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.

Acknowledgment. The author wishes to thank the National Research Council of Canada and the Petroleum Research Fund for financial support. We are grateful to Mrs. V. Boon for many of the nmr measurements and to Mrs. S. Bagley for elemental analyses.

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.

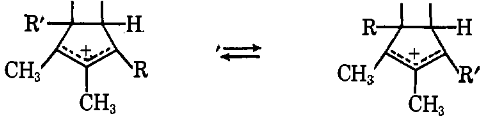
Directly Observable Carbonium Ion–Carbonium Ion Rearrangements. II. Kinetics and Equilibria in the Interconversion of Tetraalkylcyclopentenyl Cations

T. S. Sorensen

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.



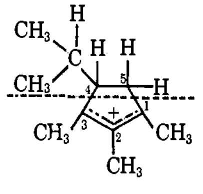
I, R = ethyl; R^1 = methyl II, R = methyl; R^1 = ethyl
III, R = isopropyl; R^1 = methyl IV, R = methyl; R^1 = isopropyl
V, R = *t*-butyl; R^1 = methyl VI, R = methyl; R^1 = *t*-butyl
VII, R = isopropyl; R^1 = ethyl VIII, R = ethyl; R^1 = isopropyl
IX, R = *t*-butyl; R^1 = isopropyl X, R = isopropyl;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

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

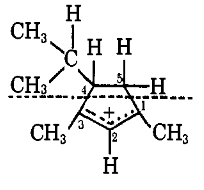
---

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

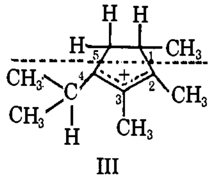
rate of the equilibration reactions of the tetraalkyl series would be predicted to be much faster than those measured for the trialkyl series[1] since the equilibration mechanism of the former should involve lower energy intermediates. (2) The presence of a methyl group at C2 would be predicted on past precedent[2] to give an extra stabilization to the tetraalkyl system, thereby hopefully allowing one, in combination with the above argument, to measure equilibria involving *t*-butyl groups (not possible in the trialkyl series[1]). (3) If the equilibrium reactions are rapid, one should then be able to measure enthalpy differences for the ion "pairs" using the van't Hoff relationship. (4) The disposition of the alkyl groups at the carbonium ion centers of the ring in the tetraalkyl series would be *subtly different*, particularly in the nonbonded interactions, from those of the trialkyl series. If the ring is numbered as below, using the methyl *vs.* isopropyl examples, then the comparison



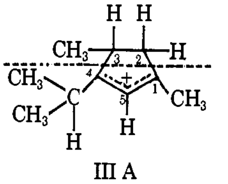
IV



IVA



III



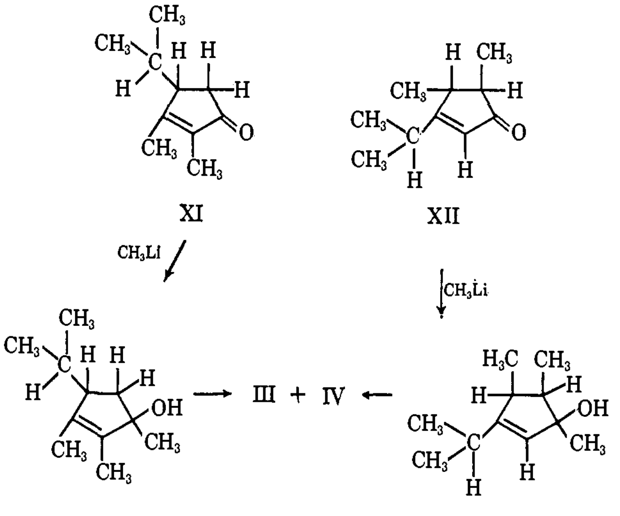
IIIA

in the tetraalkyl series is a 1,3- *vs.* a 2,4-dialkyl one, while in the trialkyl series it is a 1,3- *vs.* a 1,4-dialkyl comparison.

In this study, as in the previous one,[1] it was considered imperative that one obtain unequivocal evidence for true equilibrium behavior in these ion "pairs."

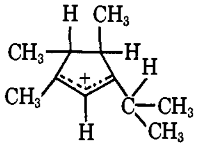
Results and Discussion

Synthetic Sequences. The ion system III–IV was chosen as a representative case to show that the ion concentrations reached a true equilibrium. Toward this end, two different isopropyl-substituted ions were synthesized. The starting materials are two ketones, XI and XII, formed simultaneously from the isomerization of l-thujone in concentrated sulfuric acid.[7] Treatment of these with methyllithium, and repeating the procedure on the crude alcohol in the case of XI, yielded



XI XII XIII XIV

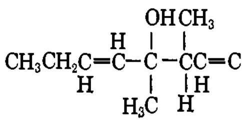
the corresponding tertiary alcohols which were isolated by microdistillation. The corresponding carbonium ions were prepared by the extraction of the alcohols from a hexane solution by a small volume of sulfuric acid and, from either alcohol XIII or XIV, the same ion mixture was observed after 1 hr at 35°. In 100% sulfuric acid, the initially formed ions, corresponding to the heterolysis of the hydroxyl group, persist long enough to be easily observed by nmr spectroscopy and the kinetics of the approach to equilibrium can be followed. It is worth noting that ion XV, from alcohol



XV

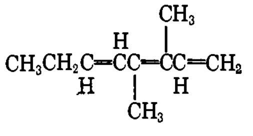
XIV, while initially observed, is completely isomerized to III–IV after a short time.[2] The ion "pairs," VII–VIII and IX–X, were obtained by adding ethyllithium and *t*-butyllithium, respectively, to the ketone XI. In these cases also, the alkyllithium addition was repeated once on the crude alcohol, since some enolization[1] accompanies addition. The ions were prepared in an identical manner with the methyl case above.

The ion "pairs," I–II and V–VI, were prepared by the cyclization of appropriately substituted trienes. In the ethyl case, I–II, the addition of crotylmagnesium chloride to hex-3-en-2-one, using the simultaneous addition method,[8] gave a good yield of 3,4-dimethylocta-1,5-dien-4-ol (XVI), in which, as expected from previous



$\mathrm{CH_3CH_2CH{=}CH{-}C(OH)(CH_3){-}CH(CH_3){-}CH{=}CH_2}$

XVI

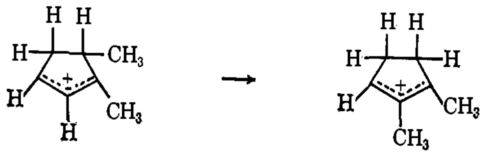


$\mathrm{CH_3CH_2CH{=}CH{-}C(CH_3){=}C(CH_3){-}CH{=}CH_2}$

XVII

---

[2] At least three separate examples are known which show that a cyclopentenyl ion with a C2 methyl group is thermodynamically more stable than an isomer with a proton at this position. Deno, *et al.*, were first to note this,[3] but perhaps a better example is the quantitative isomerization of i to ii.[4,5] Another example is found in the present work



i ii

(see Results and Discussion). A similar type of stabilization can be shown from basicity measurements of polyalkylbenzenes[6] and is in any case not unexpected.

[3] N. C. Deno, N. Friedman, J. D. Hodge, and J. J. Houser, *J. Am. Chem. Soc.*, **85**, 2995 (1963).

[4] T. S. Sorensen, *Can. J. Chem.*, **43**, 2745 (1965).

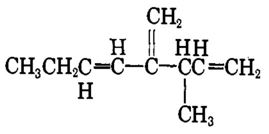
[5] G. A. Olah, C. U. Pittman, Jr., and T. S. Sorensen, *J. Am. Chem. Soc.*, **88**, 2331 (1966).

[6] D. A. McCaulay and A. P. Lien, *ibid.*, 73, 2013 (1951).

[7] R. H. Eastman and A. V. Winn, *ibid.*, **82**, 5908 (1960).

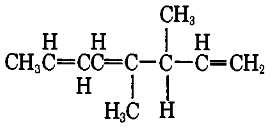
[8] T. S. Sorensen, *Can. J. Chem.*, **42**, 2781 (1964).

reports,[9] the allylic Grignard reagent adds to give the α-methylallyl product. The dehydration of the alcohol



$CH_3CH_2CH{=}CH{-}C({=}CH_2){-}CH(CH_3){-}CH{=}CH_2$

XVIII

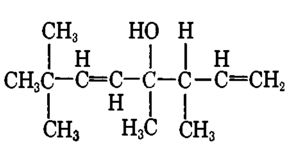


$CH_3CH{=}CH{-}CH{=}C(CH_3){-}CH(CH_3){-}CH{=}CH_2$

XIX

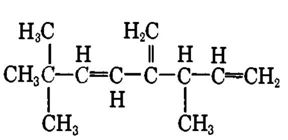
XVI to the conjugated triene XVII was successful, with the aid of preparative vpc, but the yield of this triene is very poor. The major acid-catalyzed dehydration products are the incompletely conjugated trienes, 4-methylene-3-methylocta-1,5-diene (XVIII) and 3,4-dimethylocta-1,4,6-triene (XIX), which can be separated by fractional distillation. They were identified by analysis and ultraviolet spectroscopy: XVIII, peak at 233 mμ in hexane (ϵ_{max} 17,900) and XIX, peak at 240 mμ in hexane (ϵ_{max} 22,300); and by nmr spectroscopy (see Experimental Section). Woodward's rules predict a λ_{max} of 227 mμ for XVIII and 232 mμ for XIX. The vpc conditions used for the isolation of XVII are recorded together with a trace of the chromatogram in the Experimental Section. This triene shows an ultraviolet spectrum with λ_{max} 278.5 mμ (ϵ_{max} 28,000) and shoulders at 269 and 289 mμ (ϵ_{max} 23,200 and 21,000), respectively. These three peaks are very characteristic of conjugated trienes; *cf.* 2,6-dimethyl-1,3,5-heptatriene with peaks at 262, 272, and 282.5 mμ.[8] The nmr spectrum (in τ values) shows peaks at 9.06, 8.94, and 8.82 (area 3, CH_3 of the ethyl group), 8.13 (area 6, methyl groups at C3 and C4), 7.91, 7.79, and 7.67 (part of the ethyl CH_2 absorption), and a complex region 2.7–5.1 (the alkene protons). This spectrum is exceedingly similar to that of 4-methylocta-1,3,5-triene, previously reported.[1] Addition of XVII from the gas phase to sulfuric acid yielded, as expected, the cyclopentenyl cations I–II.

Addition of crotylmagnesium chloride to 5,5-dimethylhex-3-en-2-one yielded the alcohol, 3,4,7,7-tetramethylocta-1,5-dien-4-ol (XX), and as before, the dehydration yielded considerable amounts of the incompletely conjugated triene, 4-methylene-3,7,7-trimethylocta-1,5-diene (XXI). This triene was separated from the remainder of the crude dehydration product by virtue of a much lower boiling point. The compound shows an ultraviolet maximum in hexane at 233 mμ (ϵ_{max} 17,700); *cf.* with XVIII above. The nmr spectrum is described in the Experimental Section and is in excellent agreement for this structure.



$CH_3C(CH_3)_2{-}CH{=}CH{-}C(OH)(CH_3){-}CH(CH_3){-}CH{=}CH_2$

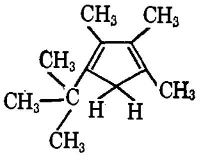
XX



$CH_3C(CH_3)_2{-}CH{=}CH{-}C({=}CH_2){-}CH(CH_3){-}CH{=}CH_2$

XXI

The higher boiling dehydrated material proved to be a mixture of cyclopentadienes, presumably formed by cyclization of the initially formed conjugated triene. This example is the first one where the triene cyclization reaction has occurred so rapidly that mere catalytic amounts of strong acid in a neutral solution is sufficient to bring it about. This method therefore has potential application for the synthesis of cyclopentadienes. The major cyclopentadiene component is probably 1,2,3-trimethyl-4-*t*-butylcyclopentadiene (XXII), although the exact nature of the cyclopentadiene mixture depends upon the distillation procedure.



XXII

Rapid fractionation yields a mixture of at least three dienes, as determined from an nmr spectral analysis, while slow fractionation appears to cause extensive thermal rearrangement with isomer XXII, the major component of the highest boiling fractions. That thermal rearrangements occur at elevated temperatures is also confirmed by vpc experiments. The structure of the cyclopentadienes follows from their mode of formation, hydrogenation to give 1-mole uptake,[10] and the ultraviolet spectrum, 242.5 mμ (ϵ_{max} 5200) for the unfractionated material, the low intensity absorption being characteristic of cyclic dienes. The nmr spectrum (in τ values) of the highest boiling fraction has peaks at 8.84 (*t*-butyl), 8.30 and 8.15, (methyl), and 7.31 [a multiplet with J = 1.5 cps, the methylene group at C5 (*cf.* 1-methylcyclopentadiene with a multiplet at 7.30[11]). There are also a number of smaller peaks belonging to other isomers but these major peaks can be attributed to the cyclopentadiene XXII, the only one with a methylene group at C5. The final structure proof is the fact that the expected cyclopentenyl ions are formed when the dienes are added to sulfuric acid and that essentially the same diene mixture is again obtained from recovery experiments. The thermal rearrangement of alkylcyclopentadienes has been investigated recently.[11]

Analysis of the Ions. The nmr spectra of the equilibrated ion mixtures are shown in Figure 1 (A–E), and are very clean, more so even than in the trialkyl cases. The nmr assignments are made as shown in Figure 1 and are recorded in Table I, using tetramethylammonium cation as an internal rererence.[12] The assignment is unequivocal; this is made possible because, in all cases, a nonequilibrium mixture of the two ions was initially observed[13] so that one can follow the increase or decrease of peaks due to one or the other isomer as the equilibrium is approached, thereby establishing which nmr peaks are due to a particular isomer.

---

(9) J. F. Lane, J. D. Roberts, and W. G. Young, *J. Am. Chem. Soc.*, **66**, 543 (1944).

(10) The tetrasubstituted bond remaining is expected to be inert to atmospheric pressure hydrogenation. A triene would have absorbed at least 2 moles of hydrogen.

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

(12) N. C. Deno, H. G. Richey, Jr., N. Friedman, J. D. Hodge, J. J. Hauser, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).

(13) In the case of the preparation of III–IV, VII–VIII, and IX–X, one starts initially with a single ion. When the triene XVII was added to sulfuric acid, the initial mixture was fractionally richer in isomer II than that present in the equilibrium mixture. The most interesting case, however, was found using the mixed trimethyl-*t*-butylcyclopentadienes (probably mainly XXII). The initial protonation *does not* yield the equilibrium mixture, giving initially about 70% VI and 30% V. We have previously suggested[4] a kinetically controlled protonation in connection with another carbonium ion preparation. In the above example, this nonequilibrium protonation can be attributed to a steric inhibition to protonation at that carbon atom bearing the *t*-butyl group (see XXII).

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

Compd	CH_3 on Cl, C3	CH_3 on C2	CH_2 or CH on C4 or C5^e	CH_3 on C4 (J, cps)	Other (J, cps)
I	7.16^{a,b}	7.87^a	6.73^{a,c} 6.55^{a,c}	8.54 8.67 (7.8)	CH_3 of ethyl group 8.50 8.62 (6.9) 8.73
II	7.16^{a,b}	7.87^a	6.73^{a,c} 6.55^{a,c}	...	CH_3 of ethyl group 8.91 9.03 (6.9) 9.14 CH_2 of ethyl group 7.7–8.3 (m)
III	7.15^{a,b}	7.87^a	6.51^{a,c} 6.66^{a,c}	8.55 8.68 (7.8)	CH_3 of isopropyl group 8.61, 8.63 8.72, 8.74 (6.6)
IV	7.15^{a,b}	7.87^a	6.51^{a,c} 6.66^{a,c}	...	CH_3 of isopropyl group 8.79, 9.38 8.90, 9.49 (6.6) CH of isopropyl group 7.2–7.7 (m)
V	7.10^{a,b}	7.71	6.62^{a,c}	8.53^d 8.65 (7.2)	CH_3 of t-butyl group 8.54
VI	7.10^{a,b}	7.87	6.62^{a,c}	...	CH_3 of t-butyl group 8.95
VII	7.17^{a,b}	7.86^a	6.69^{a,c}	...	CH_3 of isopropyl group 8.60 8.71 (6.6) CH_3 of ethyl group 8.93 9.05 (7.2) 9.17 CH_2 of ethyl group 7.2–8.3^a (m)
VIII	7.17^{a,b}	7.86^a	6.69^{a,c}	...	CH_3 of ethyl group 8.47 8.58 (6.6) 5.69 CH_3 of isopropyl group 8.76, 9.48 8.88, 9.37 (6.9) CH of isopropyl group 7.2–8.3^a (m)
IX	7.12^{a,b}	7.70	6.68^{a,c} 6.60^{a,c}	...	CH_3 of t-butyl group 8.52 CH_3 of isopropyl group 8.75, 9.50 8.87, 9.38 (7.2)
X	7.12^{a,b}	7.86	6.68^{a,c} 6.60^{a,c}	...	CH_3 of isopropyl group 8.53, 8.59 8.64, 8.70 (6.9) CH_3 of t-butyl group 8.94

[a] Superimposed peaks from both isomers. [b] Broad. [c] Very broad. [d] This half of the peak is actually buried. The relative areas have been measured and agree closely with those calculated. These areas are based on the equilibrium mixture spectra. [e] And other CH_2 and CH groups in the same relation to the enylic ion.

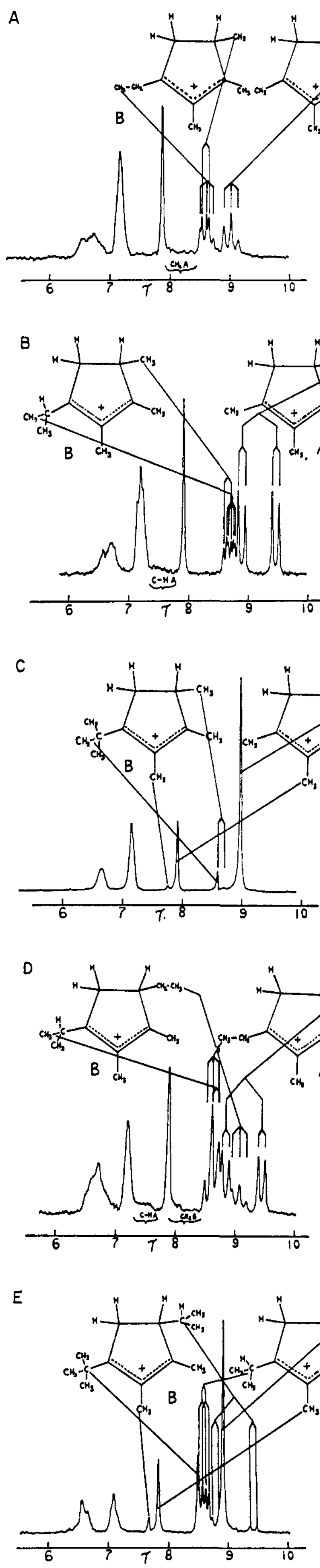


Figure 1. The nmr spectra of the equilibrium mixtures of the ions (sweep width 500): A, I-II; B, III-IV; C, V-VI; D, VII-VIII; E, IX-X.

Only in the case of I-II is there any indication of extraneous polymeric material and the amount is small. The actual curves, where comparisons can be made, are, as one might expect, very similar to the nmr spectra of the corresponding trialkyl compounds.[1] The actual nmr peaks used to calculate the relative amounts of the

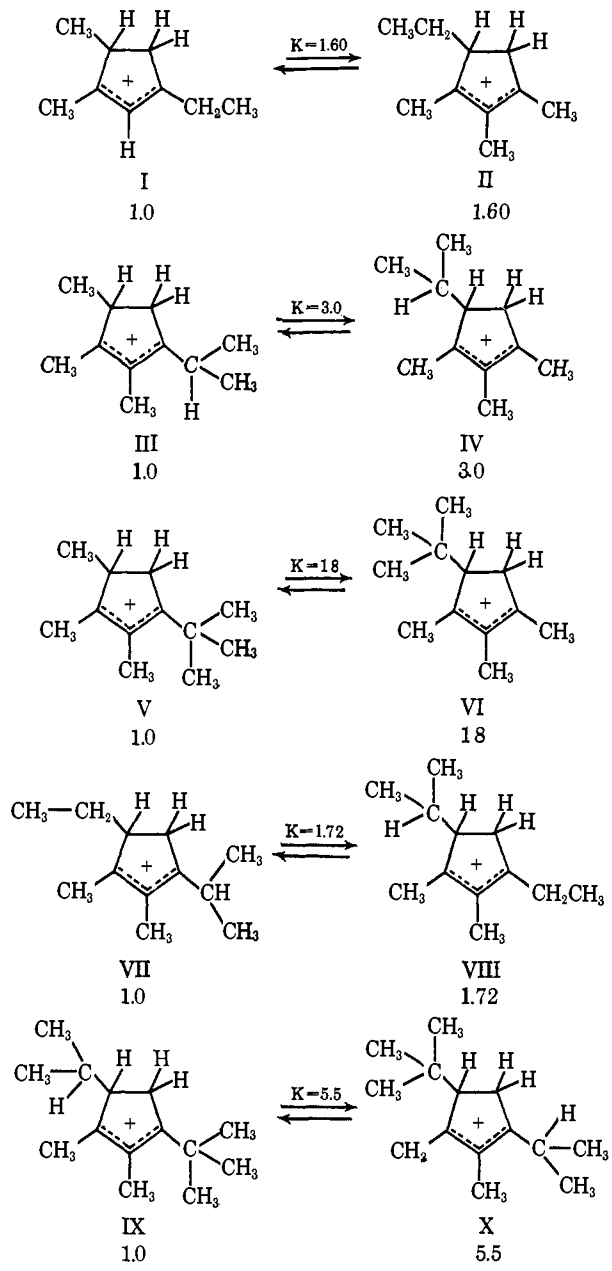


Figure 2. The structures of and the equilibrium constants for the equilibrated ions.

two isomers in the equilibrium mixture are listed in the Experimental Section. The nmr measurements and the area analyses were carried out as described in paper I.[1]

The compounds with an isopropyl group at C4 consistently show the very large separation of the two isopropyl methyl peaks previously noted[1] in paper I. This effect reaches its maximum with the carbonium ions; for example, the separation in IV is 0.59 ppm, in VIII, 0.605 ppm, and in IX, 0.63 ppm. One can also relate the nmr chemical shifts, in terms of increased charge density,[14] with the stability of the two isomeric ions. For example, in I-II, III-IV, and VII-VIII, K is reasonably small and one observes that the C2 methyl groups in the isomeric ions overlap completely so as to form a single peak. However, in V-VI and IX-X, this absorption occurs at τ 7.71 and 7.70, respectively, in the less stable isomers compared to the "normal" τ 7.86-7.87 in the more stable isomers.

Table II and Figure 2 show the equilibrium constants[15] obtained for the five ion "pairs" at 35 ± 2° along with the corresponding ΔF,[15] ΔH, and ΔS values.

Table II. Entropy-Enthalpy-Free Energy Differences between Isomeric Ions at 35 ± 2°

Ions	K^a	$-\Delta F$,[a] kcal/mole	$-\Delta H$,[b] kcal/mole	ΔS, eu
I-II	1.60	0.29	0.2 ± 0.2	± Small
III-IV	3.0	0.67	0.6 ± 0.3	± Small
V-VI	18	1.76	1.5 ± 0.6	± Small
VII-VIII	1.72	0.33	0.3 ± 0.2	± Small
IX-X	5.5	1.04	1.4 ± 0.5	± Small

[a] Within ±10%. [b] The error represents the maximum scatter from a series of runs. The actual uncertainty in these values is even greater (see Discussion).

Table III shows the variation of K with solvent. For the range listed in this table, the III-IV equilibrium constant is, within experimental error, the same in each solvent. This also applies to V-VI. Several of the solvents used for the latter determination show nmr spectra with a fairly high background noise level. One has no problem assigning a maximum size to the peaks of the minor isomeric ion but one has very little idea how small they might be.

Table III. Effect of Solvent on K and ΔH at 35 ± 2°

Compd	Solvent, %	K	ΔH,[a] kcal/mole	$k_r + k_f$, sec^{-1}
III-IV	H_2SO_4, 94.7	3.0 ± 0.3	0.7	
	H_2SO_4, 89.3	2.8 ± 0.3	0.5	
	H_2SO_4, 83.2	3.1 ± 0.3	..	
	H_2SO_4 in CF_3COOH, 20 w/w	2.7 ± 0.3	...	
V-VI	H_2SO_4, 101.5	15 ± 2	...	$\sim 2 \times 10^{-4}$
	H_2SO_4, 95.3	18 ± 2	1.2	$\sim 1.4 \times 10^{-3}$
	H_2SO_4, 89.9	17 ± 2	1.8	$\sim 10^{-2}$
	H_2SO_4, 83.8	11^b	...	
	H_2SO_4 in CF_3COOH, 20 w/w	10-11[b]		
	H_3PO_4, 115	At least 10[b,c]	...	

[a] These values are the average of several determinations. They have been combined in Table II and the over-all range of error given there. [b] To be regarded as lower limits. They may well be twice this large (see Results). [c] Limited solubility makes the determination of K virtually impossible. One can, however, assign a lower limit to K based on the size of the large t-butyl peak compared to the maximum size possible for the smaller one.

Enthalpy Calculations. Enthalpy values were obtained from the usual van't Hoff relationship. For I-II, III-IV, and VII-VIII, the temperatures used were −20, 0, 35, 80, and 120°. For V-VI and IX-X, the maximum temperature possible was 70° since a competing rearrangement reaction becomes very fast above this temperature. The experimental difficulties, mainly area analysis, which are intrinsic to each equilibrium value determination are of course magnified in the ΔH calculation. In addition, the lower temperature

[14] T. S. Sorensen, *J. Am. Chem. Soc.*, **87**, 5075 (1965), and references therein.

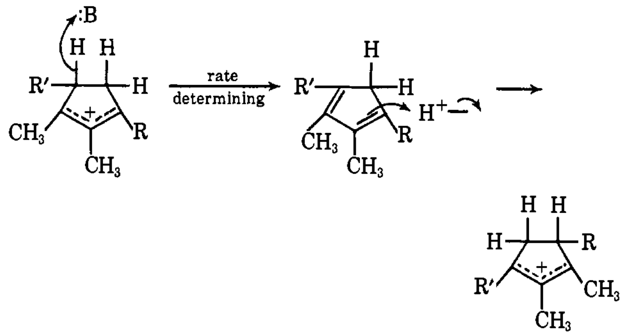
[15] The experimental uncertainty should be well within the stated limit of *ca.* ±10%. This limit is well within the scatter of a number of runs.

nmr spectra signals are broadened by viscosity effects and, at the higher temperatures, the signal-to-noise ratio becomes substantially less and in certain cases, the nmr lines are even sharper than those measured at 35°. One has therefore to contend with large changes in the shape of the nmr lines as a function of temperature. At −20°, a good deal of hand resolution of broad, overlapping peaks was carried out.

These low-temperature problems could be alleviated to some extent by choosing an acid concentration where the equilibration reaction of the ions was slow. The sample is then kept at the low temperature long enough for equilibration at this temperature; one can then carry out the nmr measurements at 35° providing the measurements are made quickly. Similarly, high-temperature runs can be quenched and again measured quickly at 35°. The calculation of the time necessary to reach equilibrium was made by taking the known rate of this reaction, which was determined at 35°, and trebling this time (using >99% approach to equilibrium) for each 10° rise or fall in temperature.

The actual uncertainty in the value of ΔH is even larger than the experimental scatter used to assign the error in Table II and it is within the bounds of possibility that the absolute errors may be plus or minus the values recorded for ΔH. Besides the uncertainties discussed above, one knows that the solvent structure may change considerably with temperature; for example, H_0, which could be considered as a measure of solvent structure, is appreciably temperature dependent.[16] The large viscosity change has already been mentioned and either of these changes could be envisioned as having an effect on K, *i.e.*, even if K is temperature dependent, this may not in fact be related to enthalpy changes. The fact that ΔH itself may be temperature dependent is a further uncertainty. Nevertheless, the variation of K *vs.* temperature is always in one direction and the magnitude of ΔH bears a reasonable relation to ΔF; in fact, these two quantities are well within the large experimental error of being the same and this fact is significant in a negative sense.

Rates of Equilibration of the Ions. The equilibration reaction rate constants ($k_r + k_f$) were determined for V–VI and are listed in Table III; however the rough values of the rate constants for the other ions appear to be very similar. For comparable acid strengths, these isomerization reactions are therefore about 50–100 times faster than those observed for the corresponding trialkyl ions (paper I).[1] The dependence of rate on H_0 has not yet been accurately determined but the slope of the plot of log ($k_r + k_f$) *vs.* H_0 appears to be less than one.



The isomerization mechanism may be simply a deprotonation–protonation reaction in two separate steps or with a gradation toward a push–pull type of reaction.

Acids considerably stronger than sulfuric have found considerable use in carbonium ion preparations, notably fluorosulfonic acid and combinations of this with antimony pentafluoride.[17] For the present study, however, sulfuric acid is admirably suited since we desire that the equilibration reactions be fairly rapid (for ΔH measurements) but not so rapid as to preclude rate measurements altogether.

Deuterium Exchange. The ions, III–IV, were also prepared in deuteriosulfuric acid. The H–D exchange is much slower in the tetraalkyl case compared to the corresponding trialkyl compounds;[1] this is, however, completely consistent with the greater stability of the tetraalkyl ions. In 95.1% deuteriosulfuric acid, the isopropyl methine proton exchange is simultaneous in both isomers since the rate of equilibration is much greater than the rate of H–D exchange. At 80°, the exchange has a half-life of *ca.* 15 min; at 90°, *ca.* 8 min. The substitution of the C4 proton is complete at 60° within 12 min, and this rate seems to be, as expected, similar to the rate of the isomerization reaction. There is thus a considerable difference between the rate of exchange of the β-CH proton on the ring at C4 and that of the isopropyl group. The exchange rate of these same protons in the trialkyl system[1] was so rapid that it was not really possible to distinguish between the two; however, we do not think that the exchange rates could have been very different.

The deuterium exchange of the methylene protons at C5 and the methyl protons at C1 and C3 is significant at 90°: about one-half of the methyl signal has disappeared after 40 min at this temperature. There thus appears to be considerably less discrimination between deuterium substitution of CH, CH_2, and CH_3 groups, compared to the trialkyl system.

The fact that deuterium appears in the methine position of the C4 isopropyl group of IV and that the same mixture of ions is obtained from two different starting materials is proof that a true equilibrium is involved in these rearrangements.

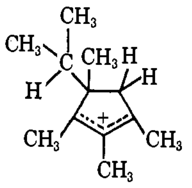
Competing Rearrangement Reaction. While it is easy to obtain equilibrium constants for V–VI and IX–X, and even ΔH values, the latter measurement is hampered by a competing rearrangement reaction. This rearrangement is reasonably clean (~80%); however, a further slower rearrangement of this ion makes it impossible to obtain a quantitative conversion. The kinetics of the rearrangement appear to be approximately first order in V–VI, $t_{1/2}$ of 14 min at 80°, and the rearrangement rate does not appear to be appreciably acid dependent. The nmr spectrum (in τ values) of the rearranged product shows the following peaks and relative areas: 9.57, 9.45, 8.97, and 8.85 (J = 6.6 cps, relative area 6), 8.65 (relative area 3), 7.87 (relative area 3), 7.10 and 7.26 (broad, relative area 6), and 6.67 and 6.85 (very broad, relative area 2). The ion is tentatively assigned the structure XXIII. Similarly, the rearrangement product from IX–X has peaks and relative areas (in τ values): 9.57, 9.46, 8.93, and

---

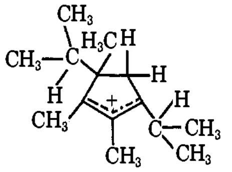
(16) F. A. Long and M. A. Paul, *Chem. Rev.*, **57**, 946 (1957).

(17) G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 2997 (1965).

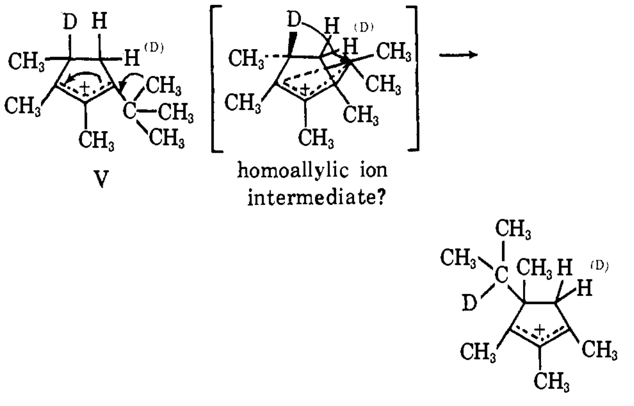
8.81 (J = 6.9 cps, relative area 6), τ 8.68 and 8.57 (J = 6.9 cps, relative area 6), τ 8.63 (relative area 3), 7.86 (relative area 3), 7.28 and 7.16 (very broad and unsymmetrical, relative area 3), and 6.69 and 6.61 (very broad, relative area 2). This ion is assigned the structure XXIV. When the rearrangement of V–VI is carried out in 100% deuteriosulfuric acid, deuterium appears in the methine part of the C4 isopropyl group of the product, as evidenced by the appearance of singlet isopropyl methyl peaks. At this temperature and concentration of deuteriosulfuric acid, the exchange of the original C4 proton in V–VI is very rapid but the methylene exchange at C5 is only about the same rate as that of the rearrangement. This evidence can be rationalized by the following mechanism (a hydride shift from C5 would be expected to give a mixture of protons and deuterons in the isopropyl methine position).



XXIII



XXIV



This reaction corresponds to a type of neopentyl rearrangement in which it will be possible to measure directly the kinetics and activation parameters for the *ion to ion* part of this classical rearrangement.

The structure of the further rearrangement product of XXIII has not yet been determined. It might be noted at this point that the analogous *t*-butyl compound in the trialkyl series[1] also underwent a rearrangement, apparently by a different mechanism.

Recovery Experiments. The equilibrium mixture solution of V–VI was added to aqueous base according to the usual procedure.[18,19] There was recovered a 72% yield of monomeric cyclopentadienes whose nmr spectrum is virtually identical with that of the mixture of dienes obtained from the original dehydration of XX and which were used to prepare V–VI. The recovered hydrocarbons, when put back into sulfuric acid, regenerated the original V–VI ion mixture in quanitative yield. The above ions are representative of those in this work and this recovery serves to show that these ions can be "recovered."

Ultraviolet Spectra. The ultraviolet spectral data for the ions studied in this work are reported in Table IV. The first and the last entries are for pure compounds; the remainder are equilibrium mixtures. In the case of V–VI and IX–X, the equilibrium lies far enough to one side so that the absorption peak λ_{max} will represent that of the major isomer.

Table IV. Ultraviolet Spectra of the Carbonium Ions

Compound	λ_{max},[a] mμ	ϵ_{max}[b]
1,2,3,4-Tetramethyl-cyclopentenyl cation	294	13,000
I–II equilibrium mixture	296.5	15,000
III–IV equilibrium mixture	299	17,000
V–VI equilibrium mixture	303	15,000
VII–VIII equilibrium mixture	301.5	19,000
IX–X equilibrium mixture	310	13,000
1,4-Diisopropyl-2,3-dimethylcyclo-pentenyl cation	304	. . .

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

In Figure 3 we have plotted the λ_{max} of these ions and, in a separate curve, those of the ions in paper I,[1] against the number of carbon atoms in the molecules (only the trend is regarded as significant and is likely an accidental accompaniment of some more fundamental cause). The relationship is remarkable in that there is no change in the number or position of alkyl substituents throughout a series. It is also notable that methyl substitution at C2 gives on the average a +12-mμ increase to the λ_{max} (compare the separation of the two curves). The effect of methyl substitution at this "inactive position" has been noted previously[19] in similar ions and has also been observed in the spectra of protonated alkylbenzene compounds.[20] Moreover, this result is in complete agreement with theory.[21]

There are, of course, differences in the ground-state energies of these ions but the most reasonable explanation of the λ_{max}–number of carbon atoms correlation would involve energy differences between the excited states: the more carbon atoms, the more delocalization in the excited state and the lower the energy of this state. Since steric interactions may increase as the number of carbon atoms increase it is also possible that the λ_{max} increase is somehow associated with this.

Rationalization of the Magnitude of the Equilibrium Constants. The solvent studies reported in paper I have been further extended to include sulfuric acid–trifluoroacetic acid and phosphoric acid systems and while these solvents produce rather poor quality nmr spectra, with resultant large experimental uncertainties, there is no indication that K values are appreciably different than those in the straight sulfuric acid systems.

---

(18) N. C. Deno, C. U. Pittman, Jr., and J. O. Turner, *J. Am. Chem. Soc.*, 87, 2153 (1965).

(19) T. S. Sorensen, *Can. J. Chem.*, 42, 2768 (1964).

(20) G. Dallinga, E. L. Mackor, and A. A. V. Stuart, *Mol. Phys.*, 1, 123 (1958).

(21) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, N. Y., 1961, p 231.

Thus, we again propose that the solvent and the counterion are unimportant[22] in determining the equilibrium concentrations of the two ions. The enthalpy and free energy differences would then be properties of the ions themselves. For the following discussion ΔF and ΔH are equated (see previous discussion).

A discussion of steric and/or resonance and inductive stabilization effects must include a comparison with the results of the previous paper.[1] Both ion series provide for the same internal comparison of alkyl groups and the resulting K values are within experimental error of being the same: I–II in the tetraalkyl series has K equal to 1.6 while the analogous compound in the trialkyl series had K equal to 1.5. For III–IV, the values of K are 3.0 and 2.7, respectively. While the two series provide for identical alkyl group comparisons, they do not necessarily have identical differences in the nonbonded interactions in each case. The representations in the introductory section show that ions IV and IVA have quite similar structures (hydrogen for methyl at C2) while III and IIIA are less similar; specifically, the isopropyl group is between a methylene group and an sp^2 carbon methyl group in III but next to a tetrahedral carbon methyl group and a proton on an sp^2 carbon in IIIA. The exact implications of this difference, in energy terms, are as usual difficult to assess; we wish only to emphasize the fact that there are differences. Actually, a study of molecular models of these ions leads one to the conclusion that III and IIIA have fewer nonbonded interactions than their corresponding isomers, yet these are the less stable isomers.[23]

In the comparisons, *e.g.*, III–IV, the C4 alkyl group is also different in the two ions but any inductive or conjugative effect caused by this difference is assumed to be of secondary importance as far as interaction with the allylic ion is concerned. It seems unreasonable, at least in the ground-state description, to suggest that differences in the alkyl group at C4 would have an effect on conjugative delocalization, and if inductive effects were dominant, these would be predicted to favor the less stable ion in these series (assuming the usual inductive order for alkyl groups).

The amazing consistency of derived and experimental $-\Delta F$ values also seems to argue against the operation of a purely "steric effect:" $-\Delta F$ for methyl *vs.* isopropyl is 0.67 kcal/mole, $-\Delta F$ for methyl *vs.* ethyl is 0.29 giving a calculated $-\Delta F$ for ethyl *vs.* isopropyl of 0.38. Experimentally, this value is 0.33. Again, $-\Delta F$ for methyl *vs.* *t*-butyl is 1.76 kcal/mole, giving a calculated $-\Delta F$ for isopropyl *vs.* *t*-butyl of 1.09; experimentally this value is 1.04. Indeed, one has no hesitation in predicting that K for the ethyl *vs.* *t*-butyl system (the remaining permutation) will be very close to 11, equivalent to a $-\Delta F$ value of 1.47 kcal/mole. The experimental free energy differences can be expressed quite well by the following equation, an *exponential* rather than an *additive* function

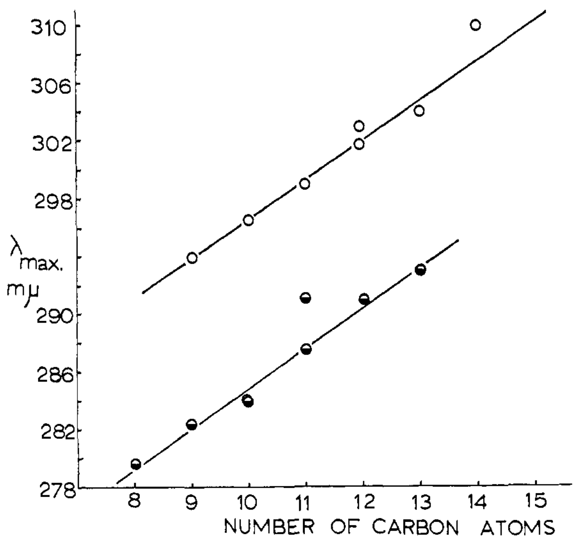


Figure 3. Correlation of the $\lambda_{\max}$ of a series of 1,3,4-trialkyl-substituted cyclopentenyl cations (lower line) and a series of 1,2,3,4-tetraalkyl-substituted cyclopentenyl cations (upper line) with the number of carbon atoms in the cations.

$$-\Delta F = \frac{(2.6)^{3-x_1}}{10} - \frac{(2.6)^{3-x_2}}{10}$$

where x_1 and x_2 are the number of β-protons on the C1 and C3 alkyl groups ($x_1 > x_2$). We can attach no great theoretical significance to this equation for several reasons: (1) there are also β-protons at C4 and C5 in all of the ions, (2) differential inductive stabilization effects are expected to also contribute to ΔF values, (3) it would seem that "steric effects" must contribute to some extent in determining ΔF, and (4) it is felt intuitively that if C–H hyperconjugative delocalization were important, then C–C hyperconjugation would also be reasonably important.

Previously, the largest reported discrimination between a methyl group and a *t*-butyl group in a chemical reaction or equilibrium, not involving obvious steric interactions, was a factor of about three.[24] One of the closer analogies to the present work concerns the protonation equilibria of 1,3,5-trialkylbenzenes.[25] However, the *t*-butyl and methyl-substituted compounds, after correcting for differing partition coefficients, are reported to have identical pK_B values. This study again lacks the internal comparison used in this work.

In conclusion, we would suggest that these $-\Delta F$ differences provide the best evidence yet observed in support of the hyperconjugative order (differential CH–CC hyperconjugation). It should be emphasized, however, that the system is a rather extreme one and that under the circumstances the $-\Delta F$ differences might not be considered very large. Certainly one should not try to rigorously extrapolate these data to systems where a considerably smaller fractional positive charge is involved at the carbon atom bearing the alkyl groups. More results will be required before we are prepared to undertake an interpretation of the quantitative aspects of this work, including the apparent fit of the data to an exponential function. The whole question of the theoretical validity of using *t*-butyl, isopropyl, ethyl,

---

(22) Many examples are known in which the nature of the solvent *is* an important factor in determining the position of an equilibrium. Examples include the solvent-dependent conformational equilibria of vicinal dihalocyclohexanes and the solvent-dependent K values for keto–enol tautomerism.

(23) A good deal of caution must be used in evaluating nonbonded interactions. Equilibrium studies of many other systems, for example, the base-catalyzed isomerization of carbonyl compounds, serve to show that reasonably large effects on K are caused by what appear to be fairly small changes in molecular structure between isomers.

(24) M. J. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962, p 110.

(25) D. A. McCaulay and A. P. Lien, *Tetrahedron*, **5**, 186 (1959).

and methyl groups as a criterion for the existence of hyperconjugation is being considered since it is not at all clear what mathematical relationship, if any, governs this order. Of particular concern is the degeneracy loss inherent in hyperconjugation calculations involving ethyl and isopropyl groups.

Experimental Section

The experimental details (machines, sample preparation, vpc columns, etc.) are identical with those of paper I.[1] The nmr temperature control was calibrated using the methanol and ethylene glycol standard samples, both before and after each measurement. Measurements are accurate to ±2° of the stated values. The low-temperature samples were kept up to 2 weeks in a cryostat to allow equilibration prior to being measured. Measurements at 35° require about 1 hr for complete equilibration and higher temperature runs progressively less.

3-Isopropyl-4,5-dimethylcyclopent-2-en-1-one (XII) and 2,3-dimethyl-4-isopropylcyclopent-2-en-1-one (XI) were prepared by the procedure of Eastman and Winn.[7]

1,4,5-Trimethyl-3-isopropylcyclopent-2-en-1-ol (XIV), 1,2,3-trimethyl-4-isopropylcyclopent-2-en-1-ol (XIII), 1-ethyl-2,3-dimethyl-4-isopropylcyclopent-2-en-1-ol (XXV), and 1-*t*-butyl-2,3-dimethyl-4-isopropylcyclopent-2-en-1-ol (XXVI) were prepared by the addition of the appropriate alkyllithium reagent to the ketone in a manner similar to that described in paper I.[1] As before, the latter three compounds required a second alkyllithium treatment in order to completely form the alcohol. In the latter three compounds the addition probably gives mainly the *trans*-addition product (nmr analysis). The nmr and infrared spectral results are in complete agreement with the expected structures and are available upon request. XIII showed the following physical properties: bp 42° (0.1 mm), yield 85% (*Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.51; H, 11.58). XIV showed the following physical properties: bp 38–40° (0.1 mm), yield 85% (*Anal.* Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.68; H, 2.11). XXV showed the following physical properties: bp 41–44° (0.05 mm), yield 82% (*Anal.* Calcd for $C_{12}H_{23}O$: C, 79.06; H, 12.17. Found: C, 78.88; H, 11.99). XXVI showed the following physical properties: bp 50–52° (0.05 mm), yield 55% (small-scale reaction with considerable hold-up on distillation) [*Anal.* Calcd for $C_{14}H_{26}O$: C, 79.90; H, 12.46. Found: C, 81.14; H, 13.64 (some dehydration has probably taken place during distillation)].

3,4,7,7-Tetramethylocta-1,5-dien-4-ol (XX) was prepared by the addition of crotylmagnesium chloride to 5,5-dimethylhex-3-en-2-one[26] using the simultaneous addition method described[8] previously. From 25 g (0.2 mole) of the ketone, 36.20 g (0.4 mole) of crotyl chloride, and 9.72 g (0.4 g-atom) of magnesium, there was obtained 24.4 g (70%) of the title compound, bp 72–74° (8 mm), $n^{20}\mathrm{D}$ 1.4530.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.17. Found: C, 78.86; H, 12.09.

The infrared spectrum exhibits a peak (hydroxyl stretch) at 3610 cm^{-1}. The nmr spectrum (in τ values) shows peaks at 9.08 and *ca.* 8.97 (J = 6.6 cps, the methyl group at C3), 8.99 (the *t*-butyl group), 8.83 (area 3, the methyl group at C4), 8.39, (area 1, the hydroxyl proton), a multiplet centered at 7.90 (area 1 the proton at C3), and a complex series of peaks 3.9–5.2 (area 5, the alkene protons).

Dehydration of 3,4,7,7-tetramethylocta-1,5-dien-4-ol (XX) (12 g, 0.067 mole) in 100 ml of dry benzene and 20 mg of *p*-toluenesulfonic acid (as the hydrate) was heated to the reflux temperature for a few minutes and then 80 ml of benzene–water slowly distilled over (*ca.* 1 ml of water, 80% was collected). Ether was added, and the resulting solution was washed with sodium carbonate solution and dried over potassium carbonate. After solvent removal the residue was distilled through a 1-m spinning-band column (*ca.* 8 mm), employing a 20:1 reflux ratio. The following fractions were collected: (1) 49–50.5°, 0.4 g; (2) 51–53°, 1.8 g; (3) 53–61.5°, 1.3 g; (4) 62–63°, 0.8 g; (5) 63.5–65.5°, 0.8 g; (6) 66–71°, 1.3 g; (7) 71–73°, 1.8 g; residue, 1.8 g; total, 10.0 g (theoretical 10.8 g).

The nmr spectrum of each fraction was obtained. Fraction 2 (17%) is virtually pure 4-methylene-3,7,7-trimethylocta-1,5-diene (XXI), the product of dehydration into the C4 methyl group. Fractions 4, 5, 6, and 7 (44%) consist of cyclopentadienes formed by the cyclization of the presumed initially formed conjugated triene. The nmr spectrum of fraction 7 is reported under Results. The other fractions contain these and other peaks, the relative strengths of the peaks varying depending upon the fraction concerned. In fractions 4 and 5, the strongest *t*-butyl peak is at τ 9.05; in fraction 6, at τ 8.84. When fraction 5 was subjected to preparative vpc at 180°, the recovered product was much richer in the isomer with the τ 8.84 peak, indicating that extensive thermal rearrangements are occurring. Rapid distillation of the crude dehydration product at low temperatures (eliminating thermal rearrangements) under high vacuum yielded a mixture which contains almost equal amounts of the τ 8.84 and the 9.05 compounds. The use of larger quantities of *p*-toluenesulfonic acid results in the formation of larger quantities of residual material. Distillation of the alcohol from a trace of iodine gives about a 50% yield of XXI; the higher boiling fractions are yellow oils boiling over a wide temperature range and showing no promise of being the desired conjugated triene.

Anal. Calcd for (fraction 4) $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.57; H, 12.35.

4-Methylene-3,7,7-trimethylocta-1,5-diene (XXI) shows a refractive index of $n^{22}\mathrm{D}$ 1.4618, bp 51.5° (8 mm). The nmr spectrum (in τ values) shows peaks at 8.96 (area 9, the *t*-butyl group), 8.88 and 8.76 (J = 7.2 cps, area 3, the methyl group at C3), and a multiplet centered at about 6.9 (area 7, the alkene protons). The infrared spectrum shows three distinctive peaks at 890, 912, and 970 cm^{-1}.

3,4-Dimethylocta-1,5-dien-4-ol (XVI) was prepared in 78% yield by the addition of crotylmagnesium chloride to hex-3-en-2-one[1,27] using the simultaneous addition method described previously,[8] bp 63–64° (8 mm), $n^{23}\mathrm{D}$ 1.4568.

Anal. Calcd for $C_{10}H_{18}O$: C, 77.88; H, 11.7. Found: C, 77.89; H, 11.54.

The nmr spectrum (in τ values) shows peaks at 9.09, 8.98, and 8.86 (J = 7.2 cps, the methyl group at C8), 9.07 and 8.96 (J = 6.6 cps, the methyl group at C3), 8.83 (the methyl group at C4), 8.44 (the hydroxyl proton), 7.5–8.5 (the protons at C3 and C7), and a complex series of peaks 3.9–5.2 (the alkene protons). The areas appear to be in the correct ratios but overlap too much for an accurate area analysis.

Dehydration of 3,4-dimethylocta-1,5-dien-4-ol (XVI) was accomplished by using the procedure given above for the dehydration of XX, using 12 g (0.078 mole) of alcohol, 100 ml of benzene, and 20 mg of *p*-toluenesulfonic acid. The following fractions were collected using a 1-m spinning-band column (8 mm) and a 20:1 reflux ratio: (1) 34–37°, 0.2 g; (2) 37–39°, 2.0 g; (3) 39–45°, 1.8; (4) 45–46.5°, 0.8 g; (5) 46.5–53°, 0.8 g; (6) 53–60° (mainly 60°), 3.0 g; residue, 1.8 g; total, 10.4 g (10.6 g theoretical). The tail fractions from several runs were combined and redistilled to yield a fraction, bp 59–60° (8 mm), which was used for the isolation of the conjugated triene.

4-Methylene-3-methylocta-1,5-diene (XVIII). The nmr and ultraviolet spectra show that fraction 2 is the title triene, $n^{25}\mathrm{D}$ 1.4676

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.48; H, 12.25.

The ultraviolet spectrum is reported under Results. The infrared spectrum shows three distinctive peaks at 890, 912, and 965 cm^{-1} (*cf.* XXI). The nmr spectrum (in τ values) shows peaks at 9.10, 8.99, and 8.88 (J = 6.6 cps, the methyl group at C8), 8.90 and 8.79 (J = 6.6 cps, the methyl group at C3), a complex series of peaks at 7.6–8.5 (area 2, the methylene protons at C7), a multiplet centered at 6.92 (area 1, the proton at C3), and a complex series of peaks from 3.8 to 5.3 (area 7, the alkene protons).

3,4-Dimethylocta-1,4,6-triene (XIX). The nmr and ultraviolet spectra show that fraction 4 is the title triene, $n^{24}\mathrm{D}$ 1.4833.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.97; H, 12.30.

The ultraviolet spectrum is reported under Results. The infrared spectrum shows distinctive peaks at 720, 912, and 960 cm^{-1}. The nmr spectrum (in τ values) shows peaks at 8.95, 8.91, 8.83, and 8.79 (area 3, J = 7.2 cps, with secondary coupling, J = 2.4 cps, the methyl group at C8), 8.33 (the methyl group at C4 and one-half of the methyl group at C3), 8.21 (the other half of the C3 methyl group), a multiplet centered at 7.20 (area 1, the proton at C3), and a complex series of peaks at 3.5–5.3 (area 6, the alkene protons).

3,4-Dimethylocta-1,3,5-triene (XVII). The fraction, bp 59–60° (8 mm), from the dehydration, was analyzed by vpc. The chroma-

---

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

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

togram and the experimental conditions are shown in Figure 4. The fraction indicated by the vertical marks (a colorless, air-sensitive liquid) was found to be the desired triene XVII, n^{25}D 1.5292; the ultraviolet and nmr spectra are reported under Results. The infrared spectrum shows three distinctive peaks at 900, 960, and 985 cm^{-1}.

Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.01; H, 12.00.

Recovery Experiments. An approximate 8% w/v solution (0.857 g in 10 ml of 96% sulfuric acid) of the carbonium ion "pair" V–VI was prepared and decomposed (30 g of potassium hydroxide, 200 ml of ice–water, 50 ml of ether, more ice as addition proceeds) as previously described.[18,19] There was recovered 0.613 g (72%) of product, bp 82–85° (9 mm). The product is virtually identical in composition with that formed from the dehydration of the alcohol XX (nmr analysis). When put back into sulfuric acid the ions V–VI were again formed.

Area Calculations. The nmr peaks used to calculate the relative amounts of each isomer in the ions I–II, III–IV, and V–VI are essentially the same as those for the corresponding trialkyl ions, reported in the Appendix of part I.[1] For VII–VIII, the higher field isopropyl doublet was used to calculate the relative amount of isomer VIII. This area multiplied by two (the remaining isopropyl methyl group and the methyl part of the ethyl group) was subtracted from the rest of the area in the τ 8.4–9.3 region; the remainder represents the nine protons of isomer VII. In this analysis, one of the ions (VII) is obtained by difference and the experimental error is certainly larger than in the other ion "pairs." For IX–X, the relative amounts of the two isomers were calculated directly from the areas of the respective C2 methyl groups. Some rough resolution (hand estimated) of these peaks was necessary in the low-temperature spectra and even a minor amount in the higher temperature spectra.

Acknowledgments. The author wishes to thank the National Research Council of Canada and the Petroleum Research Fund for financial support. The author is also grateful for the technical assistance provided by Mrs. V. Boon and Mr. P. Campbell.

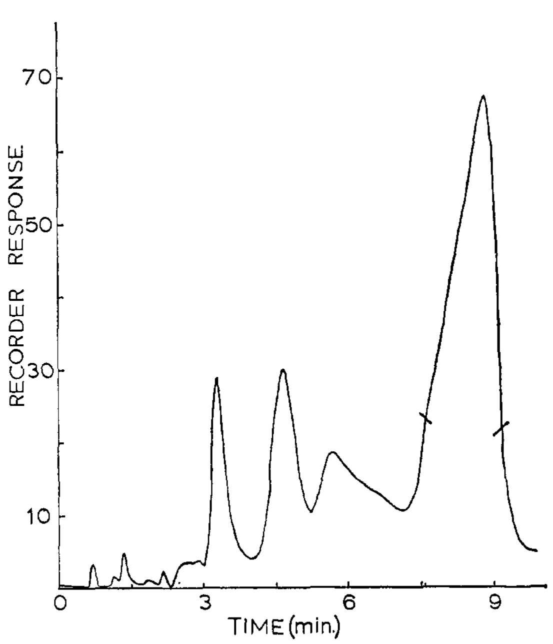


Figure 4. The preparative vapor phase chromatogram of the fraction used to isolate the triene XVII: column, 145°, collector, 165°, injector, 230°, He flow rate *ca.* 200 cc/min, injector sample, *ca.* 0.15 ml.

A Nuclear Magnetic Resonance Study of Transmission of Electronic Effects. Ethylbenzenes, Dihydrocinnamic Acids, and *cis*- and *trans*-Cinnamic Acids[1]

Thomas A. Wittstruck[2] and Edward N. Trachtenberg

Contribution from the Chemistry Department, Clark University, Worcester, Massachusetts 01610.

Received October 25, 1966

Abstract: The proton magnetic resonance spectra of a series of *meta*- and *para*-substituted styrenes, ethylbenzenes, dihydrocinnamic acids, and *cis*- and *trans*-cinnamic acids have been determined in acetone solution. Based on analysis of the β-hydrogens of the styrenes, it is concluded that perturbations in their chemical shifts are caused mainly by inductive and resonance effects rather than by electric and magnetic field effects. Comparison of internal chemical shifts in the various acid series to those in the styrenes and ethylbenzenes reveals that *trans*-cinnamic acids show marked conjugation when substituted with electron-releasing groups, that the side chains of *cis*-cinnamic acids are sufficiently twisted out of coplanarity with the phenyl ring as to markedly dampen conjugation, and that electronic effects can be effectively transmitted from the phenyl ring to the β-carboxyl group of the dihydrocinnamic acids through solvent.

Numerous papers have appeared in the past few years dealing with the origin of the chemical shift. Attempts have been made to relate it to specific substituent properties such as electronegativity[3] or dipole moment[4] as well as to correlate it with more general expressions of substituent ability to affect electronic density such as, for example, the well-known

---

(1) Taken in part from the Ph.D. dissertation of T. A. Wittstruck.

(2) National Science Foundation Cooperative Fellow, 1964–1965.

(3) (a) H. S. Gutowsky and C. J. Hoffman, *J. Chem. Phys.*, **19**, 1259 (1951); (b) H. S. Gutowsky, D. W. McCall, B. R. McGarvey, and L. H. Meyer, *J. Am. Chem. Soc.*, **74**, 4809 (1952); (c) L. H. Meyer and H. S. Gutowsky, *J. Phys. Chem.*, **57**, 481 (1953); (d) J. N. Shoolery, *J. Chem. Phys.*, **21**, 1899 (1953); (e) B. P. Dailey and J. N. Shoolery, *J. Am. Chem. Soc.*, **77**, 3977 (1955); (f) A. L. Allred and E. G. Rochow, *ibid.*, **79**, 5361 (1961); (g) J. R. Cavanaugh and B. P. Dailey, *J. Chem. Phys.*, **34**, 1099 (1961); (h) H. Spiesecke and W. G. Schneider, *ibid.*, **35**, 722 (1961); (i) K. L. Williamson, *J. Am. Chem. Soc.*, **85**, 516 (1963); (j) T. Schaefer, *Can. J. Chem.*, **40**, 1 (1962).

(4) (a) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **80**, 1728 (1958); (b) S. Reddy, J. H. Goldstein, and L. Mandell, *ibid.*, **83**, 1300 (1961).