delocalized only into the π system of the triple bond and not further into the benzene ring. The slight decrease in enthalpy of activation which does result from replacing the γ-methyl group of Ib with the phenyl group of Ie (0.9 kcal/mole) may reflect the increased stabilization of the radicals produced by that fraction of Ie which happens to be in a rotational state at the instant of decomposition in which the p orbitals of the phenyl group and the p orbital of the terminal radical sp^2 carbon atom are coplanar or nearly so.

The inability of a triple bond to transmit the resonance-stabilizing effect of a phenyl group on a carbonium ion has been indicated earlier in studies by Kochi and Hammond[24] in which they solvolyzed *m*- and *p*-2-phenylethenyl and 2-phenylethynylbenzyl tosylates. They found that the σ_p and σ_p^+ values for the 2-phenylethenyl group were -0.070 and -1.00, respectively, whereas for the 2-phenylethynyl group, σ_p and σ_p^+ had values of 0.165 and -0.03. Thus, the phenyl group conjugated with the benzyl cation through an intervening double bond at the *para* position serves as an excellent electron reservoir ($\sigma_p^+ - \sigma_p = -0.93$) whereas when the conjugating link is a triple bond, the phenyl group only contributes modestly to the added stabilization of the benzyl cation ($\sigma_p^+ - \sigma_p = -0.19$). Here, as in the case of the radical discussed in this paper, free and independent rotation about both bonds between the triple bond and the two phenyl groups precludes through conjugation of the γ-phenyl group with the benzylic cationic center.

Acknowledgment. It is a pleasure to thank the donors of the Petroleum Research Fund for a grant (PRF No. 603-A4) administered by the American Chemical Society which financed the greater part of this work.

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[24] J. K. Kochi and G. S. Hammond, *J. Am. Chem. Soc.*, 75, 3452 (1953).

Directly Observable Carbonium Ion–Carbonium Ion Rearrangements. I. Kinetics and Equilibria in the Interconversion of Trialkylcyclopentenyl Cations

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Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada. Received February 9, 1967

Abstract: The kinetics of several observable carbonium ion–carbonium ion reversible rearrangements in an alkyl-substituted cyclopentenyl system have been measured. By conducting these reactions in variable acid concentrations and in deuterated acids, it has proven possible to suggest a plausible mechanism for the rearrangements. The equilibrium constants for these reversible reactions have been obtained in a variety of acid concentrations and a preliminary discussion of the possible structural features responsible for the varying *K* values is presented. An unrelated rearrangement involving the *t*-butyl-substituted ions is also described and a detailed measurement and comparison of the nmr and ultraviolet spectra of these ions are presented.

Physical chemical studies of carbonium ion rearrangements have almost exclusively[1] involved a kinetic or product study of the general sequence

$$\begin{array}{l}\text{starting material}\\ \text{(neutral molecule of}\\ \text{known structure)}\end{array} \longrightarrow \left[\begin{array}{l}\text{ionic transition}\\ \text{states of deduced}\\ \text{structure}\end{array}\right] \longrightarrow \begin{array}{l}\text{product}\\ \text{(neutral molecule of}\\ \text{known structure)}\end{array}$$

This paper reports the study of a rearrangement where the starting material and products are both carbonium ions and while these correspond to no known transition-state intermediates, both in structure and solvating solvent, it may be possible in the future to make certain direct correlations with these.

Previous work[1a-d,f,g,2,3] has shown that cyclopentenyl cations are readily prepared in highly acidic solution and that they appear to be more stable than other allylic cations. A study of deuterium substitution in some nonrearranging cyclopentenyl cations has also been made.[1a]

This study originated from an attempt to test the relative ability of alkyl groups in stabilizing carbonium ion centers, and it was considered that the cyclization of dienylic ions of structure A (a known reaction type[1b,c,f,h]) would lead to two cyclopentenyl ions whose relative amounts would be determined by their thermodynamic stabilities.

This hypothesis proved to be wrong. However, it was observed that the proportion of the two ions in the mixture *slowly changed* but eventually reached a constant value. Furthermore the reaction was clean, *i.e.*, no further significant products or polymer formed during this change, except where R was *t*-butyl.

This study reports the experimental evidence showing that the two ions reach a true equilibrium, reports the

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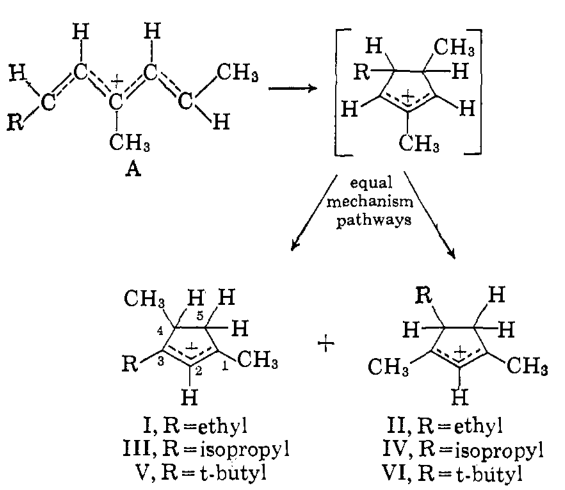
[1] Exceptions include some recent ion rearrangement studies given in the following references: (a) N. C. Deno, N. Friedman, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, 85, 2995 (1963); (b) T. S. Sorensen, *Can. J. Chem.*, 42, 2768 (1964); (c) N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *J. Am. Chem. Soc.*, 87, 2153 (1965); (d) N. C. Deno and J. J. Houser, *ibid.*, 86, 1741 (1964); (e) N. C. Deno and C. U. Pittman, Jr., *ibid.*, 86, 1744 (1964); (f) T. S. Sorensen, *Can. J. Chem.*, 43, 2744 (1965); (g) T. S. Sorensen, *J. Am. Chem. Soc.*, 87, 5075 (1965); (h) G. A. Olah, C. U. Pittman, Jr., and T. S. Sorensen, *ibid.*, 88, 2331 (1966).

[2] N. C. Deno, D. B. Boyd, J. D. Hodge, C. U. Pittman, Jr., and J. O. Turner, *ibid.*, 86, 1745 (1964).

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



I, R=ethyl
III, R=isopropyl
V, R=t-butyl

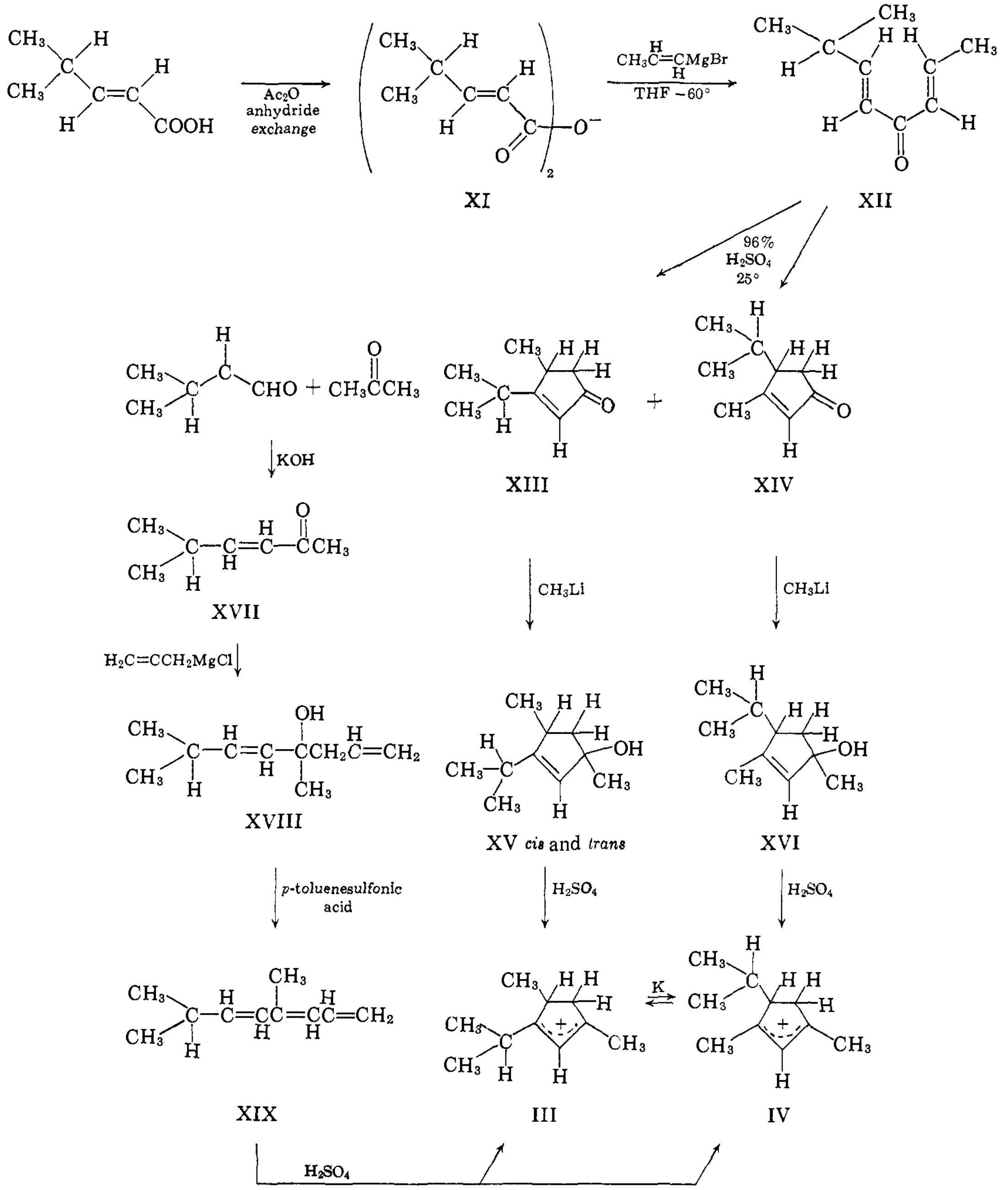
II, R=ethyl
IV, R=isopropyl
VI, R=t-butyl

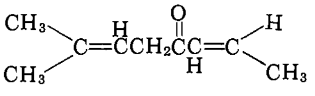
rate of interconversion of the ions as a function of the acid strength, and investigates the magnitude of K when R = ethyl, isopropyl, and *t*-butyl and in two cases where R = isopropyl, and an ethyl group (VII and VIII) or an isopropyl group (IX and X) is present at C1.

Results

Synthetic Sequences. The ion system (III–IV, R = isopropyl) was chosen for the complete study primarily because it was possible to obtain the most reliable nmr data integrations of the two isomeric ions in the mixture and thus to obtain better kinetic and equilibrium data. The synthesis of the two pure carbonium ions was undertaken in order to follow the presumed approach to equilibrium from the two directions. The synthetic sequence is given below.

The dienone XII in the sequence is easily isomerized on heating to the β,γ-unsaturated ketone, 7-methylocta-2,6-dien-4-one (XX). At the distillation temperature under aspirator vacuum (80°), this reaction is quite rapid, and it was not possible under these conditions to isolate the pure cross-conjugated ketone.





$(CH_3)_2C=CHCH_2COCH=CHCH_3$

XX

The conditions for the Nazarov cyclization[4,5] are usually formic acid–phosphoric acid but these were unsuccessful for us, possibly because of solubility problems. The sulfuric acid procedure gives homogeneous conditions, is very convenient, and can be monitored using an aliquot of the solution in an nmr tube and following the rearrangement by the appearance of the cyclic ketone peaks. The yield under these conditions was, however, only 28%. As expected, both of the possible products were obtained, the mixture containing about 38% XIV and 62% XIII. The two ketones were easily separated by preparative vpc in spite of their similar structures. The physical and spectroscopic properties of the two ketones are in excellent agreement with that expected and nmr spectroscopy serves quite easily to distinguish the two.

The addition of methyllithium is essentially quantitative in both instances and the alcohols were isolated by microdistillation. The alcohols were preferred over the dienes as starting materials, principally because cyclopentadienes are prone to undergo thermal double bond rearrangements.[6] To ketone XV, it was also possible to add ethyllithium and isopropyllithium although in these two cases a second treatment with the alkyllithium reagent was required since about 10% enolization accompanies addition. Two treatments would therefore give essentially quantitative (99%) conversion to the alcohol.

The triene synthetic route starts with the known 5-methylhex-3-en-2-one (XVII). The literature preparation[7] of this ketone yields a mixture of α,β- and β,γ-unsaturated isomers which could be very simply separated by adding the mixture to concentrated sulfuric acid, pouring the resulting solution onto ice, and distilling the unchanged α,β isomer, the β,γ isomer being converted either to the α,β isomer or to the higher boiling 5-hydroxy ketone.

The addition of allyl Grignard reagent, using the simultaneous addition method, follows previous examples[8] on related compounds as does the dehydration of the alcohol[8] to the conjugated triene XIX, which was isolated from the isomeric trienes of the crude reaction product by preparative vpc (vapor phase chromatography). The corresponding trienes, with an ethyl group and a *t*-butyl group in place of the isopropyl group, were synthesized by the same route; the *t*-butyl ketone (analogous to XVII) has been reported[9] and is obtained pure since there is no possibility of a double-bond shift. The ethyl ketone, prepared by the literature route,[10] is a mixture of *cis*- and *trans*-α,β-unsaturated and the β,γ-unsaturated ketone; the *trans*-α,β-unsaturated ketone is the highest boiling of the three and can be obtained nearly pure (nmr and vpc analysis) by careful fractionation. The chromatograms showing the peaks corresponding to the desired conjugated trienes are given in the Experimental Section. The physical and spectroscopic properties are in excellent agreement with their proposed structures and resemble very closely 4-methyl-1,3,5-heptatriene, which has previously been reported[8] from this laboratory. The actual geometry of the trienes is unimportant as far as the carbonium ion work is concerned, but by analogy with previous work[8] and the observed multiplicity of the vpc chromatogram, a tentative assignment can be made; ethyl triene mixture of 3,4-*trans*,5,6-*trans* and 3,4-*cis*,5,6-*trans*; isopropyl triene (XIX) all *trans;* and *t*-butyl triene all *trans.* The ultraviolet spectra are practically identical with one another with the characteristic three peaks for a conjugated triene in each case.[8]

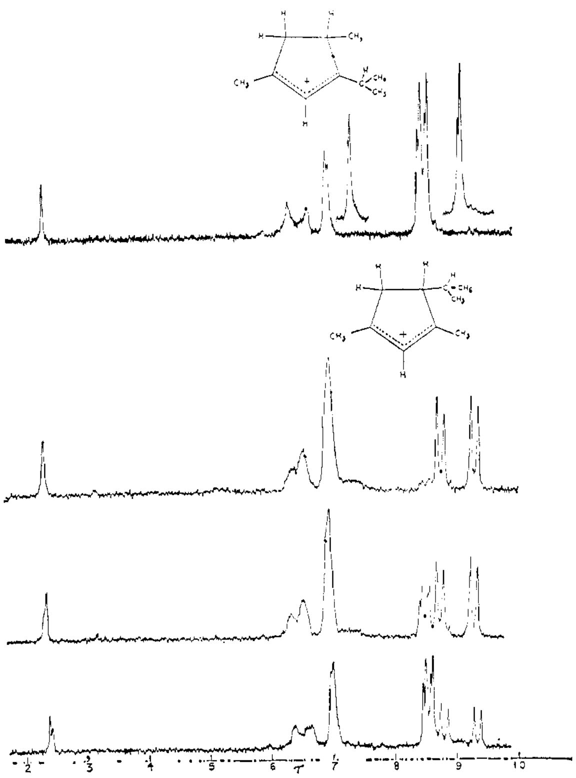


Figure 1. Top curve, ion III; the additional curves are those obtained after deuterium substitution and they are displaced on the scale only for ease of portrayal; second, ion IV; third, the equilibrium mixture of III and IV; and bottom curve, the initial mixture obtained from the cyclization of XIX.

Preparation and Analysis of the Ions. The triene XIX and the ethyl and *t*-butyl analogs were added to the sulfuric acid from the gas phase as has been previously described for similar trienes.[1b] No effort was made toward securing the presumed initially formed dienylic ions and the additions were made at 15–25°; indeed lower temperatures cause considerable polymerization, a phenomenon also noted previously with 4-methyl-1,3,5-heptatriene.[1b] The alcohols, XV, XVI, etc., being less volatile, were dissolved in hexane and slowly extracted into a small volume of sulfuric acid, appropriate corrections being made for the dilution of the sulfuric acid caused by the dehydration of the alcohol. The nmr spectra of the carbonium ions were relatively easy to interpret and the spectra of the isopropyl series in 96% sulfuric acid are shown in Figure 1 (35°). The top two curves are of the pure cations III and IV. The bottom curve is the mixture

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(4) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 1430 (1952).

(5) L. de Vries, *J. Org. Chem.*, **25**, 1838 (1960).

(6) S. McLean and P. Haynes, *Tetrahedron*, **21**, 2329 (1965).

(7) R. Heilmann, G. de Gaudemaris, and P. Arnaud, *Compt. Rend.*, **242**, 2008 (1956).

(8) T. S. Sorensen, *Can. J. Chem.*, **42**, 2781 (1964).

(9) K. N. Campbell, *J. Am. Chem. Soc.*, **59**, 1982 (1937).

(10) E. D. Bergmann and C. Resnik, *J. Org. Chem.*, **17**, 1291 (1952).

initially obtained from the cyclization of XIX (as the dienylic cation). The remaining curve shows the two ions at equilibrium concentrations. The complete numerical assignments for all of the ten ions are given in Table I, using tetramethylammonium cation (τ 6.90) as the internal reference.[3] In many cases, peaks from the two ions in the equilibrium mixture overlap or are superimposed on one another and these can be identified only as due to a certain type of proton. In general, the positions of various nmr peaks are similar to those previously reported for related ions.[1b,c,3] The signals of the methyl protons at C1 or C3 (τ ~7) and the methylene and methine protons (τ 6–7) are generally very broadened but the remainder are quite sharp considering the viscosity of the solvent. The actual nmr peaks used to calculate the relative amounts of the two isomers are given in the Appendix.

Table I. Nmr Data for the Carbonium Ions (τ, ppm)

Compd	CH$_3$ on C1, C3	H on C2	CH$_2$ or CH on C4 or C5^d	CH$_3$ on C4 (J, cps)	Other (J, cps)
I	$7.04^{a,b}$	2.38	$6.45^{a,c}$ $6.63^{a,c}$	8.51 8.63 (7.2)	CH$_3$ of ethyl group 8.48 8.59 (6.6) 8.70
II	$7.04^{a,b}$	2.42	$6.45^{a,c}$ $6.63^{a,c}$	...	CH$_3$ of ethyl group 8.89 9.01 (6.9) 9.12 CH$_2$ of ethyl group 7.6–8.3 (m)
III	$7.03^{a,b}$	2.37	$6.40^{a,c}$ $6.61^{a,c}$	8.49 8.61 (7.2)	CH$_3$ of isopropyl group 8.53 8.65 (7.2)
IV	$7.03^{a,b}$	2.40	$6.40^{a,c}$ $6.61^{a,c}$	...	CH$_3$ of isopropyl group 8.77, 9.32 8.88, 9.43 (6.6) CH of isopropyl group 7–8 (m)
V	$7.01^{a,b}$	2.33	$6.40^{a,c}$ $6.53^{a,c}$ $6.68^{a,c}$	8.43 8.55 (7.2)	CH$_3$ of *t*-butyl group 8.55
VI	$7.01^{a,b}$	2.42	$6.40^{a,c}$ $6.53^{a,c}$ $6.68^{a,c}$	...	CH$_3$ of *t*-butyl group 8.91
VII	...	2.35^{a}	$6.61^{a,c}$	8.49 8.61 (7.2)	CH$_3$ of ethyl group^a 8.48 8.59 (6.6) 8.70 CH$_3$ of isopropyl group 8.52 8.63 (6.6)
VIII	7.05^{b}	2.35^{a}	$6.61^{a,c}$	...	CH$_3$ of ethyl group^a 8.48 8.59 (6.6) 8.70 CH$_3$ of isopropyl group 8.77, 9.33 8.88, 9.44 (6.6) CH of isopropyl group 7.1–7.6 (m)
IX	...	2.35^{a}	$6.42^{a,c}$ $6.63^{a,c}$	8.53 8.64 (6.6)	CH$_3$ of isopropyl groups^a 8.53 8.64 (6.6)
X	7.06^{b}	2.35^{a}	$6.42^{a,c}$ $6.63^{a,c}$	...	CH$_3$ of isopropyl groups^a 8.53 8.64 (6.6) CH$_3$ of second isopropyl group 8.76, 9.34 8.87, 9.45 (6.6) CH of second isopropyl group 7.2–7.6 (m)

^{a} Superimposed peaks from both isomers. ^{b} Broad. ^{c} Very broad. The relative areas have been calculated and agree within experimental error with that calculated. These areas are based on the equilibrium mixture spectra. ^{d} And other CH$_2$ and CH groups in the same relation to the enylic ion.

The isomerization reactions were carried out at constant temperature in the nmr tubes, these being protected from light, since light catalysis in carbonium ion reactions has been reported.[1g,11] The integrations were performed by recording the spectra a number of times at varying sweep widths, tracing the curves on bond paper, and weighing the paper. All experiments were carried out in duplicate. In the area analysis of I ⇄ II, a rough correction was made for polymeric material, which creates a general increased base line in the τ 8–9 region. These corrections were small and do not grossly affect the results. Listed in Figure 2 are the best values for the equilibrium constants determined for the ions in 96% sulfuric acid. Listed in Table II are the equilibrium constants in various concentrations of acid and a listing of the rate constants ($k_r + k_f$), representing the approach to equilibrium; in the isopropyl case, this approach was measured starting with both pure ions. The kinetics were measured at 25.4°, and the data were analyzed for reversible first-order kinetics, the fit being reasonable considering the experimental uncertainties in the area measurement. Since K is known, both k_r and k_f can be separately calculated. As mentioned previously, the isomeric ion pair III ⇄ IV was the only case where the complete study (starting from both pure ions, complete acid variation, etc.) of the kinetics was to be made.

Table II. Kinetic and Equilibrium Data at 25.4° in H$_2$SO$_4$

% acid	Starting compd	$k_r + k_f$,^{a} sec^{-1}	K^a	$-\Delta F$,^{a} kcal/mole
94.7	III or IV	3.2×10^{-5}	2.7 ± 0.2	0.59
89.3	III or IV	1.2×10^{-4}	3.0 ± 0.3	0.65
83.2	III or IV	4.5×10^{-4}	2.8 ± 0.3	0.61
94.7	Nonequilibrium mixture of I and II	$\sim 1.5 \times 10^{-5}$	1.5 ± 0.2	0.24
94.7	VII	3×10^{-5}	2.4 ± 0.3	0.52
94.7	IX	8×10^{-5}	2.8 ± 0.3	0.61

^{a} Errors are estimated from the scatter of a number of duplicate measurements, about ±10%.

It was also mentioned in the introductory section that when the triene XIX and the ethyl and *t*-butyl analogs were used as starting materials, a nonequilibrium mixture of the two cyclopentenyl ions was obtained. When triene XIX was used, the initial ratio was 56% III, 44% IV (see Figure 1). With the ethyl triene, the initial ratio was 46% I, 54% II, and for the *t*-butyl triene, 61% V and 39% VI.

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(11) Private communication from Professor H. J. Dauben, Jr.

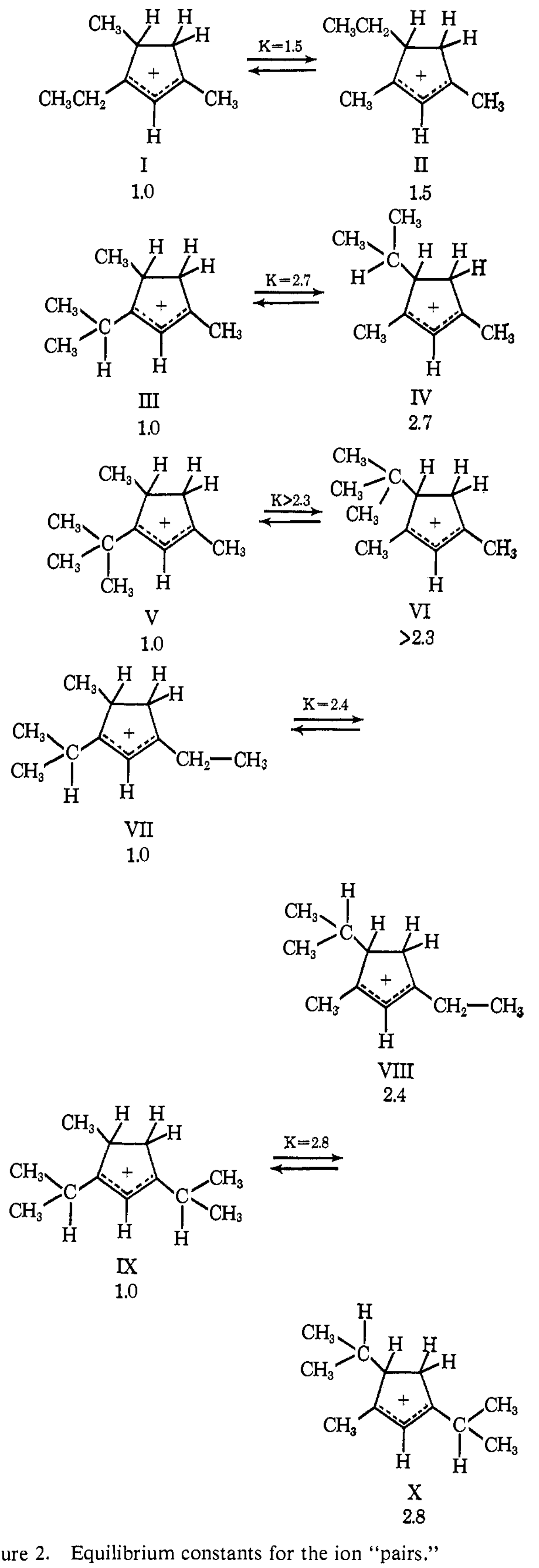


Figure 2. Equilibrium constants for the ion "pairs."

The carbonium ions were also prepared in deuterated sulfuric acid of varying concentrations. Figure 3 portrays the rough half-life limits for H–D exchange in varying concentrations of deuteriosulfuric acid, and one would expect these ranges to be valid for the CH_3, CH_2, and CH groups of all 1,3,4-trialkylcyclopentenyl cations. The results give only an order of magnitude measurement since in most cases the isomerization is occurring at a similar rate to the H–D exchange, thus precluding accurate measurements of the latter. Also, no correction has been made for the fact that a methyl group, for example, will show an isotope effect after one proton has exchanged, and the exchange is therefore not strictly first order. A correction has been applied for the equilibrium concentration of protons in the deuteriosulfuric acid.

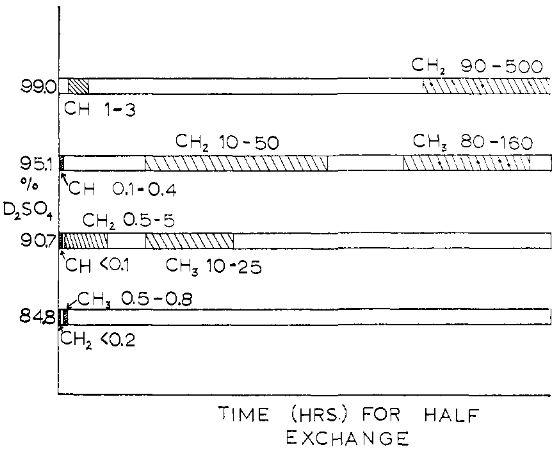


Figure 3. Half-life ranges for deuterium substitution in 1,3,4-trialkylcyclopentenyl cations as a function of the acid concentration.

In spite of the inexactness, these data are very valuable as an aid in elucidating the mechanism of the isomerization reaction. Table III lists the approximate kinetic and equilibrium data obtained in the deuteriosulfuric acid solvent. The equilibrium constants for the deuterated ions are quite similar to their proton analogs; however the uncertainty in the area calculation is greater; for example, the methyl group at C4 in III is only partly exchanged in the higher deuteriosulfuric acid concentrations and the correction for this is inexact.

When the kinetic data obtained in deuteriosulfuric acid are analyzed for reversible first-order kinetics, a straight line is not observed. The rate of isomerization slows down as the deuterium substitution proceeds; the initial curvature is most pronounced in the higher acid concentrations and becomes close to a straight line in the 85% acid. The rate constants listed in Table III are crude approximations of a very complex reaction; the values for the concentrated acid are determined from the approximate straight line observed after the initial curvature while those in the weakest acid are straight line approximations of the observed data. A more sophisticated treatment of the results is unwarranted at this time in view of the uncertainties in the area measurement. The figures are still useful in that they give a rough idea of the rate slowdown, represented in the last column by an unspecified isotope effect. The curvature (or rate slowdown) actually correlates very well with the observed substitution of hydrogen by deuterium at C5 of the ions. Thus, in the weaker acid, where deuterium exchange at C5 occurs before most of the isomerization, the best approximation to a straight line (but a much slower rate) is observed. However, in the 95% acid, hydrogen exchange at C5

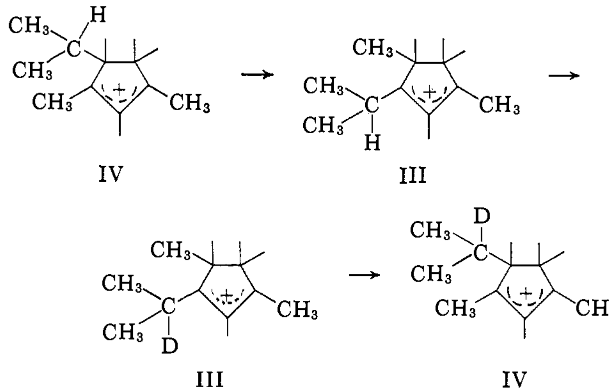
Table III. Kinetic and Equilibrium Data at 25.4° in D_2SO_4

% acid	Starting compd	Order of magnitude, $k_r + k_f$,[a] sec^{-1}	K	Time for half-exchange of H at C2, hr	Time for half-exchange of isopropyl proton in IV, hr	Approx isotope effect (unspecified)
95.1	III	~3 × 10^{-6}	2.8 ± 0.3	~36		10
95.1	IV	~5 × 10^{-6}		~110	~170	6
90.7	III	~9 × 10^{-6}	3.2 ± 0.5	~25		9
90.7	IV	~2 × 10^{-5}		~40	~48	5
84.8	III	~5 × 10^{-5}	2.8 ± 0.5	~3		6
84.8	IV	~5 × 10^{-5}		~7	~10	6
91.3	Nonequilibrium mixture of 50% I and 50% II	. . .	1.4 ± 0.2	~16	. . .	. . .
99.7	1,3,4-Trimethylcyclopentenyl cation	*b*	*b*	~640	. . .	. . .
95.7		*b*	*b*	~35	. . .	. . .
91.3		*b*	*b*	~13	. . .	. . .
90.7	VII	~8 × 10^{-6}	2.3 ± 0.5	~15	. . .	. . .
90.7	IX	~2 × 10^{-5}	3.2 ± 0.5	~8	. . .	. . .

[a] Plots are all curved near the origin. See Results for the evaluation of these data. [b] K is, of course, 1.

has a half-life of 10–50 hr and the rate of the isomerization in 95% protiosulfuric acid has reciprocal rate constants of the same order of magnitude.

The remaining columns of Table III list the D–H exchanges which occur only because the ions are interconvertible. Deno, *et al.*,[1a] have previously shown that the proton on the 2 position in 1,3-dialkylcyclopentenyl cations is *not* exchanged. Similarly, the methine proton of the isopropyl group at C4 in IV (γ to the carbonium ion) is not exchanged except by conversion of IV to III, being exchanged in III (β to the ion), and then reisomerizing to its original position in isomer IV with deuterium exchange effected. These sequences are shown below.



The rate is actually measured by observing the rate at which the isopropyl doublets in isomer IV are converted to singlets. These D–H exchange half-lives should be related therefore to the rate of the isomerization reactions and not to the actual rate of deuterium exchange.

For protons which are never in a position β to the ion in either isomer, no D–H exchange has been observed. The isopropyl methyl protons, for example, are either γ or δ to the ion and are not noticeably exchanged. This finding also agrees with that of Deno, *et al.*[1a]

The cation pair, V ⇄ VI, undergoes a competing rearrangement reaction, besides the isomerization already discussed, and it was not possible to obtain the equilibrium concentrations of the ions; even in 83% sulfuric acid, where the equilibration reaction is fairly rapid, all that can be said is that K is greater than 2.4 (immediately on formation of the ions, K was about 0.65). A detailed nmr spectral study of this rearrangement suggests strongly that it is ion V which is actually unstable; however since VI can be isomerized to V, complete rearrangement is eventually observed. This conclusion is based mainly on the fact that the *t*-butyl peak of ion V disappears quite rapidly compared with this same peak in ion VI; indeed the disappearance of the *t*-butyl peak of ion VI correlates well with the calculated rate of the isomerization reaction. The final products of the rearrangement, formed in about 50% yield, the rest being mainly polymer, are the equilibrium concentrations of 1,2,3-trimethyl-4-isopropylcyclopentenyl cation XXI and its isomer XXII. The identity of the product with the two ions mentioned was proven by an independent synthesis of these.[12,13] The products XXI and XXII are half-formed in about 1 week at 25°. However, the half-life for the disappearance of V is only about 6 hr at the same temperature. The intermediate ion is characterized by a strong nmr signal at τ 8.58, but its identity can hardly be established from this. The assignment of peaks to this ion is complicated because VI persists in solution well beyond the point where the final products XXI and XXII show up so one has at least four ions in solution at one time.

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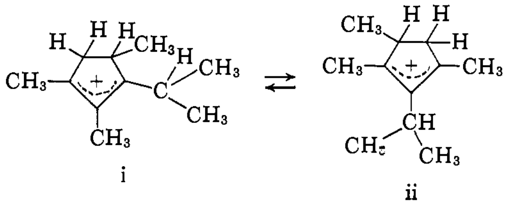
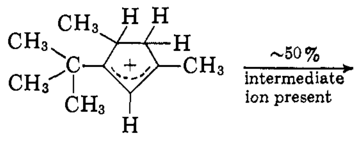
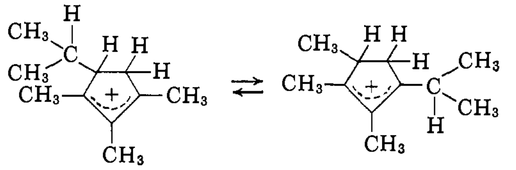
(12) Part II in this series: *J. Am. Chem. Soc.*, **89**, 3794 (1967).

(13) What appears to be most remarkable is the appearance of the isopropyl group solely on the "outside" of the methyl group, corresponding to a movement of a methyl group from the *t*-butyl group to C5 of the ring. There is no reason to believe that the isopropyl group of the ions i ⇄ ii, which might be formed by a more reasonable shift of a methyl group from *t*-butyl to C2, would not be completely stable. Yet, these or any of the other possible products are, within expeimental error, not observed.



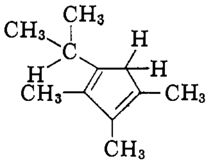


V



XXI XXII

Recovery Experiments. The neutral products from the ion pair XXI ⇄ XXII, produced both by the rearrangement of V and by an independent synthetic route,[12] were recovered using the standard techniques for this.[1b,c] In this instance, only a vpc analysis was performed but the results in the following paper,[12] and previous examples, are sufficient to show that all these ions are "recoverable." The vpc analysis shows one main peak with a retention time of 5.0 min (~80%), and two small peaks with retention times of 4.5 and 3.8 min[14] at 87°. The large peak is quite likely due to the diene XXIII, which can be formed from both ions.



XXIII

Ultraviolet Spectra. The ultraviolet spectra were measured in 96% sulfuric acid, using the pure ions where available or a mixture of the two isomers in two cases, and are recorded in Table IV. The results are quite similar to those previously reported for other cyclopentenyl cations.[1b,15]

Table IV. Ultraviolet Spectra of the Carbonium Ions

Compound	$\lambda_{\max}$,[a] mμ	$\epsilon_{\max}$[b]
1,2,4-Trimethylcyclopentenyl cation	279.5	12,000
I-II (1:1)	282.5	17,000
III	284	17,000
IV	284	13,000
V-VI (60:40)	291	13,000
VII	287.5	17,000
IX	291	21,000
1-*t*-Butyl-3-methyl-4-isopropylcyclopentenyl cation	293	. . .

[a] ±0.5 mμ. [b] Assuming no side reactions during the ion formation.

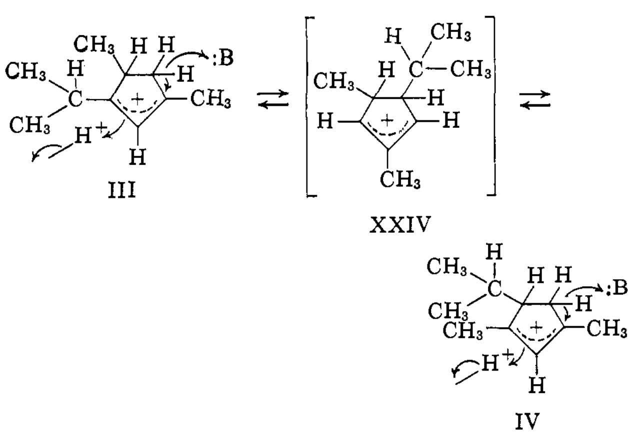
Discussion

The evidence (freezing-point depression, pK_a studies, etc.) that substituted cycloalkenols or cycloalkadienes form cations in sulfuric acid has already been given.[15] The concentration of a dialkylcyclopentadiene and its cation are equal in 35% sulfuric acid.[16] The lowest acid concentration used in these studies is 83%, about 5.5 H_0 units above the pK_a. In any case, the ultraviolet spectral data listed in Table IV are explicable only on the basis of ion formation.

The data reported under Results give unequivocal evidence for a true equilibrium in the isomerizations: (1) the same per cent composition is obtained starting with both pure ions, and (2) deuterium substitution in the isopropyl hydrogen of IV can only occur if this ion is converted to III and is then reisomerized to IV.

Mechanism of the Isomerization Reaction. The dependence of the rate of isomerization on acidity is shown in Figure 4 where the Hammett acidity function is used as an acidity measurement. Figure 4 also gives a rough indication of how the rate of deuterium substitution is affected by acid change (H_0 values for deuteriosulfuric acid are assumed to be similar to those of protiosulfuric acid[17]). It is immediately obvious that the rate of deuterium substitution shows a much greater slope[18] than that of isomerization. This was qualitatively apparent even from a cursory study of the isomerization reactions in the deuterated acid. In 96% deuteriosulfuric acid, for example, deuterium substitution of the C1 and C3 methyl groups is incomplete even after essentially complete equilibration of the two ions. In the 85% acid however, CH_3 substitution by deuterium is nearly complete before most of the isomerization process has started. The mechanism of deuterium substitution has been postulated as a simple deprotonation–protonation step.[1a] The protonation equilibria of aliphatic cyclopentenyl ions has also been found to follow the H_0 acidity function although the data on this are rather fragmentary.[16] The slope of near 1 found in these studies, for deuterium substitution as a function of acidity, is therefore entirely consistent with this simple mechanism. The large difference (a factor of about 10) between CH, CH_2, and CH_3 exchange is also in line with the well-known trend of carbonium ion intermediates to form the more substituted alkene on hydrogen ion elimination.

Since acid–base equilibria with base attack at C5 appear to have approximate unit slope, the smaller slope for the isomerization reaction (0.59) is consistent with the following mechanism, a concerted acid–base termolecular process leading to the pseudosymmetrical



III XXIV IV

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[14] Two further small peaks with retention times of 2.9 and 3.3 min were observed in the chromatogram of the product formed by rearrangement of ion V.

[15] N. C. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2998 (1963).

[16] N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).

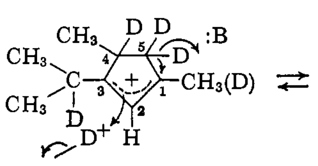
[17] E. Hogfeldt and J. Bigeleisen, *J. Am. Chem. Soc.*, **82**, 15 (1960).

[18] These slopes would be negative in the conventional sense since log *k* usually increases as $-H_0$ becomes a bigger number. In this study, "specific catalysis" questions are concerned with bases rather than acids.

ion XXIV, which can then form either ion by a similar reverse mechanism. The increase in rate as the acid strength decreases requires the base-initiated (HSO_4^- or H_2O) deprotonation step, as expected, to be the more important. An alternative mechanism, which avoids the implication of adding a proton to an already charged species, would involve deprotonation at C5, protonation at the less basic center C3 to give the intermediate ion XXIV, and then the reverse of these steps. Under steady-state conditions this might also yield a log k *vs.* $-H_0$ slope different from the slope of the rate of deuterium substitution.

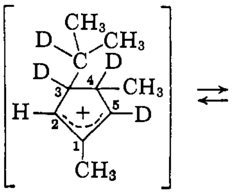
The above mechanisms also rationalize well the observed isotope effect on the isomerization rate, since this effect is best correlated with deuterium substitution at C5 (see Results). Both of the above mechanisms postulate a rate-determining, bond-breaking step at C5 in the transition state and a slower rate would be expected in the deuterated case. The isotope effects are very complex; however, since the base and acid both contain deuterium, a deuterium solvent isotope effect might be expected and deuterium is also present at other positions in the carbonium ion (besides C5), mainly the β-C–H protons.

The above mechanism is also consistent with the rate of deuterium substitution at C2. The best conditions to observe this substitution are in the isomerization of III in 85% deuteriosulfuric acid. Under these conditions, deuterium exchange has occurred at C5 before any isomerization has taken place so that the plot of the kinetic data is much closer to a straight line.

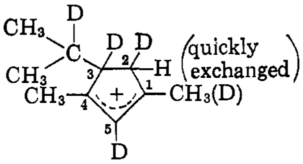


III in 85% D_2SO_4

Deuterium substitution occurs very rapidly in the positions indicated. Note that the CH_2 or CD_2 protons or deuterons at C5 are nonequivalent. One has no way of knowing whether this is significant, however.



XXIV



IV

Half-deuterium substitution at C2 (C5 in the above formula) corresponds to half-isomerization assuming no reverse process (initially a good assumption).

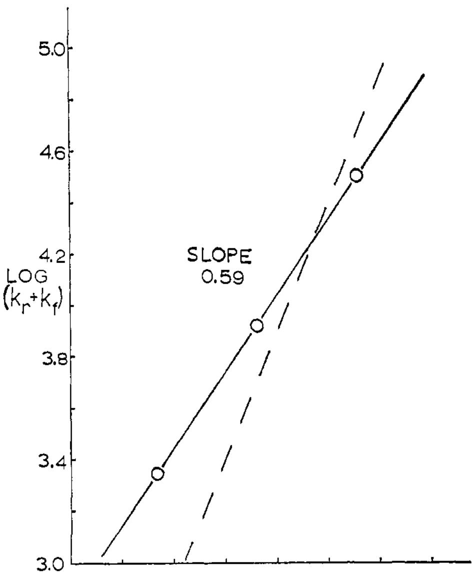
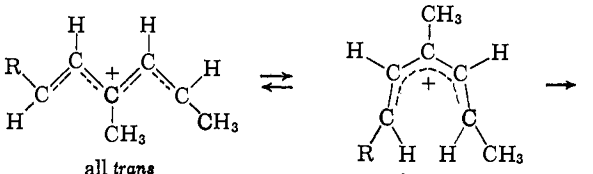


Figure 4. Solid line, the acid dependence of the logarithm of the rate constants for isomerization using the Hammett acidity function. Dashed line, the rough acid dependence of deuterium substitution (logarithm of the rate constants) using the same acidity function. Note that the scale for the ordinate is the same in this case but the numbers and the caption apply only to the solid line.

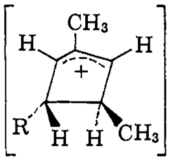
Under these conditions the value of the half-life for deuterium exchange at C2 is about 3 hr at 25° while $t_{1/2}$ for the forward isomerization reaction is also about 3 hr. This process is shown above.

The intermediate ion XXIV is a most logical intermediate in the dienylic ion cyclizations[1b] and the interesting fact is that the equilibrium mixture of cyclopentenyl ions is not initially formed (see Results). Also, when the triene cyclizations are made in deuteriosulfuric acid, no appreciable deuterium enters at C5 of the ions, as required by the isomerization mechanism (1D,1H at this position) discussed above. This latter result seems to be explained only by assuming a hydride shift process. Previously we have (erroneously it appears) represented this type of hydrogen shift in several other cases[1b,f,g] as a reversible protonation–deprotonation reaction. The hydride shift could be a direct 1,3 shift or two 1,2 shifts,[20] possibly concerted. This is shown below; the reaction can also proceed in the same way to give the other isomer.

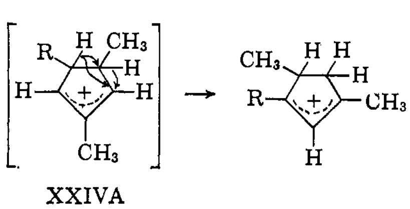


all *trans*

s-cis, s-cis isomer (predicted conrotatory process during cyclization[19])



XXIVA



XXIVA

The nonequilibrium formation of the cyclopentenyl cations and the negligible deuterium substitution can be

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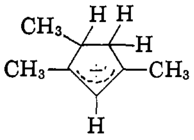
(19) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965).

(20) The hydride shifts occurring in the propyl cation produced by deamination provide direct analogies for these processes; *e.g.*, see G. J. Karabatsos and C. E. Orzech, Jr., *ibid.*, **84**, 2838 (1962).

rationalized if it is assumed that the cyclization and hydride-transfer reaction is a concerted, exothermic process where the intermediates XXIV and XXIVA are structurally similar but differ in their solvation and in their internal energy, the ion intermediate XXIVA undergoing hydride shifts before it is solvated and deactivated as in XXIV.[21] The factors which direct the hydride shifts to give the nonequilibrium mixtures are not clear. However, the observed order, greater nonequivalence in the direction *t*-Bu > i-Pr > Et, would suggest that the reaction may prefer to initiate a double hydride shift where charge is developed preferentially at a carbon substituted by a methyl group and progressively less in the opposite direction depending upon whether R is Et, *i*-Pr, or *t*-Bu.

The isomerization of ion XXV[16] represents an interesting case of a reaction involving considerable structural change but where the product is identical with the reactant. The isomerization is shown clearly by the deuterium substitution at C2 and in the methyl group at C4, both substitutions not occurring unless isomerization takes place. Indeed, the isomerization can be nicely followed by following the deuterium exchange at C2. The $k_r + k_f$ values for the ions I $\rightleftarrows$ II and VII $\rightleftarrows$ VIII, are similar to the isopropyl case studied in detail and the mechanism of the isomerization is assumed to be the same. The $k_r + k_f$ value for IX $\rightleftarrows$ X appears to be somewhat greater than the above.



XXV

Position of the Equilibrium. It had been hoped that a direct comparison of methyl, ethyl, isopropyl, and *t*-butyl groups could be made; however the instability of the last group in these ions has precluded this. The results, as far as they go, show very clearly, however, that the ion stabilities, for whatever reason, follow the Baker–Nathan order.

The nature of the solvent is one of the factors which might be expected to affect the equilibrium positions. This was one of the reasons therefore for varying the solvent from 84 to 96% sulfuric acid and for using a deuterated solvent. The results show that within experimental error, the *K* values are the same in all of these solvents. It might be considered that the change from 96 to 84% sulfuric acid would not be very great in terms of solvent structure, but this is not the case.[22] At 84%, sulfuric acid is composed mainly of HSO_4^- and H_3O^+ ions (similar to a molten salt), while the 96% acid is largely molecular H_2SO_4. At both these concentrations, the solvent is very highly structured but the structure changes considerably with acid concentration. We also have other results[12] in 100% sulfuric acid, which are the same as those in 96% and lower per cent acid solutions. Also, if specific proton hydrogen-bonding solvation effects were very important in determining *K*, one might have expected that the equilibria in deuteriosulfuric acid might have been different from those in the proton acid. This is not to say that solvation of the ions is unimportant, but only that it may be unimportant in determining *K*.

Any specific effects of the counterion (HSO_4^-) in determining *K*, which might be important if ion pairing were important, can probably be discounted. The dielectric constant for pure sulfuric acid is 100 at 25°[23] and aqueous solutions of sulfuric acid would be expected to have a value even greater than this.

Having to some extent discounted external factors, one might rationalize the observed *K*'s either by differential steric interactions, which will also include steric effects which could, for example, decrease the planarity of the ion system, etc., or one might rationalize the *K*'s solely by the usual inductive and resonance stabilization effects.

It is worth emphasizing that these ion comparisons (for example, as evidence for differential CH–CC hyperconjugation) have an internal comparison, as opposed to the usual studies where the kinetics or equilibria of a series of *different ions* are compared. One example among literally hundreds is the measurement and comparison of the K_{diss} values of 4-methyl- and 4-*t*-butyltriphenylchloromethanes.[24] In our work, each ion duo pits one group directly against the other. It is true that one may then compare the *K* values for a number of ion "pairs" but this is not necessary: each pair contains a comparison in itself.

The ΔF values (the free energy difference) between the two ions in each system are reported in Table II. The activity coefficients for the individual ions are assumed to be the same, a fairly safe assumption in view of their structural similarity. Equilibrium constant values (or ΔF) should not strictly be used to discuss hyperconjugation in the resonance or theoretically calculated stabilization energy sense. There are reasons[12] to believe, however, that ΔS differences are small so that $\Delta F \sim \Delta H = \Delta E$.

It is not the intention to dwell too long on a discussion of steric and/or inductive-resonance effects since the following paper[12] presents a different system with different steric interactions and which shows remarkably the same *K* values. The following two points are relevant however: (1) an examination of molecular models (Courtaulds) would indicate that the less stable isomer in each series has, if any, the fewer nonbonded interactions; and (2) the comparison of isopropyl *vs.* methyl in the three systems III–IV, VII–VIII and IX–X gives within experimental error the same value of *K*, even though one has presumably made small changes in the nonbonded interactions of the molecules.

Nmr Spectra. The cause of the marked broadening of the nmr peaks due to the methyl protons at C1 and C3 in cyclopentenyl cations has been somewhat of a puzzle ever since this fact was noted in the original preparations of this ion type by Deno and co-workers.[3] These authors concluded that the broadening was due to coupling from hydrogens on nearby α-carbons (β-hydrogens in our terminology). Certain results from the present work shed some further light on this matter.

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(21) This argument is analogous to the "hot carbonium ion" description used to explain the variation in products formed in reactions where carbonium ions are presumed intermediates; *e.g.*, see K. L. Servis and J. D. Roberts, *J. Am. Chem. Soc.*, **86**, 3773 (1964), and references therein.

(22) T. F. Young, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 12, 81 (1951).

(23) R. J. Gillespie and E. A. Robinson, *Advan. Inorg. Chem. Radiochem.*, **1**, 386 (1959).

(24) N. N. Lichtin, P. E. Rowe, and M. S. Puar, *J. Am. Chem. Soc.*, **84**, 4259 (1962).

In Figure 1, top curve, the shape of the C1 methyl group of III (and the C3 isopropyl and C4 methyl) is shown after deuterium substitution only at C4 and the isopropyl CH. We believe that the important coupling actually occurs between protons on the methyl groups at C1 and the protons on the *opposite* side of the allylic system (at C4 and the isopropyl C–H). The above example is the only one in our studies where this degree of sharpness has been observed and it is the only one where both of these positions are completely deuterium substituted (but where those on the same side at C2 are not).

The nmr spectra of cyclopentenyl ions show remarkable[1b,c,3] constancy of resonances for groups at fixed positions in this system. The present results add further information. For example, the proton at C2 is found between τ 2.33 and 2.42 in all ten ions. The methyl group at C3 is found from τ 7.01 to 7.06 in all of the cases studied. A methyl group one carbon removed from an ion center occurs from τ 8.49 to 8.59 in all cases, even though the group is methyl, ethyl, isopropyl, or *t*-butyl. A methyl group two carbon atoms removed from the ion center occurs from τ 8.91 to 9.01 except in the case of an isopropyl group at C_4, which shows an unusual nonequivalence of the two methyl groups (0.63-ppm separation in the best case). This spectrum has been rationalized[25] in terms of a preferred conformation for the isopropyl group, which sets one methyl group directly in the diamagnetic region of the allylic cation.

It is even possible to correlate the small differences in the C2 proton resonances with the relative stability of the two isomeric ions: for example, in I–II, τ 2.38 for I, τ 2.42 for II; in III–IV, τ 2.37 and τ 2.40; and in V–VI, τ 2.33 and 2.42, respectively, with the greatest difference in the last (*t*-butyl *vs.* methyl) case. This is supported by noting that the methyl group at C4 resonates at 0.06 ppm lower in the less stable isomer of the V–VI pair than in any of the other compounds. Very good correlations of the deshielding of nmr $^{\delta+}$C–H and $^{\delta+}$C–CH_3 resonances, as a function of the positive charge density on these carbon atoms, have previously been observed[1g,26a,b] in a carbonium ion series.

Experimental Section

Melting points and boiling points are uncorrected. Ultraviolet spectral measurements were made using a Perkin-Elmer Model 202 spectrophotometer or a Beckman DK-1 spectrophotometer. Infrared spectral measurements were made on all neutral compounds in dilute carbon tetrachloride solution using a Perkin-Elmer Model 337 spectrophotometer. Gas chromatography separations were made using the Aerograph "Autoprep," Model A-700, employing a 12 ft × $^3/_8$ in. column of 30% Carbowax 20 M on 60–80 Chromosorb W, HMDS treated. The analytical vpc results were obtained on an Aerograph "Hy-Fi," Model 600, employing a 6 ft × $^1/_8$ in. column of 5% SE-30 on Chromosorb W.

The nmr spectra were obtained on a Varian Associates A-60 spectrometer equipped with a variable-temperature probe. The neutral compounds were measured as *ca.* 10% w/v solutions in carbon tetrachloride using tetramethylsilane as internal reference. Hydroxyl signals where present were pinpointed by shaking these solutions with heavy water. Tetramethylammonium cation (τ 6.90) was used as the internal reference[3] in the ion studies. Other workers have suggested τ 6.87 for this reference.[26c]

The ion solutions (*ca.* 10% w/v) were prepared either by the gas-phase addition procedure, previously described[1b] (used for the trienes), or by extraction of the compounds (generally the alcohols) from a hexane (CaH_2 dried) solution by sulfuric acid, also previously described.[1g] In the latter case, the two layers generally separated out quite well, and a dropper could be used to take off the lower acid layer. When emulsification occurred, the hexane was removed under reduced pressure as in ref 1g. In general, the solvent extraction was carried out at 0° and took only a few minutes; the gas-phase addition was carried out at about 15° and took a little longer. When the kinetics were very rapid, crude corrections were applied to include the time necessary to prepare the sample. In several cases, both preparative procedures were used on the same compound with essentially the same result. Most of the ion solutions were yellow to orange initially but darkened considerably with time, although this did not seem to affect the quality of the nmr spectra.

The reactions were conducted in the nmr tubes, these being protected from light using aluminum foil and the tops sealed with tape. The constant-temperature bath is accurate to ±0.02°. The nmr measurements were made at 35 ± 2°. Only in the case of the fastest reactions might this difference be important and in these cases all measurements were made as rapidly as possible (about 3 min). The area analysis was carried out as described under Results.

Aqueous H_2SO_4 and D_2SO_4 concentrations were obtained by titration with standard alkali. Deuteriosulfuric acid (96–98%, 99.1 ± 0.05% D) was obtained from Fluka A.G. and more dilute solutions were prepared by appropriate dilution with heavy water. The deuterium substitution was followed by measuring the decreasing area of the peaks, using peaks not being substituted as reference areas or in several cases, particularly where all protons are being exchanged, with no standard other than using the same machine settings. The latter procedure is probably justified since the kinetics, in any case, cannot be measured very accurately for a number of reasons (see Results).

Recovery Experiments. An approximately 10% sulfuric acid solution of the ion "pair" XXI–XXII (2 ml of solution), from both sources discussed under Results, was added through a hypodermic syringe to a well-stirred, ice-cold solution of concentrated potassium hydroxide (25 ml) with about 5 ml of hexane also present. The hexane layer was separated and dried over magnesium sulfate. Vpc analyses were carried out on this extract using both the preparative and the analytical column.[5] The retention times for the analytical column are reported under Results. Only one broadened peak was observed using the preparative column (135°) but this result is consistent with the facile thermal rearrangement of these dienes.[6]

4-Methylpent-2-enoic acid was prepared by the standard route,[27] bp 101–103° (7–8 mm), $n^{27}\mathrm{D}$ 1.4457.

4-Methylpent-2-enoic Anhydride (XI). A solution of 102 g (1 mole) of acetic anhydride and 228 g (2 moles) of the above acid was heated to reflux, slowly distilling off the acetic acid formed through a 1-m spinning-band column. Toward the end of the reaction, the distillation temperature slowly rose and a fraction, bp 110–142°, was collected and discarded. This fraction contains some of the anhydride of the isomeric β,γ-unsaturated acid. The main fraction (*ca.* 125 g, about 60% yield based on several runs) was collected at 142–146° (7–8 mm), $n^{23.5}\mathrm{D}$ 1.4704. The nmr spectrum is very similar to that of the acid, and the infrared spectrum shows the characteristic carbonyl doublet at 1750 and 1800 cm^{-1}.

7-Methylocta-2,5-dien-4-one (XII). A solution of propenylmagnesium bromide was prepared from 24.3 g (1 g-atom) of magnesium and 121 g (1 mole) of redistilled propenyl bromide (mixture of *cis* and *trans* isomers) using a total of 500 ml of purified tetrahydrofuran. This solution was added over a 3-hr period from a heated dropping funnel to a well-stirred solution of 260 g (1.23 moles) of 4-methylpent-2-enoic anhydride in 200 ml of tetrahydrofuran cooled to below −50°.[28] The solution was initially flushed with nitrogen and then protected from the atmosphere. The resulting mixture was allowed to warm to 0° overnight in the refrigerator and then decomposed by pouring it into cold ammonium chloride solution. The aqueous solution was extracted with ether (two 300-ml portions); the ether was washed with saturated sodium carbonate solution (two 200-ml portions) and twice with water and the ether solution dried over magnesium sulfate. Rapid distillation of the residue after solvent removal yielded a fraction, bp 88–135°, about 70 g, followed by a fraction of about 80 g, bp 145°, which is

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[25] T. S. Sorensen, to be published.

[26] (a) G. Fraenkel, R. E. Carter, A. McLachlan, and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5846 (1960); (b) T. Schaefer and W. G. Schneider, *Can. J. Chem.*, **41**, 966 (1963); (c) D. G. Farnum, M. A. T. Heybey, and B. Webster, *J. Am. Chem. Soc.*, **86**, 673 (1964).

[27] A I. Vogel, "A Textbook of Practical Organic Chemistry," 3rd ed, Longmans, Green, and Co., New York, N. Y., 1956, p 464.

[28] H. Normant, *Advan. Org. Chem.*, **2**, 40 (1960).

recovered anhydride. A large pot residue (~65 g) remains. The first fraction was carefully redistilled through a 1-m spinning-band column (10 mm) to yield the following fractions (using a 10:1 reflux ratio): (1) 39–79.5°, mainly 70–79.5°; (2) 79.5–82.0°; (3) 82–91.5°, very unstable, rapidly polymerizes in air; and (4) >91.5°, mostly 4-methyl-2-pentenoic acid. Fraction 2 (17 g, 12% yield based on the propenyl bromide) is a mixture of about two parts of the cross-conjugated dienone XII to one part of the unconjugated dienone XX. When the distillation is carried out more rapidly, an essentially pure dienone XII is obtained. The infrared spectrum shows a peak at 1670 cm^{-1}, normal for a cross-conjugated ketone. The nmr spectrum (in τ values) shows peaks at 8.87 and 8.98 (J = 6.6 cps, area 6, isopropyl group), two peaks at 8.06 and 8.17 (J = 6.6 cps, each of which is a narrow doublet with J = 1–2 cps, area 3, the methyl group at C1), a heptet centered at 7.60 (J = 6.6 cps, area 1, the isopropyl proton), and a complex region 2.9–4.2 (area 4, the alkene protons).

Anal. Calcd for $C_9H_{14}O$: C, 78.14; H, 10.21. Found: C, 78.18; H, 10.21.

3-Methyl-4-isopropylcyclopent-2-en-1-one (XIV) and 3-Isopropyl-4-methylcyclopent-2-en-1-one (XIII). The dienone XII described above (15.0 g, 0.11 mole) was added over a 30-min period through a dropper to 150 ml of concentrated sulfuric acid kept at 0°. After 2 hr at room temperature, the mixture was added dropwise over a 30-min period to 1.5 l. of well-stirred ice–water. The organic material was extracted into ether (three 250-ml portions) and the ether solution washed with dilute sodium hydroxide and dilute sodium chloride solutions and then dried over anhydrous magnesium chloride. After removal of the solvent, the residue was distilled (7–8 mm) through a microdistillation column to yield 4.2 g (28%) of a very pale yellow liquid, bp 80–90°.

The product is XIV–XIII *ca.* 38:62 mixture (by vpc determination) of the two ketones. They can be quantitatively separated by preparative vpc using the $^3/_8$-in. column previously described. The column was operated at 165°, the collector at 180°, the injector at 275°, the helium flow rate was *ca.* 200 cc/min, and 0.10–0.15-ml samples were used at each injection. Under these conditions the retention times are 25.5 min for XIII and 30.2 min for XIV.

3-Isopropyl-4-methylcyclopent-2-en-1-one (XIII). The infrared spectrum shows a carbonyl doublet about 1695 and 1720 cm^{-1}, a characteristic of many cyclopentenones.[29] The ultraviolet spectrum in hexane shows a single peak (only the $\pi \rightarrow \pi^*$ transition was measured) at 221 mμ (ϵ_{max} 15,100). The nmr spectrum (in τ values) shows peaks at 8.89 and 8.78 (J = 6.6 cps, area 3, the methyl group at C4), 8.84 and 8.72 (J = 7.2 cps, area 6, the isopropyl group), a complex region from 6.8 to 8.3 (CH and CH_2 protons), and a triplet 4.18 (J = 1 cps, area 1, the proton at C2).

Anal. Calcd for $C_9H_{14}O$: C, 78.14; H, 10.21. Found: C, 78.18; H, 10.63; $n^{21.5}D$ 1.4790.

The ketone forms a red 2,4-dinitrophenylhydrazone derivative, mp 130–133° (from 95% ethanol).

Anal. Calcd for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70. Found: C, 56.41; H, 5.71.

3-Methyl-4-isopropylcyclopent-2-en-1-one (XIV) solidifies at about 0°, $n^{21.5}D$ 1.4807.

Anal. Calcd for $C_9H_{14}O$: C, 78.14; H, 10.21. Found: C, 78.04; H, 10.19.

The infrared spectrum shows a similar characteristic doublet, at 1680 and 1715 cm^{-1}, for the cyclopentenone structure. The ultraviolet spectrum in hexane shows a single peak (only the $\pi \rightarrow \pi^*$ transition was measured) at 222 mμ (ϵ_{max} 14,200). The nmr spectrum (in τ values) shows peaks at 9.38, 9.27, 9.04, and 8.93 (J = 6.6 cps, area 6, the isopropyl group), 7.93 (area 3, the methyl group at C3), broad absorption >7 (CH_2 and CH protons), and a multiplet at 4.13 (J = ~1 cps, area 1, the proton at C2).

The ketone forms a red 2,4-dinitrophenylhydrazone derivative, mp 151–152° (from 95% ethanol).

Anal. Calcd for $C_{15}H_{18}N_4O_4$: C, 56.59; H, 5.70. Found: C, 56.38; H, 5.54.

1,3-Dimethyl-4-isopropylcyclopent-2-en-1-ol (XVI). A solution of methyllithium (4 ml of 1.62 M, 0.0065 mole) was added to a cold (0°) stirred solution of ketone XIV (0.580 g, 0.0042 mole) in 10 ml of dry ether. The solution became slightly yellow during the addition but was again nearly colorless at the end. After 1.5 hr at 0°, the solution was poured into ice-cold dilute sodium carbonate solution. The aqueous solution was extracted with ether (three 25-ml portions), and this was dried over potassium carbonate. Distillation of the residue (*ca.* 0.1 mm), after removal of the ether, yielded a colorless liquid with a camphor-like odor, bp 34–35°, yield 0.52 g (70%).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.09; H, 12.03.

The infrared spectrum shows the expected hydroxyl peak at 3620 cm^{-1} and only a small peak in the carbonyl region. The nmr spectrum (in τ values) shows peaks at 9.32, 9.21, 9.15, and 9.04 (J = 6.6 cps, area 6, the isopropyl group at C4), 8.74 (area 3, the methyl group at C1), 8.36 (area 3, the methyl group at C3), a complex series of peaks for the CH_2 and CH protons, and a multiplet, area 1, at 4.70 (the proton at C2).

1,4-Dimethyl-3-isopropylcyclopent-2-en-1-ol (XV), **1-ethyl-3-isopropyl-4-methylcyclopent-2-en-1-ol (XXVI), and 1,3-diisopropyl-4-methylcyclopent-2-en-1-ol (XXVII)** were prepared in the same way as above using the appropriate alkyllithium compound. In these cases, a second alkyllithium treatment (using one-half the amount used originally) was performed on the crude material obtained after the ether evaporation (see Results). The reaction was again worked up as before. Physical properties were as follows: XV, bp ~32° (~0.1 mm), 70% recovered yield, mixture of *cis* and *trans* isomers (*Anal.* Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.79; H, 12.00); XXVI, bp ~48° (0.25 mm), 65% recovered yield, mixture of *cis* and *trans* isomers (*Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 77.99; H, 11.99); and XXVII, bp 45–47° (0.1 mm) (*Anal.* Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 79.45; H, 12.10).

Hex-3-en-2-one was prepared according to the literature,[10] a fraction, bp 135–137° (662 mm), $n^{26}D$ 1.4387, being used. The nmr spectrum of this fraction shows that less than 5% of the β,γ-isomer is present, and the spectrum is completely consistent with the title structure.

5-Methylhex-3-en-2-one (XVII) was prepared according to the literature,[7] a fraction, bp 148° (665 mm), $n^{26}D$ 1.4364, being obtained. This material is about 70% α,β-unsaturated and 30% β,γ-unsaturated ketone, and the separation of these by distillation appears to be impossible. The mixture was accordingly added dropwise to concentrated sulfuric acid at 0°, and the resulting solution was left for 1 hr at 25° and then poured onto ice. This mixture was extracted several times with ether, and the ether was dried over magnesium sulfate. After removal of the ether, distillation of the residue gave the pure (nmr) α,β-unsaturated ketone with a good recovery yield.

5,5-Dimethylhex-3-en-2-one was prepared in good yield by the literature[9] method, bp 158–160° (665 mm), $n^{23}D$ 1.4409 [lit.[9] 78–80° (40 mm), $n^{20}D$ 1.4430].

4-Methylocta-1,5-dien-4-ol (XXVIII), 4,7-Dimethylocta-1,5-dien-4-ol (XVIII), and 4,7,7-Trimethylocta-1,5-dien-4-ol (XXIX). The addition of the allyl Grignard reagent to these ketones was performed in a manner similar to that described previously for the addition of this reagent to pent-3-en-2-one.[8]

XXVIII showed the following physical properties: bp 62.5–63° (10 mm), $n^{26}D$ 1.4520, yield 25 g, 67% from 0.268 mole of ketone. The nmr spectrum (in τ values) shows peaks at 9.13, 9.01, and 8.88 (J = 7.2 cps, area 3, CH_3 of ethyl group), 8.81 (area 3, the remaining methyl group), 8.48 (area 1, the hydroxyl proton), 7.85 and 7.72 (J = 7.8 cps, area ~2, the methylene protons at C3), 7.8–8.22 (a complex series of peaks of area *ca.* 2, the methylene protons of the ethyl group), and a complex series of peaks at 3.8–5.2 (area 5, the alkene protons). The infrared spectrum shows peaks at 3620 (OH stretch) and 1640 cm^{-1} (double-bond stretch). Of the remaining, a series of three peaks at 920, 973, and 996 cm^{-1} are prominent.

Anal. Calcd for $C_9H_{16}O$: C, 77.14; H, 11.4. Found: C, 77.00; H, 11.12.

XVIII showed the following physical properties: bp 68.5–69° (10 mm), $n^{26}D$ 1.4495, yield 18 g, 67% from 0.175 mole of ketone. The nmr spectrum (in τ values) shows peaks at 9.06 and 8.95 (J = 6.6 cps, area 6, isopropyl methyl peaks), 8.81 (area 3, the remaining methyl group), 8.42 (area 1, the hydroxyl proton), 7.83 and 7.72 (J = 6.6 cps, area 2, the methylene protons at C3), 7.5–8.0 (a complex series of peaks, the isopropyl CH), and a complex series of peaks at 3.8–5.2 (area 5, the alkene protons).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.88; H, 11.7. Found: C, 77.76; H, 12.00.

XXIX showed the following physical properties: bp 80.5–81° (15 mm), $n^{21}D$ 1.4496, solidifies about −10°, yield 26 g, 84% from 0.184 mole of ketone. The nmr spectrum (in τ values) shows peaks at 9.00 (area 9, the *t*-butyl group), 8.80 (area 3, the remaining methyl group), 8.09 (area 1, the hydroxyl proton), 7.84 and 7.72 (J = 7.2 cps, area 2, the methylene protons at C3), and a complex series of

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(29) P. Yates and L. L. Williams, *J. Am. Chem. Soc.*, 80, 5896 (1958).

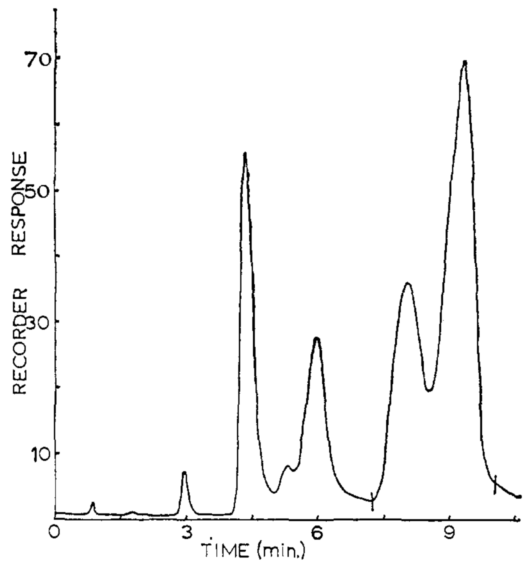

Figure 5. Preparative-scale vapor phase chromatogram of the crude dehydration product from XXVIII: column 130°, collector 150°, injector 210°, He flow *ca.* 200 cc/min, sample size 0.1 ml.

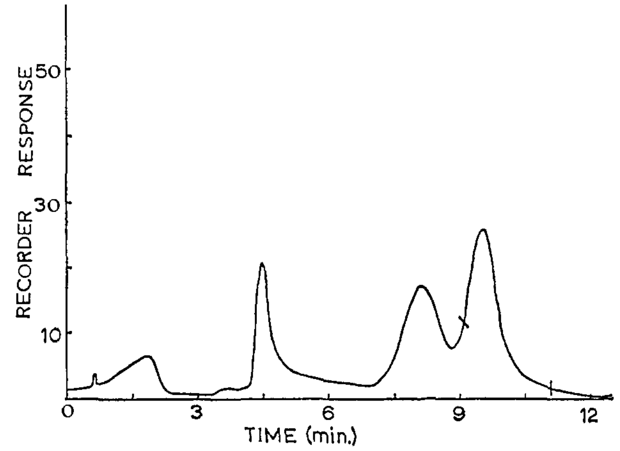

Figure 6. Preparative-scale vapor phase chromatogram of the crude dehydration product from XVIII: column 135°, collector 150°, injector 210°, He flow *ca.* 200 cc/min, sample size 0.1 ml.

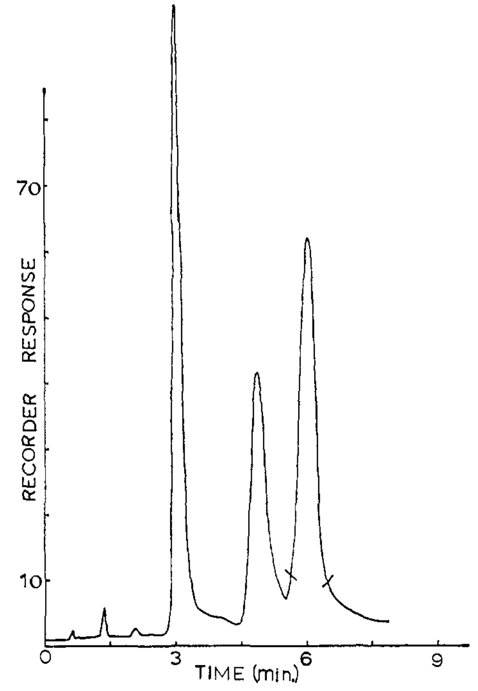

Figure 7. Preparative-scale vapor phase chromatogram of the crude dehydration product from XXIX: column 150°, collector 165°, injector 220°, He flow *ca.* 200 cc/min, sample size 0.1 ml.

peaks at 4.0–5.2 (area 5, the alkene protons). The infrared spectrum shows the expected hydroxyl stretch peak at 3620 cm^{-1} and a double bond stretch at 1645 cm^{-1}. Characteristic, strong peaks are also found at 920, 980, and 1000 cm^{-1}.

Anal. Calcd for $C_{11}H_{20}O$: C, 78.57; H, 11.9. Found: C, 78.45; H, 11.85.

4-Methylocta-1,3,5-triene (XXX). The alcohol XXVIII (10 g, 0.07 mole) in 50 ml of dry benzene was dehydrated as described previously,[5] using 0.025 g of *p*-toluenesulfonic acid. A crude distillate, bp 50–65° (10 mm), was obtained which still contained some of the original alcohol. The preparative vapor phase chromatogram is shown in Figure 5 and is very reminiscent of that obtained in the dehydration of 4-methylhepta-1,5-dien-4-ol. Accordingly, the fraction indicated by the vertical marks was collected and is a mixture of the *cis* and *trans* isomers of the title compound. The preparative collection conditions are indicated in Figure 5; the sample size was generally 0.10 ml for each injection. The product is a colorless liquid, n^{20}D 1.5300, which is rapidly polymerized by air.

Anal. Calcd for C_9H_{14}: C, 88.45; H, 11.55. Found: C, 88.13; H, 11.98.

The ultraviolet spectrum in hexane shows the characteristic triplet of conjugated trienes at 260, 269.5, and 281 mμ, (ϵ_{max} 30,000, 40,000, and 31,000), respectively (*cf.* with 4-methylhepta-1,3,5-triene). The infrared spectrum shows strong peaks at 1625, 985, 960, and 900 cm^{-1}. The first peak is considerably weaker than the others. The nmr spectrum (in τ values) is very simple and clean with peaks at 9.10, 8.98, and 8.85 (J = 7.2 cps, area 3, CH_3 of ethyl group), 8.18 (area 3, the remaining methyl group), 7.96, 7.84, 7.73, and 7.61 (J = 7.2 cps, area 2, the CH_2 protons of the ethyl group), and a complex series of peaks at 3.0–5.3 (area 6, the alkene protons). Several peaks centered at about τ 5 appear to be characteristic for $C{=}CH_2$ protons in these conjugated trienes (based on the nmr spectra of all three trienes).

4,7-Dimethylocta-1,3,5-triene (XIX). The alcohol XVIII was dehydrated as above to yield a crude distillate, bp 60–82° (10 mm), which still contained some of the original alcohol. The preparative vapor phase chromatogram is shown in Figure 6 along with the conditions used for the collection. After experimentation, it was determined that the fraction indicated by the vertical marks was mainly the title compound (nmr analysis). This fraction was again put through the chromatograph to completely remove the compound responsible for the peak showing up just to the left of that due to the desired compound, using the same experimental conditions as the first time. The product is a colorless liquid which is rapidly polymerized by air.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.41; H, 11.98.

The ultraviolet spectrum in hexane shows peaks at 261, 270.5, and 282 mμ (ϵ_{max} 33,000, 43,100, and 33,900), respectively (*cf.* XXX). The infrared spectrum shows strong peaks at 1620, 985, 963, and 900 cm^{-1} (*cf.* XXX). The first peak is considerably weaker than the others. The nmr spectrum (in τ values) is very clean and definitive, showing peaks at 9.03 and 8.92 (J = 6.6 cps, area 6, the isopropyl methyl groups), 8.18 (area 3, the remaining methyl group), 8.02, 7.90, 7.79, 7.68, 7.57, 7.46, and 7.35 (area 1, CH of the isopropyl group), and a complex series of peaks at 3.1–5.2 (area 6, the alkene protons).

4,7,7-Trimethylocta-1,3,5-triene (XXXI). The alcohol XXIX was dehydrated in a similar manner to XXVIII, to yield a crude distillate, bp 60–75° (10 mm), which still contains some of the unreacted alcohol. The preparative vapor phase chromatogram is shown in Figure 7 along with the conditions used for the collection. After experimentation, it was determined that the fraction indicated by the vertical marks was the title compound, probably the all-*trans* isomer. The product is a colorless liquid, n^{20}D 1.5103.

Anal. Calcd for $C_{11}H_{18}$: C, 87.93; H, 12.07. Found: C, 87.43; H, 12.19.

The ultraviolet spectrum in hexane shows peaks at 261.5, 270.5, and 282 mμ (ϵ_{max} 34,200, 45,600, and 34,800), respectively (*cf.* XXX and XIX). The infrared spectrum shows strong peaks at 1625, 987, 967, and 900 cm^{-1} (*cf.* XXX and XIX). The first peak is considerably weaker than the others. The nmr spectrum (in τ values) is reasonably definitive and clean; peaks are found at 8.95 (area 9, the *t*-butyl group), 8.18 (area 3, the remaining methyl group), and a complex series of peaks 3.2–5.2 (area 6, the alkene protons). A small peak at τ 9.12 is probably extraneous.

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Appendix

The actual nmr peaks used to calculate the relative amounts of the two isomers are as follows: I $\rightleftarrows$ II, the ethyl CH_3 group of isomer II was used to calculate the amount of II; the ethyl CH_3 group and C4 methyl group of isomer I were used to calculate the amount of I. Both these areas are well separated. The only uncertainty in this analysis is the position of the ethyl CH_2 group in isomer II; the peaks appear around τ 7.6–8.3, and it is not certain how much is under the ethyl CH_3 and C4 methyl peaks of this same isomer. The integration figures would suggest that most of it is in the above-quoted region so the uncertainty in the calculations should be quite small.

For III $\rightleftarrows$ IV, either one or two of the isopropyl CH_3 groups in isomer IV was used to calculate the amount of IV. If both were used, then the amount of isomer III was calculated from the relative area of the isopropyl CH_3 and C4 methyl groups of this isomer. If only the highest field isopropyl CH_3 of isomer IV was used, this area was subtracted from the rest of the area (including the second isopropyl CH_3 doublet of IV and the above peaks from III); the resulting area then represents the peaks of isomer III.

For V $\rightleftarrows$ VI, the two *t*-butyl groups are well separated; the lower field one (isomer V) overlaps with half of the split C4 methyl group of this same isomer so that this peak represents 10.5 protons against 9 for the high-field *t*-butyl peak of VI. The protons at C2 in the individual isomers are at sufficiently separate positions to enable these to also be used for area measurements. The agreement between the two measurements is good.

For VII $\rightleftarrows$ VIII, the high-field isopropyl CH_3 group of isomer VIII is used to calculate the amount of VIII. This area is multiplied by two (the remaining isopropyl CH_3 group and the ethyl CH_3 group of this isomer) and subtracted from the remaining area in the τ 8.48–9 region. The residual area represents the twelve protons of isomer VII. The above area calculation suffers because one isomer is calculated by difference, and the experimental error is certainly larger than in the other cases.

For IX $\rightleftarrows$ X, the high-field isopropyl CH_3 group of isomer X is used to calculate the amount of X. This area is multiplied by three (the remaining isopropyl CH_3 at C4 and the two isopropyl CH_3 groups at C1 of this isomer) and subtracted from the remaining area in the τ 8.53–9 region. The residual area represents the 15 protons of isomer IX.

Directly Observable Carbonium Ion–Carbonium Ion Rearrangements. II. Kinetics and Equilibria in the Interconversion of Tetraalkylcyclopentenyl Cations

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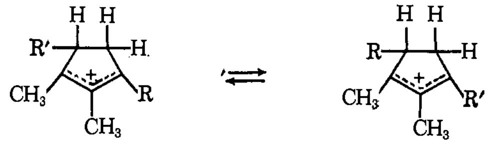
Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada. Received February 9, 1967

Abstract: A series of methyl, ethyl, isopropyl, and *t*-butyl tetrasubstituted cyclopentenyl cations have been prepared in which a facile equilibration takes place to yield both the 1,3- and the 2,4-dialkyl allylic cations. This system pits the various alkyl groups against one another and the results provide probably the best evidence yet obtained in support of the hyperconjugative order. This paper reports the value of the equilibrium constants so obtained, the kinetic rate constants of the equilibration reactions, the variation of equilibrium constants with temperature and solvent, the preparation of several of the ions in a deuterated acid solvent, and a detailed comparison of these quantities with those observed previously in a trialkyl series. In the *t*-butyl-substituted ions an additional rearrangement was found, corresponding to a directly observable neopentyl-type rearrangement. The position of the ultraviolet absorption maximum of these ions shows a remarkable correlation with the number of carbon atoms in the ion. Finally, a new cyclopentadiene synthesis was inadvertently discovered.

A study of the kinetics and equilibria of a tetraalkylcyclopentenyl cation series of the following structures was undertaken both for the intrinsic interest of this system and to complement and extend the work on a trialkylcyclopentenyl cation series,[1] principally the role of various alkyl groups in stabilizing these ions.

The tetraalkyl series was expected to show a number of differences compared to the trialkyl series. (1) The



I, R = ethyl; R^1 = methyl II, R = methyl; R^1 = ethyl
III, R = isopropyl; R^1 = methyl IV, R = methyl; R^1 = isopropyl
V, R = *t*-butyl; R^1 = methyl VI, R = methyl; R^1 = *t*-butyl
VII, R = isopropyl; R^1 = ethyl VIII, R = ethyl; R^1 = isopropyl
IX, R = *t*-butyl; R^1 = isopropyl X, R = isopropyl; R^1 = *t*-butyl

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(1) Part I: T. S. Sorensen, *J. Am. Chem. Soc.*, **89**, 3782 (1967).