HYDRATION STUDIES OF SUBSTITUTED STYRENES

by

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Abstract

The rates of hydration of styrene, p-cyclopropylstyrene, p-divinylbenzene, α,p-styrylethanol, m-divinylbenzene, and α,m-styrylethanol were studied in 3.83 M perchloric acid at 25°C. The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values for p-cyclopropylstyrene at 25° C were 19.3 Kcal/mole and -8.0 e.s.u., respectively. The σ^{+} values for each of these substituents were found to be -0.439 for p-cyclopropyl, -0.152 for p-vinyl, -0.046 for p-hydroxyethyl, +0.146 for m-vinyl, and +0.059 for m-hydroxyethyl.

The data for p-cyclopropylstyrene substantiates a previous conclusion that the cyclopropyl substituent interacts by a resonance mechanism and that hybridization change of the reacting carbon is an insignificant factor in these reactions.

Introduction

The structure of carbonium ions in solution constitutes an active field of research.[1,2] Of primary concern to many chemists is the nature of bonding in carbonium ions. The stimulation for research into carbonium ion structure involving certain cyclic systems was initiated by Meerwein,[3] who studied the rearrangement of camphene 1 to isobornyl chloride 2. To account for the observed results in this
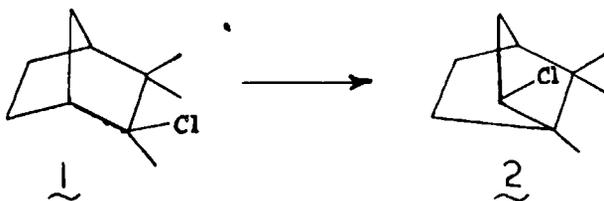
rearrangement, Wilson[4] suggested that the carbonium ion formed after the departure of the chloride ion might be represented as 3 and 4, and that 3 and 4 must be equilibrating rapidly.
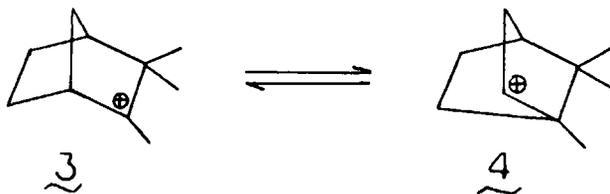
Furthermore, he suggested that 3 and 4 might be considered to be a mesomeric species which is represented by 5. Carbonium ions which can be depicted like 5 are called nonclassical carbonium

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$\underset{\sim}{5}$
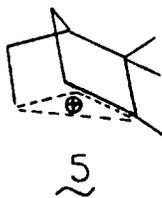
ions. Bartlett[1] has defined such an ion as follows: "An ion is nonclassical if its ground state has delocalized bonding σ-electrons."

Although the camphene chloride-isobornyl chloride problem still remains unsettled,[5,6] the nonclassical ion concept prevails and has successfully explained various experimental results[1,2] involving enhanced solvolysis rates, stereochemical results, radioactive labeling data, etc.

The cyclopropylcarbinyl system[7,8,9] is one of the most familiar systems in nonclassical ion studies. The enhanced rate of solvolysis observed in these systems can be explained in terms of the nonclassical ion concept which is similar to hyperconjugation.[10] In hyperconjugation, the p-orbital of the cationic carbon overlaps with the σ-bonding orbital of an adjacent carbon atom in the same plane. Roberts, Bennett and Armstrong[11] illustrate hyperconjugative stabilization as follows:

●   Carbon

Ⓡ   Alkyl group

o   Hydrogen

Hyperconjugation differs from nonclassical ion participation mainly

in that the electrons in the latter are more mobile due to strained

spatial arrangement of the carbon atoms. As pointed out by Gould:[12]

"The regions of maximum electron density (in the cyclopropyl ring)

lie well outside the ring instead of on the straight lines connecting

the carbon nuclei." These electrons are therefore capable of

anchimeric assistance[13] which is responsible for the enhanced

rate of solvolysis. If the anchimeric assistance interpretation is

correct, electron delocalization will give rise to a more stable

transition state, consequently, the enhanced rate of solvolysis

can be accounted for.

Brown,[6,14,15] however, is not satisfied with the anchimeric

assistance interpretation, but believes that relief of steric

strain associated with the change in hybridization of the reacting

carbon atom on going from reactant to product is an alternative

explanation which can account for the enhanced rate of solvolysis

in this and other systems.

It is therefore desirable to investigate the cyclopropyl-carbinyl system more thoroughly in the hope of throwing further light on the nature of the electronic interactions of the cyclopropyl substituents.

Discussion

The enhanced rate[7,8,9] of solvolysis observed in the cyclopropylcarbinyl system can very well be explained as being due to the relief of steric strain.[6] However, if the reaction center is farther remote from the cyclopropyl ring, the relief of steric strain effect should be less pronounced than in those systems in which reaction centers are located next to the cyclopropyl ring. In considering such a factor, the best model for testing the steric effect in the nonclassical resonance interaction seems to be 8, cyclopropylbenzene with any desirable reaction center
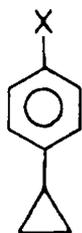
X=any desirable reaction center

attached <u>para</u> to the cyclopropyl group. Model 8 provides the desirable location of the reaction center which is remote to the cyclopropyl ring and therefore it minimizes any steric interaction effect between the two groups, but it facilitates the continuity of any electronic effect by transmitting it through the benzene ring.

Recently, Jones and Jones[16] studied the solvolysis reaction of <u>p</u>-cyclopropylphenyldimethylcarbinyl chloride.

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They pointed out that the data for the p-cyclopropyl substituent

indicate too large a rate enhancement of the electron supplying

ability of this group as compared to any other alkyl groups to

be explained by the normal hyperconjugation interpretation, and

that the data indicate that nonclassical ion participation by

the cyclopropyl group took place in the rate determining step.

This participation in valence bond terminology can be visualized

as follows:
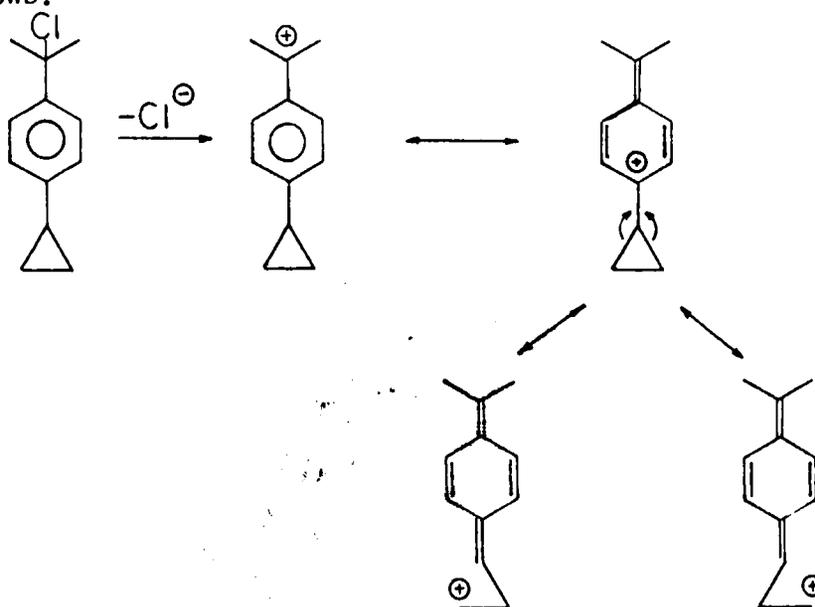
i.e., the empty p-orbital created by the departure of the chloride

ion interacts with the σ-bonding electrons of the cyclopropyl

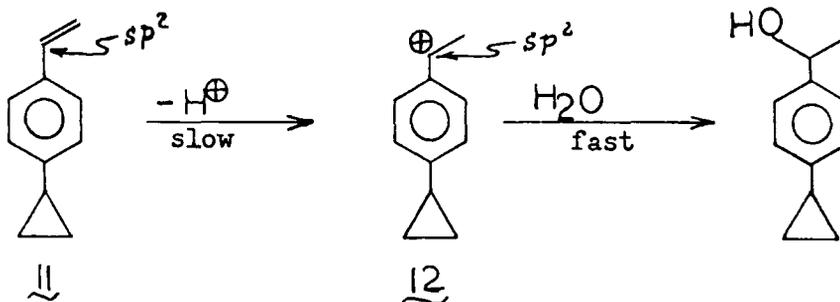ring through the π-electrons of the benzene ring.

Nevertheless, one may still argue that the enhanced rate

of solvolysis of p-cyclopropylphenyldimethylcarbinyl chloride is

not entirely due to the electron supplying ability of the cyclo-
propyl group; one may argue that the change in hybridization of
the orbitals of the reacting carbon can be responsible for the
rate enhancement.[17] As is shown below, the reacting carbon atom
in 9 has an $\underline{sp}^3$ configuration (bond angle $109\frac{1}{2}°$), and the reacting
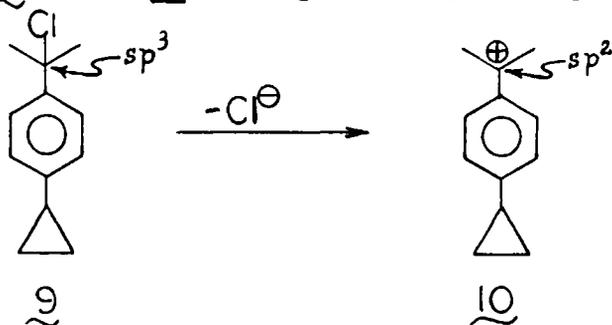
carbon atom in 10 has an $\underline{sp}^2$ configuration (bond angle 120°).

To clarify the hybridization effect, the hydration of
p-cyclopropylstyrene 11 was studied. The protonation of p-cyclo-

propylstyrene, 11, gives rise to 12. Yet no change in hybrid-
ization of the two reacting carbons occurs. Schubert, Lamm and
Keeffe[18] presented evidence that the rate-controlling protonation
of styrene from $H_3\overset{\oplus}{O}$ gives the carbonium ion directly, $\underline{i.e.}$,

$$H_3\overset{\oplus}{O} + PhCH=CH_2 \longrightarrow H_2O + Ph\overset{\oplus}{C}H-CH_3 \xrightarrow{-H^{\oplus}} PhCH-CH_3$$
$$\underset{OH}{}$$

but not

$$H_3\overset{\oplus}{O} + PhCH=CH_2 \rightleftharpoons H_2O + [Ph\overset{\overset{\overset{H}{\diagup}}{\oplus}}{C}H\text{---}CH_2] \xrightarrow{-H^{\oplus}} PhCH-CH_3$$
$$\underset{OH}{}$$
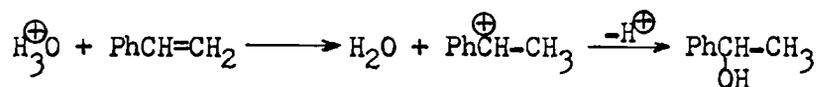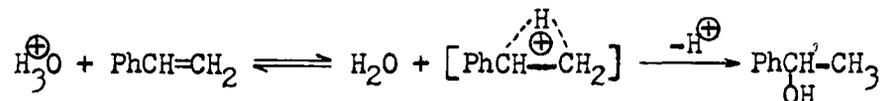
Therefore, it can be seen that any rate enhancement observed as compared with the unsubstituted styrene will be mainly due to electronic effects.

Hydration studies of p-cyclopropylstyrene were carried out at 25°, 9° and 0° C using 31.86% (3.83 M) perchloric acid solution. The rate of hydration of p-cyclopropylstyrene at any other temperature can be extrapolated by plotting the rate vs. the absolute temperature shown in Table I.

Table I

Rate of Hydration of p-Cyclopropylstyrene in 31.86% (3.83 M) Perchloric Acid at Different Temperatures with $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ Calculated at 25° C

Temperature °C	$10^4 k_{obsd} sec^{-1}$	$\Delta H^{\ddagger}$ (Kcal/mole)	$\Delta S^{\ddagger}$ (e.s.u.)
25	7.04±0.14	19.3	-8.01
9	1.08±0.04		
0	0.327±0.006		

When p-cyclopropylstyrene is subjected to an acidic environment, there is a possibility that the cyclopropyl ring may be opened to give p-propenylstyrene 13.
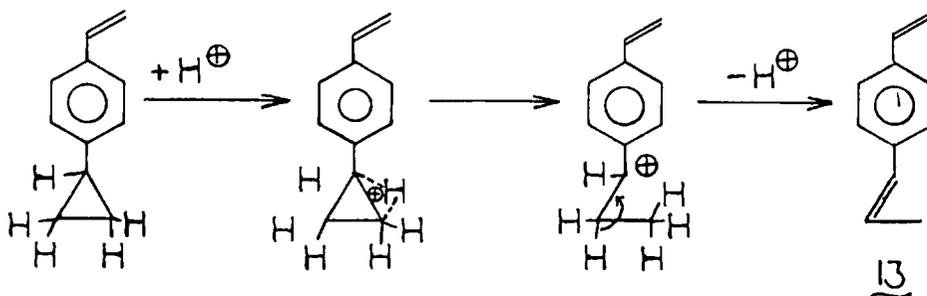
It was assumed that the shape of the ultraviolet spectra of p-2-propenylstyrene and p-divinylbenzene should be very similar to each other. p-Divinylbenzene was chosen for study because it is readily available by separating the commercial product.[19] It was observed that p-cyclopropylstyrene shows a unique spectrum throughout the course of the kinetic measurement with λ_{max} around 260 mμ. This spectrum is different from that obtained from ,p-divinylbenzene, which has a λ_{max} around 280 mμ. Two rates of hydration of p-divinylbenzene were obtained.

λ_{max} 279 mμ

k_1=rate of protonation of p-divinylbenzene

λ_{max} 252 mμ

k_2=rate of protonation of α,p-styrylethanol
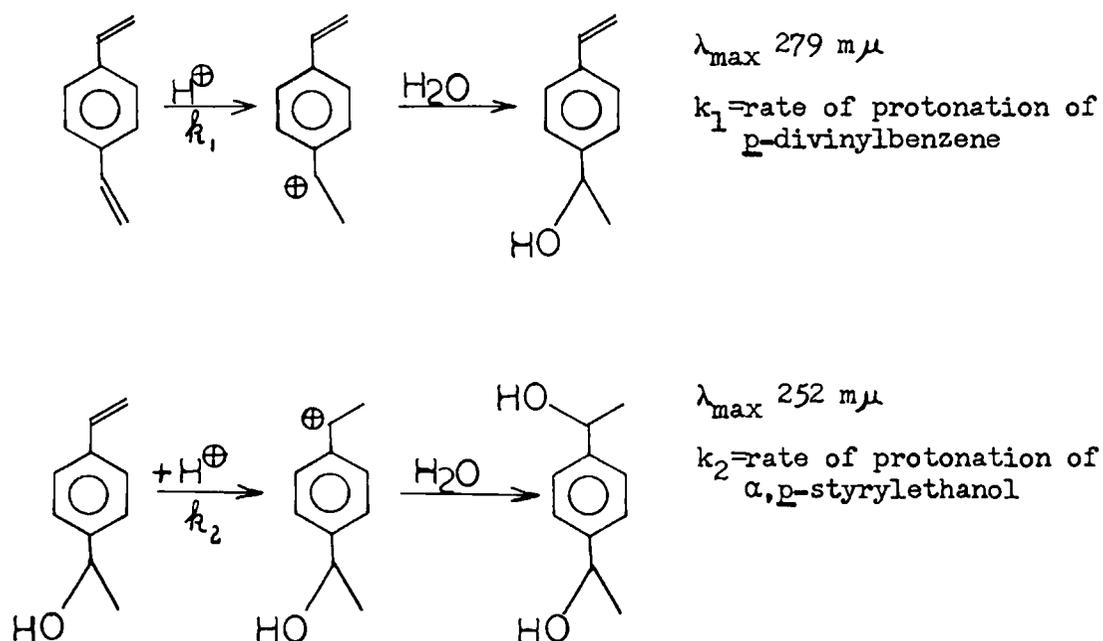
m-Divinylbenzene was also studied to see what kind of effect the meta-ethylene group may exert on the styrene. Attempts were made to obtain the two rates, namely:

λ_{max} 239 mμ

k_3=rate of protonation of m-divinylbenzene

λ_{max} 239 mμ

k_4=rate of protonation of α,m-styrylethanol
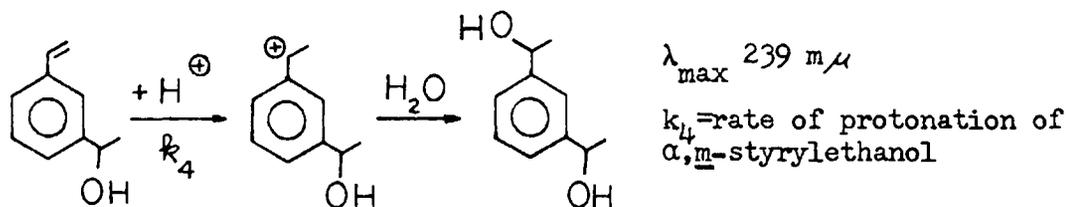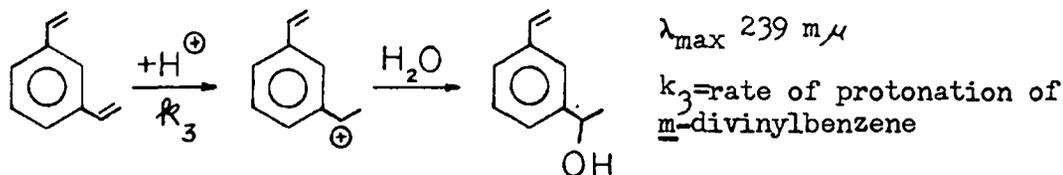
However, no break on the slope of the log Optical Density vs. Time plot was observed. This is apparently due to the fact that k_{3obsd}=k_4 and therefore the second stage of the hydration reaction, k_4, occurred at the same apparent rate as the first stage, k_3.

The rate data and calculated σ^+ values of the compounds studied are listed in Table II. The hydration rates of m- and p-divinylbenzene listed have been corrected for the symmetry factor. The ρ value for this reaction is -3.42.[18]

Table II

Rates of Hydration of Styrene, p-Cyclopropylstyrene, p-Divinylbenzene, α,p-Styrylethanol, m-Divinylbenzene, and α,m-Styrylethanol in 3.83 M $HClO_4$ and the Corresponding σ^+ Values

Compound	$10^4 k_{obsd} \ sec^{-1}$	σ^+
Styrene[a]	0.222±0.003	0.0
p-Cyclopropylstyrene	7.040±0.14	-0.439
p-Divinylbenzene	0.735±0.01	-0.152
α,p-Styrylethanol	0.319±0.004	-0.046
m-Divinylbenzene	0.070±0.003	+0.146
α,m-Styrylethanol	0.140±0.049	+0.059

[a]Agrees with the value reported by Schubert, Lamm and Keeffe[18]

From Table II, p-cyclopropylstyrene is shown to be 32 times more reactive than the model compound styrene; 9.6 times faster than p-divinylbenzene; 22 times faster than α,p-styrylethanol; 101 times faster than m-divinylbenzene and 50 times faster than α,m-styryl-ethanol. This observed marked rate enhancement along with a large degree of electron supplying ability σ^+ value of -0.439, does point to the fact that the p-cyclopropyl group is indeed capable of strong resonance interaction which helps in stabilizing the transition state of the solvolysis reaction by using its σ-bonding electrons to overlap with the p-orbitals of the aromatic ring. The data

indicate that the effect of hybridization change at the reaction center in the solvolysis of the p-cyclopropylphenylcarbinyl systems is insignificant and that the rate enhancement is mainly due to the electronic effect because, within experimental error, the σ^+ value of -0.439 for a p-cyclopropyl substituent obtained from the hydration of p-cyclopropylstyrene agrees with the σ^+ value of -0.410 for the same substituent obtained from the solvolysis of p-cyclopropylphenyldimethylcarbinyl chloride reported by Jones and Jones.[16] Since a negative σ^+ value indicates that the substituent is an electron donating group and a positive σ^+ value indicates that the substituent is an electron withdrawing group. Table II indicates that the C=C group in p-divinylbenzene and in α,p-styrylethanol is functioning as an electron supplying group, but the same group in m-divinylbenzene and in α,m-styrylethanol serves as an electron withdrawing group.

The equilibrium between p-cyclopropylstyrene and α,p-cyclopropylphenylethanol, namely,
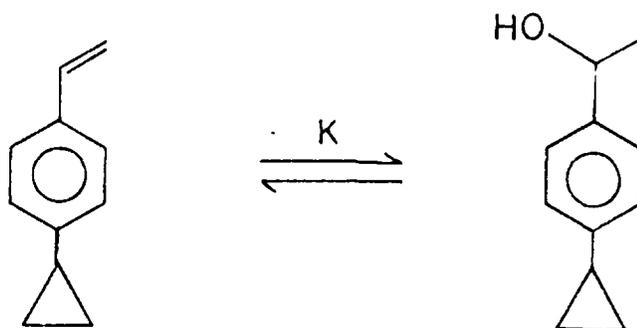
within experimental error, was found to be greater than 99% in favor

of the hydrated form and, therefore, it is not necessary to correct

the rate data in Table II for this effect.

Experimental

General

Ultraviolet spectra of solutions in 95% ethanol were determined with Cary Models 11 and 14 recording spectrophotometers. Nuclear magnetic resonance (nmr) spectra of carbon tetrachloride solutions with tetramethylsilane as reference were determined at 60 Mc with a Varian Model A-60 nmr spectrometer. Infrared spectra of carbon tetrachloride solutions were determined with a Perkin-Elmer Model 137 infrared recording spectrophotometer. The micro-analysis was performed by Huffman Laboratories Inc., Wheatridge, Colorado. All boiling points are uncorrected. Magnesium sulfate was employed as a drying agent.

Preparation of Styrene

Commercial styrene (Matheson Coleman and Bell) was washed with sodium hydroxide solution, water, dried, and distilled from calcium hydride to give material having b.p. $50°/25$ mm.

1,3-Dibromo-1-phenylpropane

The procedure of Corbin, Hahn and Schechter was employed.[20] In a two liter, three necked flask fitted with a stirrer and two reflux condensers were placed 100 g. (0.5 mole) of 1-bromo-3-phenyl-

propane (Eastman Organic Chemicals), 94 g. (0.53 mole) of N-bromo-
succinimide, 1.5 g. of benzoylperoxide and 600 ml. of carbon tetra-
chloride. The mixture was heated with a flame to initiate the
reaction. After the spontaneous reaction subsided, heating and
stirring was continued until most of the N-bromosuccinimide had
reacted. The mixture was cooled and filtered. The precipitate
was washed with carbon tetrachloride. The combined carbon tetra-
chloride layers were concentrated by distillation at water aspirator
pressure at 40-50° to give 140 g. of crude material.

Cyclopropylbenzene

In a 500 ml. three-necked round-bottomed flask equipped
with stirrer and thermometer were placed 250 ml. of dimethylform-
amide and zinc-copper couple prepared from 66 g. (1 g.-atom) of
zinc,[21] the mixture was cooled in ice-water, and 140 g. of
1,3-dibromo-1-phenylpropane obtained from the preceeding experiment
without purification was added at a rate to maintain the temperature
at 7-9°. The highly exothermic reaction has an induction period,
the end of which is characterized by a rapid temperature rise. At
this point, the addition of the 1,3-dibromo-1-phenylpropane was
stopped, and was resumed only after the temperature had stopped
rising. The mixture was stirred for thirty minutes after addition
was completed, poured into 500 ml. of water, and steam distilled
until the condensate was homogeneous. The organic layer was
extracted with ether, washed with water, dried, concentrated and
distilled to give 48.3 g. (0.408 mole, 81%) of material, b.p. 156-160°,

n_D^{27} 1.5258. (lit.[20] b.p. 169-171°, n_D^{26} 1.5306-1.5418). The nmr spectrum shows peaks at 0.1-0.5 ppm (four-hydrogen multiplet, cyclopropyl methylene hydrogens), 1.1-1.6 ppm (one-hydrogen multiplet, tertiary cyclopropyl hydrogen), and 6.4-6.9 ppm (five-hydrogen multiplet, aromatic hydrogens).

p-Bromophenylcyclopropane

The method of Levina et. al.,[22] was employed. To a solution of 16.6 g. (0.14 mole) of phenylcyclopropane in 85 ml. of chloroform cooled in Dry Ice-acetone was added dropwise with stirring a solution of 22 g. (0.275 mole) of bromine in 55 ml. of chloroform. After the completion of addition, the mixture was stirred in Dry Ice-acetone for an additional four hours, then washed with aqueous sodium sulfite, followed by aqueous sodium bicarbonate. Drying, concentration, and distillation yielded 21.7 g. (0.11 mole, 78%) of material, b.p. 98-99°/7 mm. (lit.[22] b.p. 116°/15 mm.). Gas chromatography showed only one peak.[b] The nmr spectrum of the pure liquid shows peaks at 0.2-0.9 ppm (four-hydrogen multiplet, cyclopropyl methylene hydrogens), 1.3-1.75 ppm (one-hydrogen multiplet, tertiary cyclopropyl hydrogen), and 6.6 and 7.13 ppm (two two-hydrogen doublets, J=8.5 c.p.s., aromatic hydrogens, further split by the benzylic proton, J=ca. 1-2 c.p.s.).

b. A column packed with Silicone Rubber GE-SE 30 suspended on (base-washed) Chromosorb P was employed.

p-Cyclopropylstyrene

To a Grignard solution prepared from 2.2 g. (0.09 g.-atom) of magnesium and 19.7 g. (0.1 mole) of p-bromophenylcyclopropane in anhydrous ether under nitrogen was added dropwise 5.86 g. (o.133 mole) of freshly distilled acetaldehyde in 15 ml. of anhydrous ether. After the addition was complete, the mixture was stirred for an additional $\frac{1}{2}$ hour and left overnight. The mixture was poured onto ice, decomposed with ammonium chloride, and extracted with ether. The ether layer was washed with aqueous sodium bicarbonate, dried, concentrated and distilled to give 4.4 g. (0.032 mole, 32%) of material, b.p. 31-110°/7 mm. The infrared spectrum shows a strong band at 1680 cm^{-1} (conjugate C=O). The pure liquid nmr spectrum shows a singlet at 1.94 ppm (three-hydrogen, CH_3-$\overset{O}{\overset{\|}{C}}$-), and a multiplet at 6.4-6.9 ppm (four-hydrogen, aromatic hydrogens) which corresponds to p-cyclopropylacetophenone. It is likely that auto-disproportionation is responsible for the formation of this ketone. Of this material, 11.1 g. was reduced with ca. 1 g. (0.018 mole) of lithium aluminum hydride. The reaction mixture was decomposed with water, dried and concentrated to give 10 g. of material. Gas chromatography of the crude mixture[b] shows five peaks in the ratio of 1:1.8:4.5:2.5:10.8. The third peak was collected and found to be p-cyclopropylstyrene. The infrared spectrum shows a strong band at 1635 cm^{-1} indicating the presence of (C=C) group, and the band at 1680 cm^{-1} (C=O) has disappeared. The nmr spectrum shows absorptions

b. A column packed with Silicone Rubber GE-SE 30 suspended on (base-washed) Chromosorb P was employed.

at 0.6-0.97 ppm (four-hydrogen multiplet, cyclopropyl methylene

hydrogens), 1.62-2.01 ppm (one-hydrogen multiplet, tertiary cyclo-

propyl hydrogens), 6.4-6.8 and 5.0-5.8 ppm (^{H}C=C^H_H group), and

7.28 and 6.98 ppm (two two-hydrogen doublets, J=8 cps, aromatic

hydrogens).

 <u>Anal</u>. Calc. for $C_{11}H_{12}$: C, 91.60%; H, 8.40%.

Found: C, 91.90%; H, 8.20%.

Separation of <u>m</u>- and <u>p</u>-Divinylbenzene

Gas chromatography[c] shows that the commercial divinylbenzene

(Matheson Coleman and Bell) consisted of three major components,

components two and three being only partially separated. The

compounds were collected and their nmr spectra were determined.

The nmr spectrum of peak two shows absorptions at 6.38-6.84 and

5.03-5.75 ppm (six-hydrogen, two ^{H}C=C^H_H groups), and at 7.14-7.35 ppm

(four-hydrogen, aromatic hydrogens), and is consistent with the

spectrum of <u>m</u>-divinylbenzene.[19] The nmr spectrum of peak three

shows absorptions at 6.37-6.82 and 5.00-5.72 ppm (six-hydrogen,

two ^{H}C=C^H_H groups), and at 7.22 ppm (four-hydrogen singlet, aromatic

hydrogens), and is consistent with the spectrum of <u>p</u>-divinylbenzene.[19]

Gas chromatography[d] of the <u>m</u>- and <u>p</u>-divinylbenzene shows only one peak.

 c. A column packed with Ucon LB-550-X suspended on (base-
washed) Chromosorb P was employed.

 d. A column packed with 3% ECNSS-N by weight on 100/120
mesh Gas-Chrom Q was employed.

Standardization of 3.83 M Perchloric Acid

A stock solution was prepared by dilution of 70% perchloric acid (Mallinckrodt Chemical Works, A.R. grade) and assayed by titration with 0.8934 M sodium hydroxide which had been standardized against potassium hydrogen phthalate.

Kinetic Procedure

First order rate constants for the hydration of styrene, p-cyclopropylstyrene, m-divinylbenzene and p-divinylbenzene, (ca. 10^{-4}-10^{-5} M in 3.83 M perchloric acid were determined by the ultraviolet spectrophotometric method.[23] The decrease in absorbance with time was recorded, the measurements being made in the region 248 mμ for styrene, 260 mμ for p-divinylbenzene, and 239 mμ for m-divinylbenzene where these compounds have a high extinction coefficient. All infinity points were taken after at least ten half lives.

Tables of Experimental Data

Table I

Run 8. The Hydrolysis of Styrene in 3.83 M
Perchloric Acid at 25° C.

Time, min.	Optical Density	% Unreacted
0	2.175	100.0
88	1.94	88.9
157	1.715	78.3
213	1.61	73.3
273	1.50	68.1
332	1.36	61.5
409	1.239	55.7
506	1.12	50.1
583	0.99	44.0
707	0.855	37.6
881	0.68	29.3
1023	0.59	25.1
1206	0.46	18.9
(Infinity point)	0.06	0.0

Table II

Run 12. The Hydrolysis of Styrene in 3.83 M
Perchloric Acid at 25° C.

Time, min.	Optical Density	% Unreacted
0	1.074	100.0
57	1.00	93.0
125	0.927	86.2
213	0.833	77.3
279	0.76	70.4
335	0.72	66.7
399	0.645	59.6
471	0.590	54.4
532	0.525	48.3
598	0.498	45.8
721	0.440	40.3
833	0.380	34.7
1066	0.280	29.1
1199	0.228	20.3
(Infinity point)	0.012	0.0

Table III

Run 1. The Hydrolysis of p-Cyclopropylstyrene
in 3.83 M Perchloric Acid at 25° C.

Time, min.	Optical Density	% Unreacted
0.0	0.91	100.0
1.0	0.847	92.6
2.5	0.812	88.5
3.5	0.78	84.7
5.0	0.735	79.5
6.0	0.712	76.8
7.0	0.68	73.0
8.0	0.651	69.6
10.0	0.600	58.8
12.0	0.559	53.9
14.0	0.517	49.5
16.0	0.48	47.5
17.0	0.463	43.7
(Infinity point)	0.058	0.0

Table IV

Run 2. The Hydrolysis of p-Cyclopropylstyrene
in 3.83 M Perchloric Acid at 25° C.

Time, min.	Optical Density	% Unreacted
0	0.717	100.0
1	0.687	95.5
3	0.638	88.2
5	0.59	81.0
7	0.542	73.9
9	0.499	67.5
11	0.472	63.4
13	0.439	58.5
15	0.405	53.4
17	0.37	48.2
19	0.349	45.1
21	0.327	41.8
23	0.30	37.8
25	0.278	34.5
(Infinity point)	0.047	0.0

Table V

Run 2. The Hydrolysis of p-Cyclopropylstyrene
in 3.83 M Perchloric Acid at 9° C.

Time, min.	Optical Density	% Unreacted
0	1.915	100.0
14	1.74	90.3
27	1.625	84.0
39	1.50	77.1
52	1.40	71.6
68	1.27	66.4
80	1.18	59.4
93	1.095	54.7
106	0.995	49.2
118	0.925	45.3
132	0.855	41.4
(Infinity point)	0.105	0.0

Table VI

Run 5. The Hydrolysis of p-Cyclopropylstyrene
in 3.83 M Perchloric Acid at 9° C.

Time, min.	Optical Density	% Unreacted
0	1.043	100.0
22	0.93	88.5
48	0.805	75.7
65	0.727	67.8
81	0.657	60.7
101	0.60	54.8
120	0.53	47.7
139	0.474	42.0
159	0.429	37.4
180	0.378	32.2
198	0.352	29.6
(Infinity point)	0.062	0.0

Table VII

Run 1. The Hydrolysis of p-Cyclopropylstyrene
in 3.83 M Perchloric Acid at 0° C.

Time, min.	Optical Density	% Unreacted
0	1.682	100.0
24	1.640	97.4
54	1.592	94.5
73	1.525	90.4
100	1.454	86.1
121	1.393	82.3
143	1.350	79.7
165	1.296	76.4
186	1.242	73.1
208	1.140	66.9
(Infinity point)	0.045	0.0

Table VIII

Run 3. The Hydrolysis of p-Cyclopropylstyrene
in 3.83 M Perchloric Acid at 0° C.

Time, min.	Optical Density	% Unreacted
0	1.462	100.0
28	1.418	96.9
53	1.360	92.8
77	1.290	87.9
103	1.237	84.2
127	1.172	79.6
152	1.128	76.5
179	1.061	71.8
205	1.027	69.4
233	0.960	64.7
(Infinity point)	0.040	0.0

Table IX

Run 1. The Hydrolysis of p-Divinylbenzene
in 3.83 M Perchloric Acid at 25° C.

Time, min.	Optical Density	% Unreacted
0	0.663	100.0
34	0.491	73.1
56	0.414	61.1
82	0.337	49.1
105	0.276	39.5
130	0.218	30.5
161	0.180	24.5
186	0.151	20.0
209	0.127	16.3
251	0.104	12.7
277	0.088	10.2
316	0.072	7.7
(Infinity point)	0.023	0.0

Table X

Run 2. The Hydrolysis of p-Divinylbenzene
in 3.83 M Perchloric Acid at 25° C.

Time, min.	Optical Density	% Unreacted
0	0.651	100.0
27	0.507	76.8
46	0.425	63.6
69	0.358	52.8
90	0.299	43.3
119	0.236	33.2
140	0.205	28.2
172	0.163	21.4
194	0.140	17.7
226	0.114	13.5
251	0.102	11.6
284	0.086	9.0
332	0.073	7.1
(Infinity point)	0.03	0.0

Table XI

Run 2. The Hydrolysis of α,p-Styrylethanol
in 3.83 M Perchloric Acid at 25° C.

Time, min.	Optical Density	% Unreacted
0	1.696	100.0
23	1.625	95.6
46	1.563	91.7
70	1.497	87.7
91	1.438	84.0
111	1.378	80.3
130	1.328	77.2
150	1.277	74.0
169	1.239	71.7
190	1.179	68.0
210	1.125	64.6
(Infinity point)	0.084	0.0

Table XII

Run 3. The Hydrolysis of α,p-Styrylethanol
in 3.83 M Perchloric Acid at 25° C.

Time, min.	Optical Density	% Unreacted
0	1.594	100.0
24	1.530	95.8
48	1.464	91.5
70	1.411	88.1
90	1.367	85.2
110	1.309	81.4
129	1.256	77.9
149	1.216	75.3
169	1.170	72.3
189	1.123	69.3
209	1.079	66.4
(Infinity point)	0.062	0.0

Table XIII

Run 2. The Hydrolysis of m-Divinylbenzene and
α,m-Styrylethanol in 3.83 M Perchloric Acid
at 25° C.

Time, min.	Optical Density	% Unreacted
0	2.032	100.0
101	1.866	91.8
231	1.659	81.5
386	1.480	72.6
500	1.359	66.6
632	1.210	59.2
740	1.110	54.2
1384	0.686	33.2
1513	0.599	28.8
1637	0.547	26.3
1757	0.500	23.9
1848	0.464	22.1
(Infinity point)	0.018	0.0

Table XIV

Run 3. The Hydrolysis of m-Divinylbenzene and
α,m-Styrylethanol in 3.83 M Perchloric Acid
at 25° C.

Time, min.	Optical Density	% Unreacted
0	1.853	100.0
129	1.737	93.9
283	1.498	81.3
403	1.351	73.6
529	1.187	65.0
639	1.082	59.5
1281	0.624	35.4
1409	0.538	30.9
1532	0.48	27.9
1640	0.428	25.1
1744	0.406	24.0
1933	0.319	19.4
2036	0.297	18.2
(Infinity point)	0.001	0.0

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