sub>E</sub> 2	H <sub>2</sub> O	55
Phenylacetylene	Hydration	-18.2	A-S <sub>E</sub> 2	H <sub>2</sub> SO <sub>4</sub>	44
4-ethynyl-d-anisole	Hydration	-20.1	A-S <sub>E</sub> 2	H <sub>2</sub> SO <sub>4</sub>	58
4-ethynylanisole	Hydration	-21.6	A-S <sub>E</sub> 2	H <sub>2</sub> SO <sub>4</sub>	44
Styrene	Hydration	-25.0	A-S <sub>E</sub> 2	HClO <sub>4</sub>	56

TABLE V (continued)

Compound	Reaction	$\Delta S^\ddagger$ e.u. <sup>a</sup>	Mechanism	Solvent	Ref
<u>m</u> -Methylstyrene	Hydration	-28.0	A-S <sub>E</sub> 2	HClO <sub>4</sub>	57
<u>p</u> -Chlorophenyl- acetylene	Hydration	-33.6	A-S <sub>E</sub> 2	H <sub>2</sub> SO <sub>4</sub>	44

<sup>a</sup>Calculated at 25° and unit proton activity.

in the activated complex. This increase in order would yield negative  $\Delta S^\ddagger$  values. The loss of entropy contributed by each water molecule frozen in the transition state is between 5 and 6 e.u.<sup>40</sup> Therefore, one would expect more negative  $\Delta S^\ddagger$  values for A-2 type mechanisms than those exhibited by A-1 mechanisms (cf. Table V).

The third mechanistic scheme being considered, A-S<sub>E</sub>2, has been observed to exhibit entropies of activation from zero to very negative values (cf. Table V).

The entropy of activation (at  $H_0 = 0.0$ ) calculated from the data in Table I, associated with the compound under study, is -27.4 e.u. at 25°C (cf. Table IV). From the above discussion and by comparing this value with those listed in Table V, it can be seen that it would be impossible to eliminate any of the reaction schemes being considered based on this information.

#### The Effect of Structure on the Rate of Rearrangement

Substituents affect the rate of a reaction by altering the electron density about the reaction center. For example, it has been found that reactions which proceed by a carbonium ion intermediate proceed in such a manner that an increase of electron density at the reaction center will help facilitate it. Thus, substituents that bring about such an increase will cause an increase in the reaction rate.

The extra thermodynamic free energy relationship developed

by Hammett allows one to classify reactions according to how substituents affect them.

$$\log \frac{k}{k_0} = \sigma \rho$$

This equation allows one to calculate the rate or equilibrium constant,  $k$ , associated with the reaction of any one of the substituted derivatives, from the values of  $k_0$ , for the unsubstituted compound and the two parameters  $\sigma$  and  $\rho$ .<sup>41</sup> Rho,  $\rho$ , is the reaction constant and is a measure of the sensitivity of a given reaction series to ring substituents. It is dependent upon the nature of the reaction and the conditions under which it takes place. Sigma,  $\sigma$ , is the substituent constant, and is characteristic only of the substituent. It is a measure of the total electrical effects of a substituent when it is attached to a benzene ring. A positive value for sigma,  $\sigma$ , indicates that the substituted group is electron--withdrawing with respect to hydrogen. A negative sigma,  $\sigma$ , value indicates that the group is electron--donating with respect to hydrogen. While the sigma values tend to hold true for meta and para substituents, the treatment fails for ortho substituents. This is because in ortho compounds, steric effects are present in addition to the electrical effects.

Hammett used the dissociation reaction of benzoic acid to formulate this relationship.<sup>41</sup> Collecting the equilibrium constants of a number of substituted benzoic acids and arbitrarily setting rho,  $\rho$ , for this reaction series as unity, he was able to define a set of substituent constants,  $\sigma$ . With this set of sigma values, rho values

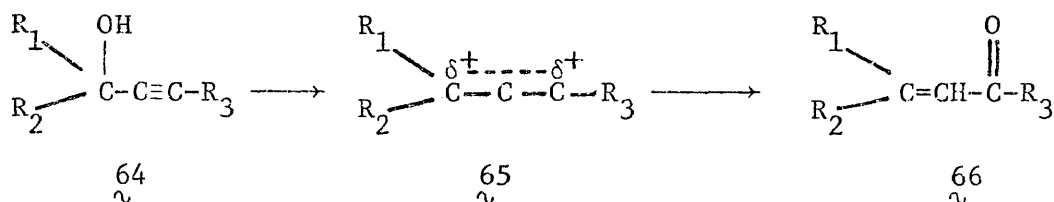
for other reactions could then be obtained as long as the rates of two substituted compounds were known. Since rho,  $\rho$ , is the slope of the plot of  $\log k_{\text{relative}}$  versus  $\sigma$ , a slope steeper than unit indicates that the reaction has a greater sensitivity to substitution than benzoic acid (a positive value for  $\rho$ --indicating that the rate of the reaction series is enhanced by electron-withdrawal). A slope of opposite sign (a negative value for  $\rho$ ) indicates that the rate of the reaction series is enhanced by electron-donation.

Although the sigma constants calculated by Hammett were used successfully in a number of different systems, it later became clear that their success was limited to those reactions in which there was little or no resonance interaction of the substituent with any charge developed at the reaction center. Thus, two new sets of sigma values were needed--one for cases in which an electron-releasing group interacts with a developing positive charge at the reaction center and one for cases in which an electron-withdrawing group interacts with a developing negative charge.<sup>41</sup>

In 1958, Brown and Okamoto<sup>42</sup> devised a scheme for defining a new substituent constant,  $\sigma^+$ . They had noticed that while the solvolysis rates of meta-substituted 2-phenyl-2-propyl chlorides in 90% aqueous acetone at 25° correlated well with Hammett calculated sigma constants, the para-substituted compounds did not. They contributed this behavior to the resonance interaction para-substituents are expected to show with the developing charge at the reaction center. Using the solvolysis of 2-phenyl-2-chloropropane, under the

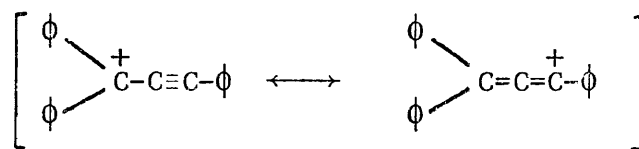
conditions previously stated, as the standard reaction and the Hammett  $\sigma_m$  constants, they derived a rho value for a meta-substituted reaction series. From this reaction constant, they were then able to obtain a new set of  $\sigma$  values for the para-substituents. These sigma-plus,  $\sigma^+$ , values are useful in any reaction system where positive charge is generated in conjugation with the para position of an aromatic ring. Some examples of reactions correlating with  $\sigma^+$  may be seen in Table VI.

Although substituent effects on 1,1-diphenyl-2-propyn-1-ol have not yet been studied, they have been determined for a similar compound. Schiavelli, et al.,<sup>43</sup> studied the rate of rearrangement of a series of triarylpropargyl alcohols, 64a-f, under conditions similar to the ones in this study. The same reaction schemes as



- a.  $R_1 = R_2 = R_3 = \phi$
- b.  $R_1 = R_2 = \phi$      $R_3 = p-CH_3\phi$
- c.  $R_1 = R_2 = \phi$      $R_3 = p-Cl\phi$
- d.  $R_1 = R_2 = \phi$      $R_3 = p-CH_3O\phi$
- e.  $R_1 = R_3 = \phi$      $R_2 = p-CH_3O\phi$
- f.  $R_1 = R_3 = \phi$      $R_2 = p-Cl\phi$

those described earlier in this paper were proposed. The results are summarized in Figures 3, 4, and 5. A plot of  $\log k$  ( $H_0 = 0.0$ ) versus  $\sigma^+$  yields  $\rho = -1.8$  for substituents in a 1-phenyl ring and  $\rho = -1.7$  for substituents in a 3-phenyl ring. The negative  $\rho$  value supports reaction Scheme A where a charge delocalized cation is involved. It tells one that electron-donating substituents increase the rate



through resonance. Scheme B would not be expected to exhibit the substituent effects observed unless a step after protonation at carbon was the slow step. This appears to be highly unlikely when compared with the hydration of p-chlorophenylacetylene and p-methylphenylacetylene which are known to be hydrated by just such a mechanism. The rate of hydration of substituted phenylacetylenes correlated with  $\sigma^+$  constants gives a  $\rho$  value of  $-3.84^{44}$  (cf. Fig. 5). The two substituted phenylacetylenes mentioned above are hydrated to the corresponding ketone 575 and 180 times slower than the corresponding  $\phi_4\text{c}$  and  $\phi_4\text{b}$  undergo rearrangement under the same conditions.<sup>44</sup> From the  $\rho$  value for the triarylpropargyl alcohols and from the data in Table VI, it can be predicted that the  $\rho$  value for a series of substituted diphenylpropargyl alcohols would be at least as negative. If you compare similar systems (cf. Table VI), it can be seen that an increase in charge stabilizing groups (such as in the case of going from benzhydrol to the triphenylcarbinyl system) causes a decrease

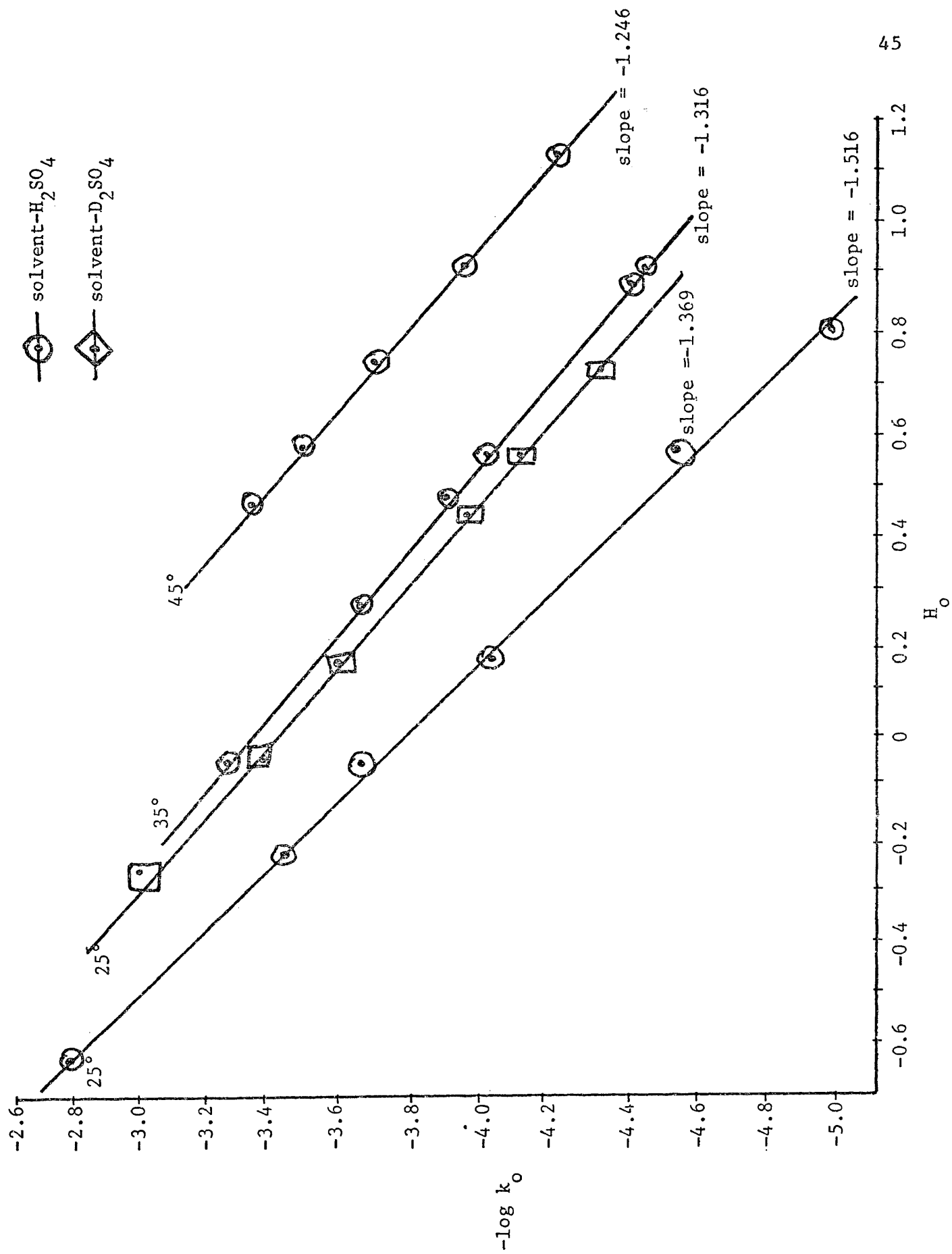


Fig. 3. Acidity Dependence of the Rearrangement Reaction of Triarylpropargyl Alcohol

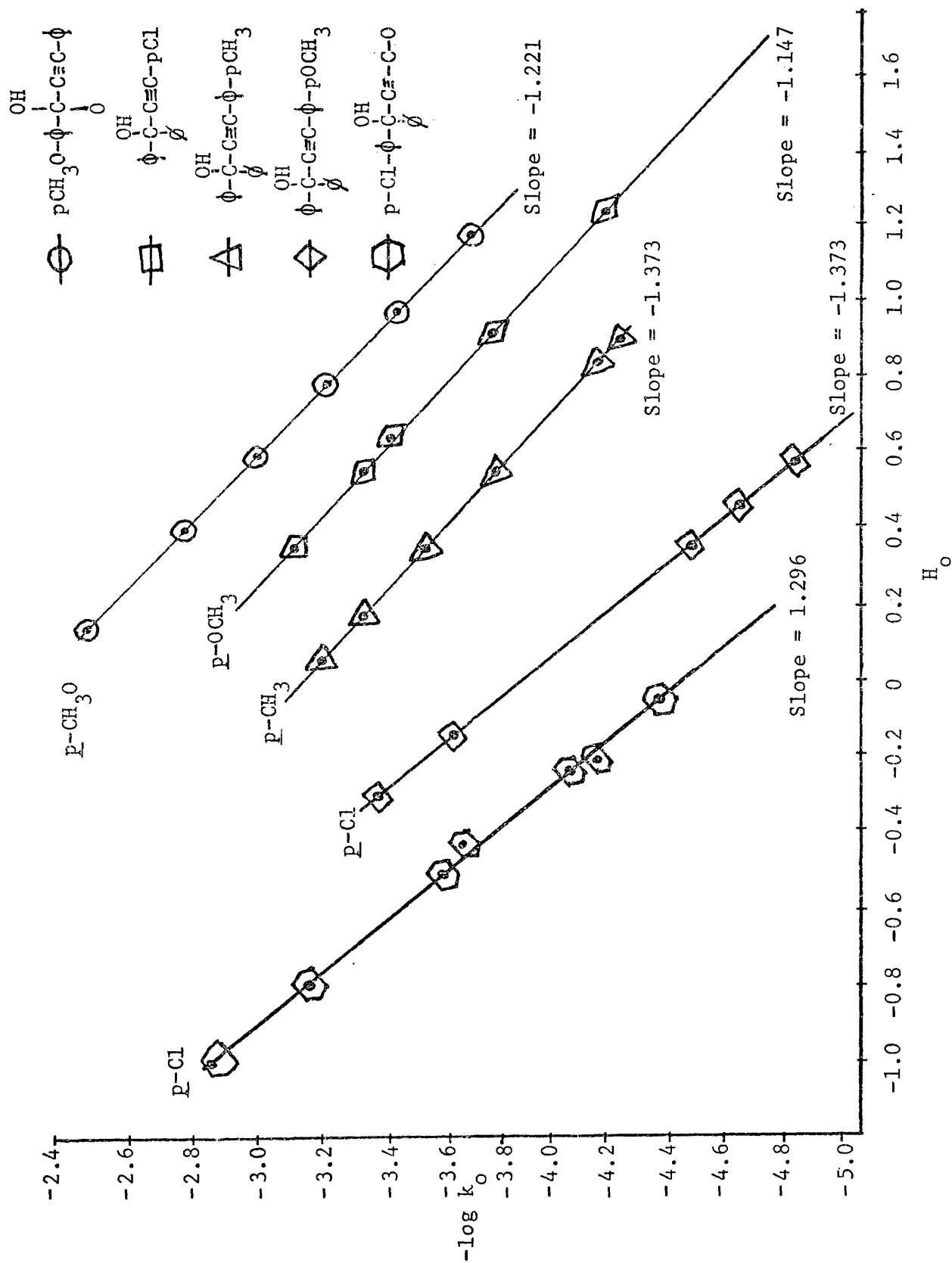


Fig. 4. Acidity Dependence of the Rearrangement Reaction of Substituted Triarylpropargyl Alcohols at 25°

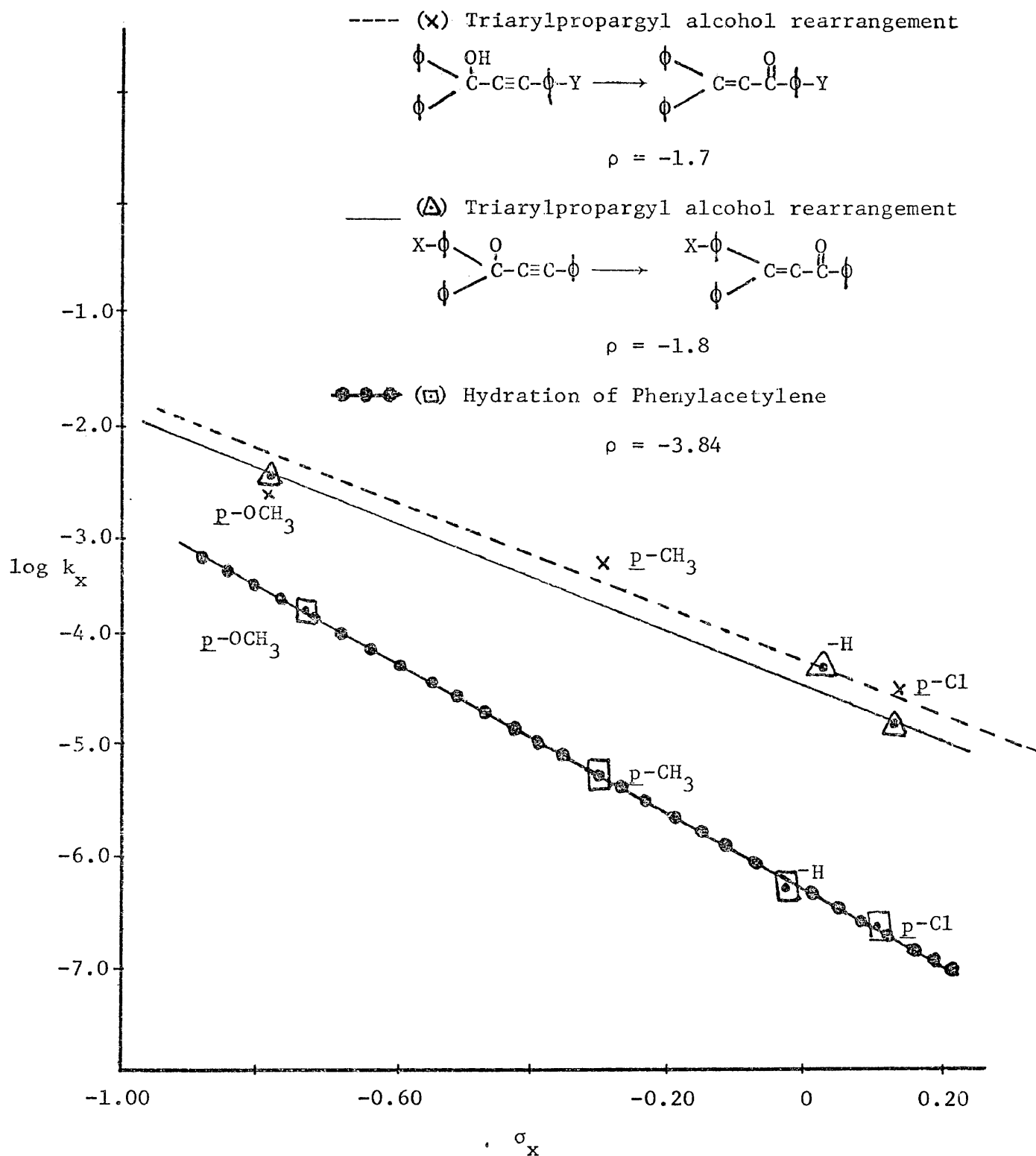


Fig. 5. Substituent Effects in the Rearrangement of Triarylpropargyl Alcohols and in Phenylacetylene Hydration at 25° at  $H_0 = 0.0$

TABLE VI

SUMMARY OF DATA FOR SELECTED REACTIONS CORRELATED WITH  $\sigma^+$ 

Substrates	Rho, $\rho$	Solvent	Reaction	T	Ref
t-Cumylchlorides	-4.54	90% aqueous acetone	solvolysis	25°	42a
	-4.67	EtOH	solvolysis	25°	59
Benzhydrol	-6.67	aqueous H <sub>2</sub> SO <sub>4</sub>	ionization-equilibrium	25°	60
p-Alkylbenzhydrol Chloride	-4.63	EtOH	solvolysis	25°	61
p-Halobenzhydrol Chloride	-4.11	70% aqueous acetone	solvolysis	25°	61
Benzdydryl Chloride	-4.06	2-propanol	solvolysis	25°	62,63
	-4.05	EtOH	solvolysis	25°	64
Triphenylcarbinols	-3.64	aqueous H <sub>2</sub> SO <sub>4</sub>	ionization-equilibrium	25°	60
Triphenylcarbinyl- chlorides	-2.34	40% EtOH 60% Et <sub>2</sub> O	solvolysis	25°	65
	-2.57	40% EtOH 60% Et <sub>2</sub> O	solvolysis	60°	66

TABLE VI (continued)

Substrates	Rho, $\rho$	Solvent	Reaction	T	Ref
X-C <sub>6</sub> H <sub>4</sub> CH(OH)CH=CHCH <sub>3</sub>	-2.97	60% aqueous dioxane	acid-catalyzed rearrangement	30°	66
$\alpha$ -Phenylethylchloro-carbonate	-2.87	toluene	thermal rearrangement	80°	61
t-Cumylhydroperoxide	-4.57	50% aqueous EtOH	acid-catalyzed decomposition	50°	66
Styrenes	-3.42	aqueous HClO <sub>4</sub>	acid-catalyzed hydration	25°	67
<u>cis</u> -Cinnamic acid	-4.30	aqueous H <sub>2</sub> SO <sub>4</sub>	<u>cis-trans</u> -isomerization	25°	68
<u>cis</u> -Stilbenes	-3.10	5% EtOH	<u>cis-trans</u> -isomerization	25°	69a,b
Phenylbenzoyl-acetylenes	-4.30	5% aqueous dioxane	hydration	25°	69c
Phenylpropionic acid	-4.80	aqueous H <sub>2</sub> SO <sub>4</sub>	hydration	25°	69d,70
$\alpha$ -Bromostyrenes	-5.40	80% aqueous EtOH	solvolysis	120°	71
Phenylacetylenes	-3.84	5% aqueous EtOH	hydration	25°	44
	-4.30	2:1 v/v Acetic acid H <sub>2</sub> O	hydration	25°	72

TABLE VI (continued)

Substrates	Rho, $\rho$	Solvent	Reaction	T	Ref
Triarylchlorides	-2.0	80:20 v/v acetone/ H <sub>2</sub> O	solvolysis	25°	73,27a
Triarylpropargyl alcohols	-1.8	40:60 v/v dioxane/ water	acid-catalyzed rearrangement	25°	43

in the absolute value of  $\rho$ . This affects the positive charge delocalization in the intermediate. Therefore, the triarylpropargyl system with three stabilizing groups will have a smaller  $\rho$  value than a similar system, like the one studied here with just two stabilizing groups.

The Solvent Isotope Effect  
on the Rate of Rearrangement

Solvent deuterium isotope effects are an important tool for the determination of the mechanism of reactions, particularly those catalyzed by acids and bases. They are the experimentally observed effects caused by a change of solvent from water to deuterium oxide. This change in solvent from one containing a light isotope to one having a heavy isotope alters the physical properties of the solvent and solvent properties can influence the rate of reaction in solution.

There have been two different concepts used to evaluate these isotope effects associated with reaction rates and equilibria in isotopic solutions. Bunton and Shiner have developed a method for the calculation of such effects based solely on solute-solvent interactions.<sup>45</sup> They have suggested that the deuterium oxide solvent isotope effect on aqueous acid dissociation constants arises principally from changes in zero-point energy associated primarily with changes in both the number of hydrogen bonds between the solute and solvent and the hydrogen bond strength. They formulated a set of rules for determining the number of hydrogen bonds affected by the reaction.<sup>45a</sup> By combining these rules with the accepted assignments



of certain O-H vibrational frequencies in aqueous solution, they were able to construct simple models for the initial and transition states and, thus, estimate the solvent isotope effect on a system.

Their accuracy depends a great deal upon the model that they chose for the transition state. They constructed extreme transition-state models for each reaction mechanism under consideration. In a unimolecular dissociation or a bimolecular association, they considered two possible models--one in which all the partial bonds at the reaction center were considered fully "covalent" and a second in which these bonds were purely "electrostatic" in character. While neither of these models is likely to resemble the real transition state exactly, the values obtained should bracket the correct value for any given mechanism. For a bimolecular displacement, four models would be considered. Therefore, by constructing transition-state models for the various mechanisms, they could delineate between those being considered by just comparing the calculated and observed values.<sup>45b</sup>

For example, their treatment predicts a maximum solvent isotope effect for a slow proton transfer reaction to be

$k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} \approx 3.6$ .<sup>45c</sup> This number is based on a symmetrical transition-state model where the secondary solvent isotope effect was calculated from the difference in the various O-H stretching frequencies between  $\nu$  initial- $\nu$  transition. By using a value of  $\approx 6$  for the maximum isotope effect due to primary hydrogen transfer and the calculated value of 0.61 for the secondary solvent isotope effect, then the

maximum net effect will be  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = \sim 6 \times 0.61 \approx 3.6$ .<sup>45</sup> Reactions which do not involve a proton transfer in their rate-determining step will involve only secondary solvent isotope effects. Their  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$  will be small. Table VII contains several well-documented examples for the mechanisms under consideration. It is noted that  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$  for A-S<sub>E</sub>2 reactions are generally above 1.50 and that they are below unity for A-1 and A-2 reactions.

Swain and Bader<sup>46</sup> and Swain and Thornton<sup>47</sup> have viewed the origin of solvent isotope effects as a perturbation of the solvent by the solute. They uphold that D<sub>2</sub>O is more structured than H<sub>2</sub>O, due to the three additional librations it possesses. This means that it also has a greater zero point energy than H<sub>2</sub>O and possesses less optical rotation. When a solute disrupts the structure of the D<sub>2</sub>O and, thus, decreases some of these libration frequencies, it is decreasing the zero-point energies and increasing the isotope effect. The lack of solubility data prevents this treatment from being performed on the compound under investigation in this work.

The solvent deuterium isotope effect on the rearrangement of 1,1-diphenyl-2-propyn-1-ol was measured at 25°C to be +0.52. This relatively small isotope effect compares favorably with those observed for reactions in which the rate-determining step is either elimination of water or nucleophilic attack of water upon the protonated species-- A-1 and A-2 type mechanisms. It is not in agreement with the solvent

TABLE VII  
 SOLVENT DEUTERIUM ISOTOPE EFFECTS FOR  
 SELECTED ACID-CATALYZED REACTIONS

Compound	Reaction	Solvent	T	$k_{H_2O}/k_{D_2O}$	Ref
I. Rate-limiting addition of water to $SH^+$ (A-2)					
<u>cis</u> -Chalcone	isomerization	5% dioxane 3M $H_2SO_4$	25°	0.52	74
Methylacetate	hydrolysis	1.4M $H_2SO_4$	25°	0.60	75
Acetamide	hydrolysis	0.1M HCl	25°	0.67	76
Ethyl formate	hydrolysis	0.2M HCl	25°	0.73	77
Ethyl acetate	hydrolysis	-	-	0.63	79
II. Rate-limiting decomposition of $SH^+$ (A-1)					
Epoxide	hydrolysis	40% aqueous dioxane	-	0.5	78
Acetal	hydrolysis			0.37	79
Sucrose	inversion			0.49	79
Ethylorthoformate	hydrolysis			0.43	79
4-methoxy diphenyl- methyl acetate	hydrolysis	aqueous dioxane		0.53	50
Pinacol	rearrangement	1.86N $H_2SO_4$		0.45	45b, 82
t-Butyl acetate	hydrolysis	-	-	0.50	45b, 83
III. Rate-limiting triple bond protonation (A-S <sub>E</sub> 2)					
Phenylacetylene	hydration	0.5-57% $H_2SO_4$	25°	2.0-3.5 <sup>a</sup>	44

TABLE VII (continued)

Compound	Reaction	Solvent	T	$k_{H_2O}/k_{D_2O}$	Ref
Ethylthioethyne	hydration	aq. buffers	25°	2.13	80
<u>cis</u> -1-Propenyl-1-propynyl ether	hydration	.005M HClO <sub>4</sub>	25°	1.76	81
Phenylpropionic acid	hydration	32-76% H <sub>2</sub> SO <sub>4</sub>	25°	3.4-4.6 <sup>a</sup>	69d
Phenylbenzoyl-acetylenes	hydration	60-81% aq. H <sub>2</sub> SO <sub>4</sub>	25°	2.0-2.2 <sup>a</sup>	69c

<sup>a</sup>Observed effect within acidity range studied.

isotope effects observed for rate-limiting proton transfer--A-S<sub>E</sub>2 type mechanism. Therefore, this eliminates Scheme B from further consideration.

Bunton and Shiner's<sup>45</sup> theoretical treatment for secondary solvent isotope effects was performed for the possible rate-determining steps found in Scheme A. Figure 6 contains the extreme models for both the A-1 and A-2 transition states. Note that the models for A-1 would be the same for both the intramolecular rearrangement of the protonated species and the intermolecular rearrangement, (2a). The pka for the alcohol is assumed to be the same as the pka for water, 16.<sup>45b</sup> Therefore, from the equations used for estimating the stretching frequencies of the hydrogens of water donated to oxygen bases in aqueous solution and for the frequencies for the hydrogen bonds donated by acids, 3400 cm<sup>-1</sup> is calculated for the donor and acceptor frequencies for the hydroxyl group of the alcohol.<sup>45a,b</sup> The relation between the kinetic isotope effect  $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}}$  and the relevant hydrogen stretching frequencies is

$$k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = \text{antilog} \frac{\Sigma_{\nu_{\text{H}}} - \Sigma_{\nu'_{\text{H}}}}{12.53T}$$

where  $\Sigma_{\nu_{\text{H}}}$  and  $\Sigma_{\nu'_{\text{H}}}$  are the sum of hydrogen stretching frequencies (cm<sup>-1</sup>) in the initial and transition states, respectively, and T is the absolute temperature.<sup>45a</sup>

Performing the indicated calculations, one gets a value of 0.44 for the "electrostatic" A-1 model, "a"; 0.73 for the "covalent" A-1 model, "b"; 0.39 for the "electrostatic" A-2 model, "c"; and 1.06

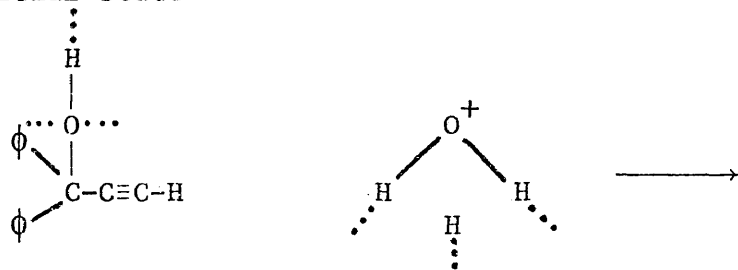
$$\begin{aligned} \text{pKa} &= 16 \\ \nu(\text{cm}^{-1}) &= 2937 + 28.8 \text{ pKa} \\ &= 3400 \text{ cm}^{-1} \end{aligned}$$

... Dangling dotted lines refer to hydrogen bonds to or from solvent water molecules

..... Electrostatic interaction

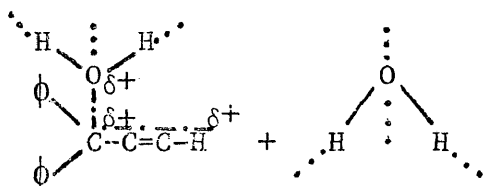
----- Covalent interaction

Initial state



$$\Sigma_{\nu_{\text{H}}} = 3(3400) + 3(2900) = 18,900 \text{ cm}^{-1}$$

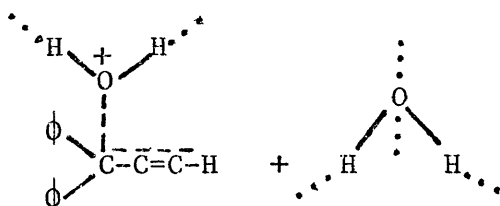
Model "a" A-1 "electrostatic"



$$\Sigma_{\nu_{\text{H}}} = 3(3400) + 4(3400) - 3600 = 20,200 \text{ cm}^{-1}$$

$$K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}} = \text{antilog} \frac{(18,900 - 20,200) \text{ cm}^{-1}}{(12.53)(298^\circ\text{k})} = \boxed{0.448}$$

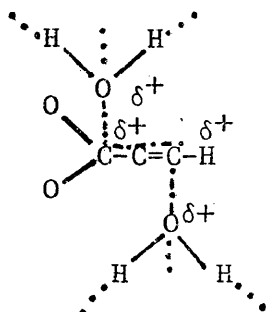
Model "b" A-1 "covalent"



$$\Sigma_{\nu_{\text{H}}} = 2(2900) + 4(3400) = 19,400 \text{ cm}^{-1}$$

$$K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}} = \text{antilog} \frac{(18,900 - 19,400) \text{ cm}^{-1}}{(12.53)(298^\circ\text{k})} = \boxed{0.734}$$

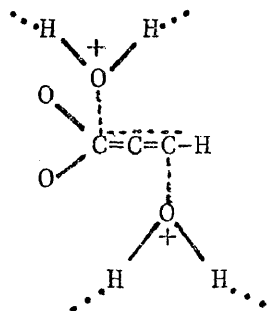
Model "c"      A-2 "electrostatic"



$$\Sigma_{\nu, H} = 3(3400) + 3(3400) = 20,400 \text{ cm}^{-1}$$

$$K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}} = \text{antilog} \frac{(18,900 - 20,400) \text{ cm}^{-1}}{(12.53)(298^\circ\text{k})} = \boxed{0.396}$$

Model "d"      A-2 "covalent"



$$\Sigma_{\nu, H} = 2(2900) + 2(2900) + 2(3600) = 18,800$$

$$K_{\text{H}_2\text{O}}/K_{\text{D}_2\text{O}} = \text{antilog} \frac{18,900 - 18,800}{(12.53)(298^\circ\text{k})} = \boxed{1.063}$$

Fig. 6. Bunton and Shiner Theoretical Treatment  
of Secondary Solvent Isotope Effects  
on 1,1-Diphenyl-2-propyn-1-ol

for the "covalent" A-2 model, "d". The values calculated for models "a" and "c" give good agreement with experimental value.

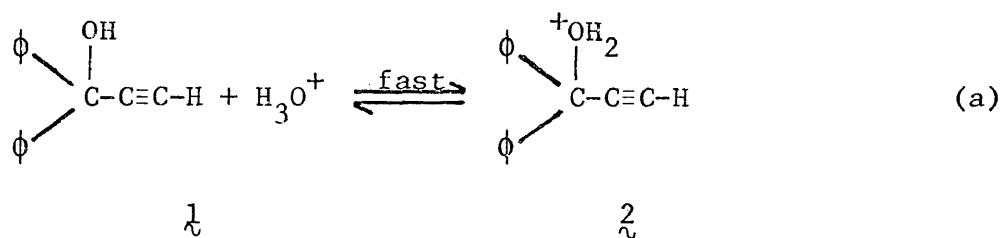
While nothing can be said in favor of one over the other, this treatment does indicate that the transition state is electrostatic in character, not covalent.

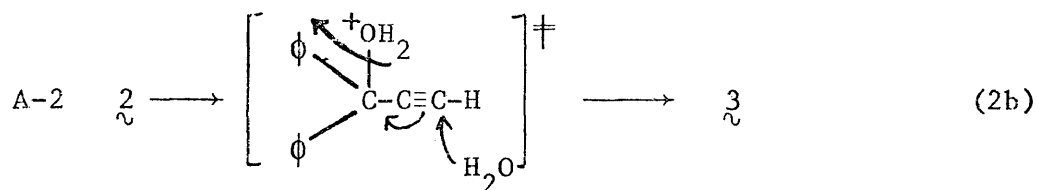
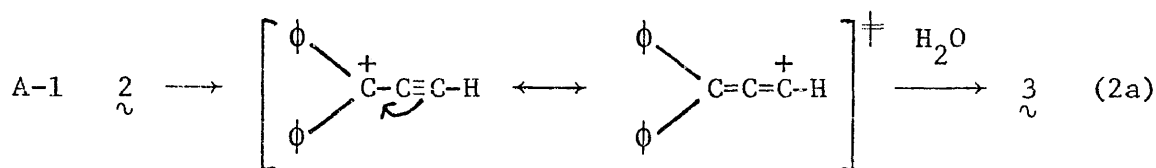
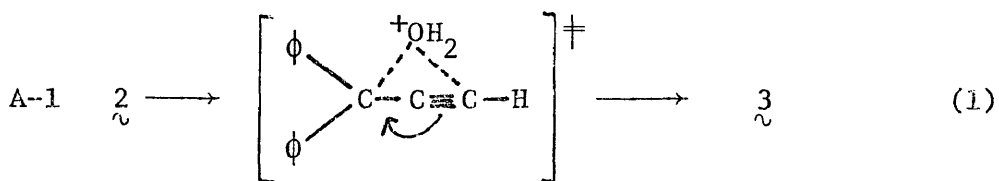
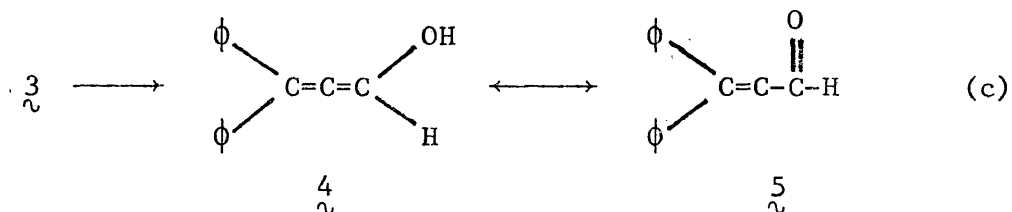
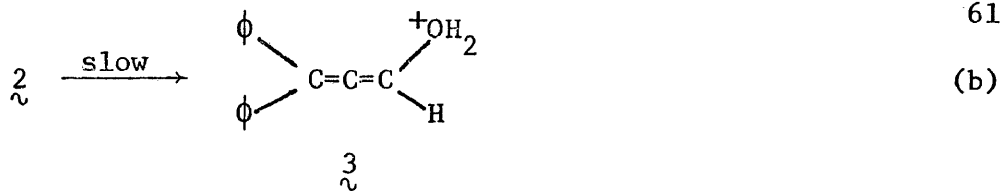
CHAPTER V

CONCLUSIONS AND PROPOSALS FOR FURTHER STUDY

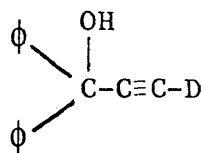
This investigation began with the knowledge that tertiary  $\alpha$ -acetylenic alcohols (which do not contain  $\alpha$ -hydrogens), when placed in moderately concentrated acid, undergo the Meyer-Schuster rearrangement reaction to  $\alpha,\beta$ -unsaturated carbonyl products. The rate of rearrangement of 1,1-diphenyl-2-propyn-1-ol in sulfuric acid to 3,3-diphenyl-2-propen-1-al was found to exhibit both first-order kinetics and linearity with the acidity function,  $H_0$  (slope = 1.17 - 1.68). These results, along with the temperature effects ( $\Delta S^\ddagger = -27$  e.u.), predicted substituent effects ( $\rho > -1.8$ ) and the secondary solvent isotope effects ( $k_H/k_D = 0.52$ ) support a mechanism like the one depicted in Scheme A--fast equilibrium formation of the protonated alcohol followed by a slow first-order rearrangement to the allenol. Within this scheme, the rearrangement may be intramolecular (as implied by 1) or intermolecular (as implied by 2a,2b).

Scheme A: ' .





A study of secondary isotope effects on this system would determine whether the rearrangement step occurs by route 2a or by either route 1 or 2b. If the rearrangement occurs according to 2a, no isotope effect would be expected. If it occurs by either 1 or 2b, an isotope effect would be expected. Nass<sup>84</sup> has prepared the deuterated alcohol and performed the necessary kinetic studies on its rearrangement.



He observed a secondary isotope effect of 0.89 at  $H_0 = 0.1$  and  $25^\circ\text{C}$ . This eliminates route 2a. He repeated the isotopic study in the more polar solvent, ethanol. The more polar solvent results in a transition state complex where the solvent molecules are not bound as tightly to the substrate. Therefore, if a heavily solvated transition state is present, like 2b, isotope effect closer to unity would be expected. This is what he found. The  $k_H/k_D$  ranged from 0.98 to 1.01 over the range of acidities he studied. These results, along with the results of the theoretical treatment of the solvent isotope effect (agreement between observed  $k_H/k_D$  and the calculated  $k_H/k_D$  for model "c"), are good supportive evidence for a mechanism like the one depicted by Scheme A with the rearrangement step proceeding by route 2b.

The definitive experiment for distinguishing between the rearrangement route 1 and 2b would be to perform the reaction in  $O^{18}$  labeled water. If the rearrangement was to proceed according to route 2b, a product containing a labeled carbonyl oxygen would be expected. If it proceeded according to route 1, an unlabeled product would be expected. The fast rate of exchange of carbonyl compounds would make this experiment difficult and tenuous, at best.

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