

at 6.1–6.3 μ was present. The n.m.r. spectrum was in general agreement though complicated by the product being a mixture of *cis-trans* isomers.

Anal. Calcd. for $C_{15}H_{24}O$: C, 81.81; H, 10.90. Found: C, 81.51; H, 10.59.

4-Methyl-2-phenylpentadienes. Addition of C_6H_5MgBr to 4-methyl-3-penten-2-one (mesityl oxide) in ether produced a 51% yield of a mixture of dienes as previously reported.¹³ An analysis of the n.m.r. spectrum of the mixture showed it to be ~65% of the 1,3-pentadiene and ~35% of the 2,4-pentadiene.

Maleic Anhydride Adducts. The cyclopentenyl cations of structure **8** were converted to the dienes by rapid dispersal in cold 10% aqueous NaOH. The dienes were ether extracted, washed, and distilled. The boiling points the dienes are listed in Table I.

(13) V. I. Esafov, *Zh. Obsch. Khim.*, **27**, 2667 (1957); *Chem. Abstr.*, **52**, 7176 (1958).

A solution of 1 g. of dienes and 0.74 g. of maleic anhydride was refluxed for 6 hr. in 4 ml. of benzene. The benzene was removed by distillation and the residue was dissolved by refluxing for 2 hr. with 5% aqueous Na_2CO_3 . The diacid adducts were precipitated by addition of the aqueous Na_2CO_3 solution to excess 10% HCl (reverse addition of the HCl to the aqueous carbonate solution resulted in the precipitation of sodium salts in two cases). The diacids were recrystallized from benzene-methanol. The yields, melting points, C and H analyses, and n.m.r. spectra appear in Table I. The n.m.r. spectra were measured in $CH_2Cl_2-CH_3OH$ solution using a Varian 60-Mc. instrument.

Acknowledgment. We are grateful to the National Science Foundation for providing funds both to support this research and to aid in the purchase of a Varian A-60 n.m.r. spectrometer.

The Intermediacy of Carbonium Ions in the Addition of Water or Ethanol to Arylalkenes

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The kinetics of the hydration of 2-arylpropenes closely resembles the kinetics of hydration of other olefinic systems. It is concluded that mechanism and transition states are similar and that no mechanistic division occurs between alkenes and arenes. In the acid-catalyzed reactions of 2-phenyl-2-butene and 2-phenyl-2-butanol with ethanol, the carbonium ion is an intermediate in the reaction with the alcohol, but not the alkene. Extrapolating this result to the hydration-dehydration reactions in aqueous systems, the carbonium ion is probably an intermediate between alcohol and the transition state.

At the time these studies were initiated, we had just established that protonation of diarylalkenes does not follow Hammett's H_0 acidity function.¹ It was thought that it would be instructive to examine rate-acidity profiles for reactions that could involve such a protonation as an initial step. The initial results² were that the kinetics of hydration of arylalkenes (and the reverse dehydration of the alcohols) follow eq. 1.

$$d \log k = -dH_0 \quad (1)$$

By this time, it was realized that this result was to be expected based on the following argument.

The difference in acidity function behavior of protonated anilines (H_0) and diarylalkyl cations (H_R') is primarily due to the strong hydrogen bonding of the protonated anilines to water, an effect not present (or much reduced) in the diarylalkyl cations.^{3,4} If

(1) N. Deno, P. T. Groves, and G. Saines, *J. Am. Chem. Soc.*, **81**, 5790 (1959).

(2) Ph.D. Thesis of Henry J. Peterson, Pennsylvania State University, 1960.

the rate-determining step in hydration of arenes was a proton addition⁵ or an internal proton migration,⁶ the migrating proton would hold part of its positive charge, the transition state would strongly hydrogen bond to water, and the fit of the data with eq. 1 would be expected. This is the usual situation since the kinetics of hydration of aliphatic alkenes,⁶ unsaturated ketones,⁷ styrenes,⁵ and α -methylstyrenes (Table I) all fit eq. 1.⁸ The dehydration of 1,1-diphenylethanol and several 2-aryl-2-propanols also fit eq. 1 as shown in Table I.

This picture of the transition state is supported by data on the effect of substituents on rates. In the hydration of styrenes, a plot of $\log k$ against σ^+ gave a slope, ρ , of -3.4 .⁵ The hydration of α -methylstyrenes gave ρ of -3.2 and the reverse dehydration of 2-aryl-2-propanols gave ρ of -3.1 (Table II). These values are a little smaller in magnitude than those for carbonium ion equilibria⁹ and those for reactions in which the transition state is believed to closely resemble a carbonium ion.¹⁰ The picture is thus of the

(3) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **82**, 2965 (1960); see also J. F. Bunnett, *ibid.*, **82**, 499 (1960).

(4) N. Deno in "Surveys of Progress in Chemistry," Vol. 2, A. F. Scott, Ed., Academic Press, Inc., New York, N. Y., 1964.

(5) W. M. Schubert, B. Lamm, and J. R. Keeffe, *J. Am. Chem. Soc.*, **86**, 4727 (1964).

(6) R. H. Boyd, R. W. Taft, Jr., A. P. Wolf, and D. R. Christman, *ibid.*, **82**, 4729 (1960), and earlier references.

(7) D. S. Noyce and co-workers, *ibid.*, **84**, 1632, 1650 (1962).

(8) The data for styrenes more precisely fit $d \log k = cdH_0$, where c is 1.23–1.33. The interpretation of this minor discrepancy³ is in accord with our views.

(9) N. Deno and W. L. Evans, *J. Am. Chem. Soc.*, **79**, 5804 (1957).

(10) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); Y. Okamoto and H. C. Brown, *J. Org. Chem.*, **22**, 485 (1957).

Table I. Rate and Equilibrium Constants for Hydration (k_1) and Dehydration (k_{-1}) at 25°. Test of Eq. 1

H ₂ SO ₄ , %	$k_1 \times 10^4$, sec. ⁻¹	$k_{-1} \times 10^4$, sec. ⁻¹	K_{eq}^a	$H_0 + \log k_1$	$H_0 + \log k_{-1}$
2-Phenylpropene					
4.8	1.7	0.12	15	-3.5	-3.8
9.8	4.3	0.4	11	-3.5	-4.6
19.6	25	1.6	18	-3.5	-4.7
29.6	126	9	18	-3.4	-4.5
40.5	880	15	10	-3.5	-4.1
2-(4'-Methoxyphenyl)propene					
4.8	71	6.1	12	-1.9	-2.9
7.1	110	17	7	-1.9	-2.7
9.8	226	36	7	-1.8	-2.6
14.1	480	120	4	-1.8	-2.4
2-(4'-Nitrophenyl)propene					
29.6	0.29	0.06	6	-6.0	-6.7
40.5	1.6	0.32	9	-6.1	-6.9
50.8	17	4.8	11	-6.1	-6.6
60.2	250	80	19	-6.0	-6.5
4-Isopropenylbenzoic acid					
20.2	0.28	0.07	5		
29.6	2.2	0.37	8		
2-(4'-Chlorophenyl)propene					
20.2	6.7	0.6	13		
2-(3'-Chlorophenyl)propene					
20.2	1.53	0.35	5.0		
2-(4'-Methylphenyl)propene					
20.2	120	23	6.0		
1,1-Diphenylethene					
15.7		6.5			-3.8
21.7		12.6			-3.9
25.5		20			-3.9
30.6		76			-3.7
34.5		180			-3.6

$$^a K_{eq} = k_1(k_{-1}a_{H_2O})^{-1}$$

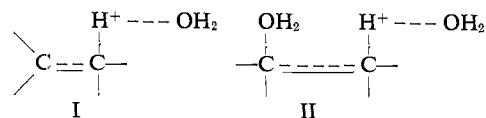
positive charge partially on the incoming (or outgoing in dehydration) proton and partially delocalized into the arene system.

Table II. Summary of σ - ρ Plots for Hydration and Dehydration

Substituent on 2-arylpropene	σ^a	Deviation of $\log k/k_0$ from $-3.05\sigma^+$	
		hydration	dehydration
4-Methoxy	-0.65	0.08	0.0
4-Methyl	-0.31	0.09	0.2
H	0	0.00	0.0
3-Chloro	0.37	-0.19	-0.3
4-Carboxy	0.45	0.29	-0.1
4-Nitro	0.78	-0.03	-0.1

^a See ref. 10.

At this point, there was still no definite evidence that a carbonium ion was an intermediate in such hydration-dehydration reactions and the past evidence⁵⁻⁷ also seems rather weak on this question. For example, the transition state could be a rate-determining proton transfer to form an intermediate carbonium ion, I, or a simultaneous addition of H⁺ and water to form the protonated alcohol, II. The fit with eq. 1 does suggest



that two to three molecules of water are hydrogen bonded to the transition state³ and this would perhaps support II, but the argument is weak.

It was inconvenient to prove definitively or disprove an intermediate carbonium ion in these aqueous reactions so recourse was taken to a similar reaction, the addition of ethanol to olefins. The following sets of experiments are interpreted to mean that in the reactions of arylalkenes with ethanol containing 10-20% H₂SO₄, the arylalkanol is in reversible equilibrium with the arylalkyl cation (the carbonium ion) and the arylalkene is not.

Hydrogen-Deuterium Exchange. 2-Phenylpropene was allowed to react with 17% D₂SO₄ in C₂H₅OD. After (1) 24% and (2) 54% of the alkene had been converted to ether, the unreacted 2-phenylpropene contained (1) 0 ± 2% and (2) 10 ± 5% of deuterium in the five exocyclic hydrogens. Thus the alkene is *not* in reversible equilibrium with the carbonium ion prior to ether formation.

Similarly, in the addition of *cis*-2-phenyl-2-butene to 11% D₂SO₄ in C₂H₅OD the formation of the ethyl ether of the arylalkyl system and the incorporation of deuterium in the starting arene could both be followed by n.m.r. spectroscopy. After 34% of the arene had disappeared, no deuterium was detected in unreacted *cis*-2-phenyl-2-butene.

These experiments and the results parallel similar experiments on the simple aliphatic alkenes.¹¹

Arylalkene Isomerization. In the conversion of *cis*-2-phenyl-2-butene to its ethyl ether in ethanol containing 15% H₂SO₄, the n.m.r. bands of the reactant diminished without any evidence of bands assignable to a *trans*-2-phenyl-2-butene. Admittedly, this is a less sensitive test in that the *cis* isomer is more stable. Cram¹² reported that in the preparation of these two isomeric arenes by acid-catalyzed dehydration of 2-phenyl-2-butanol the ratio of *cis* to *trans* is 4 to 1.

This experiment and its result parallels similar experiments on the isomeric 2-methylbutenes.¹³

Relative Rates of Ether Formation. The rates of formation of 2-phenyl-2-propyl ethyl ether were studied at 25.0° in ethanol containing 9.8% H₂SO₄. The first-order rate constant for 2-phenylpropene as reactant was 4.0 × 10⁻¹ sec.⁻¹ and for 2-phenyl-2-propanol as reactant, 4.2 × 10⁻⁵ sec.⁻¹. Thus the ether forms 105 times faster from alcohol than arene.

This result is analogous to that of Dostrovsky and Klein,¹⁴ who showed that 2-methyl-2-propanol (*t*-butyl alcohol) exchanges oxygen faster than it dehydrates. In both this work and our work on 2-phenyl-2-propanol, the results suggest that the alcohol is in rapid reversible equilibrium with the carbonium ion though it is conceivable that the reaction could be more *fruitfully described* as a displacement by water

(11) E. L. Purlee and R. W. Taft, Jr., *J. Am. Chem. Soc.*, **78**, 5807 (1956).

(12) D. J. Cram, *ibid.*, **71**, 3883 (1949); **74**, 2137 (1952).

(13) J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, *ibid.*, **75**, 1253 (1953).

(14) I. Dostrovsky and F. S. Klein, *J. Chem. Soc.*, 791, 4401 (1955).

(in the oxygen exchange) or C_2H_5OH (in the ether formation) on the protonated alcohol. To answer this question, we were led to the following experiment.

Ether Formation from (+)-2-Phenyl-2-butanol. (+)-2-Phenyl-2-butanol was placed in ethanol containing 8.5 or 15.7% H_2SO_4 and the kinetics of racemization measured at 25.0°. In both cases, the loss of optical activity fit first-order kinetics (the respective rate constants were 1.9×10^{-4} and $3.6 \times 10^{-4} \text{ sec.}^{-1}$) and the rotation reached zero and remained there. In a separate experiment, the rate of ether formation was measured in the ethanol containing 8.5% H_2SO_4 and found to be only one-fifth as fast as racemization.

The interpretation of these results is that the carbonium ion, optically inactive, is an intermediate. About 80% of this ion undergoes internal return leading to racemic alcohol and 20% reacts with ethanol leading to racemic ether. By analogy, it is inferred that the carbonium ion is also an intermediate between alcohol and transition state in the dehydration of alcohols in aqueous acid.

Experimental

Rates of Hydration and Dehydration. All kinetic experiments were conducted at 25.0°. The progress of the reaction was followed spectrophotometrically in the region 230–360 $m\mu$. For each compound, three wave lengths were used. These were spaced at least 20 $m\mu$ apart and were chosen to maximize the change in absorption during the course of the reaction. Values of k reported herein are averages of the values calculated from data at the three wave lengths. The initial concentrations of reactant, alcohol or alkene, ranged from 10^{-4} to $10^{-5} M$. At these low concentrations, the reaction mixture was homogeneous.

The extensive details of these runs appear in the Ph.D. thesis of Henry J. Peterson (The Pennsylvania State University, 1960). It is sufficient here to state that at any particular concentration of sulfuric acid, the data do not significantly deviate from eq. 2 throughout the course of the reaction.

$$dc_{ROH}/dt = -dc_{alk}/dt = k_1c_{alk} - k_{-1}c_{ROH} \quad (2)$$

Values of k_1 , k_{-1} , and K_{eq} appear in Table I. K_{eq} was calculated from the relation

$$K_{eq} = k_1(k_{-1}a_{H_2O})^{-1} \quad (3)$$

which was assumed to hold. The constancy of $\log k + H_0$ in Table I serves to demonstrate the fit of the data with eq. 1.

σ - ρ Plots. The rate constants for hydration and dehydration in 20.2% aqueous sulfuric acid were used for the σ - ρ plots. These rate constants were either directly measured or estimated by a short extrapolation using eq. 1. The fit of the data to a σ^+ plot is shown in Table II.

Dehydration of 1,1-Diphenylethanol. The final equilibrium apparently favored the alkene, 1,1-diphenylethene. The equilibrium was not stable, presumably because of acid-catalyzed dimerization of the arene. Satisfactory first-order kinetic plots were obtained only to about 1 half-life. The data are summarized in Table I.

Addition of C_2H_5OD to 2-Phenylpropene. Deuterated ethanol, C_2H_5OD , was prepared by treating C_2H_5ONa with D_2O . The n.m.r. spectrum of the distilled product, b.p. 77.4° (731 mm.), no longer contained the band at 2.58 p.p.m., characteristic of hydroxylic hydrogen.

The D_2SO_4 was prepared by introduction of SO_3 in the gas phase into stirred D_2O . The gaseous SO_3 was conducted into the D_2O chamber by a gentle stream of dry N_2 . The SO_3 was heated to eliminate potential solidification of polymeric SO_3 and to distil the SO_3 into the stream of N_2 . The apparatus was entirely of glass and the tube between the SO_3 surface and the D_2O surface was wide and capable of being flamed if polymeric SO_3 deposits developed. Any SO_3 in the exit N_2 was trapped in H_2SO_4 .

When the SO_3 was first introduced into the D_2O chamber, the N_2 stream was run intermittently to allow time for the slow absorption of the colloidal SO_3 by D_2O . As the concentration of D_2SO_4 built up, the SO_3 was distilled into the D_2SO_4 - D_2O at a more rapid rate.

The reason for avoiding direct introduction of liquid SO_3 is that if liquid SO_3 contacts D_2O on a Pyrex glass surface, the intense heat cracks the Pyrex glass. Furthermore, D_2O (or water) catalyzes the polymerization of SO_3 so that attempts to introduce liquid SO_3 through a capillary tube failed because polymer blocks the tube.

The choking fumes of colloidal SO_3 in the air are not entirely eliminated by hoods and we have found it convenient to use a standard military gas mask when handling liquid SO_3 .

A mixture of 0.6 g. of D_2SO_4 , 2.5 g. of C_2H_5OD , and 0.6 g. of 2-phenylpropene was periodically examined by n.m.r. spectroscopy. The total area of the phenyl hydrogens at 7.1 to 7.6 p.p.m. (downfield from tetramethylsilane) measured the sum of 2-phenylpropene and the ether produced by addition of C_2H_5OD . The concentration of ether was measured by the area of the quartet due to the CH_2 group in $C_6H_5C(CH_3)(CH_2D)OCH_2CH_3$. This quartet, $J = 7.5$ c.p.s., centered at 3.18 p.p.m. and was fortunately separated from the bands of the solvent, C_2H_5OD .

The difference between total moles and moles of ether gave the number of moles of 2-phenylpropene. This was used to calculate the areas of the bands due to exocyclic hydrogen in 2-phenylpropene if no H-D exchange had occurred. The per cent deuteration is directly calculable from the difference between the observed band areas and the above calculated areas. The per cent deuteration in unreacted 2-phenylpropene was the same within experimental error whether calculated from the observed band areas of the vinylic hydrogens (5.05 and 5.36 p.p.m. downfield from Me_4Si) or the methyl hydrogens (2.12 p.p.m.). The data are presented in Table III.

Racemization of 2-Phenyl-2-butanol. Optically active 2-phenyl-2-butanol ($[\alpha]^{25D} + 10.04^\circ$, completely resolved alcohol is $+17.45^\circ$)¹⁵ was added to 8.5% H_2SO_4 in ethanol and 15.7% H_2SO_4 in ethanol, both at 25°. The racemization rates fit first-order kinetics throughout the course of the reaction and the respective half-lives were 76 and 40 min. In both cases the rotation went to 0° and remained there.

(15) H. H. Zeiss, *J. Am. Chem. Soc.*, **73**, 2391 (1951).

Table III. H-D Exchange in the Addition of C₂H₅OD to 2-Phenylpropene at 25°

	—Reaction time—	
	16 hr.	188 hr.
Relative band areas		
7.1 - 7.6 (aryl H)	5.0	5.0
5.05 + 5.36 (vinyl H)	1.5	0.9
2.12 (CH ₃ on alkene)	2.3	1.2
3.18 (ether CH ₂)	0.5	1.1
Ether formed, %	25	55
Alkene remaining, % (total minus ether)	75	45
Calcd. band areas for no H-D exchange		
5.05 + 5.36 bands	1.5	0.9
2.12 band	2.3	1.0
Deuteration in 2-phenylpro- pene, %	0 ± 5	0 ± 10 10 ± 10

Rate of Reaction of Alcohol or Alkene with Ethanol. The rates of formation of the ethyl ether of 2-phenyl-2-propanol were studied at 25° in 10% H₂SO₄-90% ethanol starting with either 2-phenyl-2-propanol or 2-phenylpropene. With the alcohol as reactant, the rates fit first-order kinetics to completion and the rate constant was $4.2 \times 10^{-5} \text{ sec.}^{-1}$.

The conversion of 2-phenylpropene to the same ether was carried only to 1.5% of completion and within this narrow range the data fit first-order kinetics with a rate constant of $4.0 \times 10^{-7} \text{ sec.}^{-1}$. The formation of ether from alcohol is thus 105 times faster than formation from 2-phenylpropene.

The progress of the reaction was followed by gas chromatography. Samples were periodically quenched in aqueous NaOH and the separated organic layer dried over Na₂SO₄ and injected into the gas chromatograph (g.c.). A 14-ft. column was used at 128° and the stationary phase was O(CH₂CH₂CN)₂.¹⁶ The authentic ethyl ether of 2-phenyl-2-propanol was prepared and used to calibrate the g.c. along with authentic samples of alkene and alcohol. This proved to be an important precaution because the proportionality constant between g.c. band area and moles was quite different for the ether relative to the other two components. It is suspected that the ether cracks to ethanol plus arene on the hot wire of the detector.

(+)-2-Phenyl-2-butyl Ethyl Ether. (+)-2-Phenyl-2-butanol was prepared as described by Zeiss.¹⁵ The ether was produced by treating RO⁻K⁺, prepared by addition of ROH ($[\alpha]^{25D} + 10.04^\circ$) to potassium sand in benzene, with excess C₂H₅I in benzene. The rotation of the crude ether was $[\alpha]^{25D} + 11.01^\circ$. The mode of preparation ensured that alcohol and ether had the same configuration, and the measured rotations show that the ether has a larger specific rotation than the alcohol. These rotations of the ethyl ether paralleled results obtained by Zeiss for the methyl ether.¹⁷

2-Phenylpropyl Ethyl Ether. A solution of 13.7 g. of 2-phenylpropene in 100 ml. of 5% H₂SO₄-95% ethanol was refluxed for 5 hr. Cooling, addition to ice and water, ether extraction, alkaline wash, Na₂SO₄ drying, and distillation through a spinning-band column

(16) H. M. Tenney, *Anal. Chem.*, **30**, 2 (1958).

(17) H. H. Zeiss, *J. Am. Chem. Soc.*, **75**, 154 (1953).

produced a 33% yield of 2-phenylpropyl ethyl ether, b.p. 64.9-65.0° (2.8 mm.).

Anal. Calcd. for C₁₁H₁₆O: C, 80.5; H, 9.8. Found: C, 80.2; H, 9.9.

2-(4'-Methoxyphenyl)propene. This and the following alkenes were prepared by the Wittig synthesis. Triphenylphosphonium bromide¹⁸ (35.8 g., 0.10 mole) was added to a solution of 0.10 mole of C₆H₅Li in 400 ml. of ether. After stirring for 3 hr., a solution of 13.3 g. (0.095 mole) of 4-methoxyacetophenone in 50 ml. of ether was added over 30 min. The mixture was refluxed for 3 hr. and filtered. Water washing, drying over CaSO₄, distilling at $96 \pm 0.1^\circ$ (18 mm.), and twice recrystallizing the solid distillate from alkanes produced a 63% yield of 2-(4'-methoxyphenyl)propene. The melting point of 32-32.5° agreed with reported values.¹⁹⁻²¹

The synthesis of three other 2-arylpropenes closely followed the above procedure and the details are summarized in Table IV.

Table IV. Yields and Properties of 2-Arylpropenes Prepared by the Wittig Synthesis

Substituent on aryl ring	Yield, %	B.p., °C. (mm.)	M.p., °C.	Lit. ref. ^a
4-Methyl	73	185-187		<i>b</i>
4-Chloro	67	80-82 (9)	4-5	<i>c</i>
3-Chloro	52	95-96 (21)		<i>d</i> <i>e</i>

^a References are to melting and boiling points. ^b Reference 25. ^c D. T. Mawry, W. F. Huber, and E. L. Ringwald, *J. Am. Chem. Soc.*, **69**, 852 (1947), and ref. 20. ^d E. A. Bergmann and A. Weizmann, *Trans. Faraday Soc.*, **32**, 1330 (1936). ^e D. T. Mawry, W. F. Huber, and E. L. Ringwald, *J. Am. Chem. Soc.*, **69**, 852 (1947).

2-(4'-Nitrophenyl)propene. This was prepared in 75% yield by bromination of 4-nitroisopropylbenzene²² with N-bromosuccinimide followed by loss of HBr.²³

4-Isopropenylbenzoic Acid. This was prepared by simple dehydration of the alcohol using refluxing 0.1 M H₂SO₄.²⁴

2-Aryl-2-propanols. The unsubstituted member²⁵ and the 4-methoxy,^{21,26} 4-methyl,²⁷ 4-chloro,²¹ and 3-chloro²¹ were all prepared by the Grignard method. The 4-nitro member was prepared by oxidation of 4-nitroisopropylbenzene with CrO₃ in acetic acid.²⁸ 4-(2'-Hydroxy-2'-propyl)benzoic acid was prepared by oxidation of 1-isopropyl-4-methylbenzene with aqueous KMnO₄.^{24,29}

(18) G. Wittig and U. Scholkopf, *Ber.*, **87**, 1318 (1954).

(19) A. Behal and M. Tiffenau, *Bull. soc. chim. France*, **3**, 315 (1908).

(20) D. Seymour and K. A. Wolfstern, *J. Am. Chem. Soc.*, **70**, 1177 (1948).

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

(22) E. C. Sterling and M. T. Bogart, *J. Org. Chem.*, **4**, 25 (1939).

(23) G. Brubacher and E. Suter, *Helv. Chim. Acta*, **33**, 256 (1950).

(24) K. Auwers and G. Keil, *Ber.*, **38**, 1707 (1905).

(25) H. Schmalzfuss and M. C. Wetzel, *J. prakt. Chem.*, **109**, 158 (1925).

(26) A. J. Birch, *J. Proc. Roy. Soc. N. S. Wales*, **83**, 245 (1949).

(27) W. S. Perkin, Jr., and S. S. Pickles, *J. Chem. Soc.*, 653 (1905).

(28) H. Kwart and P. S. Francis, *J. Am. Chem. Soc.*, **77**, 4911 (1955).

(29) O. Wallach, *Ann.*, **264**, 10 (1891).

Acknowledgment. We are grateful to both the Petroleum Research Fund of the American Chemical Society and the National Science Foundation for grants supporting this work and to the National

Science Foundation for a grant supporting the purchase of the Varian A-60 n.m.r. instrument. H. J. P. received a fellowship supported by the American Cyanamid Company.

Chlorination Studies of Unsaturated Materials in Nonpolar Media. II. Competition between Ionic and Free-Radical Reactions during Chlorination of Cyclohexene¹

Marvin L. Poutsma

Contribution from the Union Carbide Research Institute, Union Carbide Corporation, Tarrytown, New York. Received December 21, 1964

Chlorination of neat cyclohexene at 25° in the dark under nitrogen produced *trans*-1,2-dichlorocyclohexane (I), 3-chlorocyclohexene (II), and 4-chlorocyclohexene (III) in a ratio of 1.95:1.00:0.60; if cyclohexane was present, chlorocyclohexane (IV) became a significant product. External illumination led to no changes in product composition. This chlorination is interpreted as a solely free-radical reaction initiated by interaction between the reactants. Chlorination under oxygen eliminated III while I and II were now produced in a ratio of 3-4:1; under these conditions reaction apparently proceeds by means of the usual electrophilic attack of halogens on unsaturated molecules which can be observed in this case only in the presence of radical chain inhibitors. For a series of dark chlorinations under nitrogen, gradual dilution of cyclohexene with nonpolar solvents (1,1,2-trichlorotrifluoroethane, carbon tetrachloride, or cyclohexane) led to increasing importance of the ionic compared to the radical pathway. The dependence of the percentage of radical reaction on olefin concentration was determined and is attributed to an over-all higher kinetic order in olefin for the radical pathway due to participation of two or more molecules of olefin in the initiation process. Initiation of radical chlorination by interaction between olefins and chlorine is an example of a class of reactions between "even" molecules which form radicals under mild conditions; such reactions are discussed. For benzene and carbon disulfide as diluents, solvent effects on the radical pathway were observed which favor addition over total abstraction and abstraction at the 3-position of cyclohexene over that at the 4-position. The relative reactivities of the 3- and 4-hydrogens of cyclohexene and the saturated hydrogen of cyclohexane toward abstraction by chlorine atom at 25° were determined to be 1.20:0.72:1.00.

Introduction

Halogenation of olefins in nonpolar solvents, such as carbon tetrachloride, is a widely used organic reaction; however, attempts to investigate the mechanism have met with serious problems of catalysis by surfaces,

water, and hydrogen halides (particularly in the case of bromine)² and have given, at best, inconclusive results. In this and the succeeding paper³ we will consider specifically the mechanistic pathways for chlorination of unconjugated (π - π or p - π) olefins, either as neat liquids or in mixture with nonpolar diluents.

A considerable body of data⁴ suggests that simple olefins and chlorine do not undergo a rapid vapor phase reaction at ambient temperatures⁵ but do react vigorously as soon as a liquid phase of products develops in the reactor. Such reaction was found to produce predominantly addition products (55-65% and 75% from 1-butene and 2-butene, respectively)^{4a} except for olefins bearing two alkyl groups on the same olefinic carbon atom in which case allylic substitution products became dominant (93% 3-chloro-2-methyl-1-propene from isobutylene).^{4b} Much of the existing data is difficult to interpret in mechanistic terms for two reasons: (1) most chlorinations have been carried to such great conversion that secondary products seriously complicate determination of the primary processes, and (2) the experimental variables of oxygen concentration and light intensity, found to be critical in the present study, have not been controlled. Taft⁷ has considered a number of possible heterolytic and homolytic mechanisms and has proposed that the observed addition: substitution ratios can best be correlated with olefin structure on the basis of an ionic mechanism. Electrophilic attack would produce a chlorocarbenium ion

(2) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, p. 520.

(3) M. L. Poutsma, *J. Am. Chem. Soc.*, **87**, 2172 (1965).

(4) (a) H. P. A. Groll, G. Hearne, F. F. Rust, and W. E. Vaughan, *Ind. Eng. Chem.*, **31**, 1239 (1939); (b) J. Burgin, W. Engs, H. P. A. Groll, and G. Hearne, *ibid.*, **31**, 1413 (1939); (c) D. V. Tishchenko and M. A. Shchigel'skaya, *J. Gen. Chem. USSR*, **7**, 1246 (1937); *Chem. Abstr.*, **31**, 6189 (1937); (d) D. V. Tishchenko, *J. Gen. Chem. USSR*, **8**, 1232 (1938); *Chem. Abstr.*, **33**, 4190 (1939).

(5) There is an efficient homogeneous process at higher temperatures (300-600°) which appears to involve radical chain reactions initiated by thermal dissociation of chlorine. This process produces chiefly allylic chlorides because, although chlorine atom apparently both adds to the double bond and abstracts allylic hydrogen atoms, the addition process is reversible whereas the abstraction process is not; cf. H. P. A. Groll and G. Hearne, *Ind. Eng. Chem.*, **31**, 1530 (1939), and D. V. Tishchenko and A. N. Churbakov, *Zh. Prikl. Khim.*, **19**, 243 (1946), as well as ref. 6a.

(6) C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957: (a) p. 359; (b) pp. 352-369; (c) pp. 48-53, 241, 242.

(7) R. W. Taft, Jr., *J. Am. Chem. Soc.*, **70**, 3364 (1948).

(1) Reported in preliminary form by M. L. Poutsma, *J. Am. Chem. Soc.*, **85**, 3511 (1963). For part I, see M. L. Poutsma and R. L. Hinman, *ibid.*, **86**, 3807 (1964).