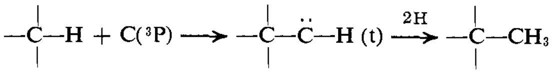
carbon atoms react with saturated hydrocarbons to give triplet carbenes which subsequently abstract two hydrogen atoms to give the eventual methyl derivatives.



$$-\overset{|}{\underset{|}{C}}-H + C(^3P) \longrightarrow -\overset{|}{\underset{|}{C}}-\ddot{C}-H\,(t) \xrightarrow{2H} -\overset{|}{\underset{|}{C}}-CH_3$$

The analogous process may be observed in the case of olefins but, as in the reported examples,[19] the yields do not exceed 2–3%. This leaves the present understanding of ground-state carbon atom chemistry in an undesirable state. Efforts are continuing to characterize this species.

Despite the confusion concerning the ground states' reactions, there is no doubt that metastable singlet states are the species responsible for allene and diene formation from olefins.

Experimental Section

The reaction system employed in this study has been described previously[20] and the modifications required for the production of thermally vaporized carbon have also appeared.[21]

Carbon vapor enriched in carbon-14 was produced by replacing the upper arcing electrode with enriched carbon-14 (0.01 Ci/g). These electrodes were obtained from the United Kingdom Atomic Energy Authority.

Products described in this paper were isolated by gas chromatography and identified by comparison of their spectral properties with known samples.

1,1,1′,1′-Tetramethylspiropentane. This compound was prepared from commercial tetramethylallene (Aldrich) by addition of dibromocarbene[22] to give 1,1-dibromo-2,2-dimethyl-3-isopropylidenecyclopropane in 33% yield. The structure of this compound was verified by a comparison of its spectral properties with those reported in the literature.[23] Reduction of the dibromo compound with sodium in wet methanol[24] gave a 32% yield of 1,1-dimethyl-2-isopropylidenecyclopropane which was identified by comparison with literature spectral data.[23] Repeating the procedure just described starting with 1,1-dimethyl-2-isopropylidenecyclopropane gave the desired 1,1,1′,1′-tetramethylspiropentane in 10% yield based on the starting allene. The spiropentane was isolated by gas chromatography on a cyanoethylsilicone column and was characterized by its spectral properties. The infrared showed no unsaturation and the parent peak in the mass spectrum was *m/e* 124 with a very intense base peak at *m/e* 109 (P − CH_3). The nmr spectrum showed two overlapping singlets of three protons each at τ 8.90 and 8.92 and an AB pattern centered at τ 9.58 (four protons).

1,1-Dimethyl-2-isobutenylcyclopropane (1). This material was prepared by a Wolff-Kishner reduction of phorone.[25] Phorone (13.8 g; 0.1 mol) (Chemical Procurement Industries) was added to a solution of 9.6 g (0.3 mol) of hydrazine hydrate (85% in water) in 100 ml of diethylene glycol and heated on a steam bath for 5 hr. Sodium hydroxide (8 g) was added and the solution was refluxed for 2 hr. Steam distillation of the reaction mixture gave a two-phase system. The organic phase was removed and dried over $MgSO_4$; subsequent distillation gave 5.7 g (0.046 mol) of **1**, bp 128° (760 mm).

Identification was accomplished by analysis of its spectral properties; the infrared spectrum exhibited unsaturation and the nmr spectra gave a broadened doublet of one proton at τ 5.18, two singlets of three protons each at τ 8.99 and 8.90, which also covered a complex one-proton absorption, and a complex pattern of two protons centered at τ 9.65.

Acknowledgment. We gratefully acknowledge the financial support of the Air Force Office of Scientific Research.

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The Equilibria between Polyenes and Polyenyl Cations

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Abstract: The equilibria between four polyenes and their conjugate acids, polyenyl cations, have been measured as a function of sulfuric acid concentration. Although polyenyl cation stability increases with increasing conjugation, the effect is smaller than stabilizing effects associated with either hyperconjugation by methyl groups or ring closure.

Certain polyenyl cations are stable species in strong acids,[1-3] which affords the opportunity of studying their equilibria with their conjugate bases as a function of acidity. These studies were initiated (1) to assess quantitatively the effect of extending conjugation on carbonium ion stability and (2) to determine the acidity function dependence of the protonation equilibria.

Exploratory studies[4] had shown that I, II, and III were 50% formed from the equilibration diene(s) at the per cent H_2SO_4 shown under each structure. In all three cases, the equilibria approximately fit eq 1.[4]

$$H_0 = pK_a + \log\,[B]/[BH^+] \qquad (1)^5$$

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(1) N. Deno and C. U. Pittman, Jr., *J. Amer. Chem. Soc.*, **86**, 1871 (1964); N. Deno, C. U. Pittman, Jr., and J. O. Turner, *ibid.*, 87, 2153 (1965).

(2) T. S. Sorensen, *ibid.*, 87, 5075 (1965); *Can. J. Chem.*, **42**, 2768, 2781 (1964); **43**, 2744 (1965)

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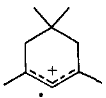
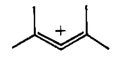
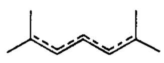
(5) Standard state for pK_a is molarity ≡ activity at pH 7. This and other aspects of eq 1 are given in L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1940, Chapter IX, and

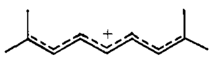
Cations II and III have been reexamined and the studies have been extended to IV and V. Cation VI[4] has been included for comparison. The data for cations II–V are presented in Table I and have been correlated with eq 1 and 2.[6]

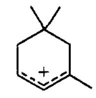

I, 35% H_2SO_4
pK_a = −1.90


II, 47% H_2SO_4
pK_a = −2.77


III, 73% H_2SO_4
pK_a = −6.32


IV, 62% H_2SO_4
pK_a = −3.82


V, 61% H_2SO_4
pK_a = −2.98


VI, ~80% H_2SO_4
pK_a = −6.8

$$H_0 - w \log a_{H_2O} = pK + \log([B]/[BH^+]) \qquad (2)$$

Best fits were obtained with eq 2 for w values of 0.5 for cation II, 0.0 for cation III (w = 0 is equivalent to eq 1), and 1.0 for cations IV and V as shown in Table I. The pK values obtained from eq 2 are shown in Table I and are probably good estimates of the pK_A of the polyenyl cations for water as the standard state. This is true partly because w is reasonably constant from 0 to 70% H_2SO_4[6] and partly because the term $w \log a_{H_2O}$ diminishes to zero in pure water so that variations in w are unimportant at small values of $\log a_{H_2O}$.

Although eq 2 is appropriate for estimating pK_A in water and for calculating [B]/[BH$^+$] ratios in 0–70% H_2SO_4, it can be expected to become invalid in the 70–100% H_2SO_4 region where w values are effectively zero, a result of invariant activity coefficients[7] and the disappearance of BH^+–H_2O interactions. In fact the w = 0 for cation III may well be due to the fact that data were measured in 72–85% H_2SO_4. If so, the pK of −6.32 for cation III is too negative. By this same argument, not much significance can be attached to the variation of w between 0 and 1 for cations III–V.

The w values of 0–1 are interpreted to mean that the polyenyl cations II–V are hydrogen bonded to three to four H_2O molecules.[8-12] In this respect, they are unlike arylcarbonium ions and protonated azulenes which generate quite different acidity functions[13,14] and which give w values of −3 when data in 0–60% H_2SO_4 are fitted to eq 2.[8] It is concluded that aliphatic polyenyl cations have considerable positive charge delocalized into methyl groups through hyperconjugation. This leads to hydrogen bonding to the negative oxygen of water to a degree comparable to that found in the Hammett indicators, $ArNH_3^+$.[8-12]

Table I. Equilibrium Data at 25°

	−Log ([B]/[BH$^+$])		
		Calcd	
% H_2SO_4	Exptl	Eq 1	Eq 2
	Cation II		
		pK = −2.95	pK = −2.77 w = 0.5
60.5	1.7	1.4	1.6
55.0	0.97	0.85	0.95
52.4	0.64	0.56	0.63
50.0	0.34	0.30	0.33
47.5	0.05	(0.05)	0.05
45.0	−0.34	−0.20	−0.24
42.6	−0.50	−0.42	−0.47
40.1	−0.77	−0.65	−0.73
	Cation III		
		pK = −6.32	
84.9	1.7	1.7	
82.3	1.3	1.2	
79.6	0.91	1.0	
77.5	0.61	0.59	
76.5	0.49	0.44	
75.5	0.33	0.32	
73.8	0.12	0.24	
72.2	−0.08	−0.14	
	Cation IV		
		pK = −4.69	pK = −3.82 w = 1.0
79.6	1.6	2.6	1.3
70.5	1.2	2.0	1.1
75.5	0.73	1.18	0.77
67.7	0.49	0.78	0.49
64.9	0.25	0.37	0.22
63.8	0.16	0.24	0.16
62.0	0.01	(0.01)	0.01
60.4	−0.12	−0.18	−0.12
57.8	−0.33	−0.49	−0.32
56.0	−0.55	−0.69	−0.46
	Cation V		
		pK = −3.46	pK = −2.98 w = 1.0
64.9	1.14	2.6	1.05
55.0	0.32	0.43	0.30
52.5	0.12	0.15	0.10
50.0	−0.09	(−0.09)	−0.16
47.5	−0.27	−0.36	−0.27
45.0	−0.46	−0.58	−0.45
42.6	−0.62	−0.82	−0.63

This strong hyperconjugation of methyl groups also shows up in stabilities of allyl cations. Each hyperconjugating methyl increases cation stability by 3–4 pK units (compare II and VI) and the same 3–4 $\log k/k_0$ is found for solvolysis of allyl chlorides.[15] It is of interest that the hyperconjugative effect per methyl is considerably larger than the conjugative effect of an added –CH=CH– unit. For example, the pK's of IV and V differ by only 0.84. The pK difference of 2.50 between III and IV (which also differ by a –CH=CH– unit) is regarded as anomalously high since it includes the unusually low stability of III, a result of extensive steric inhibition of resonance.[16]

M. A. Paul and F. A. Long, *Chem. Rev.*, **57**, 1 (1957), from which H_0 values were taken.

(6) Equation 2 is the equilibrium equivalent to rate constant equations introduced by J. F. Bunnett, *J. Amer. Chem. Soc.*, **82**, 499 (1960); **83**, 4956 (1961); J. F. Bunnett and F. P. Olsen, *Can. J. Chem.*, **44**, 1899, 1917 (1966).

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(16) The planar form of III would require a 1.60 Å interpenetration of methyl groups (N. Deno, R. Haddon, and E. Nowak, *J. Amer. Chem. Soc.*, **92**, 6691 (1970)).

Ring closures also appear to be a greater stabilizing factor than the conjugative effect of CH=CH units. This is most directly seen in the spontaneous cyclizations of dienyl cations to cyclopentenyl cations,[1,2,17] wherein the stabilizing effect of cyclization overcomes the loss of a conjugated CH=CH unit, and also in the greater stability of I relative to IV or even V.

Past discussions of carbonium ion stabilities have usually centered on resonance energy effects. The data in this paper show that other effects overshadow the simple resonance energy effect with aliphatic allylic and polyenyl cations.

Experimental Section

Chemicals. The conjugative base of II is a mixture of 1,3,5,5-tetramethyl-1,3-cyclohexadiene and 1,5,5-trimethyl-3-methylenecyclohexene. The mixture was prepared from methyllithium and isophorone.[4,18] 2,4-Dimethyl-3-penten-2-ol, the precursor of III, was prepared from methyllithium and mesityl oxide.[18] 2,6-Dimethyl-1,3,5-heptatriene, the conjugate base of IV, was prepared from $LiAlH_4$ and phorone.[1] 2,8-Dimethyl-1,3,5,7-nonatetraene was prepared from 5-methyl-2,4-heptadienal and 2-methyl-2-propenyltriphenylphosphonium chloride by the method of Sorensen.[2]

Equilibrium Measurements. A constant amount of polyene was introduced into varying strengths of aqueous H_2SO_4. The absorbtivity, A, was measured as a function of time at 25 ± 1° and at λ_{max} of the cation: II, 314 mμ (ϵ 11,900); III, 305 mμ (ϵ 19,000); IV, 396 mμ (ϵ 50,600); V, 473 mμ (ϵ 104,800). In 85–96% H_2SO_4, the cations were stable at 25°, both at the 10^{-2} M concentrations used in nmr studies[1-3] and at the 10^{-4} M concentrations used in the present study. As the acidity was reduced to levels at which cation and polyene coexisted in comparable amounts, the system rapidly decomposed. It was necessary to extrapolate the data to zero time. To improve the precision of this extrapolation, the rate laws for the decompositions were determined. This was done by varying the initial stoichiometric concentration and measuring initial rates.

Cations II and III decomposed by first-order rates and their data were extrapolated to zero time by plotting log A against time. Cations IV and V decomposed by second-order rates and their data were extrapolated to zero time using plots of A^{-1} against time. All four decomposition rates varied inversely with the h_0 acidity function[5] in the ranges given in Table I. The complete rate eq for II and III is eq 3 and eq 4 for IV and V. The data are insufficient to interpret these rate laws. Also, these rates, found at ~10^{-5} M concentration, may not obtain at higher concentration.

$$-d[R^+]/dt = k[R^+]/h_0 \qquad (3)$$

$$-d[R^+]/dt = k[R^+]^2/h_0 \qquad (4)$$

Reproducibility of the data is strongly dependent on the mode of introduction of the diene. The following procedure was adopted, not only because it gave reproducibility to within 5% but it also gave the highest A values and presumably the least decomposition and polymerization during the addition.

An acetic acid stock solution was prepared which contained about 10^{-2} mol $l.^{-1}$ of sodium acetate. An accurately measured 0.05 ml of this solution was injected through a calibrated microsyringe into 10.0 ml of the aqueous sulfuric acid. The latter was stirred vigorously by a magnetic stirrer during the injection. The syringe was wiped clean and a 0.05-ml increment added to each new concentration of aqueous sulfuric acid without dismantling the syringe. The purpose of the sodium acetate was to neutralize any trace of sulfuric acid that diffused back into the syringe.

Acknowledgment. Grateful acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the National Science Foundation for support of this work.

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Reactions of Trans-Fused Cyclopropanes. The Acid-Catalyzed Ring Cleavage of *trans*-Bicyclo[5.1.0]oct-3-ene[1]

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Abstract: The acid-catalyzed addition of acetic acid to *trans*-bicyclo[5.1.0]oct-3-ene has been studied. It was found that product-determining protonation occurred exclusively at the bridgeheads. This acid-catalyzed opening of the cyclopropane ring gave a mixture of ten products. The detailed mechanistic aspects of the formation of these products are discussed. The reactivity of trans-fused cyclopropanes is considered in relation to the presence of "twist" bent σ bonds.

Highly strained polycyclic molecules, with their multifarious chemical idiosyncrasies, have provided an almost seductive attraction for organic chemists. Mute testimony to this premise has been provided by the approximately thousand papers dealing with the properties of strained carbocyclic compounds which have been published in the last dozen years. Bicyclo[1.1.0]butane, bicyclo[2.1.0]pentane, bicyclo[1.1.1]pentane, and numerous tri- and tetracyclic small-ring compounds have been synthesized and studied. Of particular interest in relation to these compounds has been the nature of the carbon–carbon σ bond which is capable of bestowing such unusual chemical reactivity. Recently, we suggested that "bent" σ bonds should fall into two categories.[4] As shown schematically below, these bent bonds have been classified as being either "symmetrically" bent or "twist" bent.

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[1] Paper XVIII on "The Chemistry of Bent Bonds." For the previous paper in this series, see P. G. Gassman, T. J. Atkins, and F. J. Williams, *J. Amer. Chem. Soc.*, **93**, 1812 (1971).

[2] Alfred P. Sloan Foundation Research Fellow, 1967–1969.

[3] Goodyear Fellow, 1968–1969; Dow Chemical Fellow, 1969–1970.

[4] P. G. Gassman, *Chem. Commun.*, 793 (1967).