principle is not applicable to this area. It is our position that the Evans–Polanyi principle has been enormously useful in organic chemistry and it should not be abandoned in this area without giving careful consideration to the alternative possibility, namely, that the absence of significant rate accelerations does indeed correspond to the nonformation of stable bridged intermediates with the stereochemical results arising from stereochemical control by steric factors including the effect of rapid equilibration.

It is common experience in organic chemistry that the enormous possibilities for structural variations make it possible to vary almost any characteristic by small, almost continuous increments. Is it not a reasonable possibility that there will be observed a gradual change in the nature of the substitution as we proceed from a static classical cation, through a rapidly equilibrating

cation, to a bridged cation? Where will the change occur? Will it occur suddenly, only after the rate of equilibration has become so rapid that we can no longer speak of equilibration, but must speak of resonance instead? Or is it a reasonable possibility that stereochemistry may be controlled by an equilibrating ion long before we reach this extreme stage?

Before concluding, we wish once again to call attention to the recently published review and defense of the phenonium ion interpretation.[16] In order to avoid misunderstanding, it should be emphasized that no difference of opinion exists as to the experimental data; the difference of opinion is entirely one of interpretation. It is to be hoped that the availability of these two discussions will facilitate careful consideration of the alternative interpretations and the final resolution of this interesting problem.

Carbonium Ions. XVIII. Cyclizations of Pentadienyl and Heptatrienyl Cations

N. C. Deno, Charles U. Pittman, Jr., and John O. Turner

Contribution from the College of Science, The Pennsylvania State University, University Park, Pennsylvania. Received January 4, 1965

The work of Sorensen and the work described herein combine to demonstrate that the cyclization of pentadienyl cations to cyclopentenyl cations is not only a general reaction but also a nearly quantitative reaction. The studies are extended to two heptatrienyl cations, one of which cyclizes while the other does not. The latter case provides the first example of the direct observation of an aliphatic trienyl cation. Two phenyl substituted allyl cations are examined: one cyclizes, one does not. Four monoaryl carbonium ions are directly observed, two indanyls, a tetrahyronaphthyl, and the 2-phenylpropyl.

The Cyclization of Pentadienyl Cations to Cyclopentenyl Cations. In a communication,[1] the following two reactions (eq. 1 and 2) were reported. Sorensen

actions in 96% H_2SO_4 were

$$\text{(1)}$$

$$\text{(2)}$$
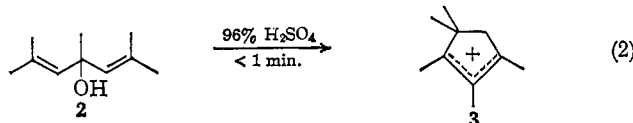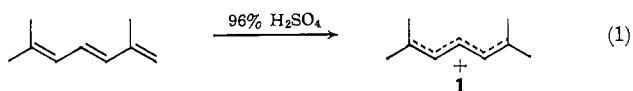
confirmed both reactions[2] and further showed that 1 slowly cyclized to the 1,2,3,4-tetramethylcyclopentenyl cation. The half-life of 1 at 25° in 96% H_2SO_4 is about 3 days, which we confirm.

Sorensen further examined homologs of 2 in which methyl groups were successively removed. The re-
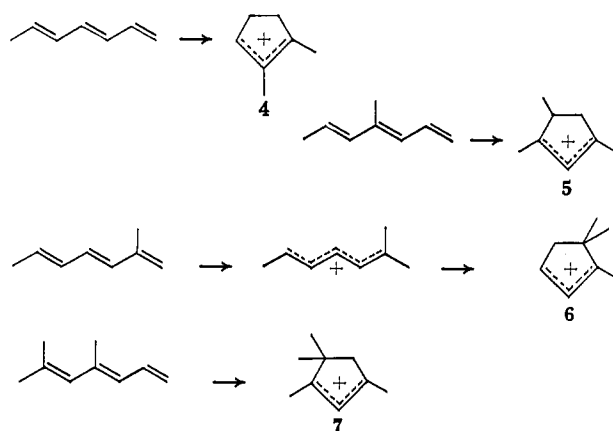
The formation of 7 has been independently confirmed by our group. The terminally alkylated allyl cations 5 and 7 were indefinitely stable whereas the trialkylated 4 and 6 were fleeting[2] in accord with past precedent.[3]

The cyclization of 2 to 3 has been extended to homologs of 2 in which the C-4 methyl has been replaced by ethyl, isopropyl, and isobutyl groups. Immediate cyclization of the dienols took place in 96% H_2SO_4 and the reaction can be represented by
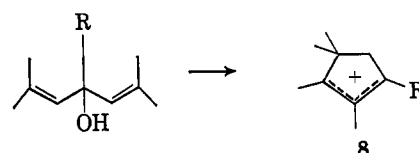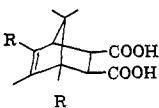
(1) N. Deno and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, 86, 1871 (1964).

(2) T. S. Sorensen, *Can. J. Chem.*, in press.

(3) N. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Houser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, 85, 2991 (1963).

| R	B.p. of diene reactant, °C.	Yield of adduct, %	M.p. of adduct, °C.	Anal. Calcd., %		Found, %		N.m.r. band positions, p.p.m.[a] —CH₃ at—		
				C	H	C	H	C-1	C-6	C-7
CH₃	78–84 (54)	76	145–146	66.6	8.0	67.6	8.4	1.04	b	0.80, 0.85
CH₃CH₂	64–65 (13)	56	158–159	67.8	8.3	67.5	8.4	1.04	1.60	0.80, 0.87
(CH₃)₂CH	65–68 (12)	57	160–161	68.5	8.6	68.5	7.9	1.01	1.70	0.80, 0.87[c]
(CH₃)₂CHCH₂	84–90 (20)	41	82–84	69.3	8.8	69.3	8.4	1.07	1.62	

[a] Band positions are in p.p.m. downfield from tetramethylsilane.   [b] The methyl group at C-5 (or C-6) was at 1.59 (or 1.70).   [c] The isopropyl doublet appeared at 1.03, $J = 6$ c.p.s.

The n.m.r. spectra of the three products appear in Figures 2–4 along with the spectrum of 3, Figure 1, which is illustrated for comparative purposes. The spectrum of 3 is now well authenticated, 3 having been obtained from several sources.[3,4] All yields of 8 were nearly quantitative as shown by the absence of extraneous bands in the n.m.r. spectra.

The structure of 8 was deduced from its n.m.r. spectrum and the spectrum of a Diels–Alder derivative. In each of the four cases, the characteristic splitting pattern of R remained intact in the spectrum of 8 showing that no rearrangement of R had occurred. The hydrogens next to the ring on R appear at 2.5–3.0 p.p.m. downfield from (CH₃)₄Si, showing that they are α to the allylic cation system. Thus R must be attached to C-1 or C-3. The remaining bands are identified in Figures 1–4 and leave as the only ambiguity the placement of R and the α-CH₃ at C-1 and C-3 or at C-3 and C-1.

The point of attachment of R was proven to be at C-1 as shown in structure 8. The cations 3 and 8 were converted to the mixture of dienes as previously described for 3.[5] One of the components of each mixture, the substituted cyclopentadiene, was capable of forming a Diels–Alder adduct with maleic anhydride. Although this one component represented only 20–30% for the case in which R is methyl, the yield of adduct was 76% showing that isomerization of the dienes took place under the conditions of the Diels–Alder reaction.

The key features in the n.m.r. spectra of the adducts (Table I) were (1) the presence of a bridgehead methyl at 1.01–1.07 p.p.m., (2) the downfield position of the α-H of R indicating it to be attached to C=C, and (3) the presence of a single methyl (for R other than methyl) α to the C=C system. These features establish the structure of the dienes and the maleic anhydrides adducts as
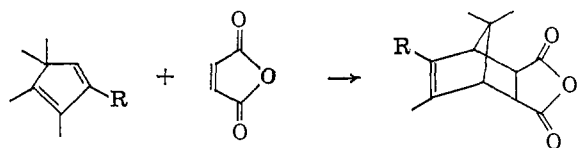
The other features of the n.m.r. spectra, such as the gem-dimethyl at C-7, were in accord with the assigned structure. It is not known whether the anhydride group is endo or exo.

Heptatrienyl Cations. The n.m.r. spectrum of 10 represents the first direct observation of a trienyl cation. This spectrum is shown in Figure 5 and some of the band positions (in p.p.m.) are indicated in structure 10. The vinyl hydrogens appeared at 6.6–7.5
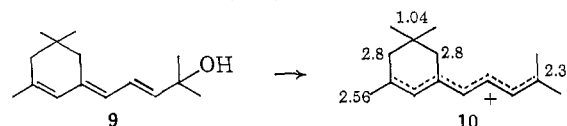
p.p.m. (Figure 5). Their total area was ~4 as calculated. It has not been possible unequivocally to assign these bands and in fact there may be more than one geometrical isomer present. The cation can be converted to a mixture of tetraenes (b.p. 68–75° at 1 mm.) in ~25% yield by rapid dispersal in aqueous alkali.[3] The recovered tetraene can be redissolved in H₂SO₄ to regenerate the n.m.r. spectrum of 10.

The ultraviolet spectrum of 10 exhibits λ_{max} 470 mμ (ϵ 2.82 × 10⁵). Simple LCAO MO theory gives orbital energies of 0, ±0.765, ±1.414, and ±1.848. The λ_{max} at 470 mμ is in agreement with the MO estimate of 523 mμ, obtained from 0.765 β and 400 mμ equivalent to 1 β.

An attempt was made to produce [(CH₃)₂C=CH–]₃C⁺. An isomeric cation of the same carbon skeleton was produced from the alcohol shown below, but it immediately cyclized to 11. This latter ion had been previously produced by a more conventional route[1] and was thus immediately recognized from its n.m.r. spectrum. The absence of extraneous bands again indicated a near quantitative yield.
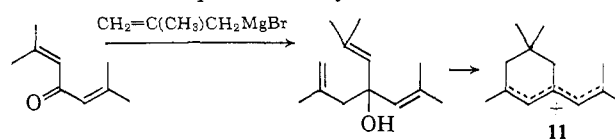
Cation 11 slowly disappears, more rapidly in 70% H₂SO₄ than 96%, and the ultraviolet spectrum reduces to that typical of cycloalkenyl cations with λ_{max} in the 300-mμ region. Presumably a further cyclization has occurred.

Monoaryl Carbonium Ions. Addition of 4-phenyl-2-methyl-1,3-pentadiene to either 96% H₂SO₄ or 23% SO₃ in H₂SO₄ gave immediately a quantitative yield of the 1,3,3-trimethylindanyl[6] cation. The n.m.r. band positions are indicated below and the areas were in accord with the assigned structure. The stability of this cation is in accord with a previous observation that

(4) N. Deno and C. U. Pittman, Jr., J. Am. Chem. Soc., 86, 1744 (1964).
(5) N. Deno, D. B. Boyd, J. D. Hodge, C. U. Pittman, Jr., and J. O. Turner, ibid., 86, 1745 (1964).

(6) Chemical Abstracts uses indanyl for the alkyl group derived from indane. The systematic name would appear to be indyl analogous to methyl from methane.
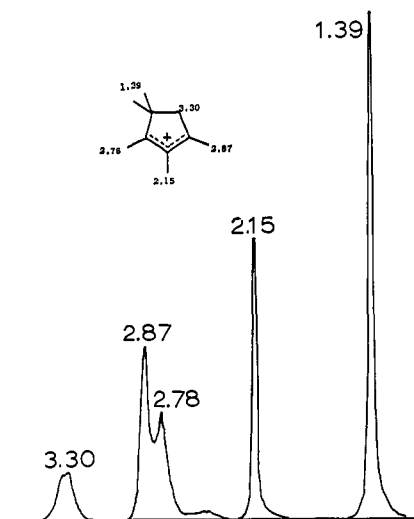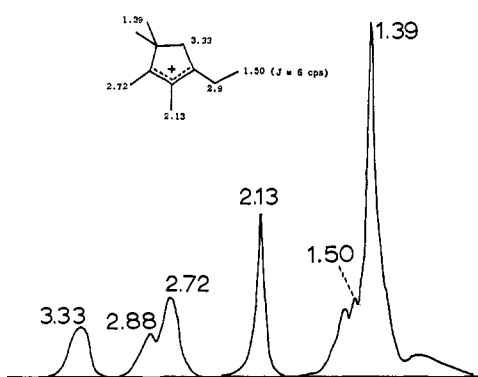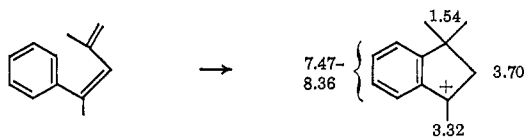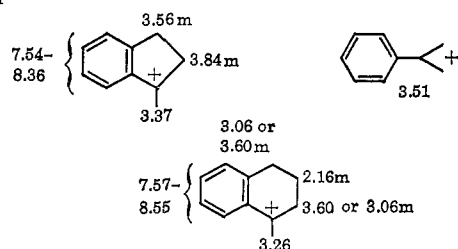
Figure 1. The n.m.r. spectrum of 8, R = methyl.

Figure 2. The n.m.r. spectrum of 8, R = ethyl.

Figure 3. The n.m.r. spectrum of 8, R = isopropyl.
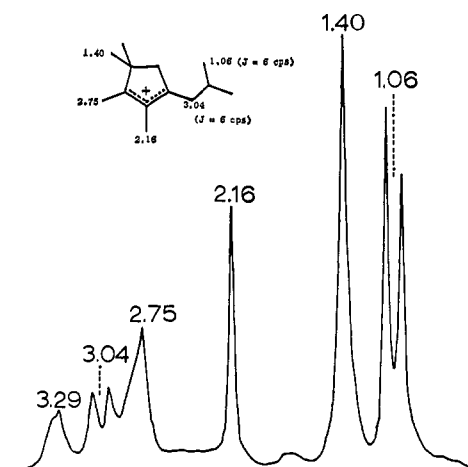
Figure 4. The n.m.r. spectrum of 8, R = isobutyl.
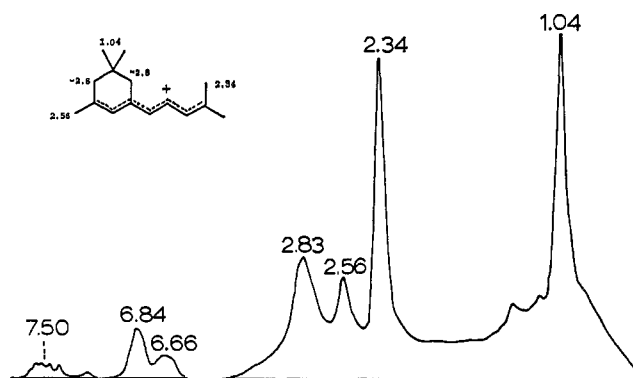
Figure 5. The n.m.r. spectrum of 10.

the 1-methylindanyl cation was half-formed in 78% H_2SO_4 and was stable in 96% H_2SO_4 for at least 1 min. at $10^{-5}\ M$.[7]

In 96% D_2SO_4 the C-2 hydrogens are completely exchanged in less than 1 min. at 25° and the hydrogens on the methyl at C-1 are half-exchanged in ~3 min.

Three other monoaryl carbonium systems were examined. 1-Methylindene formed the 1-methylindanyl cation in 96% H_2SO_4, 2-phenylpropene (α-methylstyrene) formed the 2-phenylpropyl cation in 25% SO_3–75% H_2SO_4, and 1-methyl-1,2,3,4-tetrahydro-1-naphthol formed its cation in 23% SO_3. The cation structures are shown below with the n.m.r. band positions. All band areas were as calculated.

(7) N. Deno, P. T. Groves, J. J. Jaruzelski, and M. N. Lugasch, J. Am. Chem. Soc., 82, 4721 (1960).

The letter m after the above numbers signifies a multiplet. As added precautions, 1-methylindene was recovered in 65% yield from the first cation and 1-methyl-3,4-dihydronaphthalene was recovered in 60% yield from the third cation. In both recoveries, rapid-dispersal techniques[3] were employed. Addition of the recovered arenes back into acid regenerated the n.m.r. spectrum of the respective carbonium ions.

For the 1-methylindanyl cation in 92% D_2SO_4, the hydrogens at C-2 were completely exchanged within 1 min. and the hydrogens on the methyl group

were half-exchanged in 8 min. at 25°. The exchange diminished the 3.84 band and not the 3.56 band and on this basis the 3.84 band was assigned to the hydrogens on C-2 and the 3.56 to those on C-3.

The n.m.r. spectrum of the 2-phenylpropyl cation had already been observed by Olah[8] in HF–SbF$_5$ and by Farnum[9] in ClSO$_3$H. The band positions in all three media are similar. The 2-phenylpropyl cation is chemically unstable in 96% H$_2$SO$_4$, presumably due to alkylation of its equilibrate, 2-phenylpropene. The above tetrahydronaphthyl cation was also chemically unstable in 96% H$_2$SO$_4$. The mode of decomposition appeared to be largely hydride transfer since 1-methyl-1,2,3,4-tetrahydronaphthalene could be isolated from the CCl$_4$ solution used to introduce tetrahydronaphthol into the H$_2$SO$_4$.

The following diene simply protonated as shown and did not undergo further change in 200 hr. at 25° in 96% H$_2$SO$_4$. The n.m.r. band positions of the cation are indicated below. The hydrogens at C-2 and C-3 gave identical (in shape) unresolved bands with a width at half-height of 0.14 p.p.m. The n.m.r. spectrum was identical in 80 and 96% H$_2$SO$_4$ as well as 65% SO$_3$–35% H$_2$SO$_4$. In 96% D$_2$SO$_4$ at ~25°, the hydrogens at C-2 half-exchanged in 2 hr. whereas the hydrogens of the α-methyl groups showed no appreciable exchange in 200 hr. The ultraviolet spectrum of the cation exhibited maxima at 285 and 389 mμ with ϵ 5.0 × 10^3 and 48.0 × 10^3.
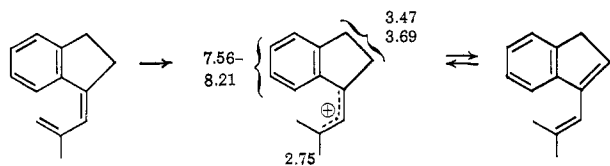
Experimental

2,6-Dimethyl-4-alkyl-2,5-heptadienols. Phorone (2,6-dimethyl-2,5-heptadiene-4-one) was treated with CH$_3$-MgBr in ether.[10] The amount of ketone in the crude product was estimated by an analysis of the band areas of the n.m.r. spectrum. The crude product was treated with a fivefold excess of hydroxylamine in aqueous ethanol to convert the by-product ketone (a combination of phorone plus the ketone from 1,4-addition) to oxime. After 2 hr. at 100°, the aqueous ethanol was further diluted with water and the dienol was extracted with pentane.

Distillation through a 10-in. Vigreux column produced an 8% yield of 2,4,6-trimethyl-1,3,5-heptatriene, b.p. 35–36° (4 mm.),[11] and 71% of 2,4,6-trimethyl-2,5-heptadien-4-ol, b.p. 38–43° (0.23 mm.).[11] The infrared spectrum of the alcohol contained an OH band at 2.97 and a C=C band at 6.16 μ. The n.m.r. spectrum was also satisfactory.

The 4-ethyl homolog was similarly obtained from C$_2$H$_5$MgBr plus phorone. The 2,4-dimethyl-4-ethyl-2,5-heptadienol, b.p. 83–88° (17 mm.), was obtained in 49% yield. The infrared spectrum contained an OH band at 2.94, a C=C band at 6.2 μ, and *no* C=O band. The n.m.r. spectrum was satisfactory.

The 4-isopropyl homolog was similarly obtained from isopropyllithium and phorone. Although the crude yield of dienol was 33%, the yield of material with b.p. 83–96° (11 mm.) was only 11%. The structure was supported by the n.m.r. spectrum of the cyclized cyclopentenyl cation, Figure 3, and the isolation from rapid-dispersal drowning of a 67% yield of material with b.p. 65–68° (12 mm.) which is in the range expected for the corresponding dienes.

The 4-isobutyl homolog was similarly obtained from isobutyllithium and phorone. A yield of 21%, b.p. 88–91° (8 mm.), was obtained. The n.m.r. spectrum, though not entirely definitive, was in accord. Introduction into 96% H$_2$SO$_4$ gave the 1-isobutyl-2,3,4,4-tetramethylcyclopentenyl cation in quantitative yield as shown by the n.m.r. spectrum of the H$_2$SO$_4$ solution, Figure 4. Rapid-dispersal drowning gave 51% of a mixture of dienes, b.p. 84–90° (20 mm.). The C and H analysis was satisfactory and the diene mixture could be quantitatively converted back to the cyclopentenyl cation on addition to 96% H$_2$SO$_4$.

Anal. Calcd. for C$_{13}$H$_{22}$: C, 87.6; H, 12.4. Found: C, 87.3; H, 12.7.

The 4-isobutenyl derivative was similarly obtained from phorone plus CH$_2$=C(CH$_3$)CH$_2$MgCl. The fraction b.p. 83–97° (14 mm.) was redistilled through a spinning-band column to produce 2,6-dimethyl-4-isobutenyl-2,5-heptadien-4-ol in 28% yield, b.p. 89–95° (5 mm.).

The 4-phenyl derivative, 2,6-dimethyl-4-phenyl-2,5-heptadien-4-ol,[12] b.p. 139–143° (13 mm.), was obtained in 41% yield from C$_6$H$_5$Li and phorone. No hydroxylamine treatment was necessary. The infrared spectrum and n.m.r. spectrum demonstrated the absence of ketone. When C$_6$H$_5$MgBr was used in place of C$_6$H$_5$Li, the product was predominantly that of 1,4-addition.

In all of the above reactions the lithium or magnesium derivative was used in 20–50% excess and the per cent yields were based on phorone.

5-(3',5',5'-Trimethyl-2'-cyclohexylidene)-2-methyl-3-penten-2-ol (**9**). Isophorone (3,5,5-trimethyl-2-cyclohexen-1-one) was treated with ethyl 4-bromo-2-butenoate and Zn in the conventional Reformatsky style. A 53% yield of ethyl 4-(3',5',5'-trimethyl-2'-cyclohexylidene)-2-butenoate was obtained, b.p. 174–185° (13 mm.). The infrared and n.m.r. spectra were satisfactory. In identifying intermediates, such as this one, we have generally replaced the conventional C and H analysis by the more definitive n.m.r. spectroscopy supported by boiling point and infrared analyses. These detailed n.m.r. spectra are for the most part presented in the Ph.D. theses of the junior authors.

A small amount of the ester was converted to the acid *via* alkaline saponification and the ultraviolet spectrum of the acid exhibited λ_{max} at 294 mμ (ϵ 41,000) as expected for a trienoic acid.

The unsaturated ester was treated with an excess of CH$_3$MgBr in ether. Conventional hydrolysis with saturated aqueous NH$_4$Cl and distillation gave a crude product, b.p. 122–145° (14 mm.). Redistillation through a spinning-band column gave a 35% yield of **9**, b.p. 81–84° (1.2 mm.). The infrared spectrum contained an OH band at 2.96 μ and no C=O band of either an ester or ketone. A broad set of C=C bands

(8) G. Olah, *J. Am. Chem. Soc.*, **86**, 932 (1964).
(9) D. Farnum, *ibid.*, **86**, 934 (1964).
(10) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1428 (1952).
(11) T. von Fellenberg, *Ber.*, **37**, 3580 (1904).

(12) B. N. Dashkevich, *Ukr. Khim. Zh.*, **21**, 335 (1955); *Chem. Abstr.*, **49**, 14711 (1955).

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_5-MgBr 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_2-Cl_2–CH_3OH solution using a Varian 60-Mc. instrument.

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

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Contribution from the Department of Chemistry, Whitmore Laboratory, Pennsylvania State University, University Park, Pennsylvania 16802. Received January 6, 1965

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 results[2] were that the kinetics of hydration of arylalkenes (and the reverse dehydration of the alcohols) follow eq. 1.

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

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 addition[5] 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 equilibria[9] 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 discrepancy[5] 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).