

dried over anhydrous sodium sulfate. The ether was evaporated and the oil gradually cooled to -20° . Crystals grown during this period were separated by filtration. The crude *trans*-1,4-dichlorocyclohexane (3.0 g.) was recrystallized from ethanol to yield 1.3 g. of pure material, m.p. $102.0-102.8^{\circ}$. The filtrate was distilled using a Todd column packed with glass helices to give a fraction, b.p. $90.5-91.5^{\circ}$ at 17 mm., n_D^{20} 1.4947, that was shown by g.l.c. to be 93% pure *cis*-1,4-dichlorocyclohexane.

***trans*-1-Bromo-2-chlorocyclohexane.**—The method of Goering and Sims was employed utilizing the reaction of hydrogen chloride

in chloroform solution with 24.6 g. of cyclohexene and 50 g. of *n*-bromosuccinimide.^{8a} Distillation gave 41 g. of material, b.p. $69-70^{\circ}$ at 8 mm. Rectification in a Todd column packed with glass helices gave 93.3% *trans*-1-bromo-1-chlorocyclohexane (64.5%), b.p. 60° at 2.6 mm. No major impurities were revealed by g.l.c.

Acknowledgment.—The n.m.r. spectra were recorded by Dr. R. King. His assistance and helpful discussions with him are gratefully acknowledged.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

Carbonium Ions. XI. Nuclear Magnetic Resonance Spectra of the Aliphatic Alkenyl Cations¹

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The nuclear magnetic resonance spectra of nine cyclopentenyl cations, six cyclohexenyl cations, and three linear alkenyl cations are presented. The areas of the bands correspond to values predicted from the structures of the ions. The positions of the bands (such as H or CH₃ on the central carbon of the allylic system or hydrogens on the carbon α to the allylic system) are invariant with structure and serve to identify these ions, either when present in complex mixtures or when produced from complex reactions. The kinetics of decomposition of carbonium ions is discussed with the view of directing attention to the critical choice of conditions necessary to achieve chemical stability.

Introduction

The discovery that the 1,3,5,5-tetramethylcyclohexenyl cation is stable in 96% H₂SO₄² opened the way to a direct study of the properties of a variety of aliphatic alkenyl (allylic) cations. Among the strictly hydrocarbon cations (excluding those with substituents such as hydroxy, chloro, etc.), chemical stability sufficient for n.m.r. studies has been achieved only with cations in which the terminal positions of the allylic system were completely alkylated. This paper presents the n.m.r. spectra of such ions. The papers immediately following will describe rearrangements, hydrogen-deuterium exchanges, ultraviolet spectra, and equilibrium studies.

Experimental

The n.m.r. spectra were recorded on a Varian A-60 instrument. The field was adjusted with an ethyl bromide sample until the resolution was between 0.005 and 0.02 parts per million (p.p.m.). The viscosity of 96% H₂SO₄ prevents the resolution obtainable in more mobile solvents. Nevertheless, the spectra were beautiful in their simplicity and examples are shown in Fig. 1-5.

The positions of the bands in the n.m.r. spectra in 96% H₂SO₄ were calibrated by reference to (CH₃)₄N⁺Cl⁻ as an internal standard (suggested by Prof. P. S. Skell and Miss Josephine de Luis). These positions are presented in Table I and are expressed as the difference in p.p.m. relative to (CH₃)₄Si. Clearly, the actual numbers depend entirely on the value chosen for the difference between (CH₃)₄Si and (CH₃)₄N⁺. A value of 3.10 p.p.m. was used, the silane at higher field, and this is based on a measured difference of 3.10 p.p.m. between (CH₃)₄N⁺ and (CH₃)₃Si(CH₂)₃SO₃H in 96% H₂SO₄ coupled with an assumed difference of zero between (CH₃)₄Si and (CH₃)₃Si(CH₂)₃SO₃H.³

This choice is not free from objection. The difference between (CH₃)₄N⁺ and (CH₃)₃Si(CH₂)₃SO₃H was 3.19, 3.17, 3.12, and 3.10 in 0, 50, 83, and 96% H₂SO₄. The latter two values were independently confirmed by Miss de Luis. An indirect comparison between (CH₃)₄N⁺ and (CH₃)₄Si was accomplished using a precision coaxial n.m.r. tube. The (CH₃)₄N⁺ was in solution in 96% H₂SO₄ in the inner tube and a 1% solution of (CH₃)₄Si in CCl₄ was in the outer tube. Appropriate corrections were made for the magnetic susceptibilities of the solvents.⁴

This method gave a difference of 2.94 p.p.m. A direct comparison between (CH₃)₄N⁺Cl⁻ and (CH₃)₄Si was accomplished in methanol and in trifluoroacetic acid giving the differences 3.28 and 3.29, respectively. Obviously, we are plagued with minor discrepancies and can only emphasize that a value of 3.10 p.p.m. was chosen for the difference between (CH₃)₄N⁺ and (CH₃)₄Si in 96% H₂SO₄.

Neither (CH₃)₄Si, (CH₃)₃Si(CH₂)SO₃H, nor CH₃SO₃H⁵ are suitable calibration standards in sulfuric acid. (CH₃)₄Si is both insoluble and unstable, (CH₃)₃Si(CH₂)SO₃H rapidly decomposes, and CH₃SO₃H exhibits variation in band position from 70 to 96% H₂SO₄.

The alkenyl cations were produced by adding the dienes to 96% H₂SO₄. Polymerization could be minimized by adding the diene through a capillary tube or as a fine film to the periphery of vigorously stirred H₂SO₄ at 0°. The syntheses of the dienes are described under the titles of the cations which they generated because in most cases the cations were better characterized than the dienes. We anticipate making a better characterization of these dienes at a later date and particularly to compare the composition of dienes when prepared by acid-catalyzed equilibration and by quenching of the cations in alkali. Most distillations were conducted using a Nestor-Faust spinning band column.

1-Alkyl-3-methylcyclopentenyl Cations.—2,5-Hexanedione was cyclized to 3-methyl-2-cyclopenten-1-one.⁶ The three dienes were made by treating this ketone with methyl, ethyl, and isopropyl Grignard reagents. The Grignard products were hydrolyzed with a small excess of hydrochloric acid. The dienes were isolated by distillation, and no attempts were made to separate the components of the diene mixtures. The three diene mixtures have been reported (methyl,⁷ ethyl,⁸ and isopropyl⁹), but in each case were prepared by other methods. The yields by the Grignard method were 44, 31, and 28%. No attempt was made to achieve optimum yields.

1-Alkyl (or Phenyl)-3,5,5-trimethylcyclohexenyl Cations.—The four dienes were prepared by addition of methyl, ethyl, isopropyl, and phenyl Grignard reagents to isophorone (3,5,5-trimethyl-2-cyclohexen-1-one). The Grignard products were hydrolyzed with saturated aqueous NH₄Cl. The dienes were isolated by distillation. The intermediate allylic alcohols can dehydrate in either of two directions to produce an endocyclic or a half exocyclic diene. The n.m.r. spectra of the methyl and ethyl derivatives showed that both dienes were present and in nearly equal amounts. This is particularly evident in the gem-dimethyl bands which were well resolved for the two dienes and had equal areas. The b.p. of each diene mixture agreed with reported values.¹⁰

(1) This research was supported in part by a grant from the National Science Foundation and in part by a grant from the Petroleum Research Fund of the American Chemical Society. A grant from the National Science Foundation supported in part the purchase of the Varian A-60 n.m.r. instrument. J. Hodge received a fellowship from the Shell Companies Foundation. All of this assistance is most gratefully acknowledged.

(2) N. Deno, H. G. Richey, Jr., J. D. Hodge, and M. J. Wisotsky, *J. Am. Chem. Soc.*, **84**, 1498 (1962).

(3) G. V. D. Tiers, Abstracts, 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960, p. 17R; G. V. D. Tiers and R. I. Coon, *J. Org. Chem.*, **26**, 2097 (1961).

(4) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p. 81.

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(6) R. M. Acheson and R. Robinson, *J. Chem. Soc.*, 1127 (1952).

(7) R. Riemschneider and E. B. Grabitz, *Monatsh.*, **89**, 748 (1958).

(8) P. Duden and R. Freytag, *Chem. Ber.*, **36**, 944 (1903).

(9) W. Treibs, *ibid.*, **66**, 610 (1933).

(10) O. H. Wheeler, *J. Org. Chem.*, **20**, 1672 (1955); J. P. Ferrin, T. B. Tom, N. L. Koslin, K. W. Greenlee, J. M. Derfer, and C. E. Board, *ibid.*, **19**, 923 (1954).

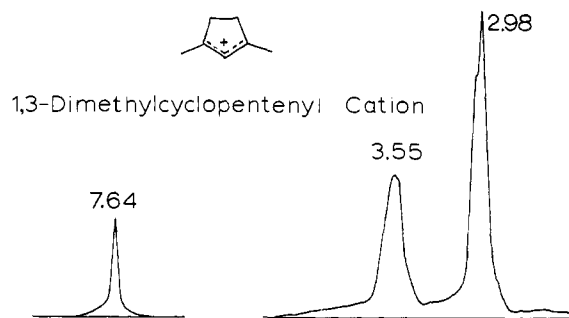


Fig. 1.—N.m.r. spectrum of 1,3-dimethylcyclopentenyl cation.

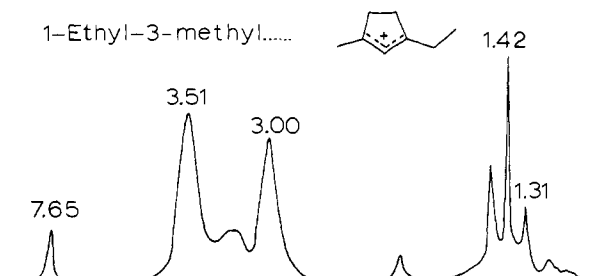


Fig. 2.—N.m.r. spectrum of 1-ethyl-3-methylcyclopentenyl cation.

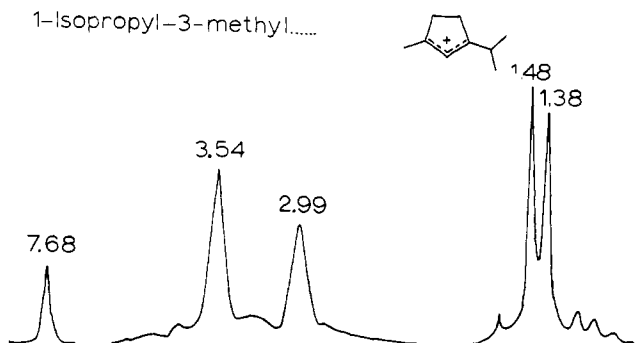


Fig. 3.—N.m.r. spectrum of 1-isopropyl-3-methylcyclopentenyl cation.

In the isopropyl derivative, the endocyclic diene predominates as indicated by the areas of the isopropyl doublet and the bands of the two vinylic hydrogens. Weak bands of the part exocyclic diene were present and an estimate from the areas of the *gem*-dimethyl bands or the vinylic hydrogen bands indicated that 70% of the diene mixture was the endocyclic diene. The initial product was contaminated with isophorone, the b.p. of the mixture being 112–113° (73 mm.). The yield of diene after correcting for the isophorone contamination was about 40%.

In the phenyl derivative, the presence of three distinct and near-equal *gem*-dimethyl bands indicated that three isomeric dienes were present in near-equal amounts. The b.p. of the mixture was 102–103° (1 mm.) and the total yield of dienes was 53%.

Anal. Calcd. for $C_{15}H_{18}$: C, 90.8; H, 9.2. Found: C, 90.6; H, 9.2.

1,3,4,4,5- and 1,2,3,4,4-Pentamethylcyclopentenyl Cations.—3-Methyl-2-butanone was converted to 3,3,4,4-tetramethyl-2,5-hexanedione by the method reported.¹¹ The diene cyclized in high yield using conditions identical to those used to cyclize 2,5-hexanedione⁸ with the exception that the solvent was a 1:1 mixture of methanol and water. The 3,4,4,5,5-pentamethyl-2-cyclopenten-1-one was characterized by the ultraviolet spectrum (λ_{max} 230 m μ , ϵ 12,300), b.p. 53–54° (1 mm.), and n.m.r. spectrum, which was in accord with the assigned structure. The yield of purified material was 72%.

Anal. Calcd. for $C_{16}H_{18}O$: C, 78.9; H, 10.6. Found: C, 78.9; H, 10.7.

The ketone was reduced with $LiAlH_4$ in ether. The crude product after hydrolysis and removal of ether exhibited an infrared spectrum with a strong hydroxyl band and no carbonyl band. The reduction was concluded to have been quantitative and the 3,4,4,5,5-pentamethyl-2-cyclopenten-1-ol was not further characterized.

(11) M. F. Ansell, W. J. Hickinbottom, and P. G. Holton, *J. Chem. Soc.*, 349 (1955).

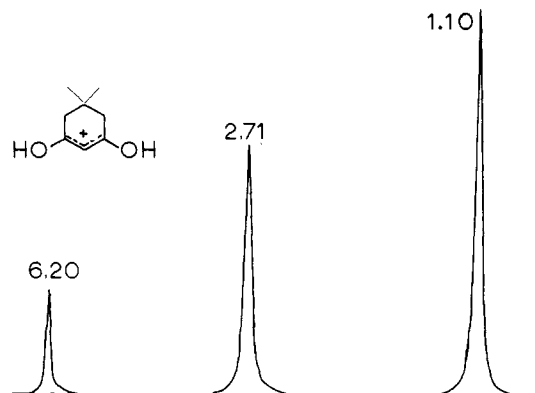


Fig. 4.—N.m.r. spectrum of 1,3-dihydroxy-5,5-dimethylcyclohexenyl cation. This is protonated dihydrodimethylresorcinol.

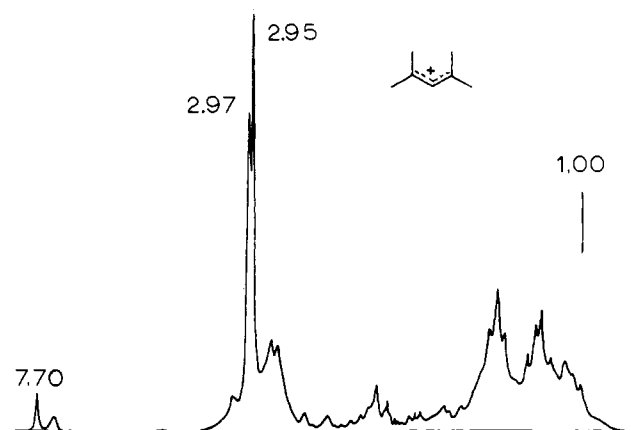


Fig. 5.—N.m.r. spectrum of 2,4-dimethylpentenyl cation showing the two sharp peaks due to the cation and the extraneous background caused by impurities.

1,3,4,4,5,5- and 1,2,3,4,4,5-Hexamethylcyclopentenyl Cations.—3,4,4,5,5-Pentamethyl-2-cyclopenten-1-one was treated with methyl lithium in ether. The product was worked up by adding water and a slight excess of hydrochloric acid. The ether extract was separated, dried, and distilled. The diene, b.p. 53–54° (10 mm.), was obtained in 44% yield. It is pure 3-methylene-1,4,4,5,5-pentamethylcyclopentene as shown by the n.m.r. spectrum. The ultraviolet spectrum in ethanol had λ_{max} 238 m μ , ϵ 18,100.

Anal. Calcd. for $C_{11}H_{18}$: C, 87.9; H, 12.1. Found: C, 87.8; H, 11.9.

2,4-Dimethylpentenyl Cation.—2,4-Dimethyl-1,3-pentadiene was prepared from mesityl oxide and CH_3MgI .¹² An n.m.r. spectrum of the diene showed bands at 1.71, 4.55, 4.72, and 5.41 p.p.m. and the areas were 8.3:1.0:0.9:1 (calcd. 8:1:1:1). These areas account for 99.5% of the total hydrogen in the n.m.r. spectrum.

2,3,4-Trimethylpentenyl Cation.—Powdered zinc chloride (50 g.) was added over a period of 30 min. to a stirred mixture of 60 g. of 2-methyl-2-butene and 175 g. of acetic anhydride. The temperature rose to 45° during the addition. The mixture was stirred for 20 hr., poured onto ice, extracted with ether, and the ether extract washed with aqueous Na_2CO_3 . After drying over $MgSO_4$, the solution was distilled to give a fraction, 20 g., o.p. 130–132°, which was 3,4-dimethyl-4-penten-2-one¹³ and a fraction, 14 g., b.p. 146–147°, which was 3,4-dimethyl-3-penten-2-one.¹³

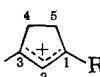




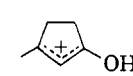
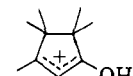
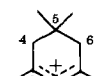
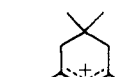
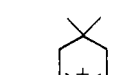
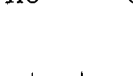
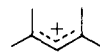
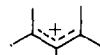
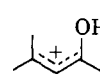
3,4-Dimethyl-4-penten-2-one (note that the unconjugated ketone was used) was added to CH_3MgI in ether. After hydrolysis with ice and dilute hydrochloric acid, the ether extract was washed with aqueous Na_2CO_3 , dried over $MgSO_4$, and distilled. The product was 2,3,4-trimethyl-4-penten-2-ol, b.p. 60–62° (27 mm.), 66% yield. The analysis is high on both C and H, perhaps due to the presence of small amounts of the diene arising from addition of the CH_3MgI to small amounts of the conjugated unsaturated ketone.

Anal. Calcd. for $C_8H_{18}O$: C, 74.9; H, 12.6. Found: C, 75.7; H, 13.0.

(12) O. N. Jitkow and M. T. Bogert, *J. Am. Chem. Soc.*, **63**, 1979 (1941). The addition of ketone to the Grignard at 0° (rather than 25°) appears to be critical.

(13) G. K. Estok and J. H. Sikes, *ibid.*, **75**, 2745 (1953).

TABLE I: N.M.R. SPECTRA OF CYCLOPENTENYL, CYCLOHEXENYL, AND LINEAR ALKENYL CATIONS

Cation	Band position in p.p.m. downfield from (CH ₃) ₄ Si						Areas	
	H on C ₂	H on C ₄ and C ₅	CH ₃ at C ₃ (and C ₁ when present)	CH ₃ on C ₂	CH ₃ of ethyl or isopropyl group	CH ₃ on C ₄ and C ₅	Exptl.	Calcd.
								
R = methyl	7.64	3.55	2.98	0.9:3.9:6	1:4:6
R = ethyl	7.65	3.51 (3.4) ^a	3.00	..	1.42 ^b	..	0.8:5.5:3.0:3	1:4 + 2:3:3
R = isopropyl	7.68	3.54 (3.4) ^c	2.99	..	1.43 ^d	..	0.84:7.9:6	1:4 + 1 + 3:6
	A	7.62	3.37	2.93	..	1.37	1:1:2:6.2 ^e :10 ^f	1:1:6:9
	B	..	3.30	2.87 2.78	2.15	1.39	1.8:6:3.1:7.0 ^f	2:6:3:6
		7.49	..	2.90	..	1.33	1.0:5.9:12	1:6:12
		..	3.2	2.81	2.15	1.38 ^d 1.34 1.28	1.2:6.1:3.0:9	1:6:3:3 + 3 + 3
		6.81	3.33	2.63	1.0:4.0:3	1:4:3
		6.65	..	2.52	..	1.32 1.25	1.0:3.0:12	1:3:12
								
R = methyl		7.62	3.06	2.84	..	1.10	0.9:3.6:6.0:6	1:4:6:6
R = ethyl		7.63	3.09	2.84	1.36 ^b	1.10	1.0:9.0:3.2:6	1:4 + 2 + 3:3:6
R = isopropyl		7.61	3.09	2.84	1.35 ^d	1.10	0.9:8.0:6.1:6	1:4 + 1 + 3:6:6
R = phenyl	7.59-8.38 ^g	3.42	2.76	1.16	6.2:1.8:1.8:3.1:6	6:2:2:3:6
		6.78	2.83 2.71	2.45	..	1.12	1.0:4.1:3.1:6	1:4:3:6
		6.20	2.71	1.10	1.1:4.0:6	1:4:6
								
		H on C ₅		CH ₃ on C ₂ or C ₄	CH ₂ on C ₃		Exptl.	Calcd.
		7.70 ^h		2.95 ^h 2.97	..		1:12.0	1:12
		..		2.95 ⁱ	2.12 ⁱ		3:14.5	3:12
		6.96		2.45 2.62 2.76	..		0.8:3.0:3.0:3	1:3:3:3

^a Center of a broad band ranging over 0.3 p.p.m. which is interpreted to be the unresolved quartet of the CH₂ of the ethyl group. ^b Center of a triplet with $J = 6.8$ c.p.s. which is typical of ethyl groups. ^c Center of a broad band ranging over 0.5 p.p.m. which is interpreted to be the unresolved septet of the CH of the isopropyl group. ^d Center of a doublet with $J = 6.6$ c.p.s. which is typical of splitting by a single hydrogen. ^e The spectrum measured 70-90 sec. after mixing already contained about 30% of the ion B as judged by the fact that the area of the 2.15 band was 1.2 times the area of the 7.62 band. Since the total aggregate band centering at 2.93 but extending from 2.7-3.2 had a total relative area of 8.8, 30% of this was subtracted out in order to estimate the area of the 2.93 band due to ion A. ^f Some arbitrariness was exercised in outlining the lower portions of this band since there was adjoining absorption. This spectrum will be shown in the following paper. ^g Bands were present at 7.59, 7.70, 7.83, 7.96, 8.06, 8.25, and 8.38. The hydrogen at C₂ was presumably one of these bands. ^h The bands and areas listed account for only 22% of the observed hydrogen; see text and Fig. 5. ⁱ The bands and areas listed account for only 40% of the observed hydrogens. The remainder occupied a broad diffuse pattern similar to that of the preceding ion, shown in Fig. 5.

Discussion

Nuclear Magnetic Resonance Spectra.—Certain characteristic bands appear in the n.m.r. spectra of the aliphatic alkenyl cations. A lone hydrogen on the central carbon of the allylic system appears at 7.5–7.7 p.p.m. with little sensitivity to alkyl substitution and little sensitivity to whether the cation is cyclopentenyl, cyclohexenyl, or linear alkenyl. Similarly, a methyl on the same carbon is equally sharp and invariant at 2.12–2.15 p.p.m.

The positions of the bands of the hydrogens on carbons α to the allylic system appear at 2.7–3.6 p.p.m. Again the variation is small between cyclopentenyl, cyclohexenyl, and linear alkenyl cations. Perhaps these small variations are related to the amount of positive charge delocalized into these hydrogens and/or the intensity of charge on the carbonium carbons. A clearer example of this effect is exhibited in the 1,1-diarylethyl cations, $\text{Ar}_2\text{C}^+\text{CH}_3$. Greater charge delocalization and less intense charge on C-1 would be expected when Ar is anisyl than when Ar is phenyl. Accordingly, the CH_3 band was at 3.25 p.p.m. when Ar was anisyl and at 3.65 p.p.m. when Ar was phenyl. An extreme case is $(\text{CH}_3)_3\text{C}^+$. Olah and co-workers found the band for this ion at 4.35 p.p.m.¹⁴

Bands due to hydrogens on carbons α to the allylic system can be as sharp as any as shown in Fig. 5 (and Fig. 1 and 2 of the following paper, no. XII of the series). However, if hydrogens are present on adjacent α -carbons, these α -hydrogen bands markedly broaden, as exhibited in Fig. 1–3. It is concluded that in the cyclopentenyl and cyclohexenyl cations a coupling occurs between such hydrogens on nearby α -carbons. Because of motion of the alkyl groups containing the α -carbons, the coupling expresses itself as a line broadening rather than a splitting.

The resolution of the CH_3 bands in the 2,4-dimethylpentenyl cation into bands of equal areas at 2.95 and 2.97 p.p.m. (Fig. 5) is under study. This nonequivalence or splitting of methyl groups is more clearly shown in the n.m.r. spectrum of the 4-methyl-2-hydroxypentenyl cation (protonated mesityl oxide), where the three methyl bands appear at 2.45, 2.62, and 2.76 p.p.m.

In the protonated α,β -unsaturated ketones, the hydrogen on the central carbon of the allylic system appears at 6.2–7.0 p.p.m., which is at somewhat lower field than general for vinylic hydrogens. Such ions are hybrids between the protonated ketone form and the hydroxyalkenyl cation form. The latter structure makes an important contribution to the hybrid.

Chemical Stability of Carbonium Ions.—The ease with which several physical properties of carbonium ions have been measured is deceptive because it depends on a thorough understanding of the chemical reactivity of such ions. The 1,3-dimethylcyclopentenyl cation (I) is typical.

Compound I is half-formed from the diene II in 35% H_2SO_4 . At this acidity, the rate of reaction of I with II is significant even in 10^{-5} M solution so that half of I + II has reacted after 170 sec. The second-order rate constant is $600 \text{ l. sec.}^{-1} \text{ mole}^{-1}$. In calculating this rate constant, no attempt was made to correct for the absorption of the dimeric ion, provisionally III. This could not have introduced much error because the rate constant, calculated from the diminution in optical density in the early stages of the reaction, was strictly constant when calculated from the equation

$$-d\text{C}_R^+/dt = k_2\text{C}_I\text{C}_{II} \quad (1)$$

(14) G. A. Olah, W. S. Tolgyesi, S. J. Kuhn, M. E. Moffatt, I. J. Gastien, and E. B. Baker, *J. Am. Chem. Soc.*, **85**, 1328 (1963).

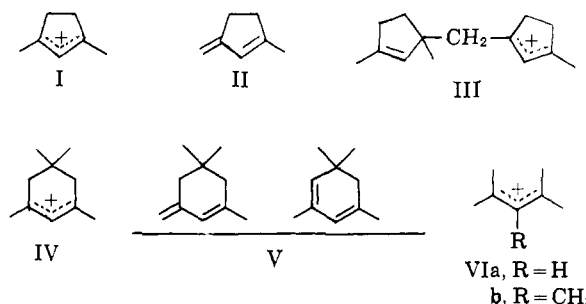
These tests of eq. 1 encompassed a tenfold variation in the initial concentration of I + II.

Using eq. 1, it is computed that in a 0.1 M solution in 35% H_2SO_4 , half of I + II disappears in 0.02 sec. so that I or II can be said to polymerize instantly in 35% acid. Using eq. 1 and the H_0 acidity function

$$H_0 = \text{p}K + \log c_B/c_{\text{BH}^+} \quad (2)^{15}$$

it can be estimated that it will take 2 days for half of I + II to disappear in either water at pH 5 or in 96% H_2SO_4 .

It is a general property of these systems that they are least stable at acidities where concentrations of carbonium ion and diene are equal.¹⁶ This principle is derived readily from eq. 1 and the restriction that the total concentration of I + II remain constant. It is for this reason that cations which are stable for days, perhaps years, in 96% H_2SO_4 are polymerized instantly in dilute acids. In the recovery of the diene mixture V from the cation IV,² it is necessary to add the solution of IV in 96% H_2SO_4 through a capillary to well stirred aqueous NaOH at 0° in order to race through the dilute acid region with all possible speed. Only in this way can the monomeric dienes be recovered, and the recovery by this technique can be quantitative.



It has been assumed that the second-order rates of disappearance were due to dimerization. There is an alternative destruction reaction that would exhibit the same rate law, eq. 1. This alternative is hydride abstraction from the diene by the alkenyl cation to produce an alkene and a dienyl cation. Dienyl cations are well known to absorb in the 400 m μ region both from LCAO MO theory and directly from experiment.¹⁷ As yet, such absorption has appeared only in traces during the destruction of the alkenyl cations described in this paper, from which it is concluded that dienyl cations are not produced.

These problems in chemical instability became particularly important in measuring the n.m.r. spectrum of the 2,4-dimethylpentenyl (VIa) and 2,3,4-trimethylpentenyl (VIb) cations. 2,4-Dimethyl-1,3-pentadiene gave different n.m.r. spectra in 96% H_2SO_4 depending on the mode of addition of the diene to the acid. When the amount of diene was reduced to a minimum and when it was added from the end of a capillary into vigorously stirred 96% H_2SO_4 at 0°, up to 50% of the total band area was due to the three bands of the 2,4-dimethylpentenyl cation (7.70, 2.95, and 2.97 p.p.m.). The spectrum shown in Fig. 5 has 22% of the hydrogen

(15) The data on alkenyl cation equilibria seem to fit this function more closely than any other as discussed in a following paper.

(16) This generalization pertains equally well to secondary carbonium ions that disappear by hydride transfer reactions of the type $\text{R}_2\text{CH}^+ + \text{R}_2\text{CHOH} = \text{R}_2\text{CH}_2 + \text{R}_2\text{CO} + \text{H}^+$.

(17) Exemplary are heptamethylcyclohexadienyl cation (W. von E. Doering, M. Saunders, H. Boynton, H. Earhart, E. Wadley, W. Edwards, and G. Laber, *Tetrahedron*, **4**, 178 (1958)); hexamethylcyclohexadienyl cation, protonated hexamethylbenzene (N. Deno, P. Groves, and G. Saines, *J. Am. Chem. Soc.*, **81**, 3790 (1959)); and a variety of protonated benzenes (C. Reid, *ibid.*, **76**, 3264 (1954), and G. Dallinga, E. L. Mackor, J. H. van der Waals, and A. V. Stuart, *Mol. Phys.*, **1**, 123 (1958)). For evidence that protonated benzenes possess the dienyl cation structure, see C. MacLean, J. H. van der Waals, and E. L. Mackor, *ibid.*, **1**, 247 (1958).

accounted for by the 2,4-dimethylpentenyl bands and was prepared by addition of the diene from a simple eye dropper. This spectrum was chosen for presentation because there was a moderate amount of diene added, the 2.95 and 2.97 bands were well resolved, and the spectrum shows the nature of the other material formed during the process of solution.

If the diene is simply added dropwise with slow stirring to 96% H_2SO_4 at 25°, none of the hydrogens present are those of the 2,4-dimethylpentenyl cation. Since

the diene is 99.5% pure (see Experimental), it is clear that dimerization (and perhaps further polymerization and rearrangement) are taking place during the process of dispersing the diene into the acid. Since the monomeric cation is stable for at least minutes, it is also clear that it should be possible to obtain a spectrum in which the 2,4-dimethylpentenyl cation bands account for 100% of the hydrogen if the diene could be introduced in a sufficiently attenuated form. This has not as yet been achieved.

[CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY, UNIVERSITY PARK, PENNA.]

Carbonium Ions. XII. The Direct Observation of Rearrangement and Hydrogen-Deuterium Exchange in Cycloalkenyl Cations¹

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Such generally accepted principles as the greater stability of tertiary over secondary carbonium ions, the increasing stability of carbonium ions with increasing α -hydrogens, and the increasing stability of alkenes with increasing alkyl substitution can be observed in a most direct way from n.m.r. spectra of cycloalkenyl cations. The rate of hydrogen-deuterium exchange into such ions is base-catalyzed so that the rate is much slower in 96% H_2SO_4 than in more dilute acids. The rearrangement of 1,3,4,4,5- to 1,2,3,4,4-pentamethylcyclopentenyl cation is also base-catalyzed, but the rearrangement of 1,3,4,4,5,5- to 1,2,3,4,4,5-hexamethylcyclopentenyl cation is not.

The properties of aliphatic carbonium ions have in the past been inferred from the rate constants and the products produced in reactions believed to proceed *via* such carbonium ions as unstable intermediates. The preparation of stable solutions of these aliphatic carbonium ions now enables the direct observation of some of these properties.

Experimental

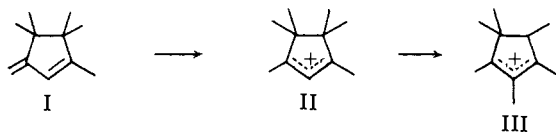
The n.m.r. spectra were recorded as described in the preceding paper.² The D_2SO_4 - D_2O solutions were prepared by combining General Chemical Co. Sulfan (SO_3 containing an unknown polymerization inhibitor) with D_2O . Several methods of effecting the combination were tried, but since none were entirely satisfactory, they are not described in detail. The problem centers around solidification of the SO_3 in the presence of small amounts of D_2O . Subsequently, Miss Josephine de Luis and Dr. P. S. Skell at Penn State slowly distilled liquid Sulfan into D_2O (stirred). This would appear to be the method of choice because the SO_3 is kept warm and liquified.

In the fast hydrogen-deuterium exchanges, some temperature control was attained by adding the dienes to the D_2SO_4 - D_2O at 35°, loading the n.m.r. tube, and immediately inserting the tube into the probe. Since the probe temperature held at $35 \pm 2^\circ$, the reactions were approximately thermostated. Slow exchanges were simply held at 25° except for short periods of measurement.

The identification of the cations are presented in the preceding paper,² as are the methods of calibrating and reporting the n.m.r. spectra.

Discussion

Rearrangements.—Addition of 3-methylene-1,4,4,5,5-pentamethylcyclopentene (I) to 96% H_2SO_4 would give on initial protonation the 1,3,4,4,5,5-hexamethylcyclopentenyl cation, II. The first spectrum observed,



1–2 min. after mixing, is that of II and this spectrum is shown in Fig. 1. The single hydrogen on C-2 at 7.49

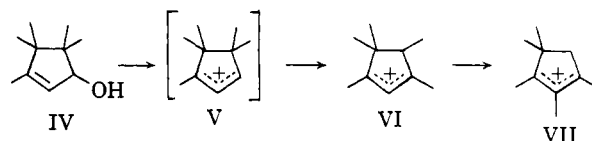
(1) This research was supported in part by a grant from the National Science Foundation and in part by a grant from the Petroleum Research Fund of the American Chemical Society. J. Hodge received a fellowship from the Shell Companies Foundation. Grateful acknowledgment is hereby made of this support.

(2) N. C. 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).

p.p.m. is definitive² as are the six hyperconjugated hydrogens at 2.90 p.p.m.

Already in Fig. 1, the incipient conversion to a new cation is apparent from the small band at 2.15 p.p.m. which is characteristically narrow and is definitive for methyl at C-2.² As time progresses, the band at 2.15 p.p.m. continues to grow concomitant with the gradual disappearance of the band at 7.49 p.p.m. This shows that the hydrogen at C-2 is being replaced by methyl. After about 1 hr., a stable n.m.r. spectrum is attained. A spectrum measured 3 hr. after mixing is shown in Fig. 2. This spectrum is entirely in accord with structure III.² The predominance of III over II at equilibrium may be associated with relief of steric repulsions and possibly with the fact that III has one more hyperconjugation hydrogen than II. The conversion of II to III takes place at the same rate in 70% H_2SO_4 as in 96% H_2SO_4 . The rate of conversion of II to III is about the same in 0.1 *M* solution, measured by n.m.r. spectra, as in 10^{-5} *M* solution, measured by ultraviolet spectra, showing that the rate of conversion is first order in II.

A similar type of rearrangement takes place when 3,4,4,4,5-pentamethyl-2-cyclopenten-1-ol (IV) is dissolved in 96% H_2SO_4 . The initially formed cation, V, was not observed. The n.m.r. spectrum after 1–2 min. is shown in Fig. 3 and approximates that expected for cation VI. The comparison of observed and calculated n.m.r. band areas has already been presented.² It is of interest that the rearrangement from the secondary to the tertiary carbonium ion is so rapid.



The spectrum of VI is not permanent, but continues to change leading to the stable n.m.r. spectrum shown in Fig. 4. The identification of this spectrum as that due to VII has been presented.² This conversion of VI to VII requires about 1 hr. for completion in 96% H_2SO_4 .