The Equilibria and Kinetics of the Cyclohexenyl–Cyclopentenyl Cation Rearrangement

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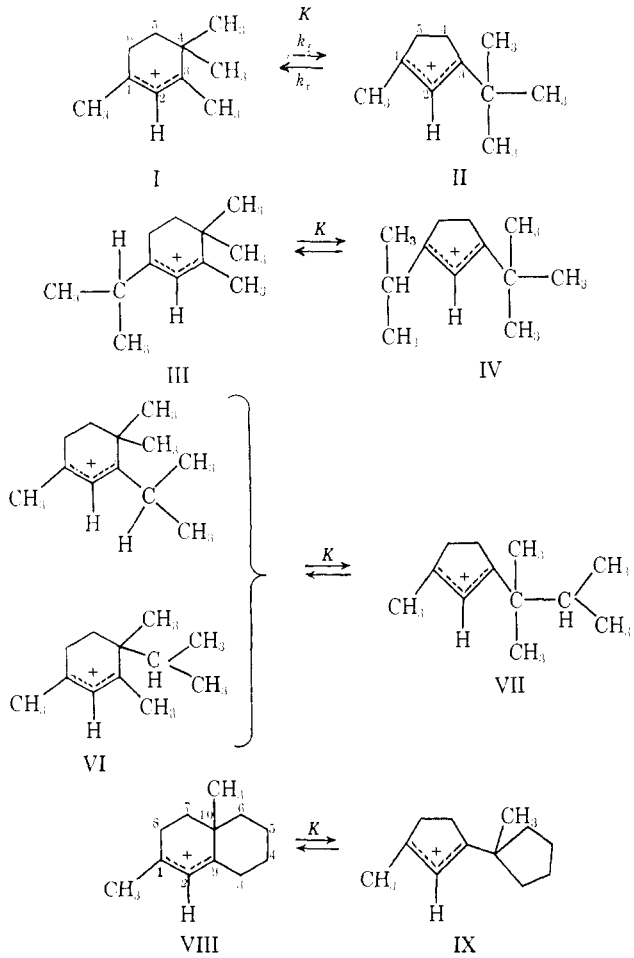
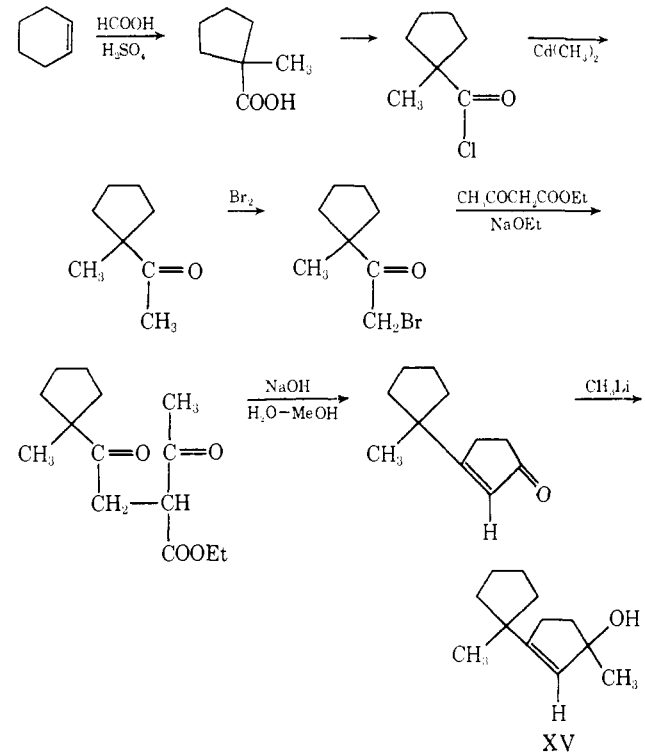
Abstract: Cyclopentenyl and cyclohexenyl cations have been observed in equilibrium with one another. The kinetics of the approach to equilibrium and the equilibrium constants have been measured in eleven different acid solvents for four series of these ions. An attempt is made to rationalize the marked stability of cyclopentenyl cations compared to the cyclohexenyl analogs.

Deno and coworkers[2a] first observed the rearrangement of cyclohexenyl to the corresponding cyclopentenyl cations. They have also shown[2b] that two mechanisms can operate in this reaction, one base catalyzed and another essentially independent of the strength of the base. The present study was initiated when it was observed that small new nmr peaks "grew" into the spectra of several *t*-butyl-substituted cyclopentenyl cations under investigation in another connection,[3] and subsequent study showed that these peaks were in fact due to cyclohexenyl cations in equilibrium with the cyclopentenyl cations. Previous studies in our laboratory have been concerned with a number of base-catalyzed carbonium ion rearrangements[3,4] where equilibrium and kinetic data could be measured over a relatively limited range of acid solvents. The reactions described in this paper were all observed to be of the base-insensitive variety and have therefore allowed the determination of equilibrium and kinetic data covering a wide variety of strong acid media.



Results and Discussion

Preparation of the Ions. The four series studied are shown below. All of the ions were prepared from the corresponding allylic alcohols which in turn were prepared by the addition of an alkyllithium to the appropriate ketone. In the case of ions I and II and VIII and IX, both ions were initially prepared and the equilibria approached from both directions. While this work was underway, the preparation of ions I and II was reported by Deno and Lastomirsky,[2b] who also measured the kinetics of II → I but who did not take into account the equilibrium nature of the reaction.



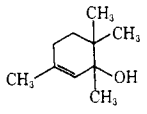
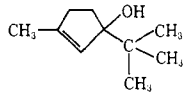
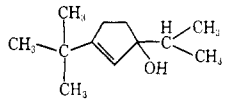
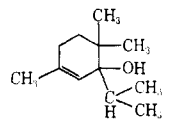
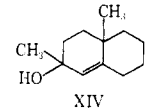
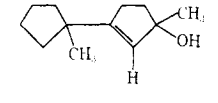
(1) Presented at the Conference on Carbonium Ions, Cleveland, Ohio, Oct 23–25, 1968.

(2) (a) N. C. Deno and J. J. Houser, *J. Am. Chem. Soc.*, 86, 1741 (1964); (b) N. C. Deno and R. R. Lastomirsky, *ibid.*, 90, 4085 (1968).

(3) T. S. Sorenson, *ibid.*, 89, 3782 (1967).

(4) T. S. Sorensen, *ibid.*, 89, 3794 (1967).

Table I

Starting compd	Ion formed	Nmr peaks of ion[a]
 X	I[b]	2.52, 1 H, C_2-H; 6.73, 2 H, partly resolved triplet, C_6-H's; 7.18, 6 H, C_1 and C_3 CH_3; 8.00, 2 H, (t), J = 6.3 cps, C_5-H's; 8.63, 6 H, C_4 CH_3
	II[b]	2.29, 1 H, C_2-H; 6.43, 2 H q, J = 2.5 cps, C_4-H's; 6.45, 2 H, C_5-H's; 6.99, 3 H (t), J = 2.5 cps, C_1 CH_3; 8.57, 9 H, C_3 t-butyl
 XII	IV ↓	2.26, 1 H, C_2-H; 6.43, 4 H (b), C_4 and C_5 H's; 8.56, 6 H (d), J = 6.6 cps, C_1 isopropyl CH_3; 8.54, 9 H, C_3 t-butyl; isopropyl CH proton *ca.* 6.3–6.7
	III	2.52, 1 H, C_2-H; 7.15 (b), C_3 CH_3; 7.99 (t), J = 6 cps, C_5-H's; rest are hidden
 XIII	V ↓	2.42, 1 H, C_2-H; 6.78, 2 H (t), J = 6 cps, C_6-H's; 7.11, 3 H, C_1 CH_3; 8.01, 2 H (t), J = 6 cps, C_5-H's; 8.64, 6 H (d), J = 6.6 cps, C_3 isopropyl CH_3; 8.59, 6 H, C_4 CH_3, isopropyl CH expected 6–7
	VI ↓	2.49, 1 H, C_2-H; 9.07 (d), J = 6.6 cps, C_4 isopropyl CH_3, rest are hidden by V
	VII	2.29, 1 H, C_2-H; 6.45, 4 H, composed of a quartet, J = 3 cps and a singlet (2 H), C_4- and C_5-H's; 6.98, 3 H (t), J = 3 cps, C_1 CH_3; 7.63–8.03, 1 H (m), C_3 isopropyl CH; 8.66, 6 H, C_3 CH_3; 9.09, 6 H (d), J = 6.6 cps, C_3 isopropyl CH_3
 XIV	VIII	2.55, 1 H, C_2-H; 6.74, 2 H (t), J = 6.5 cps, prob H's at C_8; 6.95, 2 H, v.b., prob H's at C_3; 7.19, 3 H, C_1 CH_3; 7.4–8.2, 8 H (m), C_4-, C_5-, C_6-, C_7-H's; 8.58, 3 H, C_{10} CH_3
	IX	2.32, 1 H, C_2-H; 6.41, 2 H, q, J = 3 cps, C_4-H's; 6.49, 2 H (b), C_5-H's; 7.04, 3 H (t), J = 3 cps, C_1 CH_3; 8.01, 8 H, broad multiplet, C_7-, C_8-, C_9-, C_{10}-H's; 8.56, 3 H, 3 H, C_6 CH_3

[a] 96% H_2SO_4 solvent, relative to internal tetramethylammonium cation = τ 6.90: N. C. Deno, N. Friedman, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2995 (1963). Spectra run at 100 mc, v.b. = very broad, b = broad, m = multiplet, d = doublet, t = triplet, q = quartet. Unless stated peaks are sharp singlets. [b] Also reported in ref 2b. The 100-mc spectrum has resolved some broad peaks present in the 60-mc spectrum.

Ions IV, V, and VII were identified on the basis of their nmr spectra and the exceedingly close analogy to the more completely investigated cases. Table I lists the precursers for each ion. The ketones used in the preparation of I–VI and VIII are known compounds. The alcohol XV was prepared as outlined below.

The carbonium ions were prepared either by extraction of the alcohol by the acid from a hexane solution of the former or by direct addition of the alcohol from a microlitre syringe to the cold, stirred acid. The nmr measurements were exceedingly easy in all cases since the 2 H of the cyclopentenyl and cyclohexenyl cations are well separated (*ca.* 0.2 ppm) and completely resolved. The kinetics for the first three series were conveniently carried out at 25.0°, the fourth at 0°. The temperature control at 25° is quite accurate since the samples spend about 95% of their time in a constant-temperature bath and 5% in transit (room at 25 ± 1°) or in the probe (controlled at 25 ± 1°). Excellent reproducibility could be obtained in this manner. Runs at 0 ± 1° were carried out entirely within the nmr probe and are consequently much less accurate on an absolute basis although runs done in the same day (unchanged settings) are quite reproducible.

Equilibrium values were obtained at a number of temperatures in two cases and the van't Hoff relationship was used to calculate the enthalpy difference between the two ions.

The nmr spectra of the ions are reported in Table I. The reactions themselves are exceedingly clean and, for example, in the case of I–II, starting from either pure ion, there are absolutely no nmr peaks observable other than those due to the two ions, even after several days at 25°. Indeed, the original observation of I from II was possible only because this is so. A similar situation applies to the other ions although they are not in general as stable on extended storage.

The results for I ⇄ II are presented in Table II, showing both the equilibrium constant K and the forward rate constant k_f. Runs using 97.0% H_2SO_4 and 5, 7.5, and 10% weight alcohol/volume acid solutions gave virtually identical results showing that the reaction is truly first order. The more limited results for III ⇄ IV and V, VI ⇄ VII, all isomeric ions and showing the rate enhancement for an isopropyl group at C_1 or C_3, are shown in Table III. The results for VIII ⇄ IX are given in Table IV. The percentages reported for sulfuric acids are the original concentrations. On reaction, $ROH + H_2SO_4 \rightarrow R^+ + H_2O + HSO_4^-$, 1 mole

Table II. Kinetics and Equilibria for I ⇄ II at 25.0°[a]

Acid solvent	K[b]	ΔF[c]	ΔH[c]	$k_f \times 10^4$, sec^{-1} [d]	E_a[c]
$ClSO_3H$	13.4	−1.56		3.1	
FSO_3H	13.8			3.1	
$ClSO_3H$ + 20% $Cl_2S_2O_7$	12.8			2.8	
CF_3SO_3H	14.0			2.8	
$H_2S_2O_7$ (20% fuming H_2SO_4)	11.0			2.0	
1:1 FSO_3H–SbF_5	12.4			1.6	
100.6% H_2SO_4	11.1			1.65	
97.0% H_2SO_4	10.3	−1.40	−1.45 ± 0.5	1.53	23
94.2% H_2SO_4	10.4			1.43	
89.4% H_2SO_4	11.0			1.64	
83.3% H_2SO_4	11.4			2.18	

[a] 10% w/v solutions. [b] Average of at least six measurements, probable error ±1. [c] In kilocalories per mole. [d] Probable error ±3%.

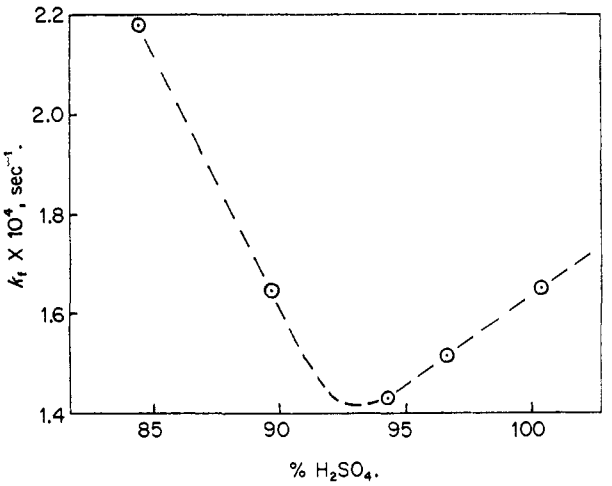


Figure 1. Plot of the forward rate constant for I → II as a function of the per cent sulfuric acid used as the solvent.

of "water" is formed and 1 mole of sulfuric acid lost. For 10% w/v solutions, this reduces the actual concentration of the acid solvent by 0.6–1% depending on the particular dilution of the acid to begin with. In order to find out whether the water generated on solvolysis of the alcohols was affecting the equilibria or the kinetics for the nonaqueous acid solvents, we used a medium consisting of the anhydride of chlorosulfonic acid ($Cl_2S_2O_5$) (sufficient to react with all of the water formed) and chlorosulfonic acid. A comparison of this medium with pure chlorosulfonic acid shows that they give almost identical results.

Table III. Kinetics and Equilibria for the Isopropyl-Substituted Ions at 25.0°

Ion	Solvent	K[b]	k_f, sec^{-1}
III ⇄ IV	$ClSO_3H$[a]	36	1.1×10^{-3} [c]
	97.0% H_2SO_4[a]	25	7×10^{-4}
V,VI ⇄ VII	$ClSO_3H$[d]	15[e]	6.1×10^{-4} [f]
	97.0% H_2SO_4[d]	17	3.8×10^{-4}

[a] 15% w/v solutions. [b] Probable error ±3. [c] Probable error ±40%. This value is an order of magnitude only since the measurements approach equilibrium from the "short" side. [d] 10% w/v solutions. [e] Defined as the ratio of cyclopentenyl to the combined cyclohexenyl total. The two cyclohexenyl ions appear to be present in about equal amounts after 24 hr and are presumably at their equilibrium values. Probable error ±3. [f] The kinetics are for combined **6** ⇄ **5**. On initial preparation, the ion VI is present to the extent of about 15% of the total. This ratio increases slightly and then both ions decrease as the cyclopentenyl ion is formed. Probable error ±5%.

Table IV. Kinetics and Equilibria for VII ⇄ IX at 0°

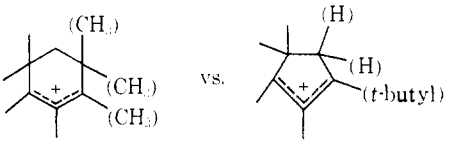
Acid solvent[a]	K[b]	ΔF[c]	ΔH[c]	$k_f \times 10^2$, sec^{-1} [d]	E_a[c]
$ClSO_3H$	0.082			6.6	22
FSO_3H	0.080	+1.52	+1.9 ± 0.5	6.8	
$ClSO_3H$ + 20% $Cl_2S_2O_5$	0.075			5.0	
CF_3SO_3H	0.083			4.4	
$H_2S_2O_7$ (20% fuming H_2SO_4)	0.075			3.1	
1:1 FSO_3H–SbF_5	0.080			3.8	
100.6% H_2SO_4	0.063			3.3	
97.0% H_2SO_4	0.059	+1.70	+1.5 ± 0.5	2.8	
94.2% H_2SO_4	0.065			3.1	
89.4% H_2SO_4	0.069			2.4[e]	
83.3% H_2SO_4				2.8	

[a] 10% w/v solutions. [b] Probable error ±0.005. [c] In kilocalories per mole. [d] Probable scatter with same machine settings ±5%, absolute accuracy for 0° about ±10%. [e] Solution supercooled.

Rates of Reaction. Two points are notable. (a) For the reactions listed in Table II and in Table IV, both of which occur at quite different rates, there is a consistent trend in "solvent effects." Thus, reactions are fastest in pure fluoro- and chlorosulfonic acid and slowest in 92–96% sulfuric acid (a factor of about 2). A similar observation has been made in still other rearrangements[5] and this trend can be regarded as a general phenomenum for the nonbase-catalyzed reactions of carbonium ions. The data for I ⇄ II at 25° are sufficiently accurate to show a curious minimum (*ca.* 93.5% sulfuric acid) in the rates for the aqueous sulfuric acid solutions. This is shown graphically in Figure 1. (b) Comparing the four series, there is a reasonably good correlation between the calculated heat of formation differences and the reaction rates. Thus, in III ⇄ IV, an isopropyl group at C_1 is expected to destabilize III (or IV) by about 0.6 kcal/mole compared to the methyl case.[3,4] In system VIII ⇄ IX, the ion IX contains a cyclopentyl group and, as is discussed later, this is expected to decrease the stability of the ion (compared to a strain-free case) by about 4 kcal/mole. The experimental energies of activation for I ⇄ II and VIII ⇄ IX are 23 and 22 kcal/mole, respectively (measured from the six-membered ion). On this simple basis, therefore, the large difference in rates observed for these two systems is mainly a consequence of the decreased stability of IX (relative to II), just as is predicted.

Equilibrium Position. The equilibrium constants are surprisingly sensitive to structural changes, particularly between I–II and VIII–IX, where a complete changeover occurs. The energy difference between a cyclohexenyl and a cyclopentenyl cation, where substituent effects are normalized, can be estimated as shown in Scheme I.

Scheme I. Relative Stability of Cyclohexenyl and Cyclopentenyl Cations



ΔF

ΔF kcal/mole

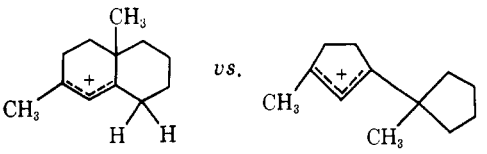
alkyl substitution at C_3	0[a]	1.8 (ref 4)
intrinsic to ring	3.2[b]	0
	3.2	1.8

[a] This assumes that there would be no difference between a methyl and hydrogen at C_4 in the cations. An alternative approach to the above scheme would be to count the number of "hyperconjugated hydrogens" present in both ions, *i.e.*, eight in cyclohexenyl *vs.* 7 is cyclopentenyl. This also favors cyclohexenyl but to what extent is unknown. [b] Adjusted to give the observed 1.4 difference for the above equilibrium.

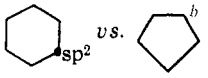
(5) Unpublished results from this laboratory. See also, D. M. Brouwer, *Rec. Trav. Chim.*, 88, 9 (1969), for a somewhat different series of acid systems.

The position of the equilibrium in VIII–IX can now be estimated (Scheme II).

Scheme II



VIII IX

	ΔF, kcal mole	ΔF
alkyl substitution[a]	0.3 (ref 4)	1.8 (ref 4)
intrinsic to ring	3.2	0
 vs. [b]	0	4
	3.5	5.8

difference = 2.3, observed 1.5-1.7

[a] The cyclohexenyl ring is approximated to an ethyl group, the 1-methylcyclopentyl to a *t*-butyl group. [b] Values taken from the American Petroleum Institute, Research Project 44, for ethylcyclopentane and methylcyclohexane. The extra strain imposed by the sp^2 carbon is difficult to estimate but would make the calculated and experimental values closer.

Of more importance to previous work on stable ion equilibria is the observation that these equilibrium constants remain relatively constant throughout the acid solvent range. Since ion formation can be unambiguously shown by freezing point depression for 100% sulfuric acid, the observation of similar spectra, k, and K values allows one to be reasonably confident that one is working with unencumbered ions in the other solvents also, *i.e.*, that counterion variations are unimportant. Of particular interest, "super" acid falls intermediate in the solvent range in both K and k. Arnett and Larsen[6] have shown that "super" acid gives large heats of formation when used to prepare carbonium ions. However, the absence of any differences in the equilibrium constant, with solvent changes, means that the differential solvation of the cations ($\Delta H_{solv\ 5} - \Delta H_{solv\ 6}$) is probably constant ($\Delta F \sim \Delta H$). This would be unlikely if there were large changes in the single values of ΔH_{solv} as one changed solvent. There are several other terms in ΔH_f, however, which may be particularly exothermic in "super" acid.

Using the van't Hoff relationship for both I–II and VIII–IX, we calculate that the enthalpy differences, within the large experimental errors, are identical with free energy differences so that the cyclohexenyl–cyclopentenyl cation differences do not arise because of entropy factors.

Although the measurements in this work are the most direct, there are several other lines of reasoning relating to the stability of these ions. For example, Deno and coworkers[7] have measured the hydrogen–deuterium exchange rates for cyclohexenyl and cyclopentenyl cations and have observed a rate ratio of *ca.* 145. This can be equated to 3 kcal/mole difference assuming only ground-state energy differences. These same workers[8] have also directly measured the pK_a of cyclopentenyl (−1.9) and cyclohexenyl (−3.2) cations and again, if the main factors affecting the equilibrium are to be found in the ions (questionable), a difference of about 1.8 kcal/mole can be derived. Finally, Roberts and Kiefer[9] have reported that cyclopentenyl bromide solvolyses faster than cyclohexenyl bromide by a factor of 1300. This is equivalent to 3.9 kcal/mole if one attributes the difference entirely to $\Delta F^{\ddagger}$ differences and that the latter difference is determined only by transition state energy differences.

(6) E. M. Arnett and J. W. Larsen, *J. Am. Chem. Soc.*, **90**, 792 (1968).
(7) See Table I, footnote *a*.
(8) N. C. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2998 (1963).

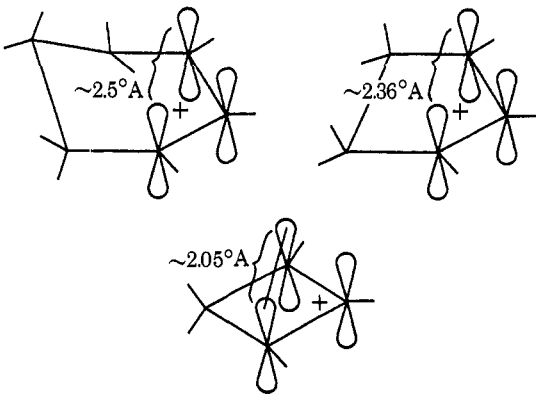


Figure 2.

Origin of the Difference. The apparent stability of a five-membered ion compared to the six might conceivably be explained by either steric effects including ring strain or by differences in the charge delocalization. The latter is much more likely since a cyclopentenyl cation (expected to be virtually planar) has eclipsed interactions at C_4 and C_5 and sp^2 bond angles substantially less than 120°, while a cyclohexenyl cation can stagger all substituents present at C_4, C_5, and C_6 and retain relatively normal hybridized bond angles (Figure 2). The enthalpy difference between ethylcyclopentene and methylcyclohexene is about 4.6 kcal/mole as compared to 6.5 for the saturated analogs.[10] Adding another sp^2 center might further reduce the difference but hardly reverse it.

The charge delocalization of cyclobutenyl cations has been postulated[11] to involve significant homocyclopropenium "character" (Figure 2), thereby placing charge at the 2 position. Similar reasoning[12] can be invoked to explain the stability differences under discussion. However, HMO calculations[13] give only 0.96 kcal/mole difference for these two ions, which hardly seems enough to overcome steric and ring strain differences. Delocalization could also occur in cyclopentenyl cations by invoking both methylene groups (C_4 and C_5) in a hyperconjugative delocalization giving a cyclic 6π-electron system as shown in Figure 3. This type of interaction in a single methylene "conductor" has been discussed

(9) E. F. Kiefer and J. D. Roberts, *ibid.*, **84**, 784 (1962).
(10) R. B. Turner and R. H. Garner, *ibid.*, **80**, 1424 (1958).
(11) T. J. Katz and E. H. Gold, *ibid.*, **86**, 1600 (1964).
(12) The 1,3-bond distance decreases, of course, as one decreases the ring size and it is implicit in a discussion by Deno that this might explain the stability differences of cyclopentenyl and cyclohexenyl cations: N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 129 (1964).
(13) Bond lengths used are (a) allyl 1.45 Å, (b) sp^2–sp^3 1.50 Å, and (c) sp^3–sp^3 1.54 Å. For cyclopentenyl, three angles of 110° and two of 105° are reasonable guesses in the absence of X-ray data. For cyclohexenyl, three 121° angles were used. The corresponding 1,3 distances are 2.36 and 2.50 Å, respectively: $\beta = S/S_0\beta_0$, using Slater $2p_z$ orbitals; $\beta = 20$ kcal.

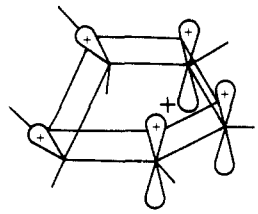
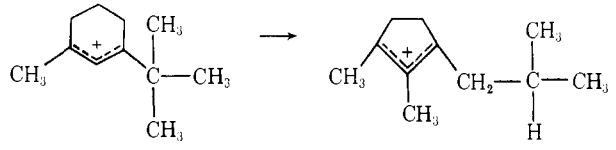


Figure 3.

by Hoffmann and Olafson.[14] The most obvious place to look for this kind of interaction would be in benzenonium ions where only a single methylene is involved. The stability of this ion relative to an open-chain pentadienylic cation is not known since pK_a measurements, hydrogen–deuterium exchange rates, etc., on these two types, must take into account the large resonance energy of benzene itself. However, rough calculations[15] seem to show that benzenonium ions are considerably more stable than one might calculate using open-chain models (about 12 kcal). The nmr chemical shift data consistently show the 2 H of cyclopentenyl cations to be at a lower field than in the corresponding cyclohexenyl cations and this of course fits both of the above hypotheses, either because of greater charge density at C_2 or because of an extra diamagnetic shielding in the cyclopentenyl cations (ring current effects). The mechanistic details of these reactions will be reported in a subsequent publication.

Recovery Experiments. In order to substantiate completely the interconversion of VIII and IX, the hydrocarbons derived from both of these ions (equilibrium conditions) were obtained by the usual recovery methods and shown to have identical glpc peaks.

Application to Other Systems. In principle, one could measure the equilibria for any two ions of n and $n + 1$ ring size. However, other factors must often be considered and, for example, the analog of II in a six-membered ring, the 1-methyl-3-*t*-butylcyclohexenyl cation (XVI), fairly rapidly rearranges to the 1,2-dimethyl-3-isobutylcyclopentenyl cation (XVII).[16] No evidence has been found for the formation of the seven-membered ion.



XVI XVII

Experimental Section

The acid solvents were purified by double distillation (FSO_3H, SbF_5, CF_3SO_3H) or used direct from commercial sources (fuming H_2SO_4, $ClSO_3H$). A mixture of $ClSO_3H$ and its anhydride was prepared and analyzed as described.[17] The actual preparation of the ions follows previous descriptions.[3] The kinetics were carried out directly in protected nmr tubes and all measurements were made at 100 mc using the acid solvent proton as a lock signal. The areas of the 2 H peaks could be determined directly from their height since the half-width at half-height and the shape of the curves were identical within experimental error. Sweep width, sweep time, and amplitude variations were made in order to show that these factors were unimportant. No absolute peak heights were used since the ion total at any time is constant. Concentration changes were expressed therefore as a ratio of the peak heights to the combined peak heights.

The nmr spectra of the neutral compounds (*ca.* 10% solutions in carbon tetrachloride, TMS internal, τ 10) were measured on a Varian Associate A-60; the spectra of the ions were measured on a Varian Associate HA-100 equipped with a variable-temperature probe. All infrared spectra were obtained on a Perkin-Elmer Model 337 spectrometer. Gas chromatography results were obtained on an Aerograph Model A-700, using a 6 ft × 0.25 in. column of 5% SE-30 on Chromosorb W. All melting points and boiling points are uncorrected. Recovery experiments were performed as described previously.[18]

Special care was taken so that all of the ketones used in the reactions were of analytical purity (glpc, nmr), since the alcohols prepared from these are difficult to characterize. For example, on glpc one invariably obtains a recording of only the dehydration products. The nmr spectra of the alcohols in some cases had to be obtained prior to distillation since distillation (besides removing a small quantity of high boiling byproducts) induces some dehydration. Satisfactory C, H analyses are therefore impossible in these cases. From a practical standpoint, the dehydration is unimportant since both the diene and the alcohol, in the following examples, produce the same carbonium ion. The actual concentration of diene present in the alcohol is important only in calculating the dilution factor appropriate for the sulfuric acid solutions.

3-Methylcyclopent-2-enone was prepared as described,[19] bp 67° (10 mm), from decomposition of the semicarbazide.

3-*t*-Butylcyclopent-2-enone was prepared as described,[20] bp 84.5–85.5° (8 mm) (lit.[20] bp 114–116° (23 mm)), except that the reaction was carried through in one step from 6,6-dimethylcarboethoxyheptane-2,5-dione. The dione, 6.0 g (0.026 mole), was dissolved in a solution consisting of 85 ml of methanol, 60 ml of water, and 5 g of NaOH and refluxed for 1 hr (bumping!). The solution was cooled, the Na_2CO_3 filtered, and an additional 10 g of NaOH was added to the solution. This solution was refluxed under a protective atmosphere for 56 hr and then most of the methanol was removed on a rotary evaporator. The residue was extracted with two 100-ml portions of ether and after drying the ether solution and removal of the ether there was obtained the crude title compound. The distillate was pure by glpc and showed the expected nmr spectrum.

3,6,6-Trimethylcyclohex-2-enone was prepared as described.[21] The crude fraction from steam distillation was carefully fractionated (18 in. spinning band column) to yield a fraction, bp 75.5–76° (8–9 mm) (lit.[21] bp 86–88° (15 mm), which was the pure ketone from glpc and nmr analysis.

10-Methyl-1(9)-octalone-2 was prepared as described,[22] bp 143.5° (15 mm) (lit.[22] bp 82–83° (0.7 mm)). The compound shows a single peak on glpc.

1-*t*-Butyl-3-methylcyclopent-2-en-1-ol (XI) and the following alcohols were prepared by the addition of the ketones (in ether or petrol) to an excess of the appropriate alkyllithium reagent at 0°. Since enolization accompanies addition several alkyllithium treatments were sometimes necessary.[3,4] The work-up and handling of these alcohols has been described.[3,4] In the above alcohol, two treatments of *t*-butyllithium were required. From 3.60 g (0.038 moles) of ketone in petrol there was obtained 2.0 g (35%) of the title alcohol, bp 32.5° (0.1 mm) (18-in. spinning band column). The alcohol solidifies at about 0° and dehydrates very easily. *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.44; H, 11.39. Nmr analysis showed τ 4.65 (1 H, quartet, J = 2 cps), 8.26 (3 H, t, J = 2 cps), 7.5–8.5 (*ca.* 4 H, complex multiplet), 9.13 (9 H).

1-Isopropyl-3-t-butylcyclopent-2-en-1-ol (XII), from 0.918 g of ketone in petrol (0.0067 mole), after three treatments with isopropyllithium, bp 47–50° (0.1 mm), yielded 0.35 g (35%). A large viscous residue remained after the distillation. The alcohol solidifies at about 0°. *Anal.* Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.17.

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Found: C, 78.32; H, 11.89. Nmr analysis showed τ 4.74 (1 H, t, J = 2 cps), 7.4–8.5 (*ca.* 5–6 H, m), 8.94 (9 H), 9.05, 9.11, 9.16, 9.22 (6 H, 2 doublets each with J = 6.6 cps).

1,3,6,6-Tetramethylcyclohex-2-en-1-ol (X), from 1.76 (0.013 mole) of ketone in ether, one treatment, bp 83–85° (10 mm), yielded *ca.* 90%. The alcohol is contaminated with *ca.* 20–30% of the diene (from nmr analysis). Surprisingly, distillation at lower pressures resulted in nearly complete dehydration. This preparation has been reported by Deno and Lastomirsky,[2] who also obtained a partially dehydrated product.

1-Isopropyl-3,6,6-trimethylcyclohex-2-en-1-ol (XIII) was prepared from 0.901 g (0.0065 mole) of ketone in ether, one treatment, bp 38–40° (0.03 mm). The alcohol is 70–80% dehydrated (nmr analysis). Nmr analysis showed (on undistilled material) τ 4.78 (1 H, m), 8.32 (3 H, broad triplet), 9.06 (7.5 H), 8.97, 9.06, 9.09, 9.16 (4.5 H, two doublets each with J = 7.2 cps), 7.7–8.8 (*ca.* 6 H, m).

2,10-Dimethyl-1(9)-octalol-2 (XIV), from 1.66 g (0.010 mole) of ketone in ether, one treatment, bp 70–74° (0.3 mm), yielded 1.67 g (93%). The product is very viscous and is presumably a mixture of *cis* and *trans* isomers. *Anal.* Calcd for $C_{12}H_{20}O$: C, 79.93; H, 11.1. Found: C, 79.78; H, 10.79. Nmr analysis showed τ 4.84 (1 H, m), 7.5–9.1 (complex series of peaks), 8.81 (*ca.* 3 H), 8.90 (*ca.* 3 H).

1-Methylcyclopentanecarboxylic acid was prepared as described,[23] bp 116–118° (20 mm) (lit.[23] bp 119° (20 mm) (after fractionation through an 18-in. spinning band column). The acid chloride was prepared in 92% yield from 37 g of the acid and excess thionyl chloride, bp 57.5–58° (15 mm).

Methyl 1-Methylcyclopentyl Ketone. The standard methylcadmium procedure[24] was carried out on 92 g of the above acid chloride to yield, after fractionation through an 18-in. spinning band column, 49.5 g (62%) of the title ketone, bp 46.5° (9 mm). This compound has been previously prepared by other methods: (lit.[25] bp 51–52° (12 mm); nmr τ 7.95 (3 H), 7.8–8.8 (8 H), a complex series of peaks), 8.83 (3 H). A single peak was observed on glpc.

Bromomethyl 1-Methylcyclopentyl Ketone. The above ketone (25.0 g, 0.2 mole), in 300 ml of dry ether was cooled to 0° and 32 g (0.2 mole) of bromine was added dropwise to the stirred solution over a 1-hr period. The resulting solution was immediately poured into ice and the ether layer was washed twice with cold water. The ether layer was dried over anhydrous $CaCl_2$. Distillation (at 8 mm) of the residue left after removal of the ether, in a Vigreux column, gave three fractions: (1) *ca.* 4 g, bp 46–100° (mainly ketone); (2) bp 100–111.5° (mainly 107–110°), 20.7 g (50%); (3) bp 111.5–117°, *ca.* 3 g (some dibromo compound). The pot residue crystallizes and is probably the dibromo ketone (from nmr analysis). Nmr analysis of the title compound showed τ 6.01 (2 H), 7.6–8.5 (8 H), 8.73 (3 H). No ketone or dibromo peaks were observed in the spectrum.

1-(3-Carboethoxy-4-oxopentanoyl)-1-methylcyclopentane. An alcoholic solution, 20.5 g (0.10 mole), of the above bromo ketone in 100 ml of dry ethanol was added dropwise over a 1-hr period to a refluxing solution consisting of ethyl acetoacetate (13.0 g, 0.10 mole), dry ethanol (300 ml), and 2.3 g (0.10 mole) of sodium (prepared in the usual order). The solution was refluxed for a further 2.5 hr and then water added to dissolve the salts formed in the reaction. Most of the ethanol was stripped off on an evaporator and the residue extracted twice (total of 200 ml) with ether. The ether solution was washed with water and dried over anhydrous Na_2CO_3. Distillation of the residue at 8 mm pressure, using an 18-in. spinning band column, gave a forerun fraction, bp up to 150°, *ca.* 9 g; a fraction bp 150–153°, 14.6 g (57%), and *ca.* 3 g of residue. The nmr spectrum of fraction 2 is reasonably consistent with the title structure if one assumes some enol content. *Anal.* Calcd for $C_{14}H_{22}O_4$: C, 66.09; H, 8.73. Found: C, 66.49; H, 9.16.

3-(1-Methylcyclopentyl)cyclopent-2-enone. The above ester, 7.3 g (0.029 mole), was dissolved in 70 ml of methanol and this was then added to a solution of 5.5 g of NaOH in 50 ml of water. The resulting solution was refluxed for about 1 hr (bumping!), cooled, and the precipitated Na_2CO_3 filtered. A further 50 ml of water, 60 ml of methanol, and 12 g of NaOH were added and the solution was refluxed for 95 hr under an inert atmosphere. After cooling, most of the methanol was removed on a flash evaporator and the residue extracted twice with two 100-ml portions of ether. The ether solution was washed with water and dried over anhydrous K_2CO_3. Distillation of the residue gave a single fraction, 1.7 g (38%), bp 92–93° (0.5 mm). Glpc analysis showed a single peak. *Anal.* Calcd for $C_{11}H_{16}O$: C, 80.42; H, 9.83. Found: C, 80.59; H, 9.91. Nmr analysis showed τ 4.19 (1 H, t, J = 2 cps), 7.2–7.9 (4 H, A_2B_2 type system), 8.26 (8 H, broad), 8.79 (3 H).

1-Methyl-3-(1-methylcyclopentyl)cyclopent-2-en-1-ol (XV). From 0.843 g (0.00514 mole) of the above ketone in 5 ml of ether and 6 ml of 2 M methyllithium in ether, as in the preparation of XI, there was obtained the title alcohol: yield 0.706 g (76%); bp 68–70° (0.05 mm). *Anal.* Calcd for $C_{12}H_{20}O$: C, 79.93; H, 11.1. Found: C, 79.58; H, 11.76. Nmr analysis showed τ 4.73 (1 H, t, J = 2 cps), 7.3–8.6 (*ca.* 13 H, a complex series of peaks), 8.73 (3 H), 8.93 (3 H).

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