The Mechanism of a Cyclohexenyl–Cyclopentenyl Cation Rearrangement

T. S. Sorensen* and K. Ranganayakulu

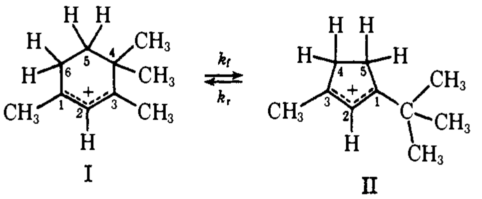
Contribution from the Department of Chemistry, University of Calgary, Calgary, Alberta, Canada. *Received April 20, 1970*

Abstract: The observable rearrangement of a cyclohexenyl to a cyclopentenyl cation involves an intermediate or intermediates which can break down in three different ways, two of these giving back the cyclohexenyl cation. The properties of this intermediate have been investigated under both direct addition conditions and steady-state kinetic conditions. The results in each case are in substantial agreement with one another. An example has been noted of a carbonium ion preparation in which the nature of the products formed is very dependent on the temperature at which the addition of the organic compound to the acid solvent is carried out.

The rearrangement of cyclohexenyl cations to cyclopentenyl cations was first observed by Deno and Houser.[1] The reaction has since proven to be very general. In some instances a measurable equilibrium state is reached in which *both* cations can be directly observed and this has allowed the various thermodynamic parameters to be measured.[2] The present study is an attempt to delineate the details of the mechanism of one of these reactions.

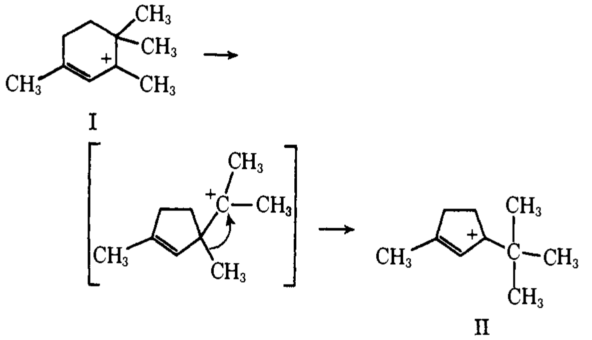
Results and Discussion

The system chosen for detailed study was the interconversion of 1,3,4,4-tetramethylcyclohexenyl cation (I) and the 1-*tert*-butyl-3-methylcyclopentenyl cation (II). The kinetics and equilibria for I $\leftrightarrows$ II, in a variety of solvents, have previously been reported.[2] This system is ideal because the ions I and II are quantitatively discernible in the nmr spectra of mixtures, having well-separated chemical-shift differences. The ions can also be prepared (*in situ*) quantitatively with no impurities or polymeric substances present. Finally, the kinetics for the interconversion of I and II occurs at a convenient rate at 25° and the equilibrium constant (K = II/I = 12) is of a magnitude that can be accurately measured.



I II

As will become clear later, at least one intermediate must be involved in this reaction. Deno and Lastomirsky,[3] although unaware at the time of the reversible nature of the reaction, proposed the mechanism shown in eq 1.



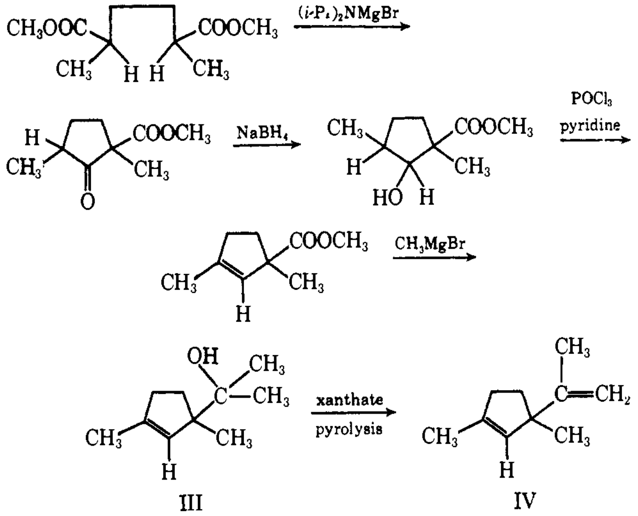
I II (1)

With this mechanism in mind, we first attempted to synthesize the intermediate ion. Subsequently, if indeed this ion was an intermediate, we hoped to measure the direct production of I and II from the intermediate, according to the modified mechanism

$$\mathrm{I} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \begin{bmatrix}\text{intermediate}\\ \text{ion}\end{bmatrix} \underset{k_2}{\overset{k_{-2}}{\rightleftarrows}} \mathrm{II}$$

The compound initially sought was III and the synthesis proceeded as shown in Scheme I.

Scheme I



III IV

The addition of III to fluorosulfonic acid (FSO_3H) at −80° led quantitatively to the protonated tetrahydrofuran compound V, characterized by its nmr spectrum.[4] The formation of this compound com-

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* To whom correspondence should be addressed.

[1] N. C. Deno and J. J. Houser, *J. Amer. Chem. Soc.*, **86**, 1741 (1964).

[2] T. S. Sorensen, *ibid.*, **91**, 6398 (1969).

[3] N. C. Deno and R. R. Lastomirsky, *ibid.*, **90**, 4085 (1968).

[4] The nmr spectrum can only be measured at low temperatures and as a consequence there is considerable viscosity broadening of the peaks. The following assignment is by no means definitive but we believe that the presence of the $>\overset{+}{O}H$ peak is very indicative. The known protonated THF compound VII also exhibits this feature.

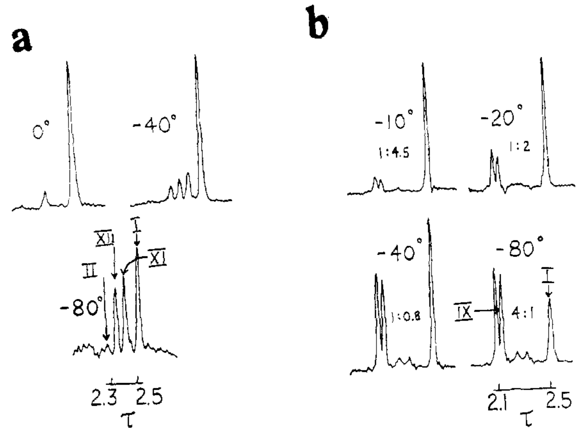
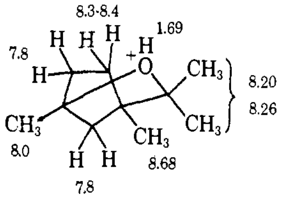
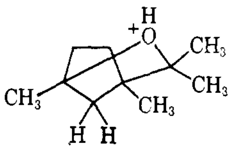


Figure 1. (a) Ion preparations from III and FSO_3H, prepared at 0, −40, and −80°. The nmr spectra were recorded at 0°. The arrows indicate the identity of the nmr peaks (the C-2 protons of each ion). (b) Ion preparations from III and FSO_3H, prepared at −10, −20, −40, and −80°. The nmr spectra were measured at −30°. The arrows indicate the identity of the nmr peaks (the C-2 protons of each ion). The relative peak areas are quoted in each case.

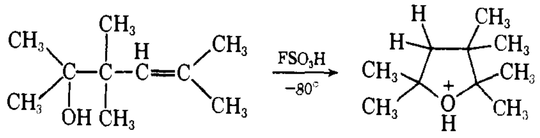


V



V

pletely parallels a similar finding[5] in the protonation of 2-hydroxy-2,3,3,5-tetramethylhex-4-ene (VI) by FSO_3H at −80°, whereby the protonated tetrahydrofuran compound VII is quantitatively formed.



VI VII

The diene IV, however, on addition to FSO_3H at −80° or to (5:1:6) FSO_3H-SbF_5-SO_2F_2 at −120° led to a mixture of I and II. The situation is complicated however since the alcohol III *does* result in a mixture of I and II when added to sulfuric acid at 0–10° or to FSO_3H *at a temperature of 0° or higher.* The ratio of I/II obtained from the alcohol protonation is quite different from that obtained from protonation of the diene. The ratios for each compound are similar however in the various solvents used for the protonation. These results are shown in Table I. All measurements were made in triplicate and the initial ratio of I/II was measured at a temperature where the subsequent equilibration reaction of these ions is negligible.

Table I. Initial Ratios of I/II

Compd	Solvent	Temp of prep, °C	Initial ratio[a] of I/II
III	FSO_3H	0	9
	96% H_2SO_4	−10	11
	96% D_2SO_4	0	12
	101% D_2SO_4	−5	11
	100% D_2SO_4	0	11
		Av =	11
IV	FSO_3H	−80	6
		−10	5.5
	FSO_3D	−80	6
	4:1 FSO_3H-SbF_5	−80	4.5
	CF_3SO_3H	−10	6
	96% H_2SO_4	−10	5.5
	96% D_2SO_4	0	6.5
	101% D_2SO_4	−5	5
	(1:5:6) SbF_5-FSO_3H-SO_2F_2	−120	6.5
		Av =	5.5

[a] Errors are estimated as ±10%.

The protonation of the diene IV might reasonably be expected to yield the intermediate ion discussed in the introductory statement. In FSO_3H-SbF_5-SO_2F_2 solvent at −120° the nmr peaks are considerably viscosity broadened, but at this temperature there is no nmr spectral evidence for the observable existence of this ion. We can be reasonably sure therefore that this intermediate ion, if formed, has a half-life of <10 min at −120°.

It might be supposed, in view of the results obtained at −80° in FSO_3H solvent, that the protonation of the alcohol III in FSO_3H at 0° leads to I and II (Table I) through the intermediacy of the protonated tetrahydrofuran compound (V). This is probably not the case however, for although the protonated tetrahydrofuran is unstable at temperatures above −80°, the products of this reaction are not simply the ions I and II. The actual reaction sequence which V undergoes, along with the rates of these reactions, is shown in Scheme II.[6]

At −80°, the reaction of III and FSO_3H leads to V which at −20° has rearranged to a mixture of ions I and IX. At 0°, the reaction of III and FSO_3H leads only to I and II (no IX or its rearrangement products). The transition range occurs starting at about −10°, where one observes products which can only have come from *both* pathways. The nmr spectral region associated with these processes is shown in Figure 1 for ion preparations at −10, −20, −40, and −80°, all measured at −30°, and for preparations at 0, −40, and −80°, all measured at 0°, after being kept at this temperature for 30 min.

The reaction sequence undergone by V is an excellent example of the observable cascade-type processes which often occur in these carbonium ion rearrangements. For example, some of the ion II is formed by the tor-

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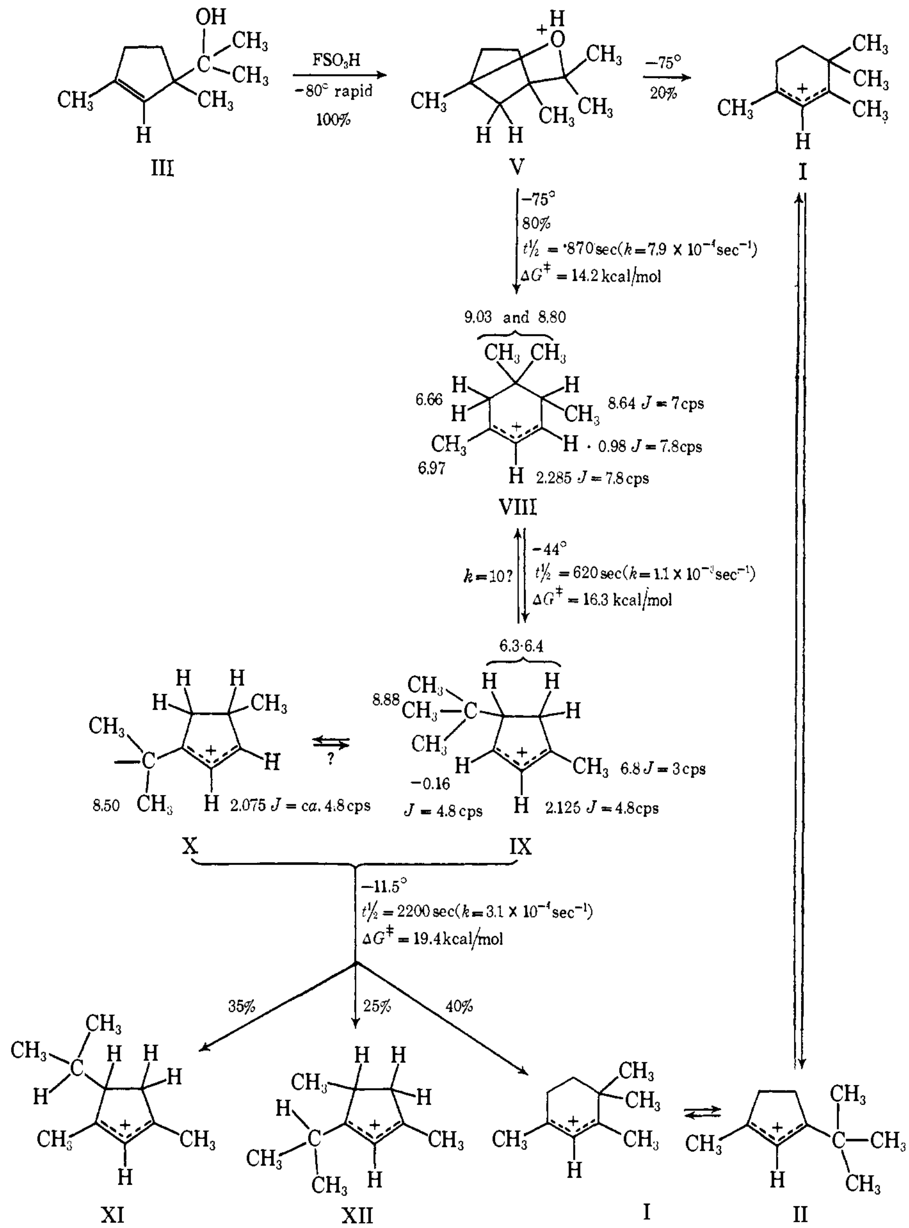
(5) T. S. Sorensen and K. Ranganayakulu, *Tetrahedron Lett.*, 659 (1970).

(6) Ions XI and XII are known compounds[7] and the identity of these ions has been established by direct comparison of their nmr spectra. Ions VIII and IX have not been reported; however in both cases the nmr spectra and chemical properties are uniquely satisfied by the assigned structures. The structure of X is less secure since this ion only appears as a transient species in small amounts. It is not known whether IX rearranges to XI, XII, and I by way of X or whether this compound represents a dead end path. There is also some indication that VIII and IX reach equilibrium concentrations with K = IX/VIII ~ 10. Too many compounds are present to be very certain of this result.

(7) T. S. Sorensen, *J. Amer. Chem. Soc.*, 89, 3782 (1967).

Scheme II



tuous path from V, in which an observable 6 → 5 → 6 → 5 transformation has occurred (the numbers referring to the ring size of the ions).

One has no real guarantee that the sulfuric acid reactions of the alcohol III (Table I) do not proceed through V, since the mechanism of the breakdown of this compound might be quite different in the weaker acid. One feels however, that since the temperature of the preparations (0 to −10°), and the ratio of I/II formed, are both similar to the FSO_3H acid preparation carried out at 0°, then the mechanism is very probably the same.

A change in the products of a reaction with a change in temperature is of course indicative of the occurrence of two processes, each having different activation energies. From the alcohol III and FSO_3H, one can envisage two competing processes (Scheme III). Process one completely dominates at −80°, process two at 25°.

Since one obtains different ratios of I and II, when starting from the intermediate generated from the alcohol or the diene (Table I), the question naturally arises as to which, *if either*, represents the behavior of the intermediate(s) occurring in the solution reaction of I $\rightleftarrows$ II. The intermediate(s) connecting I and II was depicted in the introduction in a purposely vague manner. Two reasonable, and experimentally distinguishable, possibilities exist. (1) A single unsymmetrical cation (A) (homoallylic cation) is involved, with positive charge density mainly on C-6 and C-3 but not much on C-1 (Scheme IV, Mechanism I).[8] (2) A symmetrical intermediate *or* transition state (B), corresponding to a cyclopropylcarbinyl cation, is involved with positive charge density on *both* C-1 and C-6. This category offers an unpleasant number of possible choices of detailed mechanism. For example, using *only* cyclopropylcarbinyl and/or homoallylic cations,[9] one might have these alternatives (submechanisms): (a) only one cyclopropylcarbinyl cation intermediate (B);[10] (b) two

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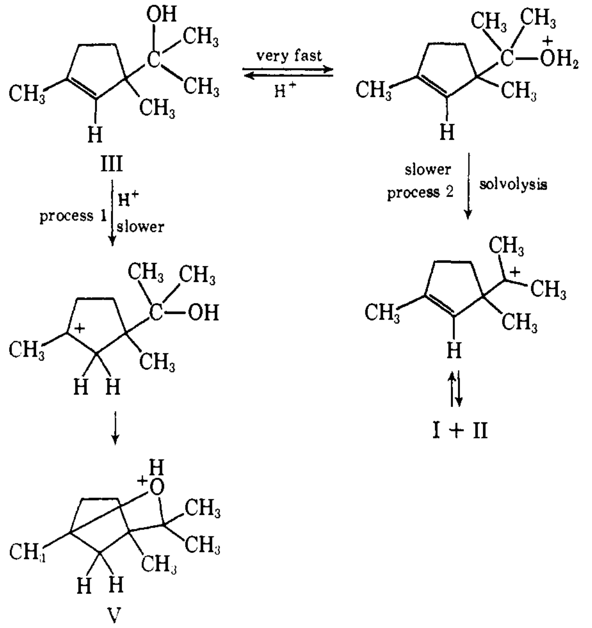
[8] This mechanism is in effect that proposed by Deno and Lastomirsky.[3]

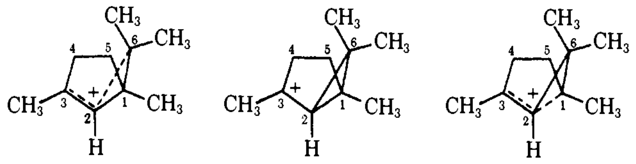
[9] C. D. Poulter and S. Winstein, *J. Amer. Chem. Soc.*, **91**, 3649, 3650 (1969).

[10] This type of cation is of course an observable species in some instances at least.[11]

Scheme III



equilibrating homoallylic cations (A and C), which would, however, have a "symmetrical" transition state resembling (a); (c) two homoallylic cations and a cyclopropylcarbinyl cation, all as intermediates;[12] (d) mixtures of the above. These detailed distinctions have been and are better investigated using simple systems. We shall hereafter use submechanism 2a for the sake of simplicity, with the expressed understanding that the arguments also apply to the other submechanisms listed, provided that the interconversion between the various intermediates is fast compared to their conversions into I and II.

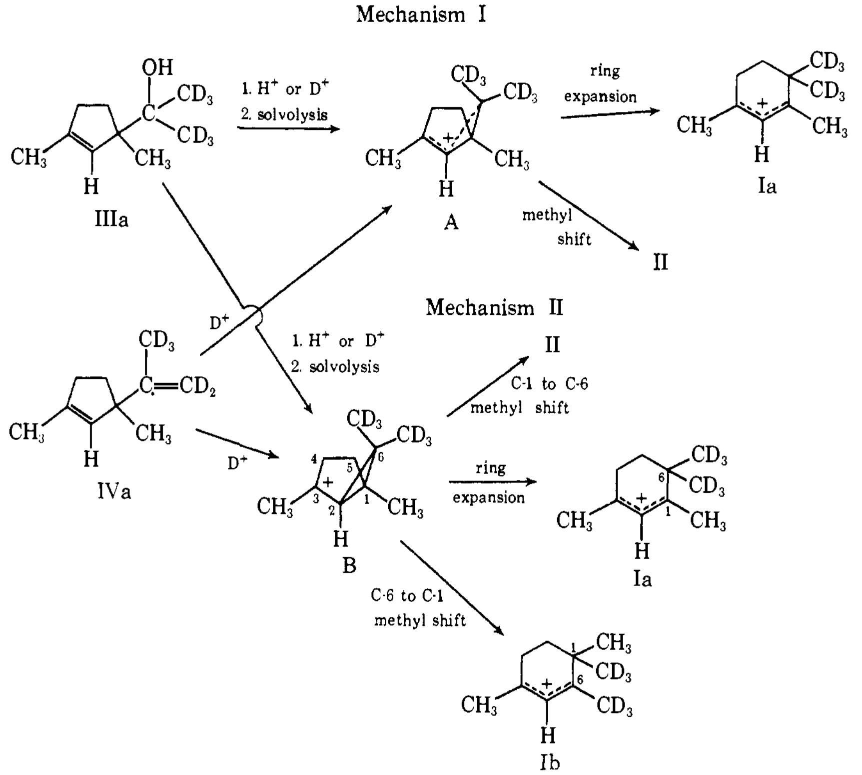

A B C

An experimental distinction between Mechanisms I and II can be made from a labeling experiment. Thus, the alcohol IIIa or the diene IVa would by Mechanism I yield the ion Ia (and II) while by Mechanism II, *both* Ia and Ib would be formed (and II). This is shown in Scheme IV. In fact, when the alcohol IIIa was added to 96, 100, or 101% D_2SO_4 at from 0 to −10° or to FSO_3D at 0 or −10°, or to the corresponding proton acids, both ions Ia and Ib were formed (and II). The amount of II formed in the reactions was identical with that found using the undeuterated alcohol (see Table I). The relative amounts of Ia and Ib formed are given in Table II. Starting from the diene IVa, the amounts of the two ions Ia and Ib formed are also given in Table II. The percentages of these ions reported in this table have been measured under conditions such that Ia, Ib, and II are not interconverting.

In the case of the alcohol IIIa therefore, at least 75% of the rearrangement is taking place *via* Mechanism II; in the case of the diene IVa, at least 60%. However, the formation of *some Ia* is entirely expected from Mechanism II so that it seems probable that Mechanism I is not operative in these rearrangements.

These experiments suffer from the problem that the behavior of the intermediate in I ⇄ II, which is presumably present at very small steady-state concentra-

Scheme IV



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(11) C. U. Pittman and G. A. Olah, *J. Amer. Chem. Soc.*, 87, 2999 (1965).

(12) This possibility seems the most reasonable to us in rationalizing the Wagner–Meerwein rearrangements.

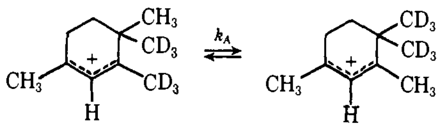
Table II. Initial Percentages of Ia and Ib

Compd	Solvent	Temp of prepn, °C	% Ia	% Ib
IIIa	96% D_2SO_4	0	18 ± 5[a]	82 ± 5[a]
	100% D_2SO_4	0	24	76
	101% D_2SO_4	−5	30	70
	FSO_3H	0	21	79
	FSO_3H	−10	19	81
			Av 22	78
IVa	FSO_3D	−80	35	65
	96% D_2SO_4	0	42	58
	101% D_2SO_4	0	41	59
			Av 39	61

[a] Similar error limits apply to the other percentages.

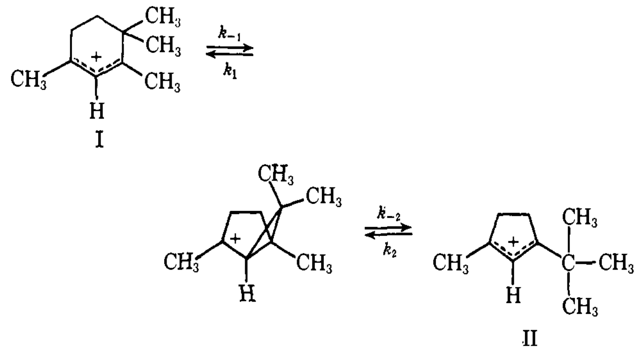
tions at equilibrium, might be completely different in structure from what we have "guessed" it to be. Alternatively, the gross structure of our proposed intermediate may be the same as the steady-state intermediate but the reactions undergone by this intermediate may be different when one forms it in macroscopic amounts in the strong acid, with the typical violent reaction characteristic of this process. We have therefore carried out three separate kinetic measurements where steady-state conditions apply. (1) The rate of the equilibration of Ia and Ib can be measured. On the basis of Mechanism I, this equilibration should only occur through the intermediacy of II. (2) The H-D substitution rate (from solvent) for the C-1, C-3, and separately the C-4 methyl groups in I can be measured. Deuterium substitution into the methyl groups of C-4 in I should occur by Mechanism I again only through the intermediacy of II. (3) The H-D substitution rate (from solvent) of the *tert*-butyl group in II can be measured very accurately. From Mechanism I, this overall rate should be much slower than k_r since only one methyl group at a time in ion I would be in an exchangeable position (ion I forming from II with rate constant k_r).

The measured foward rate constant (k_A) for the reaction Ib ⇄ Ia is $1 \pm 0.2 \times 10^{-3}$ sec^{-1} at 25° in 101% D_2SO_4. This strength of acid is high enough to ensure that no H-D substitution (from solvent) of the methyl groups takes place. The measured equilibrium constant is 0.64 ± 0.05 (theory 0.5), indicating a small isotope effect favoring Ia.

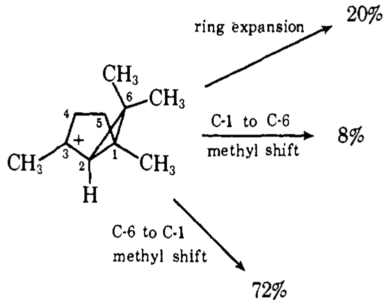


Ib Ia

The rate for the reaction I ⇄ II is much slower and this reaction does not take place to a very significant extent during the measurements needed to calculate the Ib ⇄ Ia (k_A) rate constant. In pure H_2SO_4, the I ⇄ II (k_f) rate constant has a value of 1.65×10^{-4} sec^{-1} at 25°.[2] The rate of equilibration of Ia and Ib takes place therefore at a rate about six times that for I ⇄ II. This is completely inconsistent with Mechanism I but quite plausible using Mechanism II. One can be somewhat more quantitative in comparing these two rates. Using Mechanism II, one has the following, where k_f (the overall measured rate constant for the forward reaction) $= k_1k_{-2}/(k_{-1} + k_{-2})$ and $k_r = k_2k_{-1}/(k_{-1} + k_{-2})$ using the steady-state approximation d[intermed]/dt = 0.

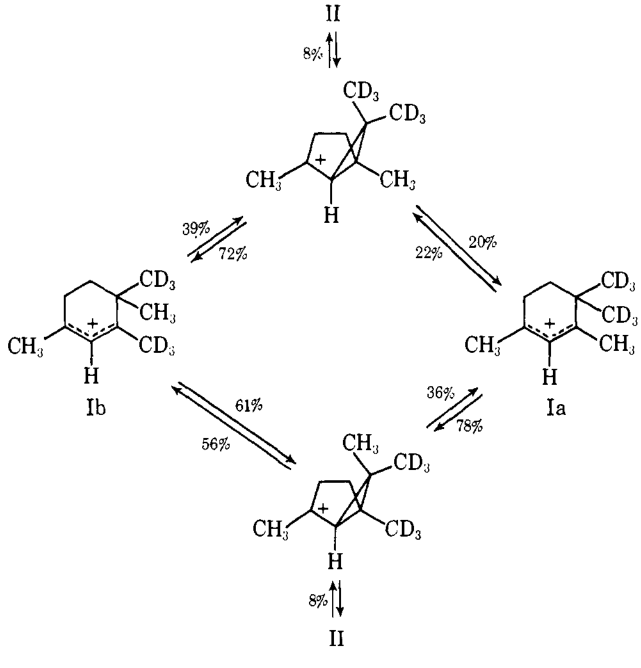


The equilibration of Ia and Ib gives a rate constant (k_A) which is not simply related to any of the above rate constants. However, one can show that the measured value of k_A is completely consistent with data obtained from the previously described direct addition experiments, using the data obtained from the alcohol III, but not that obtained from the diene IV. Briefly, these are $k_{-1}/k_{-2} = 12$ (Table I) and the percentage breakdown of the intermediate as follows (Tables I and II).



The interconversion of Ia and Ib by Mechanism II involves the following sequence (Scheme V). The percentage figures are based on the above breakdown with the appropriate statistical factors which occur with the isotopic labeling.

Scheme V



Each reaction of Ib to give the intermediate (k_1 related) is only about 30-40% efficient in leading to Ia. The calculated value of k_1 is 2.1×10^{-3} sec^{-1} at 25° (using k_f data for pure H_2SO_4[2]). The value expected for k_A would be about 0.7×10^{-3} sec^{-1}, in reasonable agreement with that measured for k_A.[13]

Scheme VI

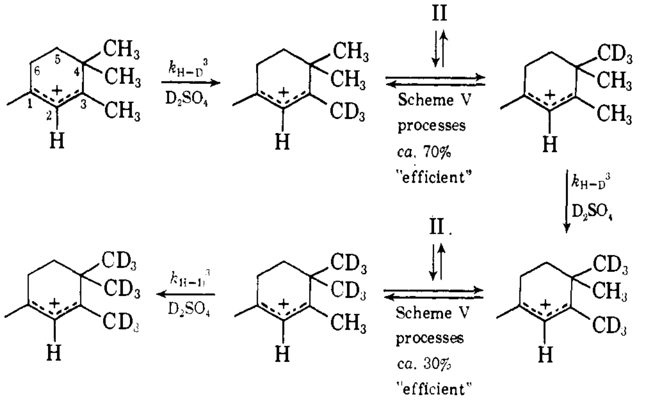


Table III. Kinetics of C-1 and C-3 Methyl Substitution in I

% D_2SO_4	$k_{H-D}^3 \times 10^3$ sec^{-1} at 25° [a,b]
95.8	0.7
93.1	1.6
88.2	8.7[c]
84.7	16[c]

[a] The chemical shifts of the C-1 and C-3 methyl groups in I are superimposed in the nmr spectrum and the rate is actually that for the H-D substitution of both groups. [b] These data are of necessity rather crude and approximate. This reaction is of course a stepwise process and quite possibly subject to an isotope effect once one or two D atoms have been substituted into the CH_3 group. [c] Extrapolated values.

Table IV. Kinetics of Deuterium Substitution into the C-4 Methyl Groups in I

% D_2SO_4	$k_{H-D}^4 \times 10^3$ sec^{-1} at 25°
84.7	1.0 ± 0.2
88.2	0.8 ± 0.1
93.1	0.5 ± 0.1
95.8	0.3 ± 0.05
% D_2SO_4	**$k_f \times 10^4$ sec^{-1} at 25°**
84.7	2.0
88.2	1.35

One can also use the data from the direct addition experiments to show that the rate of the H-D exchange from solvent to the methyl groups at C-4 in ion I is internally self-consistent. The overall reaction has the following form (Scheme VI). The only method of simplifying this sequence is to make k_{H-D}^3 (the rate constant for the base-catalyzed H-D substitution from solvent into the C-3 methyl group in I) $\gg k_1$. The value of k_{H-D}^3 can be experimentally measured in 96 and 92% D_2SO_4 and extrapolated values for it can be found for 88 and 84% D_2SO_4, using $\log k_{H-D}^3 \propto H_0$.[14] These data are given in Table III. The values agree well with similar data for other cyclohexenyl cations.[15] In Table IV, we list the rate constant, k_{H-D}^4, associated with the disappearance of the C-4 methyl proton nmr signal using four different deuterated acid solvents. The reactions, surprisingly, follow a first-order kinetic process reasonably well, to at least 75% completion. Only the results in 84% D_2SO_4 and marginally, those in 88% D_2SO_4, satisfy the requirement that $k_{H-D}^3 \gg k_1$. Simultaneous with the measurement of the C-4 methyl H-D substitution, one can measure the overall rate of I $\rightleftarrows$ II, using the C-2 proton resonance signal of each ion for the measurement. The slow formation of II also results in the loss of the C-4 methyl peak of I and we have corrected for this in the data given in Table IV.

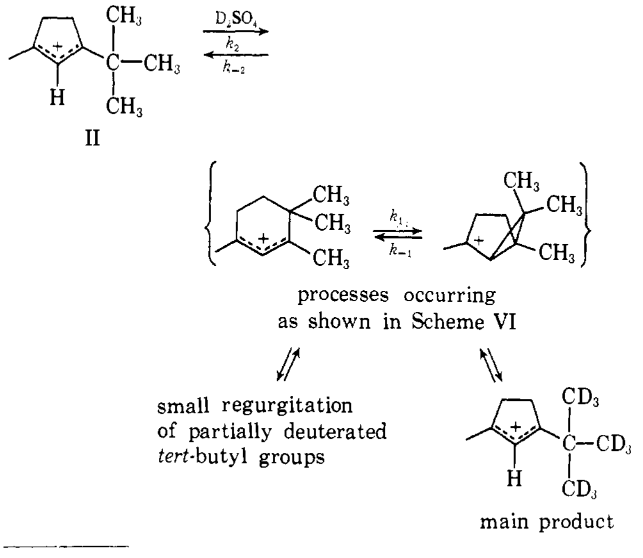
An exact comparison of k_{H-D}^4 and k_1 (calcd) is virtually impossible. The reactions in the Scheme V processes, which lead to CH_3 and CD_3 interchange, are inefficient in terms of each k_1 process and one would expect to find the k_1 (calcd) to be considerably larger than k_{H-D}^4.[16] For 84% acid, k_1 (calcd) = 2.7×10^{-3}, whereas $k_{H-D}^4 = 1.0 \pm 0.2 \times 10^{-3}$ sec^{-1} (25°). Using mechanism I, the predicted value of k_{H-D}^4 would be $< 1 \times 10^{-5}$ sec^{-1} (*i.e.*, $< k_r$).

Table V. Kinetics of the *tert*-Butyl Deuterium Substitution in II

% D_2SO_4	$k_{H-D}^{tert\text{-butyl}} \times 10^5$ sec^{-1} at 25° [a]	k_2 (calcd)
84.7	1.82	2.08
88.2	1.50	1.56
93.1	1.22	1.35
95.8	0.94	1.45

[a] Within ±3%.

Scheme VII



Finally, the rate of the H-D substitution (from solvent) into the *tert*-butyl group in II has been measured. The measured first-order rate constant, $k_{H-D}^{tert\text{-butyl}}$, associated with this reaction is given in Table V, for four different acid solvents. This reaction can be represented as follows (Scheme VII). The H-D sub-

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(13) An exact solution of the kinetic equations might give a slightly different comparison, but the experimental data are too inaccurate to make this exercise meaningful. The differentiation of Mechanisms I and II, is, however, clearcut.

(14) N. C. Deno, J. Bollinger, N. Friedman, K. Hafer, J. D. Hodge, and J. J. Houser, *J. Amer. Chem. Soc.*, 85, 2998 (1963).

(15) N. C. Deno, N. Friedman, J. D. Hodge, and J. J. Houser, *ibid.*, 85, 2995 (1963).

(16) The reaction given by k_{H-D}^4 involves two separate k_1 processes to begin with.

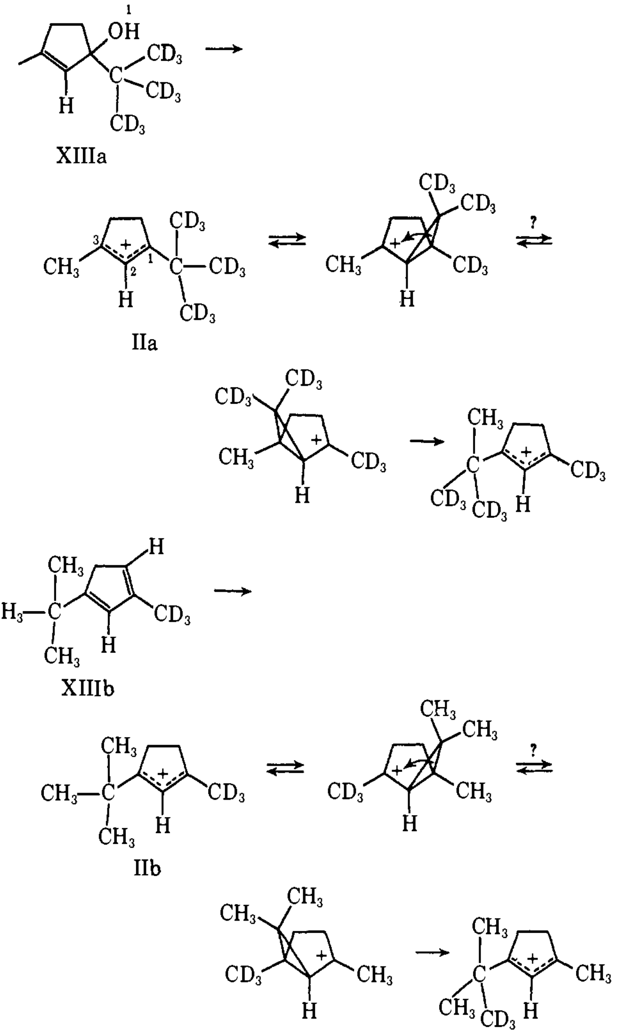
stitution rate is first order to at least 85% deuterium substitution and in the lower per cent acids is independent of the acid strength of the solvent.[17] From previous data on k_r,[2] we have calculated k_2 (using $k_{-1}/k_{-2} = 12$) and these values are also reported in Table V. It can be seen that the values of $k_{H-D}{}^{tert\text{-butyl}}$ are only slightly smaller than k_2, using the data for 84, 88, and 92% D_2SO_4. In these acids, the base-catalyzed H-D substitution from solvent into the C-3 methyl group in ion I (see Table III) is fast compared to k_2. The close identity of k_2 and $k_{H-D}{}^{tert\text{-butyl}}$ is by now expected since we know that the methyl group rearrangements in I are rapid and occur at a much faster rate than the I → II reaction (the C-3 methyl H-D base-catalyzed substitution in I is of course even faster). Each reaction of II therefore, results predominantly in the formation of a fully deuterated *tert*-butyl product. This is further confirmed by the nmr spectral results themselves, in which the decreasing *tert*-butyl peak remains relatively sharp, indicating the absence of large amounts of mixed CH_3-CD_3 *tert*-butyl groups

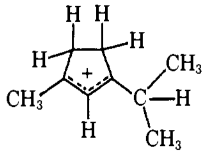
Precautionary Experiments

If the intermediate in all these reactions is indeed a cyclopropylcarbinyl cation, one might expect the possibility of a degenerate cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement. This rearrangement[18] has been reported for the related (to II) 1-*tert*-butyl-1,3,3-trimethylallyl cation system[5,9] and appears to occur in a number of other observable cyclohexenyl cation rearrangements.[19] This rearrangement would, if rapid, seriously affect all of the calculations involved in the kinetic experiments. This is shown in Scheme VIII. We therefore prepared the specifically deuterium-labeled compounds XIIIa and b, which in FSO_3H or (1:1) FSO_3H-SbF_5,[20] yield initially the ions IIa and IIb. After 48 hr at 25°, there is no detectable interchange of the C-3 and *tert*-butyl methyl groups in FSO_3H-SbF_5 solvent, as would show up in IIa by the appearance of protons in the *tert*-butyl nmr region or in IIb by the appearance of protons in the C-3 methyl nmr region.[21] Only a very small change was noted using FSO_3H solvent and this may be due to indirect D-H exchange with solvent (*via* I). A degenerate cyclopropylcarbinyl rearrangement would be expected to be independent of the strength of the acid solvent so that we are quite confident that this reaction is not occurring in sulfuric acid at any appreciable rate.

The H-D substitution (from solvent) of the *tert*-butyl group in II is an indirect process and has been shown in the Results to involve the intermediacy of I. This was further substantiated by showing that the H-D substitution (from solvent) into the isopropyl methyl groups of 1-isopropyl-3-methylcyclopentenyl cation (XIV) is very slow ($t_{1/2} > 1$ week at 25° in 93% D_2SO_4), This rate is in agreement with that expected on the basis of a much slower cyclopentenyl ⇆ cyclohexenyl cation reaction.[3] If, for example, some direct process were involved in the H-D substitution of the *tert*-butyl group in II, then one might have expected of find a similar rate for the substitution process in the isopropyl analog.

Scheme VIII





XIV

Several points relating to the proposed mechanism bear further discussion. (1) The intermediate cation prepared *via* the alcohol III appears to behave much more like the steady-state intermediate in the kinetic process than does that from the diene IV. Using IV, one obtains *both* more I (relative to II) and more ring expansion product (relative to the C-1 to C-6 methyl shift). The greater randomness in the latter case may simply mean that the intermediate(s) involved is "hotter"[22] than that produced from the alcohol. The fit of the experimental kinetic (k_f) data to theory (k_l) is actually somewhat better if one assumes a slightly

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(17) The rate of I ⇄ II is slightly solvent dependent[2] and there is a parallel between this and a slight solvent dependence noted for the H-D substitution rate.

(18) No conclusive evidence exists to show that the six methyl scrambling observed in the 1-*tert*-butyl-1,3,3-trimethylallyl cation system involves this rearrangement, but this mechanism seems the most likely.

(19) Unpublished results from this laboratory.

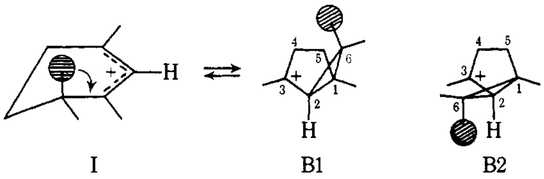
(20) Only in these very strong acids can one be fairly certain that no H-D exchange takes place between the ions and the solvent.

(21) A small amount of *tert*-butyl cation was however produced in FSO_3H-SbF_5 solvent.

(22) For example, see K. L. Servis and J. D. Roberts, *J. Amer. Chem. Soc.*, **86**, 3773 (1964), and references therein.

larger value for k_{-1}/k_{-2} than even that obtained from the direct addition experiments with the alcohol (III).

(2) The two methyl groups at C-6 in the intermediate have been assumed to migrate at the same rate. One has no easy way of measuring a possible hidden reaction which might occur if there was a preference for the same methyl group that migrated in I → intermediate B1 to be involved in the reverse step. The two methyl groups at C-6 in the intermediate B1 can be interchanged in two ways: (a) direct rotation about the C-1 to C-6 bond or (b) a conformational change leading to the ion B2. Both these processes are perhaps better accommodated using homoallylic cation structures, *i.e.*, A and C discussed previously, A for the former process and C for the latter. If the interchange of the two methyl groups is rapid, preferential migration of one of the groups, even if it occurred, would be unimportant in mechanistic terms. We have also assumed in our data treatment that the rate of migration of CH_3 and CD_3 groups is the same. Recent work by Schubert and Le Fevre[23] would indicate that this assumption is not likely to be exactly true. However, if the value for k_{CH_3}/k_{CD_3} involved in this study is similar to that reported by these authors, then the net effects on our various calculations is small.



(3) The 2-bicyclo[3.1.0]hexyl cation system proposed in this work as an intermediate or transition state in the observable ion rearrangements has also been investigated as a solvolysis intermediate.[24] This ion has previously been proposed as an intermediate in an observable rearrangement involving a cyclopentenyl cation system[25] and in the observable rearrangement of cyclohexenyl-type cations derived from longifolene.[26]

(4) The mechanism shown in this work is probably general for most of the reported cyclohexenyl–cyclopentenyl cation rearrangements. However, the rearrangement of ion VIII to ion IX, shown earlier in Scheme II, probably involves a different mechanism and other examples like this one are also known.[19]

Experimental Section

The purification of the acid solvents and the general addition procedures have been reported.[2] The method of analysis for ions I and II has also been reported.[2] All of the carbonium ion nmr spectral measurement (*ca.* 10% w/v solutions) were carried out at 100 mcps using the acid-solvent peak as a lock signal. Chemical-shift positions reported are with reference to tetramethylammonium cation, τ 6.90.[15]

The nmr spectra of the neutral compounds (*ca.* 10% solutions in carbon tetrachloride, TMS internal, τ 10) were measured on a Varian A-60 or HA-100. 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 boiling points are uncorrected. All kinetic measurements were made in duplicate or triplicate.

Measurement of Ia,b Kinetics and Initial Ratio. The nmr spectrum of I shows a sharp peak at 8.63 for the two C-4 methyl groups and a slightly broader peak at 7.18 for both the C-1 and C-3 methyl groups. In mixtures of the compounds Ia and Ib, all of the area at 8.63 is due to the one methyl group of compound Ib. Compound Ia contains all protons in the methyl groups at C-1 and C-3, Ib only one methyl (proton) group at C-1. Subtracting the peak area of the C-4 nmr region from the area of the peak at 7.18 leaves a residual area at 7.18 due to the six protons of Ia. One-half of this area gives the amount of Ia, where the amount of Ib is given by the area of the peak at 8.63. Relative peak areas were determined by multiplying peak heights by half-height half-widths using an expanded scale (generally 250-cps sweep width). The data were treated for first-order reversible kinetics. All measurements were made with the sample continuously in the nmr probe at 25 ± 1°.

Measurement of H–D Substitution in I. Deuterated aqueous sulfuric acids were prepared by adding D_2O to pure D_2SO_4 and their composition determined by titration with standard alkali. About 0.5–1% (ω/v) of tetramethylammonium cation was added to the acids to serve as a standard peak height with which to compare the peaks undergoing deuterium substitution. Simple peak height measurements were used for the C-4 methyl groups since no appreciable broadening accompanies the deuterium substitution. Simple first-order kinetics were used. All measurements were made with the sample continuously in the nmr probe at 25 ± 1°. For the C-1 and C-3 methyl groups, the substitution is accompanied by a broadening of the peak and an area calculation *vs.* time was made by tracing and weighing the peaks. In all of the H–D substitution experiments no corrections have been needed for residual proton peaks in the ions, which one might expect (but do not occur), based on the total exchangeable protons in the ions and the total deuterium atoms in the solvent. For 10% ω/v carbonium ion concentrations there are about 4 deuterium atoms/l exchangeable proton. Quite obviously a large equilibrium isotope effect is operating, favoring C–D over C–H compared to O–D and O–H.

Measurement of H–D Substitution in II and XIV. This measurement was carried out as above using the tetramethylammonium cation internal standard for reference peak heights. The H–D substitution is not accompanied by broadening of the peak and a simple peak height measurement was used to calculate the area. Simple first-order kinetics were used. The samples were kept in a thermostat bath at 25.0°. The actual time taken for the measurements (probe and room 25 ± 1°) is small compared to the total elapsed time.

2,5-Dimethyl-2-carbomethoxycyclopentan-1-one. A solution of dimethyl 2,5-dimethyladipate (50 g, 0.25 mol) in 100 ml of ether was added dropwise to a solution of diisopropylamide magnesium bromide (0.33 mol, prepared by the addition of diisopropylamine to ethyl magnesium bromide) in 200 ml of ether at 0° with stirring.[27] The reaction mixture was allowed to warm up to 25° and was then stirred for 12 hr at this temperature. Finally, the contents were refluxed on a water bath for 2 hr, cooled, and poured into 250 g of ice-dilute H_2SO_4. The ether layer was separated and the aqueous layer extracted twice more (two 200-ml portions) with ether. The combined ether extracts were washed with water, 5% Na_2CO_3 solution, and again with water before being dried over anhydrous $MgSO_4$. Fractionation of the residue gave 30 g (70%) of pure title compound, bp 90–95° (8 mm). The glc trace shows the presence of the expected cis and trans isomers.[28] The nmr spectrum also agrees well with the reported values.[28] This preparative method is much superior to that reported by Meyer, *et al.*[28]

2,5-Dimethyl-2-carbomethoxycyclopentan-1-ol. A solution of sodium borohydride (3.31 g, 0.097 mol, in 30 ml of 0.2 *N* NaOH) was added dropwise to a stirred, ice-cold solution of the ketone (29.75 g, 0.175 mol in 100 ml of methanol). The reaction mixture was stirred a further 0.5 hr and then poured into 300 ml of water. The methanol–water mixture was extracted with ether (five 150-ml portions). The combined ether extracts were washed with water (three 50-ml portions) and dried over anhydrous $MgSO_4$. The glc trace (SE 30 column) showed three major peaks, one of which

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[23] W. M. Schubert and P. H. Le Fevre, *J. Amer. Chem. Soc.*, 91, 7746 (1969).

[24] (a) M. Hanack and W. Keberle, *Chem. Ber.*, 96, 2937 (1963); (b) M. Hanack and H. J. Schneider, *Tetrahedron*, 20, 1863 (1964); (c) K. B. Wiberg and R. Fenoglio, *Tetrahedron*, 19, L1273 (1963); (d) E. J. Corey and R. L. Dawson, *J. Amer. Chem. Soc.*, 88, 1782 (1963); (e) P. G. Gassman and F. V. Zalor, *ibid.*, 88, 2252 (1966); (f) P. R. Brook, R. M. Ellman, and A. S. Bloss, *Chem. Commun.*, 425 (1968).

[25] T. S. Sorensen, *J. Amer. Chem. Soc.*, 89, 3794 (1967).

[26] D. G. Farnum and G. Mehta, *Chem. Commun.*, 1643 (1968).

[27] A. Walther, W. Treibs, and K. Michaelis, *Chem. Ber.*, 89, 60 (1956).

[28] W. L. Meyer, A. P. Lobo, and E. T. Marquis, *J. Org. Chem.*, 30, 181 (1965).

has nearly the same retention time as one of the starting ketones. Four isomeric alcohols are possible from this reduction reaction. Since reduction of the ester group might occur under forcing conditions, no attempt was made to reduce further the amount of starting ketones in the product. The nmr spectrum is complex because of the presence of isomeric alcohols. The nmr spectrum also shows peaks due to the ketones.

1,3-Dimethyl-1-carbomethoxycyclopent-2-ene. The crude product from the above reaction (*ca.* 30 g) was dissolved in 150 ml of pyridine and cooled to 0°. Phosphorus oxychloride, 30 g, was then added dropwise to this solution and the resulting mixture allowed to stand at 25° for 12 hr. The solution was finally heated on a water bath for 0.5 hr. After cooling, the mixture was poured into 600 ml of ice–water and the aqueous solution extracted with ether (four 100-ml portions). The combined ether layers were washed with water, 5% HCl, and once more with water before being dried over anhydrous $MgSO_4$. The residue was fractionated using an 18-in. spinning band column to give pure title compound: 8 g (30%); bp 67–68° (12 mm); nmr peaks 4.79 (1 H), 6.40 (3 H), 7.5–8.2 (4 H), 8.29 (3 H), 8.765 (3 H). The compound gave a single peak on glc. *Anal.* Calcd for $C_9H_{14}O_2$: C, 70.13; H, 9.1. Found: C, 70.46; H, 9.63.

1-[2-(2-Hydroxypropane)]-1,3-dimethylcyclopent-2-ene (III). An ether solution of the previous ester (2.31 g, 0.015 mol in 10 ml of ether) was added with stirring to a solution of methylmagnesium iodide (0.035 mol in 100 ml of ether) at 0°. The reaction mixture was allowed to warm up to 25° and was left at this temperature for 24 hr. Finally, the solution was refluxed on a water bath for 6 hr. The contents were poured into 100 ml of ice-cold saturated NH_4Cl solution. The aqueous layer was extracted with ether (three 100-ml portions). The combined ether layers were washed with water and dried over anhydrous K_2CO_3. Fractionation of the residue gave the title compound: 2.1 g (90%); bp 78–80° (8 mm); nmr spectrum 4.80, poorly resolved multiplet (1 H), 7.68–8.14 and 8.37–8.69 (*ca.* 4–5 H), 8.27 (3 H), 8.88 and 8.90 (6 H), and 8.98 (3 H). The compound gave a single peak on glc. *Anal.* Calcd for $C_{10}H_{18}O$: C, 77.92; H, 11.69. Found: C, 77.43; H, 11.73.

1-[2-(2-Hydroxypropane-d_6]-1,3-dimethylcyclopent-2-ene (IIIa). This compound was prepared, as above, using CD_3MgI. The six protons in the nmr spectrum of the hydrogen analog at 8.88 and 8.90 were absent. The compound gave a single peak on glc.

1-[2-(2-Propenyl)]-1,3-dimethylcyclopen-2-ene (IV). A solution of the previous alcohol (1.15 g, 0.0075 mol in 25 ml of benzene) was added to a 50-ml round-bottomed flask fitted with a condenser, protected by a $CaCl_2$ tube. Potassium metal (0.5 g, 0.012 g-atom) was cut into small pieces and added to the benzene solution. The mixture was then refluxed for 18 hr during which time most of the potassium had reacted. The solution was decanted from the excess potassium metal and the metal washed several times with dry ether. The combined organic solutions were evaporated to dryness *in vacuo* and then dry ether (20 ml) and carbon disulfide (1.5 g) were added. The mixture was allowed to stand at 25° for 2 hr. Methyl iodide (2.0 g) was then added and the contents were allowed to stand at 25° overnight. Finally, the mixture was refluxed for 6 hr. The precipitated KI was filtered off and the solvent then removed *in vacuo* from the resulting filtrate. On heating, the residue decomposed to give 0.4 g of the pure title compound, bp 90–100° (670 mm). A further 0.3 g of this compound was obtained from the forerun using preparative glc, S.E. 30 column, operating at 140° with retention time 5 min 42 sec at 60 cc/min He flow rate: nmr spectrum 4.84, broad multiplet (1 H), 5.40, broad doublet (2 H), 7.5–8.2 (*ca.* 4 H), 8.30 (6 H), and 8.90 (3 H). The two methyl groups, superimposed at 8.30 in carbon tetrachloride solvent are well separated in benzene.

1-[2-(2-Propenyl-d_5)]-1,3-dimethylcyclopent-2-ene (IVa). This diene was prepared as above and showed the absence of nmr peaks at 5.40 and an area reduction of the peak at 8.30.

1-*tert*-Butyl-d_9-3-methylcyclopent-2-en-1-ol (XIIIa). This alcohol was prepared in an identical manner with that used for the preparation of the proton analog[2] employing *tert*-butyllithium-d_9.

2-Methyl-d_3-4-*tert*-butylcyclopentadiene + Isomer (XIIIb). A solution of 3-*tert*-butylcyclopent-2-enone (2) (0.83 g, 0.0060 mol in 10 ml of ether) was added dropwise at 0° to a stirred solution of methyl-d_3-magnesium iodide (from 1.37 g of CD_3I (0.0095 mol), 0.24 g of Mg, and 15 ml of ether) over a period of 20 min. After the usual work-up (NH_4Cl solution), the residue was distilled to give 0.470 g (56%) of colorless liquid bp *ca.* 25° (0.1 mm). The glc trace shows no peak due to the starting material, only one peak appearing at a shorter retention time. From the nmr and infrared spectra, the compound is not an alcohol but the corresponding dehydration product, a mixture of two isomers in about equal amounts. On protonation of this mixture, only the one expected cation (IIb) is produced. The diene was stored under nitrogen in a freezer compartment. Dehydration of these alcohols during their attempted preparation is a common occurrence.[29]

1-Isopropyl-3-methylcyclopent-2-en-1-ol. The preparation of this alcohol followed a standard procedure previously described.[2] Two treatments of the ketone with isopropyllithium were necessary. From 1.0 g of 3-methylcyclopent-2-enone (0.005 mol) and excess isopropyllithium, there was obtained 0.42 g (23%) of the title compound, bp *ca.* 30° (0.1 mm). Some dehydration of the alcohol occurs on distillation but this in no way affects the carbonium ion produced: nmr spectrum 4.71 broad (1 H), 7.5–8.6 multiplet, 8.25 (3 H), 8.96 (1 H), 9.12 doublet, J = 6.5 cps (3 H), 9.15 doublet, J = 6.5 cps (3 H). The carbonium ion produced from this alcohol has been previously reported.[29]

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