1981

The acid-catalyzed hydration of phenylallene

Gary Wayne Long
College of William & Mary - Arts & Sciences

THE ACID-CATALYZED HYDRATION OF PHENYLALLENE

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

Gary Wayne Long

1981

APPROVAL SHEET

This thesis is submitted in partial fulfillment of

the requirements for the degree of

Master of Arts

Gary Wayne Long

Approved, May 1981

Melvyn D. Schiavelli

Trevor B. Hill

David W. Thompson

To my family

TABLE OF CONTENTS

Page

ACKNOWLEDGMENTS vi

DEDICATION iii

LIST OF TABLES vii

LIST OF FIGURES viii

ABSTRACT ix

INTRODUCTION 2

EXPERIMENTAL 18

A. INSTRUMENTATION 18

B. MATERIALS 18

C. METHODS 23

D. PRODUCT STUDY 24

RESULTS AND DISCUSSION 25

A. PRODUCT STUDIES 25

B. ACIDITY DEPENDENCE 25

C. HAMMETT DATA 33

D. SOLVENT ISOTOPE EFFECTS 35

E. BUNNETT AND OLSEN PARAMETER 38

F. ACTIVATION PARAMETERS 39

G. ISOTOPIC SUBSTITUTION 43

H. REARRANGEMENT OF PRODUCT 44

I. RELATIVE RATES 47

CONCLUSIONS 51

APPENDIX A. 52

APPENDIX B. 58

REFERENCES. 59

ACKNOWLEDGMENTS

The author wishes to express his appreciation to Professor Melvyn D. Schiavelli for his patient guidance and criticism during the course of this research. The author also wishes to thank Professor Trevor B. Hill and Professor David W. Thompson for their careful reading and criticism of the manuscript.

LIST OF TABLES

Table		Page
1.	Calculated Energies for Some $C_3H_5^+$ Cations.	4
2.	Rate Data for Phenylallenes at 25 and 45 Degrees. . . . . Centigrade.	30
3.	Acidity Dependence Data for Phenylallene Hydration. . . . . and Related Acid-Catalyzed Reactions at 25°.	33
4.	Hammett Values for Phenylallene and Related Hydration Reactions at 25°.	34
5.	Rate Data for Phenylallene and Alkyl Substituted Phenylallene in D_2SO_4/ D_2O AT 25°	36
6.	Solvent Isotope Effect Values for Phenylallene Hydration and Related Reactions at 25°.	37
7.	Bunnett and Olsen ϕ Values for Several Reactions at 25°	38
8.	Activation Parameters for Phenylallene Hydration and Related Reactions at 25°.	42
9.	Relative Rates of Hydration of Phenylacetylene, Styrene, and Phenylallene at 25°.	47
10.	Relative Rates of Hydration and Hydrochlorination of Alkyl-Substituted Phenylallenes	48

LIST OF FIGURES

Figure		Page
1.	Possible Cationic Intermediates in Allene Protonation	3
2.	Addition of Halogen and Interhalogen Compounds to Allene	
3.	Possible Cationic Intermediates in Phenylallene Protonation	13
4.	^{1}H NMR of Phenylallene Hydration Product	26
5.	^{1}H NMR of Cinnamyl Chloride Hydration Product	27
6.	^{1}H NMR of α-Methylphenylallene Hydration Product	28
7.	^{1}H NMR of γ-Methylphenylallene Hydration Product	29
8.	Substituent Effects and Temperature Dependence of Hydration of Phenylallenes	40
9.	Temperature Dependence of Alkyl Substituted Phenylallenes	41
10.	Reaction Scheme	46
11.	Enthalpy Differences	49

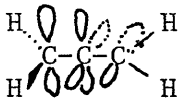
ABSTRACT

The acid-catalyzed hydration of phenylallene proceeds by a slow proton transfer mechanism with $k_{H_3O^+}/ k_{D_3O^+} = 1.80$. Observation of a large negative ρ, a negative entropy, and a linear plot of the logarithm of the rate versus H_o support this finding. Protonation leads to a perpendicular allylic cation which must rotate 90^o to form an allylic cation. The perpendicular allylic cation is partially rotated in the slow step as shown by rate enhancement from α-methyl substitution. No secondary isotope effects were observed from γ,γ-substitution.

THE ACID-CATALYZED HYDRATION OF PHENYLALLENE

INTRODUCTION

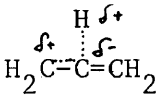
Earlier studies on electrophilic additions to allenes have considered the direction of addition, regiospecificity, and the nature of intermediates.[1] The chemistry of the cumulated double bond in allenes provides an interesting test of chemical theory. Unlike the conjugated dienes, allenes contain orthogonal π-bonds. Also unlike the conjugated dienes, they contain both sp and sp^2 hybridized carbon.



Allene

Like other olefins, allenes are a good source of electrons for electrophilic attack.

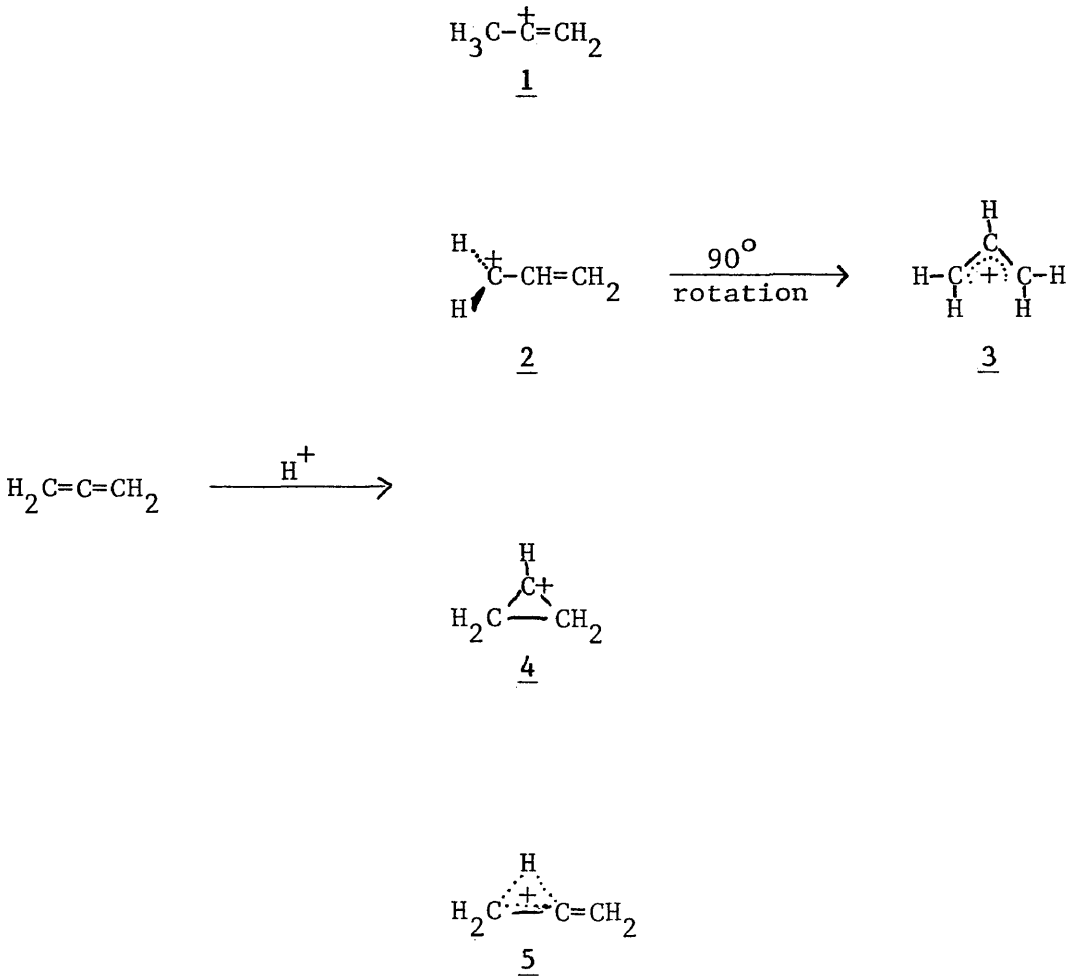
The addition of electrophile to allene can take place either at the terminal carbon to give a vinyl cation 1, or at the central carbon to give a perpendicular allylic cation 2. Other possible intermediates include the cyclopropyl cation 4 and the bridged protonated allene 5. Formation of perpendicular cation 2 can lead to allyl cation 3 by a 90^{o} rotation. A barrier to this rotation arises from the partial double bond character of the C_1-C_2 bond as the proton attacks. This partial double bond character in proton attack is shown below and possible



(Partial double bond character in proton attack on allenyl central carbon)

FIGURE 1

POSSIBLE CATIONIC INTERMEDIATES IN ALLENE PROTONATION



cationic intermediates in allene protonation are shown in figure 1 (page 3).

Molecular orbital calculations for these intermediates at the STO-3G level were carried out by Pople et al[2] and appear in table 1.

TABLE 1

CALCULATED ENERGIES FOR SOME $C_3H_5^+$ CATIONS

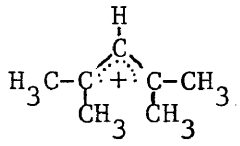
Cation		Relative Energy (kcal/mole)
2-propenyl	1	11
Perpendicular allyl	2	34
Allyl	3	0
Cyclopropyl	4	28
Bridged protonated allene	5	42

The allyl cation is the most favorable energetically. As mentioned earlier, allyl cation 3 results from rotation of perpendicular cation 2. The energy barrier of this rotation has been calculated at 42 kcal. $mole^{-1}$. Rearrangement of vinyl cation 1 to the allyl cation 3 is another possibility. This rearrangement could proceed via the bridged protonated intermediate 5 (a hydride shift), but this process has a calculated energy barrier of at least 20 kcal. $mole^{-1}$. Cyclopropyl cation 4 is not favorable energetically.

The most likely intermediate in allene protonation from an energetic standpoint is vinyl cation 1. Experimental evidence for this intermediate was presented by Aue, Davidson, and Bowers.[3] Allene was

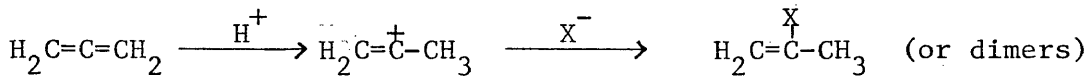
protonated by H_3S^+ in the gas phase. The cation formed from this protonation could protonate methanol directly. The cation formed from fragmentation of allyl chloride did not.

The introduction of methyl groups on allene changes the intermediate. Allenes with alkyl substituents such as 1,3-dimethylallene and tetramethylallene yield allyl cations in magic acid (SbF_5-FSO_3H) solutions at -70°C. The methyl groups apparently stabilize the perpendicular intermediate enough to allow rotation to the allylic cation.[4]



Tetramethylallene in magic acid at -70°C.

Addition of hydrogen halides and other HX to allene follows Markovnikov's rule with formation of a vinyl cationic intermediate for HF, HI, phenol, and H_2O. Addition of HBr and HCl to allene also forms the Markovnikov product with some codimerization taking place.

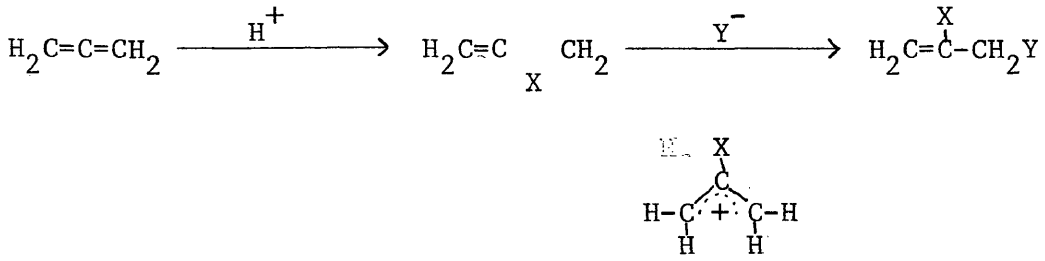


Addition of HX to allene

All of these addition reactions proceed via protonation of the terminal carbon with no evidence of a bridged proton intermediate.

Addition of halogen and interhalogen compounds to allene is analogous to the cyclic bromonium ion formed in the addition of

bromine to olefins. Cyclic bromonium ions from addition to allene have been observed in magic acid at -70°C.[5] First, there is formation of a



Addition of X_2 to allene

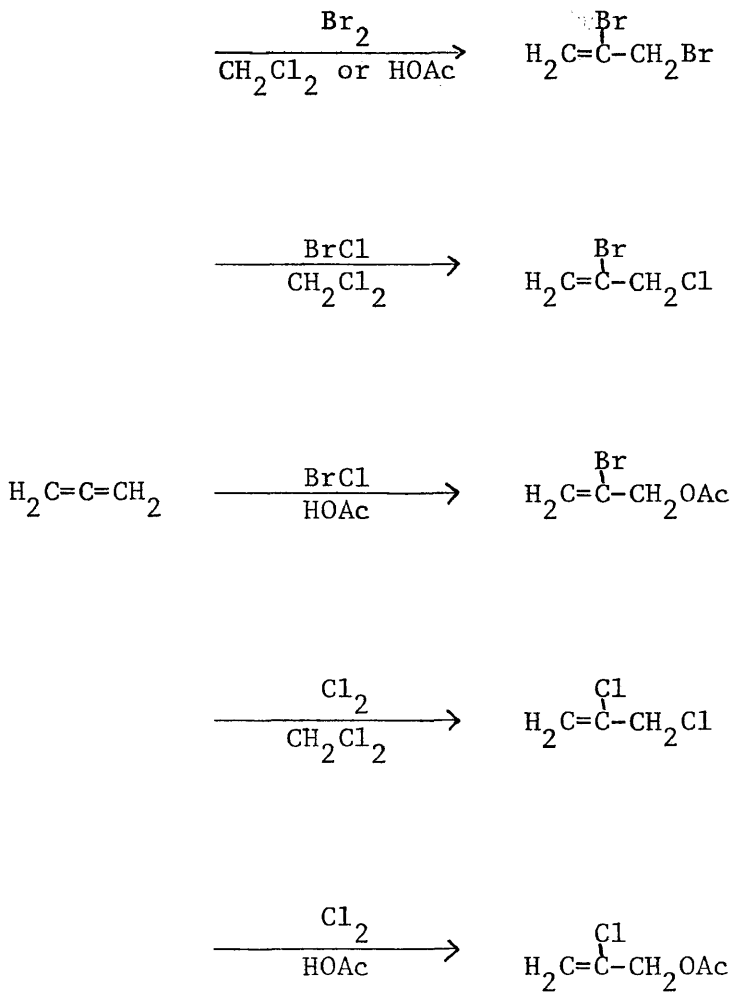
π-complex which may either collapse with nucleophile directly, or form an allyl cation which then collapses with nucleophile. If protons formed this bridged intermediate as halogens do, then one would expect anti-Markovnikov behavior for protonation as seen in halogenation. This evidence suggests a different mechanism for each reaction. Halogens are able to form cyclic intermediates because of their greater size. Addition of bromine yields 2,3-dibromo-1-propene whether the reaction is carried out in acetic acid or in inert solvents like carbon tetrachloride and methylene chloride. In interhalogen additions, the less electronegative element acts as the nucleophile. Addition of BrCl for example, gives 2-bromo-3-chloro-1-propene. In acetic acid, the product is 2-bromo-3-acetoxy-1-propene. The acetate ion competes with chloride ion as the nucleophile. In chlorine addition, the 2,3-dichloro-1-propene is formed in inert solvents and the 2-chloro-3-acetoxy-1-propene is formed in glacial acetic acid. Addition of halogen and interhalogen compounds is outlined in figure 2.

More evidence for a cyclic halonium intermediate has come from the study of α-secondary isotope effects. These effects arise from the difference in length of the C-D and C-H bonds (the C-H bond is .009 Å

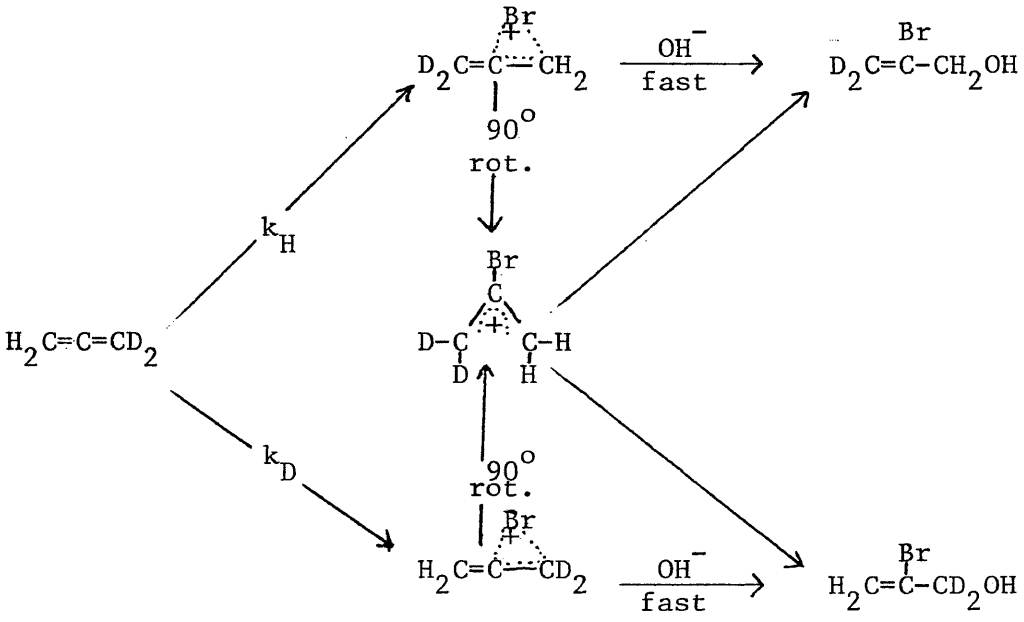
FIGURE 2

ADDITION OF HALOGEN AND INTERHALOGEN COMPOUNDS

TO ALLENE



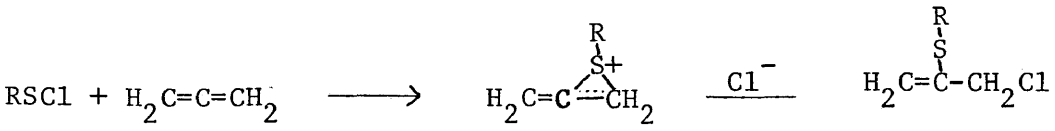
longer than the C-D bond).[6] As the hybridization of carbon changes from sp^2 to sp^3, C-H bending experiences a greater restriction than C-D bending due to the greater length of the C-H bond. The result is an inverse rate ratio $k_H/k_D < 1$. No secondary isotope effect would



Secondary isotope effect in allene addition

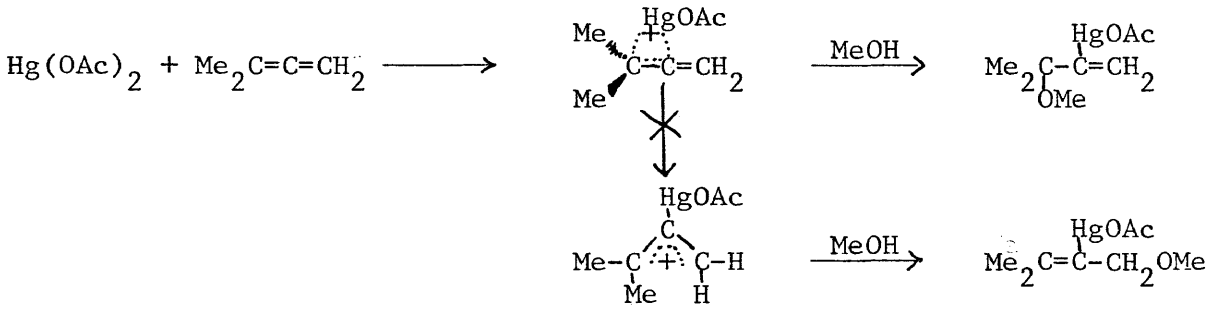
be observed if the allylic intermediate was involved as the slow step in the transition state. An inverse isotope would be predicted in the absence of the allylic intermediate. The observed value of $k_H/k_D = .83$ is in agreement with a coordination change ($sp^2 \longrightarrow sp^3$). Hypochlorous acids also show the same behavior.[5]

The addition of halogens is not the only evidence for the cyclic intermediate. The addition of 2,4-dinitrosulphenyl chlorides as well as oxymercuration are two other examples. The allylic intermediate is not observed. In the case of oxymercuration, even though C-1 is more sterically hindered than C-3, the methoxide ion attaches there because



Addition of arenesulphenyl chloride

to allene



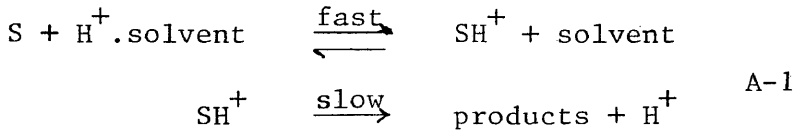
Oxymercuration of allene

(dimethylallene)

the intermediate carbonium ion is stabilized by the methyl groups.[1c]

So far, the mechanism of proton attack has not been discussed. Protonation of organic substrates may be either slow or fast. In strongly acidic media, several mechanisms have been proposed for protonation.[7]

The A-1 mechanism involves rapid formation of the conjugate acid of the substrate as a fast equilibrium step, followed by slow unimolecular decomposition of the protonated substrate. Typically, an A-1 mechanism



shows a slightly positive entropy of activation (one species becomes two).[8] Solvent isotope effects for the A-1 mechanism arise from the extent of protonation of the substrate in light and heavy solvent. Since D_3O^+ appears to be more acidic than H_3O^+, an inverse $k_{H_3O^+}/k_{D_3O^+}$ ratio would be expected. The unimolecular decomposition would not be expected to be greatly affected by the solvent change (H_2O to D_2O) since, as a rule, bonds other than SH^+ undergo rupture.

The A-2 mechanism is another possible pathway for allene protonation. It involves fast equilibrium protonation similar to the A-1 mechanism but, unlike the A-1, involves bimolecular collapse of the conjugate acid with water. In the A-2 mechanism, an inverse solvent

$$S + H^+(H_2O)_n \underset{\longleftarrow}{\xrightarrow{\text{fast}}} SH^+ + nH_2O$$

A-2

$$SH^+ + H_2O \xrightarrow{\text{slow}} \text{products} + H^+$$

isotope effect would be observed for the same reason as in the A-1, but the isotope effect is also dependent on the nucleophilicity of the solvent. Since H_2O is a stronger base than D_2O, the ratio k_{H_2O}/k_{D_2O} for nucleophilic attack should be greater than unity. The combination of the two effects would give rise to an overall $k_{H_3O^+}/k_{D_3O^+}$ ratio which depends on the magnitude of each effect. In the A-2 mechanism, a negative entropy of activation would be expected (two species become one).

Another mechanism for protonation of allenes is the Ad_E2 mechanism. In this mechanism, slow step protonation of the substrate is followed by rapid reaction of the conjugate acid. In the Ad_E2, a $k_{H_3O^+}/k_{D_3O^+}$

$$S + H^+.\text{solvent} \xrightarrow{\text{slow}} SH^+ + \text{solvent}$$

Ad_E2

$$SH^+ \xrightarrow{\text{fast}} \text{products} + H^+$$

greater than unity is expected. This effect is due to the differences in zero point energy of bond formation for hydrogen versus deuterium. A negative entropy of activation is also expected (two species become one).

To differentiate between the A-2 and Ad_E2 mechanisms, the degree of water participation in the transition state must be determined. Bunnett and Olsen[9] used the equation below to show water interaction in the transition state. It was proposed that the value of the slope (ϕ) could

$$\log k_\psi + H_o = \phi(\log[H_2SO_4] + H_o) + \log k_o$$

Bunnett and Olsen's equation

be used as a measure of the role of water in the transition state. Values of ϕ for several "calibration" reactions were determined, and using these accepted mechanisms, water interaction was deduced. It was shown that ϕ values less than 0 were indicative of no water participation. Values of ϕ between +.18 and +.56 were correlated to reactions involving water as a nucleophile, and ϕ values greater than +.58 showed water as a proton transfer agent. Values around 0 are found for hydrocarbon-like substrates with water acting as a proton transfer agent. Using these criteria, an A-2 mechanism should show a ϕ value between +.22 and +.56. A-2 and Ad_E2 mechanisms should not show values of ϕ in this range.

For allene hydration, Tidwell and Cramer[10] found a ϕ value of -.44

and for propyne hydration, a value of -.53 was found. These negative values show no water participation for this reaction in the slow step of the transition state. This ruled out the A-2 mechanism. The observation of a solvent isotope effect around 2 ruled out the A-1 mechanism, leaving the Ad_E2 as the mechanism for allene and propyne hydration.

An allene with an aromatic ring substituent presents an interesting system in which the aromatic ring is conjugated with the internal π-bond of the allene. The possible pathways for hydration of phenylallene are shown in figure 3 (next page). Each intermediate represents slow protonation of one of the allenic carbons followed by rapid collapse with nucleophile.

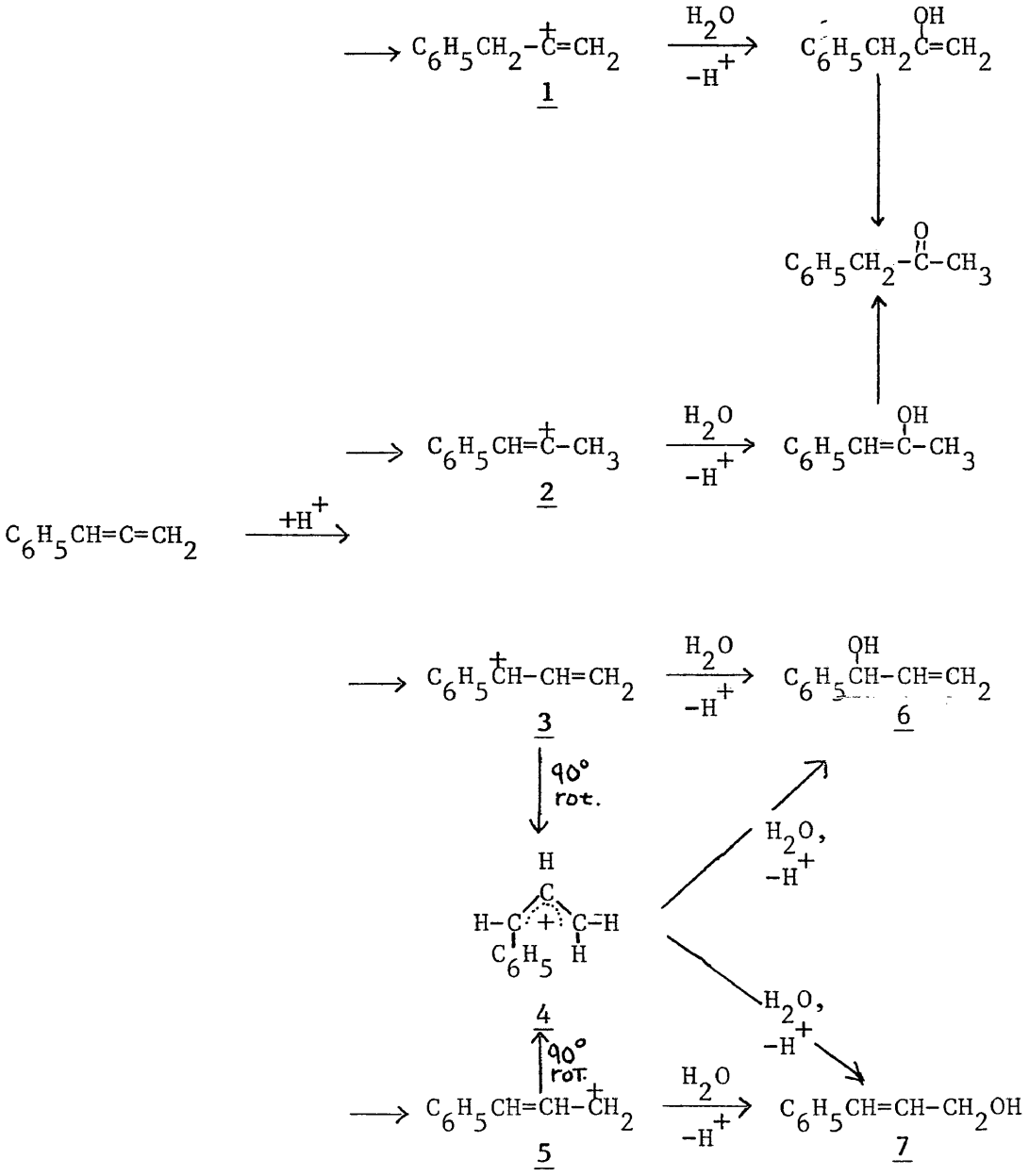
Intermediate 1 results from protonation of the carbon adjacent to the aromatic ring. The vinyl cation formed is analogous to the gas phase allene protonation product with H_3S^+. This cation would be expected to be less stable than one which is conjugated with the ring. The final product would not be an enol but would probably tautomerize to give benzyl methyl ketone as shown.

The second intermediate 2 comes from protonation of the terminal carbon. This vinylic intermediate would be stabilized more than 1 by conjugation of the double bond with the aromatic ring. Collapse with water would initially give the enol which tautomerizes to give the same ketone as does intermediate 1 (benzyl methyl ketone). The vinyl cation in allene is 11 kcal. $mole^{-1}$ less stable than the allyl cation. Rearrangement to the allyl cation from the vinyl cation by a hydride shift has an energy barrier of ca. 20 kcal. $mole^{-1}$ so that if 2 formed, rearrangement to 4 would be unlikely.[3]

Intermediate 3 results from protonation of the central carbon of

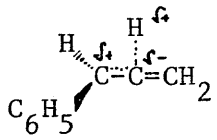
FIGURE 3

POSSIBLE CATIONIC INTERMEDIATES IN PHENYLALLENE PROTONATION



the allene. It is analogous to the perpendicular cation formed in allene protonation. The intermediate is stabilized by resonance with the adjacent aromatic ring. Intermediate 5 also results from protonation of the central carbon but is not stabilized by the aromatic ring. 5 does have the advantage of maintaining the conjugation of the internal π-bond with the aromatic ring. In systems where steric hindrance inhibits carbonium ion formation (i.e. large groups like 2,4-dinitrosulphenyl chloride) with the internal π-bond, reaction may proceed via 5.

The allylic intermediate 4 cannot be formed directly from protonation of phenylallene. Formation of 4 results from a 90^{o} rotation of 3 or 5. Just as in allene protonation, an energy barrier to rotation arises from partial double bond character of the C_1-C_2 bond as the proton attacks in the transition state. In allene, this energy barrier

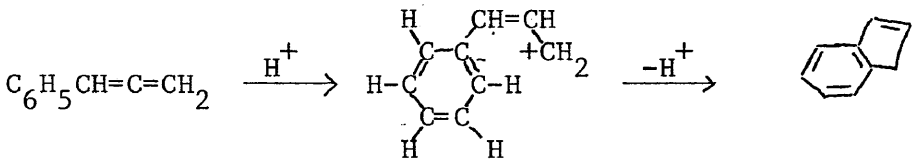


(Partial double bond character in proton attack on central carbon of phenylallene)

is great enough that the vinylic intermediate forms instead of the perpendicular form. Just as alkyl groups stabilize the perpendicular form in allene protonation, the aromatic group would be expected to do the same allowing phenylallene to form an allylic cation by rotation. Such an allylic intermediate could give rise to two products, both of which are alcohols. Alcohol 6 results from attack by water at the

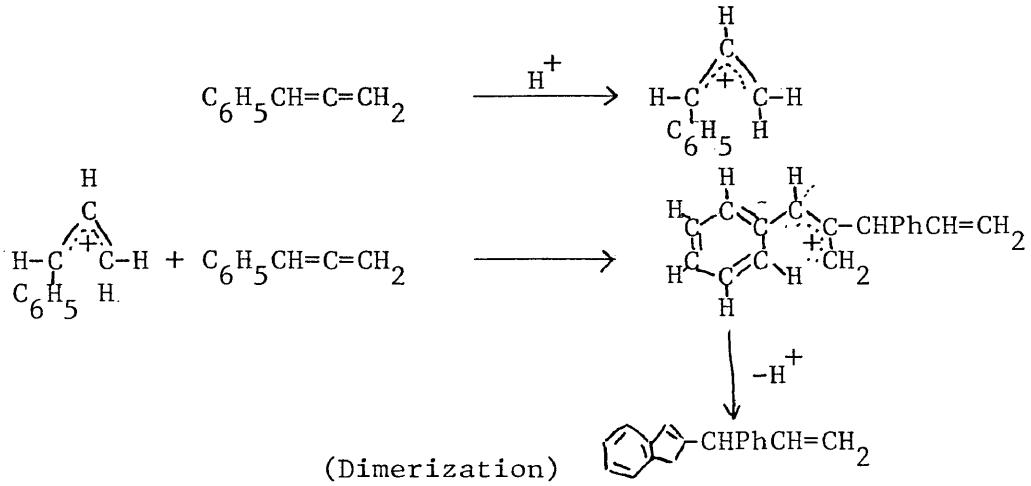
carbon adjacent to the aromatic ring. Attack at this point is more hindered than attack at the terminal carbon which leads to alcohol 7. Attack at the terminal carbon to give 7 is also favored because conjugation of the internal double bond with the ring is maintained. Formation of 7 could also arise from isomerization of 6 through the allylic intermediate 4. This effect was observed for the acid-catalyzed rearrangement of 1-phenyl-3-methylallyl alcohol (ρ= -3.1).[11,12]

These few alcohols and ketones are not the only possible products from phenylallene hydration. Arylallenes are known to undergo cyclizations to indenes.[1] A possible mechanism involves protonation at the central carbon followed by internal electrophilic substitution



Indene formation

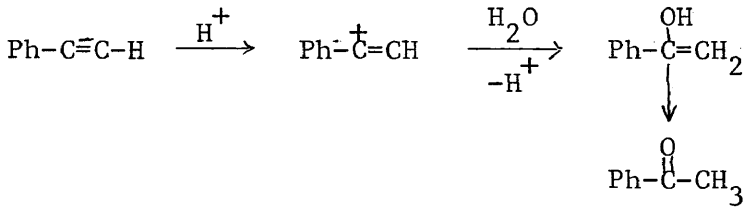
on the phenyl group. Tetraphenylallene yields 1,1,3-triphenyl indene when treated with hydrogen halides. There is also a possibility for dimerization where the carbonium ion from protonated phenylallene may



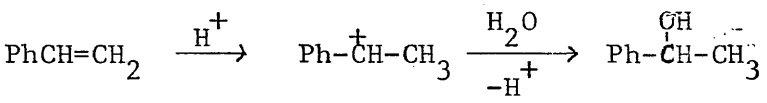
(Dimerization)

attack a second phenylallene. In the above example, the alkyl indene shown represents one of many possible products. Polymerization is also a very likely possibility.

The mechanism of phenylallene hydration has never been studied. Hydration of similar compounds such as styrene and phenylacetylene have been looked at. Since phenylallene represents an intermediate type of compound containing hybridized carbon of both types, it allows a direct comparison of the reactivity of these olefins as well as aryl acetylene. Phenylacetylene is hydrated via a vinyl cationic intermediate similar to the vinyl cation in allene hydration.[13]



Phenylacetylene hydration



Styrene hydration

Styrene hydrates via a benzyl cationic intermediate.[14] Phenylallene can give intermediates of both types.

The hydrochlorination of phenylallene in glacial acetic acid has been studied.[15] The mechanism for hydration and hydrochlorination would be expected to be similar. Comparisons of these two reactions as well as phenylacetylene and styrene hydration will be presented in the

discussion section.

EXPERIMENTAL

Instrumentation

Ultraviolet spectra were obtained using a Beckman Acta MVI spectrophotometer. Kinetic runs were done on a Gilford Model 240. Infrared spectra were done routinely on a Perkin-Elmer Model 337. The ^{1}H and ^{13}C spectra were run on a Varian FT-80A at 80 and 20 MHz. respectively. Chloroform-d was used as a solven- and lock signal.

Materials

The following procedure for the preparation of phenylallene is a general procedure for the preparation of other phenylallenes.

1. 1-phenyl-2,2-dibromocyclopropane was prepared by the method of Doering and Hoffmann.[39] 31.2 g (.3 mole) commercial styrene (Eastman), 151.8 g (.6 mole) bromoform (Fisher, distilled), 60 mL 50% NaOH, and .6 g triethylbenzyl ammonium chloride (TEBA-Chloride) were placed in a 250-mL Erlenmeyer flask and shaken for 24 hrs. at 37°. The mixture was then placed in a 1-L separatory funnul and 150 mL water and 150 mL methylene chloride added. This was shaken and allowed to stand for 1/2 hour. The methylene chloride layer was then filtered through $MgSO_4$ the methylene chloride stripped on a Buchi Roto-Vap at room temperature with a water aspirator. The crude product was then distilled (150°@ .5 mm) yielding 61.5 g (74%). ^{1}Hnmr δ 7.26 (5) aromatic, δ 2.91 (t,1,J=9.4 Hz ), δ 2.07 (2d,2,J=9.4 Hz  , J=4.4 Hz ).

2. Phenylallene was prepared by the method of Skattebol.[40] 61.5 g (.223 mole) 1-phenyl-2,2-dibromocyclopropane was placed in a 500 mL 3-neck round bottom flask. 30 mL diethyl ether (reagent) were added and the mixture was stirred and placed in an acetone-dry ice bath (later changed to chloroform-liquid N_2 both ca. -70°C.). A 50 mL addition funnel was added and the system purged with N_2. The addition funnel was charged with 190 mL (50 mL at a time) methyllithium solution (1.2 Molar in ether) under N_2. The methyllithium was added dropwise over one hour and the reaction stirred for an additional 0.5 hour. The acetone - dry ice bath was replaced with an ice-water bath and the excess methyllithium quenched by adding 150 mL of H_2O (dropwise at first then quickly). The reaction mixture was transferred to a separatory funnel, the layers separated, and the aqueous layer extracted with 2 x 50 mL ether. The etherial solutions were then filtered through $MgSO_4$ and the ether stripped on a Buchi Roto-Vap at room temperature with a water aspirator. The phenylallene was then distilled 43-45° @ .5 mm yielding 18.1 g (.156 mole, 70%). Overall yield from styrene 52%. IR strong (C=C) 1950 cm^{-1}; UV_{max} 247 nm (95% EtOH); ^1H nmr ($CDCl_3$) δ 7.19 aromatic (5), δ 6.09 (t,1,J=6.8 Hz $H\rangle C-$), δ 5.02 (d,2,J=6.8 Hz $=C\langle^{H}_{H}$); ^{13}C nmr δ209.78 (=C=), δ128.58, 126.82, 126.72 aromatic, δ 94.04 ($\rangle C=$), δ78.66 ($=C\langle$).

3. 1-(p-methylphenyl)-2,2-dibromocyclopropane prepared using procedure for 1-phenyl-2,2-dibromocyclopropane above from p-methylstyrene (Aldrich). 100-104° @ 3 mm; 29.3% yield.

4. p-methylphenylallene prepared by the same procedure as phenylallene above using 1-(p-methyl)-2,2-dibromocyclopropane. 42-45° @ .9 mm; 18.4%

yield; IR (C=C) 1950 cm^{-1}; UV_{max} 247 nm (95% EtOH); ^1H nmr δ 7.12 aromatic (4), δ 6.07 (t,1,J=5.8 Hz $_H\!\!>\!\!=$), δ 5.07 (d,2,J=5.8 Hz $=\!\!<^{H}_{H}$), δ 2.28 (s,3 ϕ-CH_3); ^{13}C nmr δ 209.73 (=C=), δ 130.62, 129.35,129.24, 126.71 aromatic, δ 93.90 ($^{\phi}\!\!>\!\!c=$), δ 78.48 ($=c<^{H}_{H}$), δ 10.5 (ϕ-CH_3).

5. 1-(p-chlorophenyl)-2,2-dibromrcyclopropane prepared from p-chlorostyrene (Aldrich) using above procedure for 1-phenyl-2,2-dibromocyclopropane b.p. 112-114° @ .9 mm; 53.8% yield.

6. p-chlorophenylallene was made from 1-(p-chlorophenyl)-2,2-dibromocyclopropane by the same procedure as phenylallene above. b.p. 48-54° @ 1.2 mm; 88% yield; ^1H nmr showed impurity 1.45 (d) and 3.75 (q), prep. GC @ 140° on Carbowax SE-40 (60 mL min^{-1} He) showed second fraction to be p-chlorophenylallene δ 7.20 aromatic (4), δ 6.07 (t, 1,J=6.8 Hz $_H\!\!>\!\!=$), δ 5.10 (d,2,J=6.8 Hz $=\!\!<^{H}_{H}$); ^{13}C nmr δ 209.83 (=C=), δ 132.48, 128.75, 128.65, 127.86 aromatic, δ 93.17 ($^{\phi}\!\!>\!\!c=$), δ 79.07 ($=c<^{H}_{H}$).

7. 1-(m-chlorophenyl)-2,2-dibromocyclopropane was prepared from m-chlorostyrene (Aldrich) using the same procedure as for 1-phenyl-2,2-dibromocyclopropane above, b.p. 114-116° @ 3 mm; 40% yield; ^1H nmr δ7.2 aromatic (4), δ 2.85 (t,1,J=9.4 Hz ), δ 2.01 (2d,2,J=9.4 Hz  , J=6 Hz ).

8. m-chlorophenylallene prepared from 1-(m-chlorophenyl)-2,2-dibromocyclopropane using the same procedure as for phenylallene above; b.p. 56-62° @ 3 mm; UV_{max} 248 nm (95% EtOH); IR strong (C=C) 1950 cm^{-1}; ^1H nmr δ 7.24 aromatic (4), δ 6.06 (t,1,J=6.8 Hz $_H\!\!>\!\!=$), δ 5.10 (d,2,

J=6.8 Hz $=\langle^{H}_{H}$); ^{13}C nmr δ209.93 (=C=), δ 135.99, 134.58, 129.67, 126.85, 126.56, 124.82 aromatic,[50] δ 93.17 ($\phi\rangle_{C=}$), δ 74.19 ($=C\langle$).

9. 1-phenyl-1-methyl-2,2-dibromocyclopropane prepared from distilled α-methylstyrene (Aldrich) using same procedure as 1-phenyl-2,2-dibromocyclopropane above; b.p. 94-98° @ 1.5 mm; 61% yield; ^{1}H nmr δ7.27 aromatic (5), δ 2.95 (t,1,J=9.4 Hz $\phi\rangle_{H}$), δ 1.91 (2d,2,J=9.4 Hz $\langle^{H}_{H}$,J=5.4 Hz $\langle^{H}_{H}$), δ 1.67 (s,3). $\langle^{CH_3}_{\phi}$).

10. α-methylphenylallene prepared from 1-phenyl-1-methyl-2,2-dibromocyclopropane using the same procedure as for phenylallene above; b.p. 40-42° @ .8 mm; 63.4% yield; IR strong (C=C) 1950 cm^{-1}; UV_{max} 247 nm (95% EtOH); ^{1}H nmr δ 7.27 aromatic (5), δ 4.96 (2d,2,J=3.2 Hz $CH_3\rangle=\langle^{H}_{H}$ J=.2 Hz $=\langle^{H}_{H}$), 2.04 (t,3,J=3.2 Hz $CH_3\rangle=\langle$).

11. 1-phenyl-3-methyl-2,2-dibromocyclopropane from distilled trans-β-methyl styrene (Aldrich) using same procedure as for 1-phenyl-2,2-dibromocyclopropane above; b.p. 104-108° @ 1.75 mm; 39% yield; ^{1}H nmr δ7.27 aromatic (5), δ4.96 (d,1,J=6.0 Hz $H\langle$), δ 3.43 (m (quintet),1, J=6.0 Hz $\langle^{CH_3}_{H}$), δ 1.42 (d,3,J=6.0 Hz $\langle_{CH_3}$).

12. γ-methylphenylallene prepared from 1-phenyl-3-methyl-2,2-dibromocyclopropane using the same procedure as for phenylallene above; b.p. 43-46° @ 1.2 mm; 45.4% yield, IR strong (C=C) 1950 cm^{-1}; UV_{max} 247 nm (95% EtOH); ^{1}H nmr δ 7.21 aromatic (5), δ 6.06 (m,1,J=3.2 Hz $\underline{H}\rangle=\langle^{CH_3}$, J=7.1 Hz $\underline{H}\rangle=\langle_{H}$), δ 5.41 (m,1,J=7.1 Hz $=\langle^{CH_3}_{\underline{H}}$), δ 1.71 (2d,3,J=3.2 Hz $H\rangle=\langle^{CH_3}$,J=7.1 Hz $=\langle^{CH_3}_{H}$).

13. Deuterophenylacetylene was made by placing 26 mL D_2O (Bio-Rad 99-77 mol%) in a 50 mL round bottom flask and purging with N_2. .150 g Na metal was added in small chunks with stirring and 9.49 g phenylacetylene (Chemical Samples) added. After stirring overnight the phenylacetylene was extracted with 3 x 10 mL ether, filtered through $MgSO_4$, and stripped on the roto-vap at room temperature with water aspirator. The phenylacetylene from this procedure was placed back in the 50 mL round bottom flask and the procedure repeated with fresh Na metal and D_2O. After filtering, the crude phenylacetylene (deuterated) was distilled b.p. 49-50° @ 30 mm; 39.5% yield; IR (≡C-D) 2600 cm^{-1}.

14. β,β-dideuterostyrene was prepared by the procedure of Brown and Gupta.[41] 5.2 g (43 mmoles) catechol borane (Aldrich) placed in a 3-neck 50 mL round bottom flask (weighed in by syringe-catechol borane air sensitive) and purged with N_2. 3.8 g (36 mmole) deuterophenylacetylene placed in a 50 mL addition funnel. Reaction flask placed in an oil bath and deuterophenylacetylene added dropwise over .5 hour with stirring. At the end of the addition, oil bath temp. raised to 70° and maintained for two hours. At the end of the two hour period, 25 mL DOAc added dropwise and the mixture refluxed for four hours (118°). After reflux, the mixture was poured over ice-water and let stand for 15 minutes. The mixture is then placed in a 125 mL separatory funnel and extracted with 5 x 20 mL pentane and the pentane extract washed with 4 x 15 mL 1N NaOH and finally with 3 x 20 mL 10% NaCl. The crude product was filtered through $MgSO_4$ and the pentane stripped on the roto-vap at room temp. with a water aspirator. β,β-dideuterostyrene was distilled b.p. 48-49° @ 26 mm; 36% yield(1.4 g); IR disappearance

of ≡C-D peak at 2600 cm^{-1}.

15. 3,3-dideutero-1-phenyl-2,2-dibromocyclopropane was prepared from β,β-dideuterostyrene using the same procedure as for 1-phenyl-2,2-dibromocyclopropane above b.p. 80-85° @ .6 mm; 53% yield.

16. γ,γ-dideuterophenylallene was made from 3,3-dideutero-1-phenyl-2,2-dibromocyclopropane using the same procedure as for phenylallene above; b.p. 38° @ 2.5 mm; 71% yield; UV_{max} 247 nm (95% EtOH); IR strong (C=C) 1920 cm^{-1}; ^1H nmr δ 7.25 aromatic (5), δ 6.14 (s,1 $\phi_H>=$), small doublet at δ 4.90 for remaining H calculated 90% deuteration.

17. Sulfuric acid-d_2 98% (Diaprep) no further purification

18. D_2O 99-77 mole% (Bio-Rad) no further purification

19. Sulfuric acid reagent 95-98% (Fisher) no further purification

20. $CDCl_3$ (Stohler Isotope Chemicals) no further purification

Methods

Stock solutions were prepared by diluting the phenylallene with 95% ethanol (EtOH). Concentrations were adjusted so that 1 mL of the stock solution diluted to 25 mL of EtOH would give one absorbance unit of deflection on the Beckman Acta (Approx. concentration 7 x 10^{-5}Molar). Since the UV_{max} of the compounds were all close to 247 nm, it was chosen as the analytical wavelength. Para-chlorophenylallene was not used

because the product of its hydration interfered with the analytical wavelength. A typical kinetic run was performed by placing 1 mL of the stock solution in a 25 mL volumetric flask and diluting to the mark with acid- The volumetric flask was inverted several times to mix the solution. Part of the solution is used to rinse the quartz cuvettes (1 cm Luminon) two or three times, the cuvettes are then filled with the solution and placed in the Gilford 240. The rest of the solution was titrated gravimetrically to determine the Wt. % acid. The lowest concentration acid was used as a blank and the temp. kept constant by a constant temperature bath (HAAKE FK). The data were input into the computer (IBM 370). Rate constants were determined by the use of a computer program by DeTar.[26]

Product Study

Phenylallene is a typical example of product study procedure. Approximately 200 mg phenylallene were placed in a 10 mL beaker and 10 mL ethanol (EtOH) added. 250 mL of the acid solution (44% for phenylallene) were placed in a 500 mL Erlenmeyer flask and allowed to stir. The ethanolic phenylallene solution was then added dropwise and stirred overnight. Extractions were carried out with EtOH and then later with CH_2Cl_2 since the ethanol peaks interfered with the product peaks in the ^1H nmr (see ethanolic product ^1H nmrs in Appendix A and CH_2Cl_2 extracts in the Discussion section figs. 4-7). Extracts were filtered through $MgSO_4$, stripped on the roto-vap, and ^1H nmr of the crude products were run on the Varian FT-80A at 80 MHz.

RESULTS AND DISCUSSION

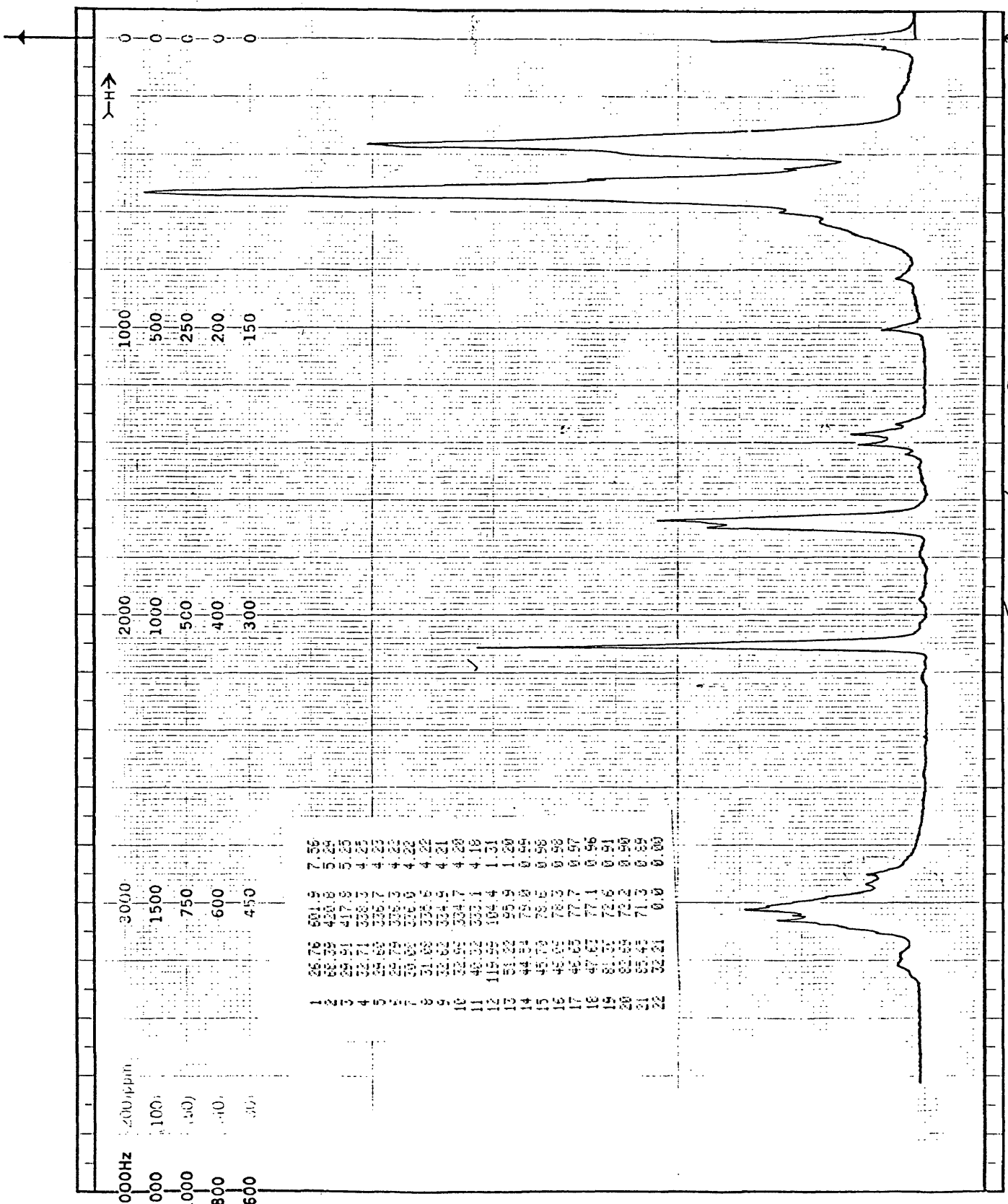
Product Studies

In the hydrochlorination of phenylallene in glacial acetic acid, cinnamyl chloride was the sole reaction product.[15] Based on this finding, cinnamyl alcohol was the expected reaction product for the hydration of phenylallene. The ^1H nmr of the reaction product did not match the ^1H nmr of cinnamyl alcohol.[21] The cinnamyl alcohol was then exposed to the hydration reaction conditions and the ^1H nmr of this product matched the ^1H nmr of phenylallene hydration. This showed cinnamyl alcohol to be a likely product of the hydration reaction. The possibility of indene being the final reaction product was ruled out by comparison of the indene ^1H nmr versus that of the hydration product.[22] The ^1H nmr's of the products of hydration of phenylallene, α-methylphenylallene, γ-methylphenylallene, and cinnamyl alcohol hydrations are shown in figures 4-7.

Acidity Dependence

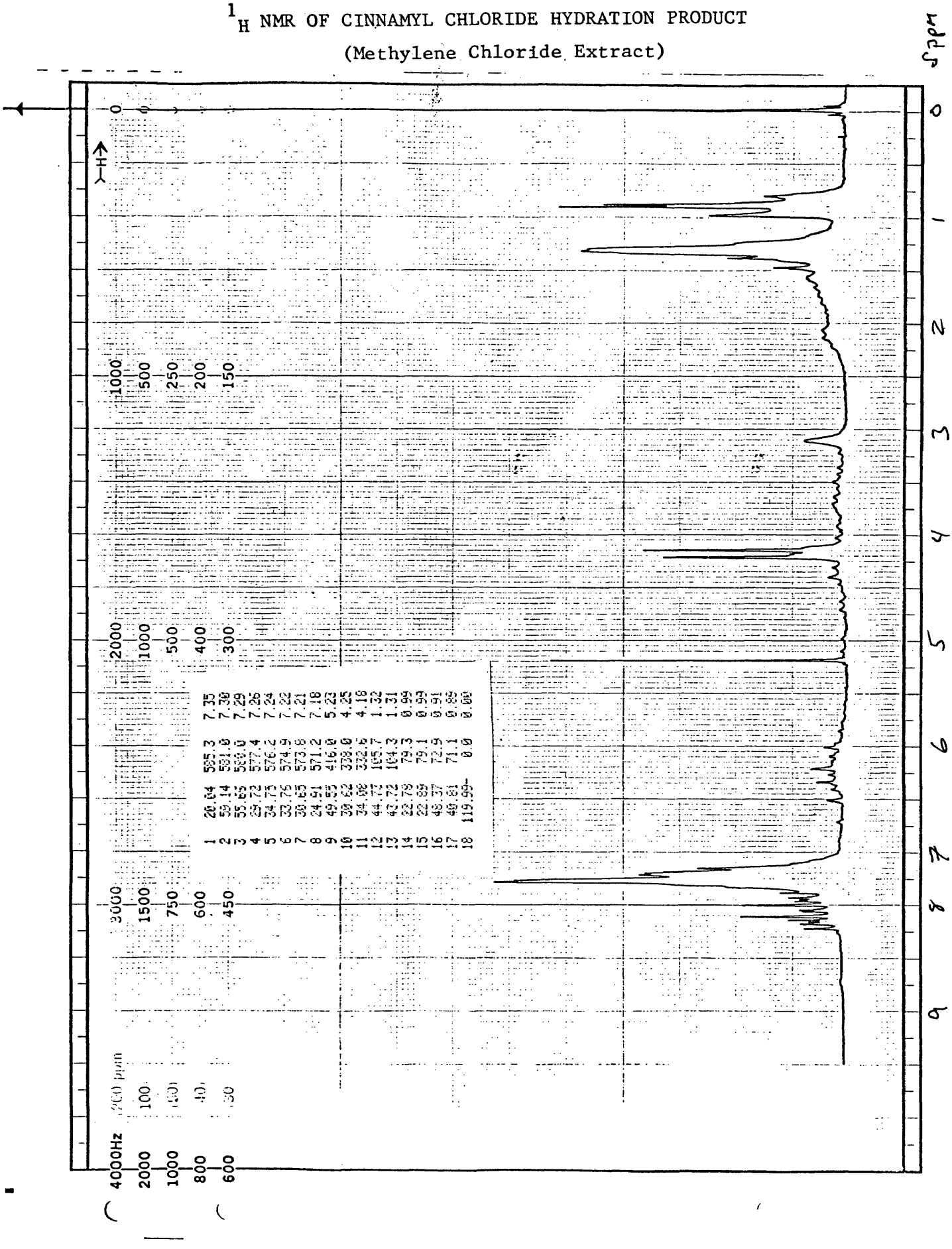
The hydration reaction kinetics show pseudo first order behavior. The hydration shows strong acid catalysis having a linear plot of the logarithm of the rate versus the acidity function $-H_o$. The slope of this line ($-d\log k / dH_o$) is -1.22 (r=.9986) for phenylallene hydration which is comparable to the values for hydration of 1-phenylpropyne (-1.30),[16] hydration of phenylacetylene (-1.24),[13] and hydration of styrene (-1.23).[14] Rate data for phenylallene, α- and γ-methylphenylallene, p-methyl-

^{1}H NMR OF PHENYLALLENE HYDRATION PRODUCT
(Methylene Chloride Extract)



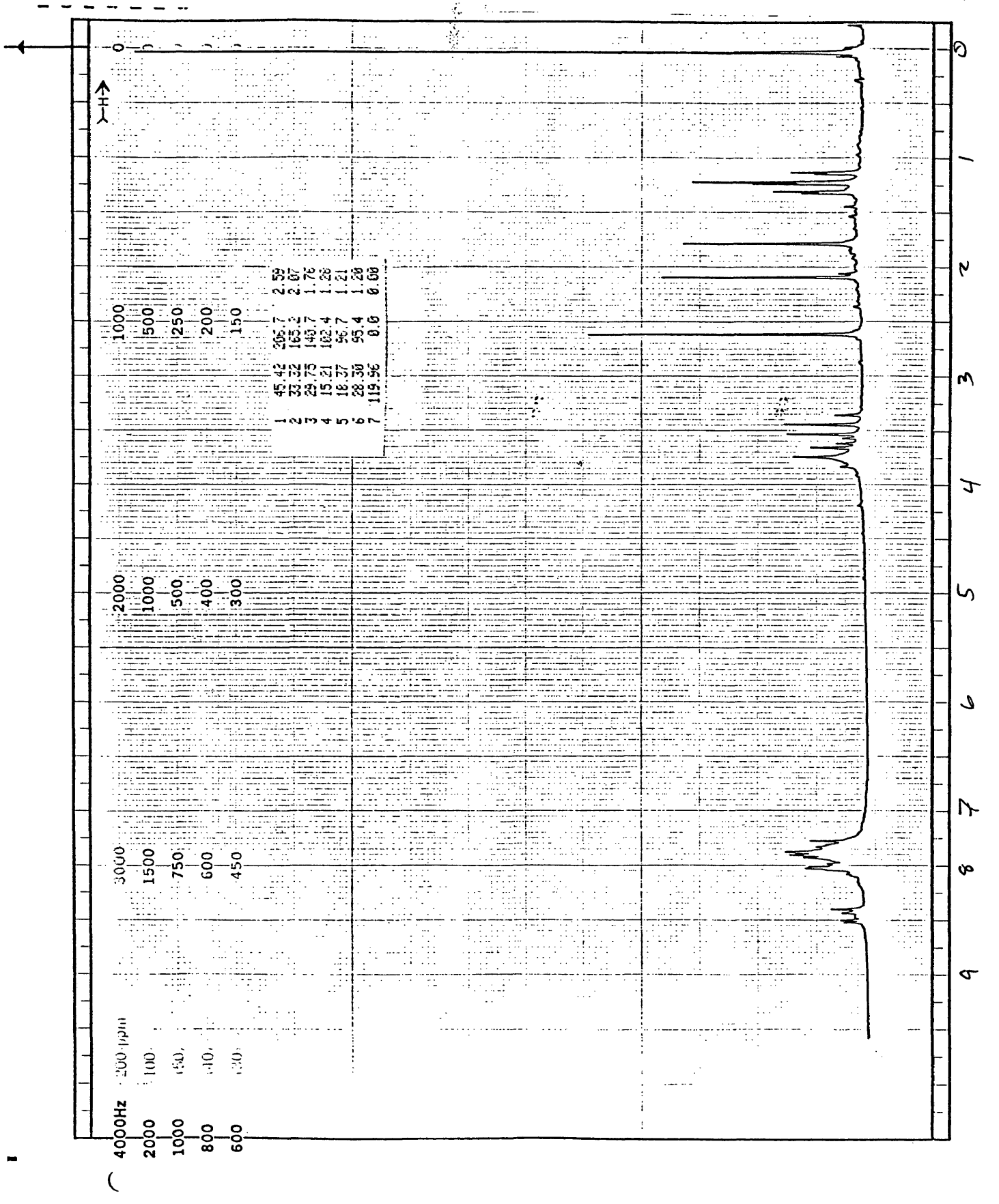
^1_H NMR OF CINNAMYL CHLORIDE HYDRATION PRODUCT

(Methylene Chloride Extract)



^{1}H NMR OF α-METHYLENEPHENYLALLENE HYDRATION PRODUCT

(Methylene Chloride Extract)



^{1}H NMR OF α-METHYLPHENYLALLENE HYDRATION PRODUCT

(Methylene Chloride Extract)

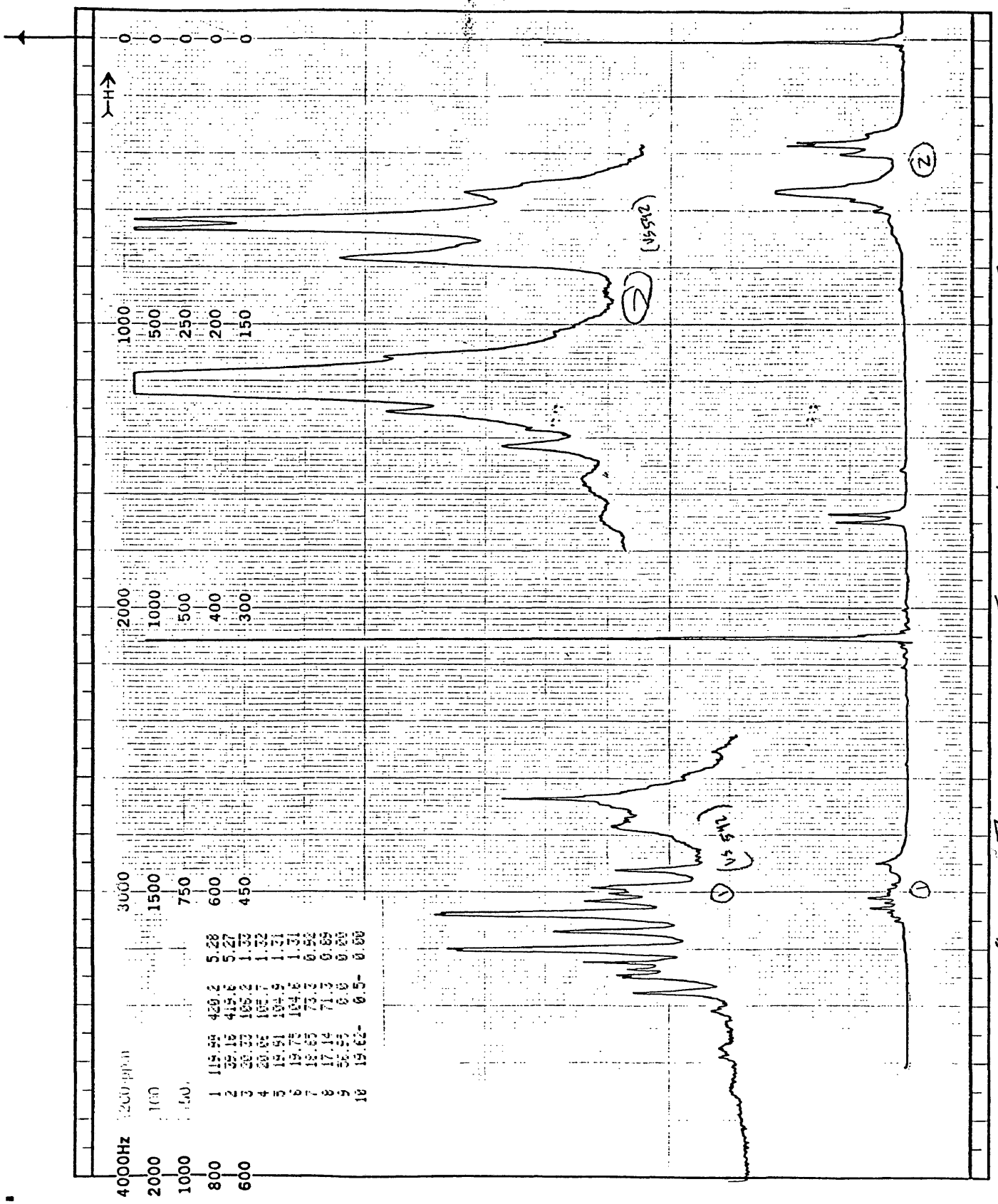


TABLE 2

RATE DATA FOR PHENYLALLENES AT 25 AND 45 DEGREES CENTIGRADE

Compound	Temp. °C	Wt. % H_2SO_4	$-H_o$	k_{obsd} x 10^5	$-\log k_{obsd}$
Phenylallene	25.2	55.60	3.98	21.578	3.6660
		54.18	3.82	14.101	3.8507
		51.78	3.63	6.9587	4.1575
		48.60	3.28	2.9938	4.5238
		50.17	3.42	4.8370	4.3154
		56.85	4.13	32.639	3.4863
	24.8	47.47	3.18	2.2348	4.6508
		46.87	3.12	1.8857	4.7245
		45.85	3.01	1.3787	4.8605
	45.2	38.40	2.43	.86085	5.0651
		40.93	2.60	1.7714	4.7517
		44.41	2.90	4.3926	4.3573
		48.62	3.28	12.862	3.8907
	45.3	45.85	3.01	5.4338	4.2649
		46.96	3.13	7.7430	4.1111
		47.97	3.23	9.2625	4.0333
m-chlorophenylallene	24.7	66.72	5.31	43.630	3.3602
		64.62	5.02	20.681	3.6844
		63.04	4.82	10.877	3.9635

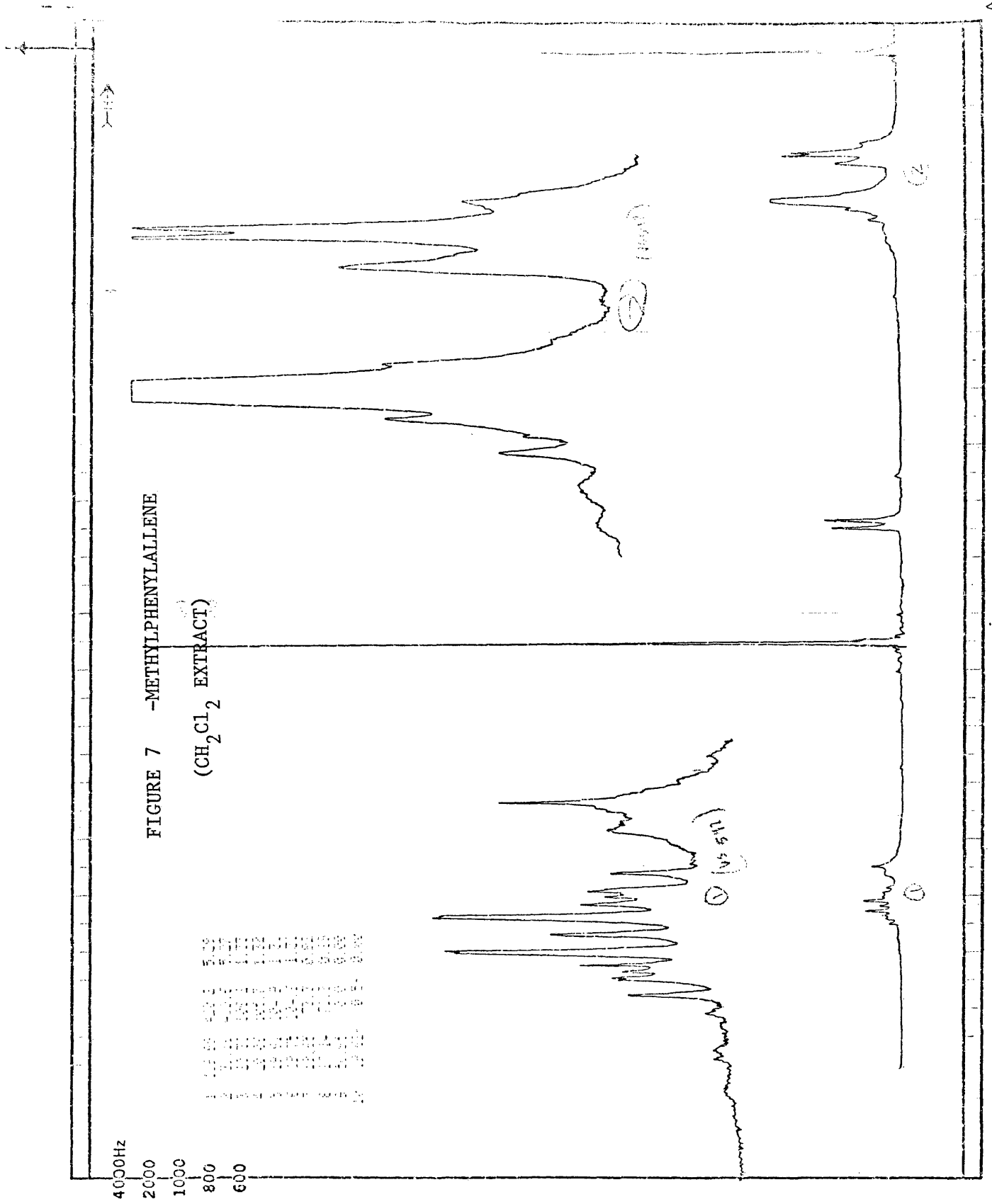


FIGURE 7 -METHYLPHENYLALLENE

(CH_2Cl_2 EXTRACT)

TABLE 2

RATE DATA FOR PHENYLALLENES AT 25 AND 45 DEGREES CENTIGRADE

Compound	Temp. °C	Wt. % H_2SO_4	$-H_o$	k_{obsd} x 10^5	$-\log k_{obsd}$
Phenylallene	25.2	55.60	3.98	21.578	3.6660
		54.18	3.82	14.101	3.8507
		51.78	3.63	6.9587	4.1575
		48.60	3.28	2.9938	4.5238
		50.17	3.42	4.8370	4.3154
		56.85	4.13	32.639	3.4863
	24.8	47.47	3.18	2.2348	4.6508
		46.87	3.12	1.8857	4.7245
		45.85	3.01	1.3787	4.8605
	45.2	38.40	2.43	.86085	5.0651
		40.93	2.60	1.7714	4.7517
		44.41	2.90	4.3926	4.3573
		48.62	3.28	12.862	3.8907
	45.3	45.85	3.01	5.4338	4.2649
		46.96	3.13	7.7430	4.1111
		47.97	3.23	9.2625	4.0333
m-chlorophenylallene	24.7	66.72	5.31	43.630	3.3602
		64.62	5.02	20.681	3.6844
		63.04	4.82	10.877	3.9635

TABLE 2 CONTINUED

Compound	Temp. °C	Wt. % H_2SO_4	$-H_o$	k_{obsd} x 10^5	$-\log k_{obsd}$
m-chlorophenylallene	24.7	61.53	4.63	5.8641	4.2318
	24.8	59.50	4.44	3.5385	4.4512
		56.40	4.11	1.2526	4.9022
	44.4	61.49	4.62	30.208	3.5199
		59.74	4.47	17.297	3.7620
		56.75	4.12	6.1831	4.2088
		55.06	3.94	4.8792	4.3116
		53.60	3.77	3.2544	4.4875
		51.56	3.57	1.4011	4.8535
p-methylphenylallene	25.5	44.24	2.88	26.264	3.5806
		41.74	2.68	15.319	3.8418
		38.20	2.42	6.8801	4.1624
		36.76	2.31	5.1367	4.2743
		45.64	2.98	35.969	3.4441
		46.70	3.12	42.400	3.3726
	44.5	29.01	1.74	5.1080	4.2917
		31.77	1.92	7.5037	4.1247
		32.27	1.98	8.9142	4.0499
		36.86	2.32	22.725	3.6435
		38.27	2.42	28.082	3.5516
		41.80	2.68	59.834	3.2230
α-methylphenylallene	25.7	16.40	.900	2.4040	4.6191
	25.5	36.28	2.30	109.65	2.9600

TABLE 2 CONTINUED

Compound	Temp. °C	Wt. % H_2SO_4	$-H_o$	$k_{obsd} \times 10^5$	$-\log k_{obsd}$
α-methylphenylallene	25.0	15.16	.780	1.6834	4.7738
		27.11	1.61	16.706	3.7771
		29.24	1.77	29.686	3.5274
	46.2	14.37	.748	8.2606	4.0830
		16.27	.899	12.117	3.9166
		8.63	.245	3.5063	4.4551
		11.79	.580	6.8205	4.1662
		20.71	1.14	25.658	3.5908
γ -methylphenylallene	25.7	24.16	1.39	.58429	5.2334
		25.52	1.49	.76648	5.1155
		29.24	1.77	2.0551	4.6872
		32.33	1.97	3.4341	4.4642
		37.03	2.32	10.008	3.9996
	46.2	25.46	1.49	4.1004	4.3872
		29.21	1.77	9.2932	4.0318
		31.74	1.93	15.250	3.8167
		32.81	2.02	16.462	3.7835
		36.78	2.33	38.118	3.4189

phenylallene, and m-chlorophenylallene appear in table 2.[49] Acidity dependence data for phenylallene hydration as well as some related reactions appear in table 3 below. The rate constants for the reactions

TABLE 3

ACIDITY DEPENDENCE DATA FOR PHENYLALLENE HYDRATION AND RELATED ACID-CATALYZED REACTIONS AT 25°

Compound	$-H_o$	$-d\log k/dH_o$	Reference
Phenylallene	3.28	1.22	This work
α-methylphenylallene	1.00	1.22	
γ-methylphenylallene	2.00	1.33	
Styrene($HClO_4$)	1.30	1.26	14
Phenylacetylene	2.50	1.13	13
Allene	4.54	1.40	10
Propyne	5.08	1.59	10
Phenylpropyne	3.35	1.30	16

in table 3 show a much steeper acidity dependence than the simple aliphatic olefins ($-d\log k/dH_o$ around unity).[24] Schubert and Lamm[14] have attributed this greater acidity dependence to solvation effects. Since the positive charge is more dispersed in the transition state of styrene hydration, the aromatic olefin would be less strongly (by water) solvated than the aliphatic olefin.

Hammett Data

The Hammett plot ($\log k/k_o = \sigma^+\rho$) shows a ρ value of -3.99 (r=.9981) for phenylallene hydration using Brown and Okamoto's σ^+ values.[25] This

strong substituent dependence of the large negative ρ indicates a positive center that is in direct conjugation with the aromatic ring in the slow step of the transition state. Similar findings were also reported for styrene hydration,[14] α-methylstyrene hydration,[18] phenylacetylene hydration,[13] and phenylallene hydrochlorination.[15] Hammett ρ values for phenylallene hydration as well as related reactions are listed in table 4.

TABLE 4

HAMMETT VALUES FOR PHENYLALLENE AND RELATED HYDRATION REACTIONS AT 25°

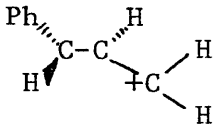
Compound	ρ	Reference
Phenylallene	-3.99	This work
Phenylacetylene	-3.84	13
Styrene	-3.58	14
α-methylstyrene	-3.20	18
Phenylpropiolic Acid	-4.77	27
Phenylbenzoylacetylene	-4.20	28
Phenylallene (Hydrochlorination)	-4.20	15

The observation of a large negative rules out vinylic intermediates 1 and 2. These intermediates are also ruled out on the grounds that

1 2

Vinylic intermediates in phenylallene hydration

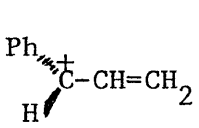
benzyl methyl ketone was not observed as a product (see introduction). Perpendicular allylic cation 5 is not formed in the rate determining step



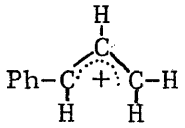
5

Perpendicular allylic cation

because the effect of changing substituents on the aromatic ring would be small. This occurs since the cation develops in the empty p-orbital which, on formation, is orhtogonal to the π-system. Rotation of 5 to allylic cation 4 would give rise to a large negative ρ value because the allylic intermediate is conjugated with the ring. Cation 3 is



3



4

Benzylic cation 3 and allylic cation 4

conjugated with the ring on formation. Cation 3 can also undergo rotation to the allylic cation 4. If protonation is the slow step, cation 3 is the only intermediate which is consistent with conjugation as the proton attacks.

Solvent Isotope Effects

In order to show which intermediate is involved in the slow step of the transition state, solvent isotope effects were studied.

TABLE 5

RATE DATA FOR PHENYLALLENE AND ALKYL SUBSTITUTED PHENYLALLENE IN D_2SO_4/ D_2O AT 25°

Compound	Wt. % D_2SO_4	Wt. % H_2SO_4	$-H_o$	k_{obsd} x 10^5	$-\log k_{obsd}$
Phenylallene	48.24	50.36	3.46	2.3871	4.6221
	50.58	52.70	3.69	5.0801	4.2941
	52.16	54.28	3.85	8.9843	4.0465
α-methylphenylallene	20.90	22.33	1.26	3.5408	4.4509
	28.28	30.04	1.81	11.265	3.9483
	36.03	38.01	2.40	61.916	3.2082
γ-methylphenylallene	29.05	30.84	1.86	2.0148	4.6958
	37.44	39.42	2.50	12.285	3.9106
	46.23	48.35	3.26	108.84	2.9632

Rate data for phenylallene and α- and γ-methylphenylallenes in deuterated solvent appear in table 5 above. If an inverse solvent isotope effect is observed, an A-1 mechanism is expected. The observation of a normal solvent isotope effect ($k_{H_3O^+}/ k_{D_3O^+} > 1$) shows either an A-2 or Ad_E2 mechanism at work. For phenylallene hydration, the solvent isotope effect is $k_{H_3O^+}/ k_{D_3O^+} = 1.80$. An A-1 mechanism is ruled out on these grounds. Solvent isotope effect

data for phenylallene, α- and γ-methylphenylallenes as well as related reactions are shown in table 6.

TABLE 6

SOLVENT ISOTOPE EFFECT VALUES FOR PHENYLALLENE HYDRATION AND RELATED REACTIONS AT 25°

Compound	Reaction	$k_{H_3O^+}/ k_{D_3O^+}$	Reference
Phenylallene	Hydration	1.80	This work
α-methylphenylallene		2.00	
γ-methylphenylallene		1.37	
Styrene (H_2SO_4)		2.27	26
Phenylacetylene		2.46	13
Phenylpropyne		2.00	16
Allene		1.75	10
Propyne		1.68	10
Cis-1-propenylpropynyl ether (triple bond hydration)		1.80	20
1-phenyl-1,3-butadiene		2.97	12
Dimethylallenyl acetate	Hydrolysis	1.46	31

If an A-2 mechanism is at work, the solvent isotope effect arises from both the nucleophilicity of the solvent ($k_{H_3O^+}/ k_{D_3O^+} > 1$), and from the equilibrium protonation ($k_{H_3O^+}/ k_{D_3O^+} < 1$).[23] If an Ad_E2 mechanism is at work, the observed solvent isotope effect comes from the differences in zero point energy of the two hydrogen isotopes as well as from secondary isotope effects.[29] Based on solvent isotope effect, it is not yet possible to differentiate between the A-2 and

Ad_E2 mechanisms.

Bunnett and Olsen Parameter

In order to find out whether an A-2 or an Ad_E2 mechanism is at work, the degree of water interaction in the transition state must be determined. If the ϕ values are in the range of +.22 to +.56, water is involved as a nucleophile in the transition state slow step and an A-2 mechanism is established. Values other than these indicate no water interaction ($\phi < 0$), or water as a proton transfer agent ($\phi > +.58$) which are consistent with an Ad_E2 or A-1. Table 7 shows ϕ values for

TABLE 7

BUNNETT AND OLSEN ϕ VALUES FOR SEVERAL REACTIONS AT 25°

Compound	Reaction	ϕ	Mechanism	Reference
Phenylallene	Hydration	-.23	Ad_E2	This work
α-methylphenylallene		-.31		
γ-methylphenylallene		-.43		
m-chlorophenylallene		-.32		
p-methylphenylallene		-.21		
Styrene		-.31		30
Phenylacetylene		-.44		30
1-phenyl-1,3-butadiene		-.31		12
Allene		-.44		10
Propyne		-.53		10
Dimethylallenyl acetate	Hydrolysis	+.60		31
p-methoxy-α-acetoxystyrene		-.12		32

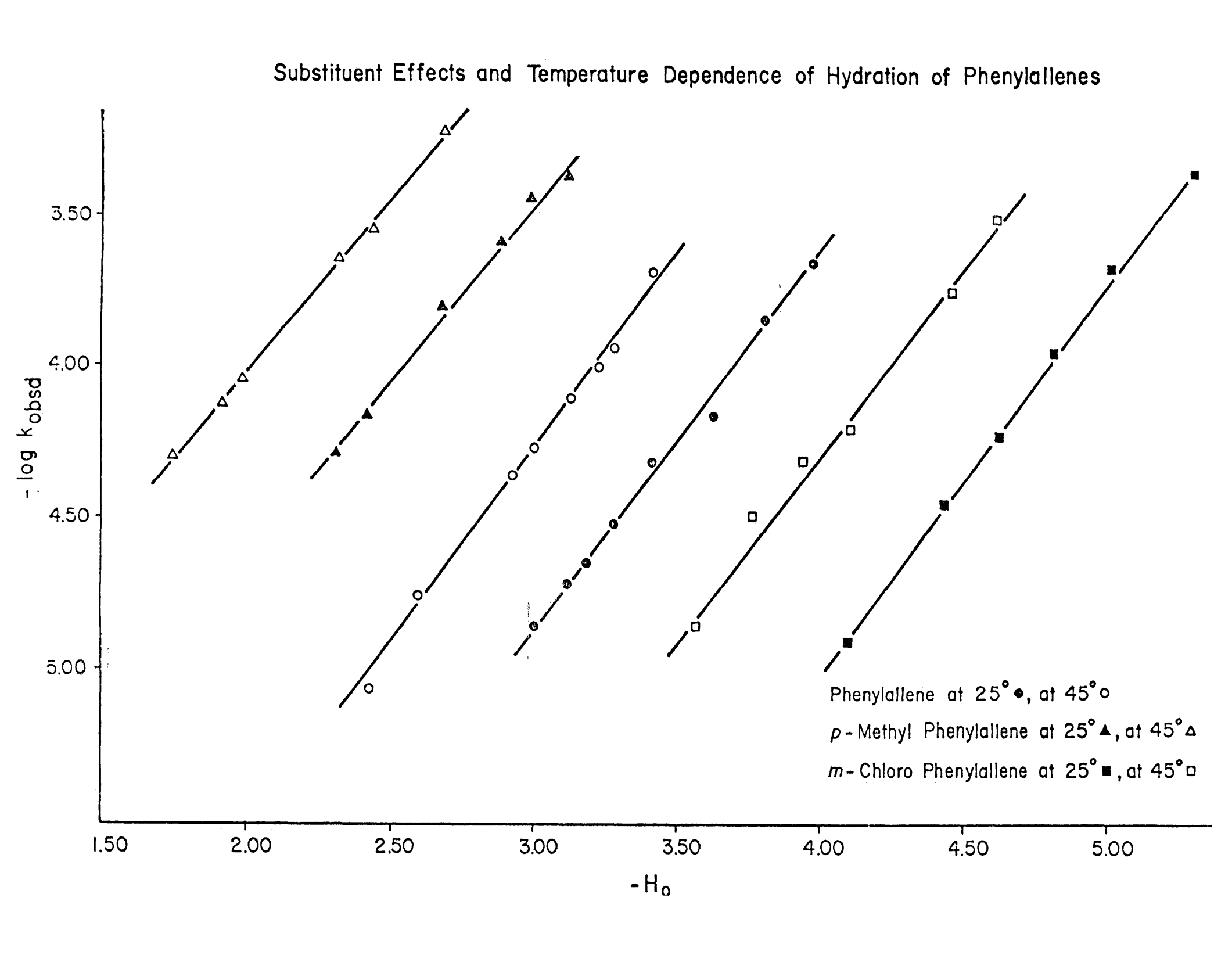
TABLE 7 CONTINUED

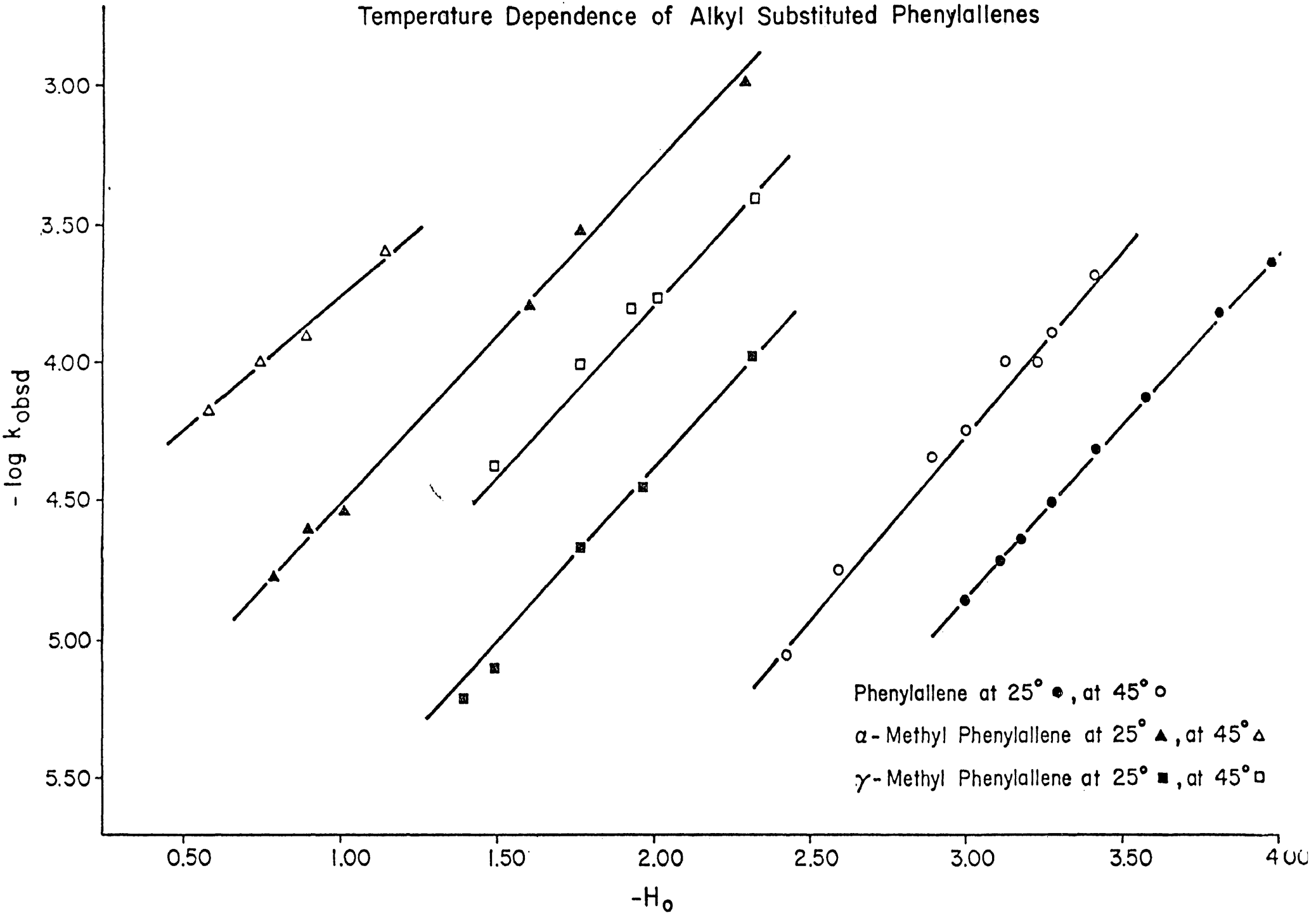
Compound	Reaction	ϕ	Mechanism	Reference
Monomethylallenyl acetate	Hydrolysis	ca. 0	Normal ester	31
α-acetoxystyrene (H_2SO_4 < 55%)		+.14	A-1	32
Ethylacetate		+.84	A-2	9

for several reactions. The ranges of ϕ values are not firmly established. There is also some question in the literature as to the significance of the ϕ values.[33,34] For example, ethylacetate hydrolysis proceeds via an A-2 mechanism in which water is involved as a nucleophile. The ϕ value of +.84 does not show water acting as a nucleophile in the slow step. Dimethylallenyl acetate shows a ϕ value of +.60 which shows water as a proton transfer agent in the slow step. This value is consistent with the reported Ad_E2 mechanism, but the finding of a more positive ϕ value for ethyl acetate shows a discrepancy in ϕ interpretation. There are other similar parameters to show the degree of water participation in the slow step, but like ϕ , none clearly show this participation in all cases. ϕ values for phenylallene hydration are comparable with other Ad_E2 mechanisms such as hydration of styrene and phenylacetylene[30] as well as hydration of 1-phenyl-1,3-butadiene.[12]

Activation Parameters

Thermodynamic activation parameters were calculated from the temperature daependence data at 25 and 45 degrees. Plots of temperature dependence data appear in figures 8 and 9 and activation parameters for


Substituent Effects and Temperature Dependence of Hydration of Phenylallenes
- log k_{obsd}
3.50
4.00
4.50
5.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
5.00
$-H_0$
Phenylallene at 25° ●, at 45° o
p - Methyl Phenylallene at 25° ▲, at 45° △
m - Chloro Phenylallene at 25° ■, at 45° □


Temperature Dependence of Alkyl Substituted Phenylallenes
3.00
3.50
4.00
4.50
5.00
5.50
- log k_{obsd}
0.50
1.00
1.50
2.00
2.50
3.00
3.50
$-H_o$
Phenylallene at 25° ●, at 45° ○
α- Methyl Phenylallene at 25° ▲, at 45° △
γ- Methyl Phenylallene at 25° ■, at 45° □

phenylallene hydration and related reactions appear in table 8 below.

TABLE 8

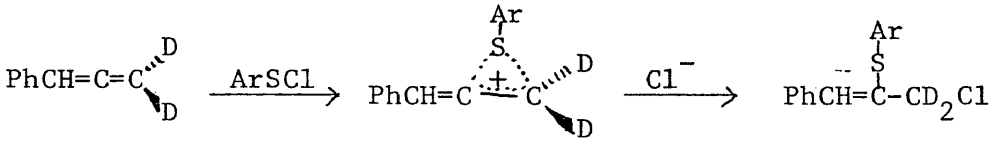
ACTIVATION PARAMETERS FOR PHENYLALLENE HYDRATION AND RELATED REACTIONS AT 25°

Compound and Reaction	$-H_o$	E_{act} kcal/mole	$H^{\ddagger}$ kcal/mole	$S^{\ddagger}$ e.u.	Ref.
Phenylallene Hydration	3.28	13.4	12.8	-36.3	This work
α-methylphenylallene	1.00	15.7	15.1	-28.5	
γ-methylphenylallene	2.00	13.5	12.9	-35.5	
1-phenyl-1,3-butadiene	-2.98	19.3	18.7	-13.0	43
Phenylacetylene	0	21.5	20.9	-18.2	44
Styrene (H_2SO_4)	3.00	18.1	17.5	-13.1	45
Styrene ($HClO_4$)	3.16	20.5	19.9	-5.0	26
p-chlorophenylpropiolic acid	0	23.7	23.1	-22.5	46
phenylbenzoylacetylene	0	18.1	17.5	-27.3	28
m-chlorophenylallene	4.50	15.9	15.3	-27.4	This work
p-methylphenylallene	2.50	14.5	13.9	-30.6	
Phenylallene Hydrochlorination (30°)		20.0	19.4	-12.7	15
Ethoxyallene Hydrolysis		60.7	60.1	-41.8	47
Benzeneboronic acid Protodeboronation	0	18.3	20	-37	48
Cis-cinnamic acid Isomerization	0	25.6	25.0	-21.0	48

The negative entropy of activation values for phenylallene hydration as well as the alkyl and aryl substituted phenylallenes reflect a greater ordering in these systems which is consistent with a bimolecular addition (Ad_E2) reaction.

Isotopic Substitution

Preparation of γ,γ-dideuteriophenylallene was carried out to test for secondary isotope effects. Okuyama and Fueno[19] studied the effect of γ,γ-dideuteration of phenylallene in the electrophilic addition of arenesulphenyl chloride. The observed isotope effect ($k_H/ k_D = .84$) was attributed to rehybridization at the terminal methylene in the slow step of the transition state (α-secondary isotope effect).



Solvent isotope effect in the addition of arene sulphenyl chloride to phenylallene

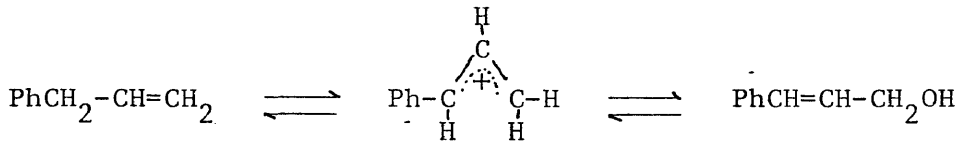
Rehybridization occurs at the terminal methylene due to the attack at the 2,3-double of the allene. Attack is at the external double bond because of steric hindrance. Rehybridization occurs with the formation of a cyclic intermediate much like the intermediate found in the addition of arenesulphenyl chloride to allene.[23]

The observation of an α-secondary isotope effect for phenylallene hydration would be indicative of either slow step protonation at the terminal methylene (Ad_E2) or the presence of the A-2 mechanism (slow

step nucleophilic attack at the terminal methylene). Protonation of the terminal methylene is ruled on the basis of the large negative Hammett ρ value. The developing positive center is orthogonal to the conjugated π-system. Attack by water at the terminal methylene in the slow step would give cinnamyl alcohol which is a likely product of hydration of phenylallene. In the hydration of phenylallene, no secondary isotope effect was observed from γ,γ-dideutero substitution. This finding rules out the A-2 mechanism for phenylallene hydration.[35] A β-secondary isotope effect represents another possibility for rate changes in hydration through hyperconjugation. This effect may be observed in an Ad_E2 mechanism such as in dimethylallenyl acetate hydrolysis ($k_H/ k_D = 1.07$), but it was not observed in phenylallene hydration ($k_H/ k_D = 1.00$).

Rearrangement of Product

The possibility of α-phenylallyl alcohol forming via an A-2 or Ad_E2 mechanism has not been discussed. If this produst does form in the slow step of the transition state and then rearrange, the measured rate may be that of rearrangement as a slow step. This possibility



Rearrangement of α-phenylallyl alcohol

was ruled out by the observation of Goering and Dilgren[36] that

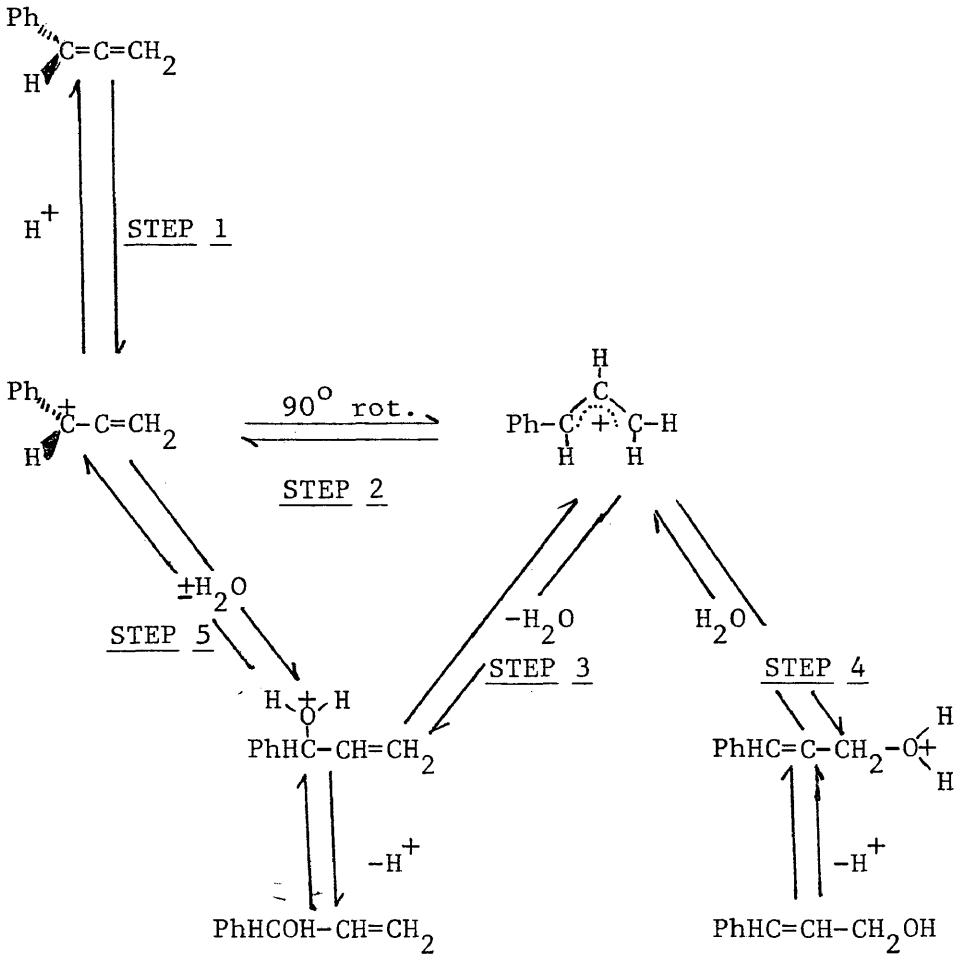
α-phenylallyl alcohol rearranged in $HClO_4$ at a rate of 1×10^3 sec^{-1} (25^o, 40% aqueous dioxane, $H_o = -3.50$). The rate of phenylallene hydration of 5.5×10^{-5} sec^{-1} under similar conditions shows that the acid-catalyzed rearrangement is not the slow step in hydration (10^8 difference). If α-phenylallyl alcohol is the product of hydration, it can be formed either by an A-2 mechanism or an Ad_E2 mechanism. The rearrangement would not be the slow step and the observation of cinnamyl alcohol as a product would be expected (as well as some α-phenylallyl alcohol). Formation of α-phenylallyl alcohol is less favored for steric reasons. Attack on the α-carbon by water is hindered by the aromatic ring. Formation of α-phenylallyl alcohol is also less favored than formation of cinnamyl alcohol since conjugation of the π-bond with the aromatic ring is maintained. Several possibilities for phenylallene hydration are presented in the reaction scheme in figure 10.

If step 1 is the slow step then an Ad_E2 mechanism is at work. A normal solvent isotope effect would be observed as well as a large negative entropy, a large negative ρ, and the absence of an isotope effect for γ,γ-dideutero substitution. If step 2 is the slow step, an inverse solvent isotope effect would have been observed. Step 2 is ruled out by the observation of a normal solvent isotope effect. Step 4 is eliminated based on the absence of an isotope effect upon γ,γ-dideuteration. Step 3 is not a likely slow step since the allylic intermediate favors the formation of cinnamyl alcohol by step 4.[12,36]

Slow carbonium ion collapse with water (5) is consistent with an A-2 mechanism. Noyce and Jorgenson[37] found an A-2 mechanism in the acid-catalyzed isomerization of p-chloro and p-nitro-cis-chalcones. Evidence included an inverse solvent isotope effect (not a condition

FIGURE 10

REACTION SCHEME



for an A-2), non-linearity of the plot of log k_{obsd} versus H_o, and a small negative ρ (-1). For p-methoxy-cis-chalcone, an A-1 mechanism was proposed due to linearity of log k_{obsd} with H_o (plot), an inverse solvent isotope effect, and an only slightly negative entropy. The observed large negative ρ value for phenylallene hydration, the linearity of the plot of log k_{obsd} with H_o, and the normal solvent isotope effect all indicate that slow proton transfer (an Ad_E2 mechanism) is the slow step. Phenylacetylene,[13] styrene,[14] and α-methylstyrene hydrations all show similar values (ρ, linear log k_{obsd} vs. H_o, and solvent isotope effect >1) to phenylallene hydration and hydrochlorination and all proceed via the Ad_E2 mechanism.

Relative Rates

Relative rates of hydration of phenylacetylene, styrene, and phenylallene are shown in table 9. This data shows phenylallene

TABLE 9

RELATIVE RATES OF HYDRATION OF PHENYLACETYLENE, STYRENE, AND PHENYLALLENE AT 25°

Compound	Relative Rate (H_o=-3.0)
Phenylacetylene	125
Styrene	101
Phenylallene	1

hydration to proceed at least 100 times slower than styrene and phenyl-

acetylene hydration. The relative rates for alkyl-substituted phenylallenes in both the hydration and hydrochlorination reactions are shown in table 10. The methyl substituent at the α-carbon enhances

TABLE 10

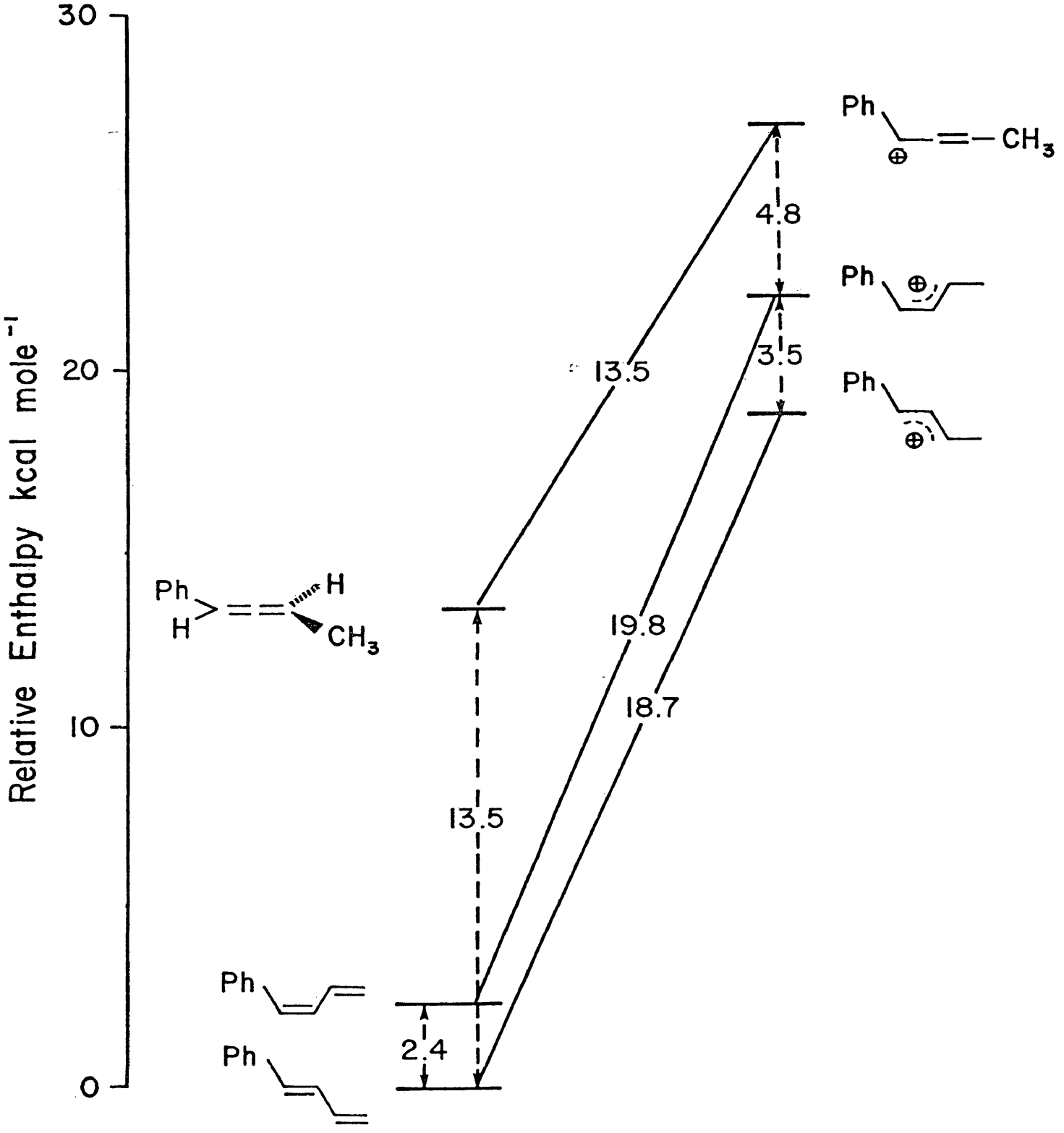
RELATIVE RATES OF HYDRATION AND HYDROCHLORINATION OF ALKYL-SUBSTITUTED PHENYLALLENES

Compound	Relative Rates	
	Hydration (25°)	Hydrochlorination (30°)
Phenylallene	1	1
α-methylphenylallene	619	4000
γ-methylphenylallene	54	20

the rate 600-fold in hydration and 4000-fold in hydrochlorination. The greater enhancement from α-substitution is consistent with an electron-deficient carbon at the alpha position. The observation of rate enhancement from γ-substitution is not expected if the intermediate carbonium ion is the perpendicular cation 5 since the methyl group would be orthogonal to the developing positive center. The observed rate enhancement from γ-substitution in both hydration and hydrochlorination indicates interaction of the methyl group at the gamma position which would be observed if the perpendicular cation is partially rotated.

Okuyama et al[38] calculated the relative enthalpies for cis- and trans-butadienes as well as for γ-methylphenylallene. Enthalpy values for cis- and trans-allylic cations and the perpendicular allylic cation

Figure 11 Enthalpy Diagram for Phenylallene and Phenylbutadiene Hydration at 25°



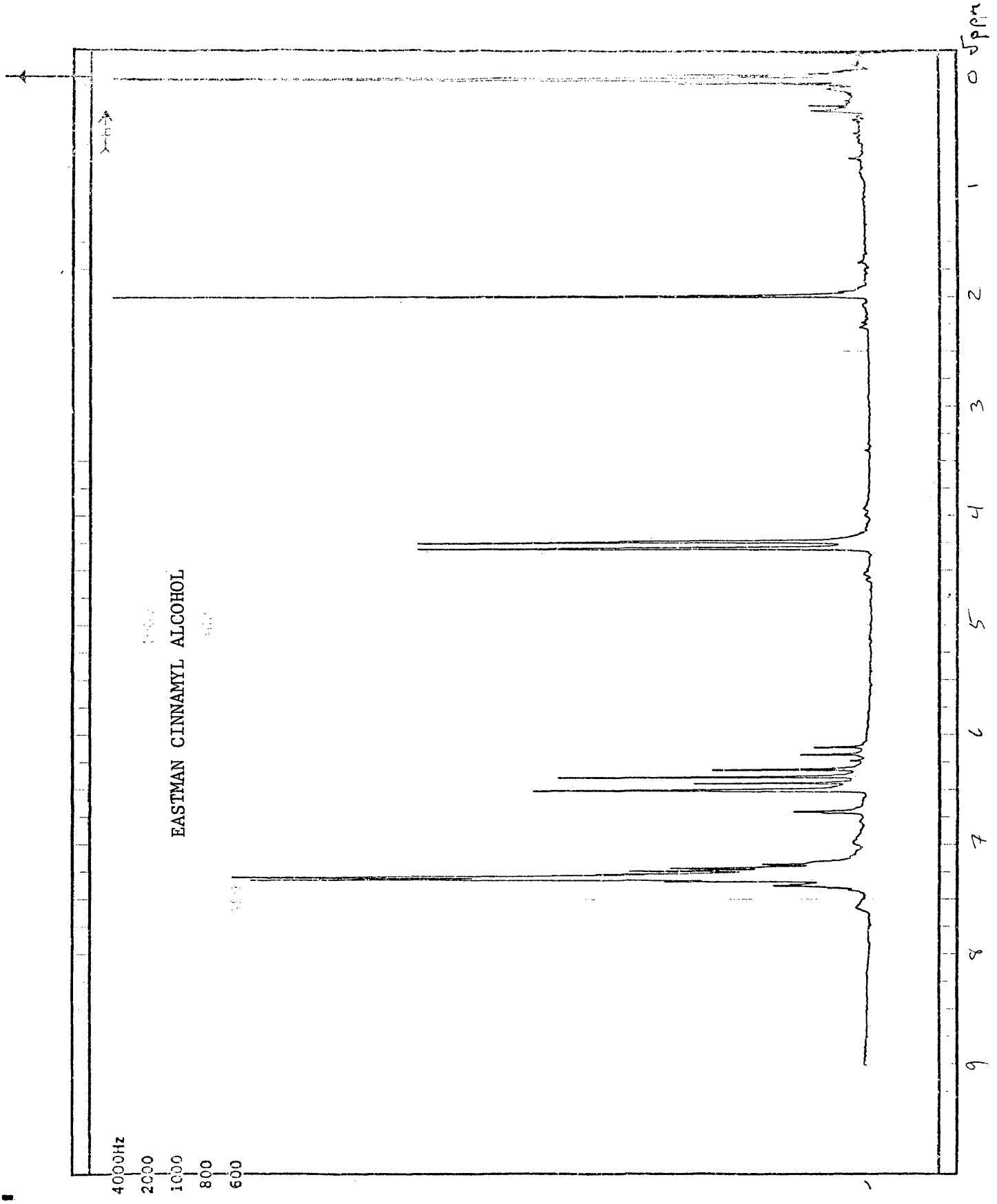
were also calculated. These relative enthalpies are shown in figure 11. The enthalpy difference between the cis-allylic and perpendicular allylic cations was calculated to be 7.6 kcal. mole^{-1}. The observed enthalpy of activation for phenylallene hydration is only 4.8 kcal mole^{-1} higher in energy than that expected for formation of the cis-allylic cation. Apparently, the degree of rotation of the perpendicular cationic intermediate in phenylallene hydration is great enough to allow a stabilization of about 2.8 kcal mole^{-1}. 1-phenyl-1,3-butadiene hydrates 90 times faster than its isomer α-methylphenylallene. This rate difference would probably be even greater if the cation in γ-methylphenylallene hydration was not stabilized by this partial rotation. In changing from γ- to α-substitution, an 11-fold rate increase is observed in hydration, whereas, the hydrochlorination reaction shows a 20-fold increase. The smaller difference in hydration shows that the γ-methyl is able to interact more in hydration than in hydrochlorination. This may indicate a greater degree of rotation in the hydration reaction. This may also arise from solvent differences.

CONCLUSIONS

Phenylallene hydrates by a slow proton transfer (Ad_E2 mechanism). The perpendicular cation that forms is partially rotated, which results in stabilization of the transition state. The cation then proceeds to react with water probably through an allylic intermediate in several subsequent fast steps. The product formed is the same product which is observed when cinnamyl alcohol is exposed to the same reaction conditions which shows cinnamyl alcohol to be a likely product. It is interesting to note that phenylallene does not react like phenylacetylene to give a vinyl cation, nor does it react like styrene to give a benzyl cation. Phenylallene reacts more like 1-phenyl-1,3-butadiene which gives an allylic intermediate. The difference between phenylallene and the phenyl-1,3-butadiene arises since the butadiene forms the allylic cation directly on protonation. The phenylallene forms a perpendicular cation on protonation which then must rotate to give an allylic cation.

The mechanism of phenylallene hydration is consistent the expected chemical behavior of cumulenes. To further look at the hydration reaction, other ring-substituted phenylallenes should be studied. Introduction of a nitro group in the para position may change the reaction mechanism by destabilizing the transition state cation. Another useful study would be to substitute a deuterum on the α-carbon to observe any rate changes.

APPENDIX A


EASTMAN CINNAMYL ALCOHOL
4000Hz
2000
1000
800
600
0 δppm
1
2
3
4
5
6
7
8
9

INDENE

IR 1012

C_9H_8 Mol. Wt. 116.16

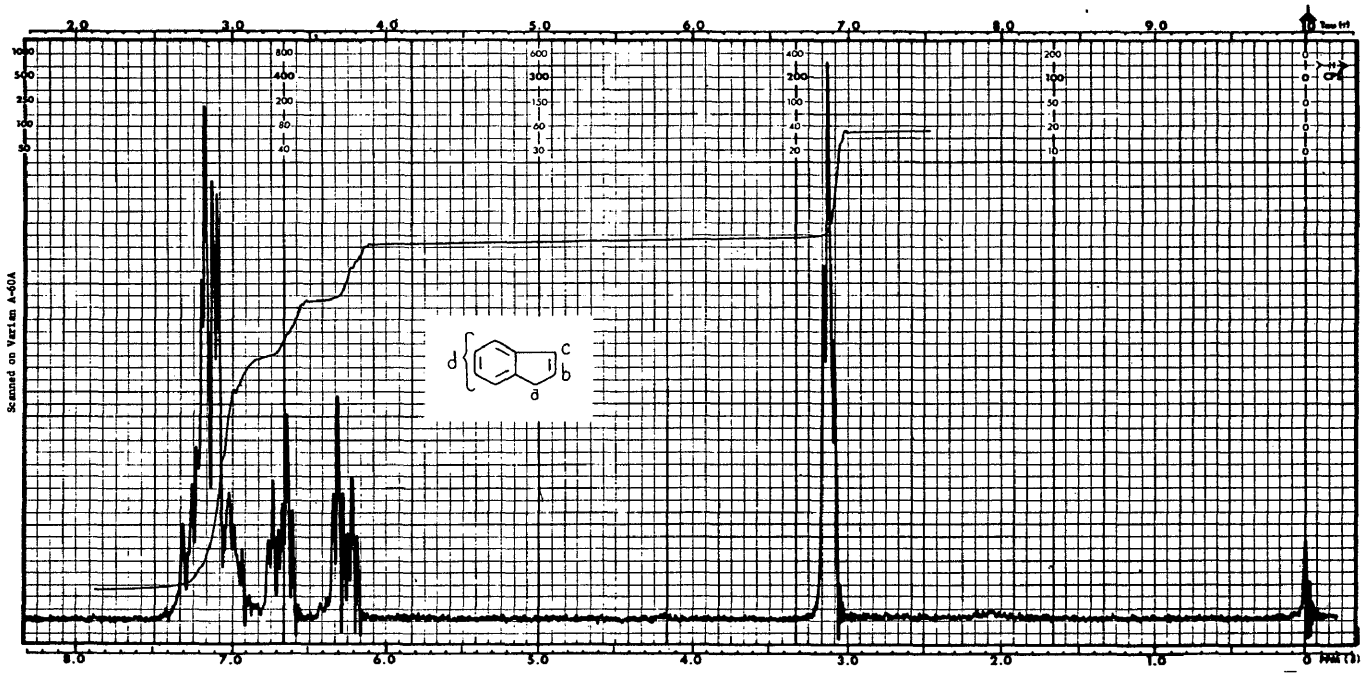
Source: Neville Chemical Company,
Neville Island, Pittsburgh, Pa.

Filter bandwidth:	4	Hz
Sweep time:	250	sec
Sweep width:	500	Hz
Sweep offset:	-	Hz
Spectrum amp:	12.5	
Integral amp:	80 (spec. amp. 1.25)	
Solvent:	CCl_4	

ASSIGNMENTS

a	3.12	h	
b	6.28	i	
c	6.68	j	
d	6.90-7.40	k	
e		l	
f		m	
g		n	

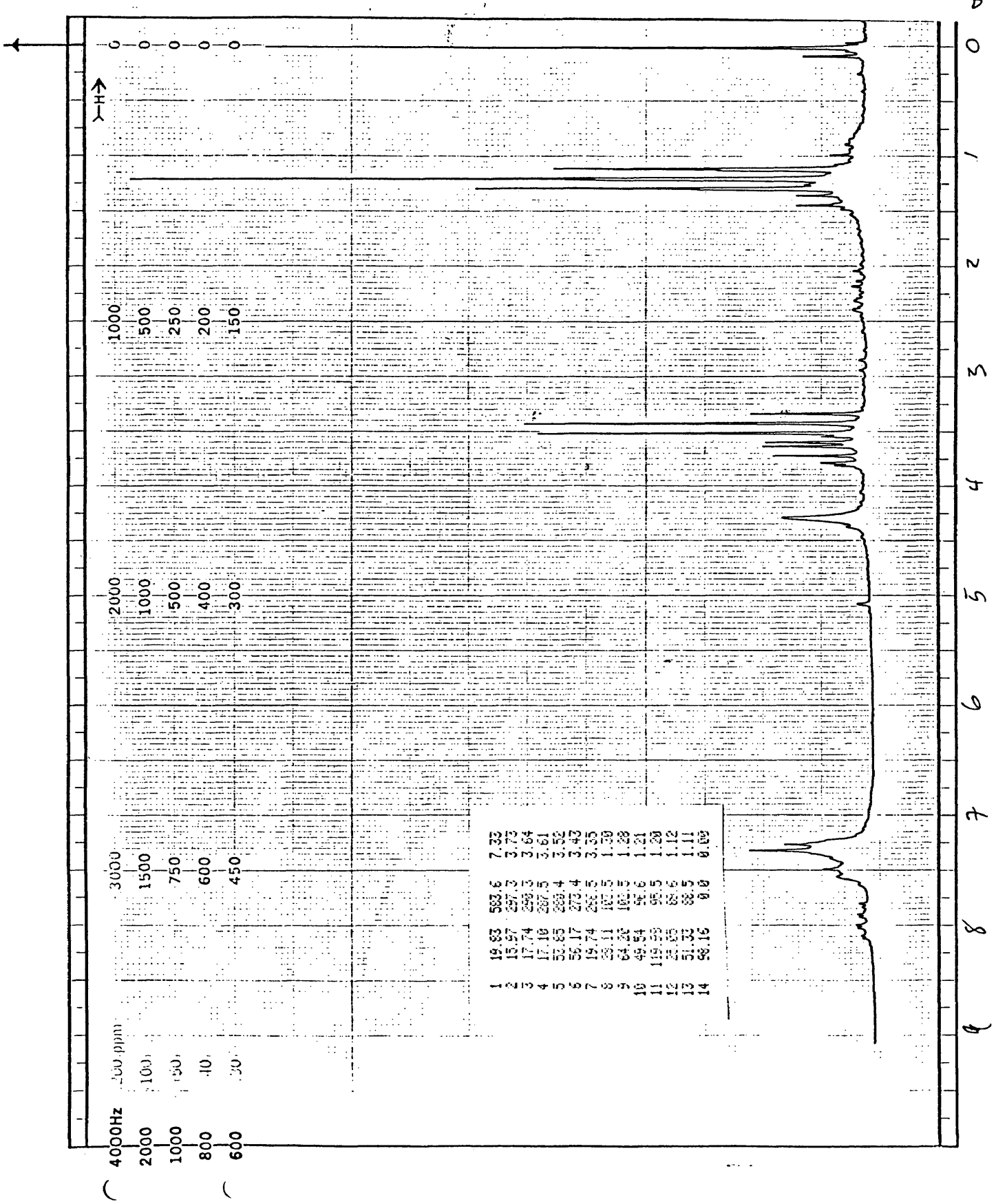
N.M.R.
© 1971



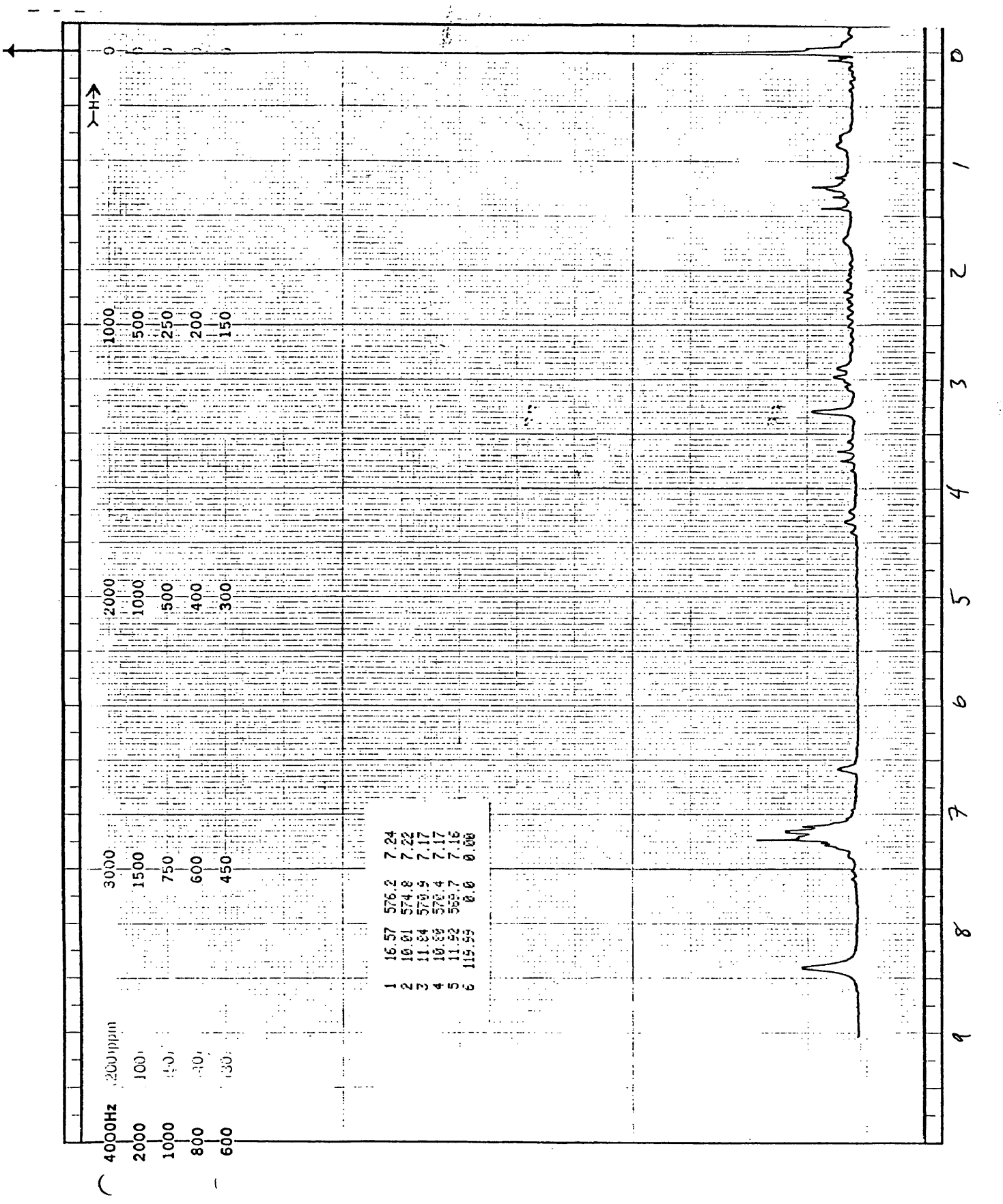
10408M

γ-METHYLPHENYLALLENE HYDRATION PRODUCT

(Ether Extract)

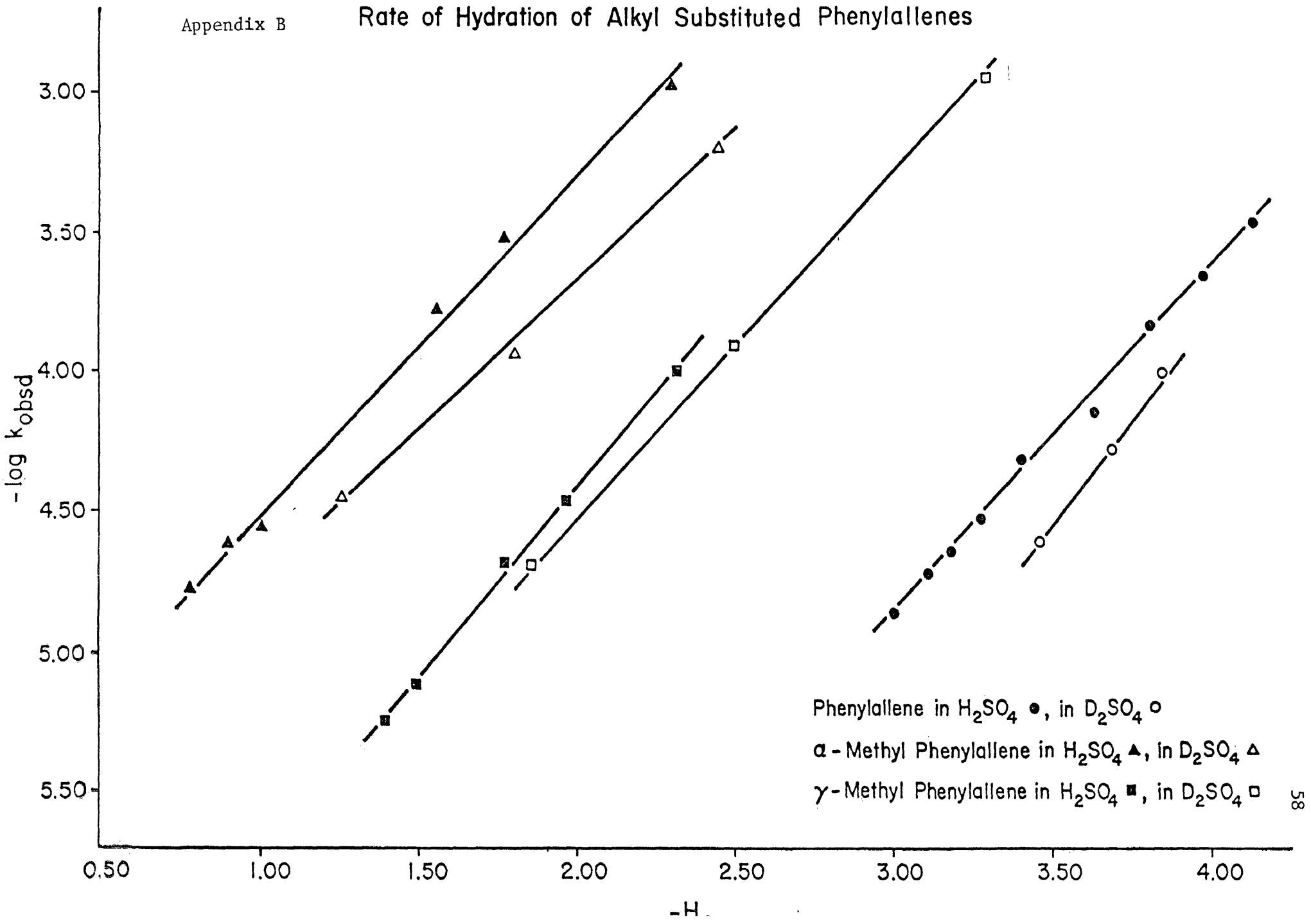


INDENE HYDRATION PRODUCT (Ether Extract)



APPENDIX B

Appendix B


Rate of Hydration of Alkyl Substituted Phenylallenes
3.00
3.50
4.00
4.50
5.00
5.50
-log k_{obsd}
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
-H
Phenylallene in H_2SO_4 ●, in D_2SO_4 ○
α-Methyl Phenylallene in H_2SO_4 ▲, in D_2SO_4 △
γ-Methyl Phenylallene in H_2SO_4 ■, in D_2SO_4 □

REFERENCES AND NOTES

(1) For review see: (A) K. Griesbaum, Angew. Chem.(Int'l. Eng. Ed.), 5, 933 (1966). (B) R. Taylor, Chemical Reviews, 67, 317 (1967). (C) P. Blake, The Chemistry of Allenes, Ketenes, and Related Compounds, John Wiley and Sons: New York, part 1, 1980, p. 350.

(2) L. Radom, P. C. Hariharan, J. A. Pople, and P. R. Schleyer, J. Am. Chem. Soc., 95, 6531 (1973).

(3) D. H. Aue, W. R. Davidson, and M. T. Bowers, ibid, 98, 6700 (1976).

(4) P. J. Stang, Progress in Physical Organic Chemistry, 10, 205 (1973).

(5) W. R. Dolbier and B. H. Al-Sader, Tetrahedron Letters, 26, 2159 (1975).

(6) A. Streitweisser, Jr., R. H. Jagow, R. C. Fahey, and S. Suzuki, J. Am. Chem. Soc., 80, 2327 (1958).

(7) For review see: M. Liler, Reaction Mechanisms in Sulphuric Acid, Academic Press: New York, 1971, pp. 168-180.

(8) Entropy of activation is only slightly positive since the overall entropy arises from a combination of proton addition (negative entropy) and decomposition (positive entropy).

(9) J. F. Bunnett and F. P. Olsen, Can. J. Chem., 44, 1917 (1966).

(10) T. T. Tidwell and P. Cramer, unpublished communication.

(11) E. A. Braude and E. S. Stern, J. Chem. Soc., 1947, 1096.

(12) Y. Pocker and M. J. Hill, J. Am. Chem. Soc., 91, 3243 (1969).

(13) D. S. Noyce and M. D. Schiavelli, ibid, 90, 1020 (1968).

(14) W. M. Schubert and B. Lamm, ibid, 88, 120 (1966).

(15) T. Okuyama, K. Izawa, and T. Fueno, ibid, 95, 6749 (1973).

(16) D. S. Noyce and M. D. Schiavelli, J. Org. Chem., 33, 845 (1968).

(17) H. C. Brown and Y. Okamoto, J. Am. Chem. Soc., 79, 1913 (1957).

(18) N. C. Deno, F. A. Kish, and H. J. Peterson, ibid, 87, 2157 (1965).

(19) T. Okuyama and T. Fueno, ibid, 95, 4090 (1973).

(20) W. Drenth and E. T. Stamhuis, Recl. Trav. Chim. Pays-Bas, 82, 394 (1963).

(21) Cinnamyl alcohol, Eastman Organic Chemicals, Rochester 3, New York.

(22) Practical Indene, Matheson, Coleman, and Bell.

(23) See introduction.

(24) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, J. Am. Chem. Soc., 82, 4729 (1960).

(25) H. C. Brown and Y. Okamoto, ibid, 79, 1913 (1957).

(26) W. M. Schubert and J. R. Keefe, ibid, 94, 559 (1972).

(27) D. S. Noyce, M. Matesich, and P. E. Peterson, ibid, 89, 6225 (1967).

(28) B. S. Noyce and K. E. DeBruin, ibid, 90, (1968), 372.

(29) C. A. Bunton and V. J. Shiner, Jr., ibid, 83, 3214 (1961).

(30) G. Modena, F. Rivetti, G. Scorrano, and U. Tonellato, ibid, 99, 3392 (1977).

(31) D. J. Scheffel, A. R. Cole, D. M. Jung, and M. D. Schiavelli, ibid, 102, 267 (1980).

(32) D. S. Noyce and R. M. Pollack, ibid, 91, 119 (1969).

(33) See ref. 7, page 175.

(34) C. H. Rochester, Acidity Functions, Academic Press: New York,1970, p. 123.

(35) Given the condition that the product of phenylallene hydration is cinnamyl alcohol, an A-2 mechanism gives rise to an -secondary isotope effect.

(36) H. L. Goering and R. E. Dilgren, J. Am. Chem. Soc., 82, 5744 (1960).

(37) D. S. Noyce and M. J. Jorgenson, ibid, 83, 2525 (1961).

(38) K. Izawa, T. Okuyama, T. Sakagami, and T. Fueno, ibid, 95, 6752 (1973).

(39) W. von E. Doering, and A. K. Hoffmann, ibid, 76, 6162 (1954).

(40) L. Skattebol, Acta. Chem. Scand., 17, 1683 (1963).

(41) H. C. Brown and S. K. Gupta, J. Am. Chem. Soc., 94, 4370 (1972).

(42) D. F. De Tar, Computer Programs for Chemistry, 1, 117 (1968).

(43) See ref. 12.

(44) M. D. Schiavelli, Ph. D. Thesis, The University of California at Berkeley, 1968.

(45) J. Durand, M. Davidson, M. Hellin, F. Coussemat, Bull. Soc. Chim. Fr., 1966, 57.

(46) See ref. 27.

(47) I. DeJonge and W. Drenth, Rec. Trav. Chim. Pays-Bas, 92, 420 (1973).

(48) M. A. Matesich, J. Org. Chem., 32, 1258 (1967).

(49) See Appendix B for plot of rate of hydration of alkyl-substituted phenylallenes

VITA

GARY WAYNE LONG

Born in Newport News, Virginia, June 29, 1957. Graduated from York High School in Yorktown, Virginia, June, 1975, B.S., Christopher Newport College, 1979, M.A. candidate, College of William and Mary, 1979-1981, with a concentration in Chemistry. During the time at William and Mary, the author was a teaching assistant in Analytical Chemistry under Drs. C. Djorjevic and S. Y. Tyree, and in Organic Chemistry under Dr. T. B. Hill. Research assistance work was carried out during one summer and one semester under Dr. M. D. Schiavelli. The author will enter the University of Texas at Austin to pursue a Ph. D. in Synthetic Organic Chemistry beginning in June, 1981.