Equilibria Studies on Tetraalkylcyclohexenyl Cations

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A cyclohexenyl cation equilibria which effectively "pits" alkyl groups against one another yields equilibrium constants in the hyperconjugative order direction; however the size of the free energy differences are only about 60% of those observed for the identical cyclopentenyl cation member. The rate of the equilibrium reaction was studied, as was the rate of several aberrant ion–ion rearrangements, one on the *t*-butyl substituted ions causing particular problems. Unfortunately, the results appear consistent with either a steric or a hyperconjugation argument.

Les équilibres entre cation cyclohexènyle qui oppose effectivement les groupes alkyles les uns aux autres, conduisent à des constantes d'équilibre de type hyperconjugaison; cependant les grandeurs des différences d'énergie libre ne sont que de 60% environ de celles observées pour le cation cyclopentényle analogue. La vitesse de l'équilibration a été étudiée ainsi que celle de plusieurs réarrangements aberrants entre ions, l'un d'eux qui s'effectue sur des ions *t*-butyles substitués, cause des problèmes particuliers. Les résultats apparaissent malheureusement compatibles aussi bien avec l'argument stérique que celui de l'hyperconjugaison.

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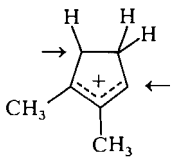
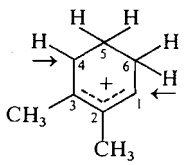
Previously it has been shown (1) that a series of equilibria involving tetraalkyl-substituted cyclopentenyl cations (eq. 1), where R^1 and R^2 are methyl, ethyl, isopropyl, and *t*-butyl groups, give an excellent correlation with the Baker–Nathan order. This result is most directly explained by either differential C—H hyperconjugation or by an unspecified steric effect or perhaps both. If steric effects are involved, then



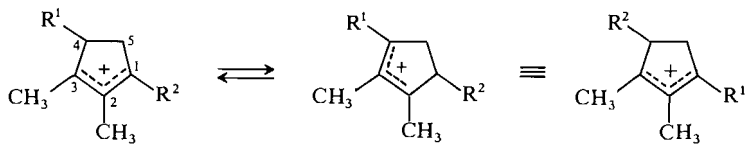


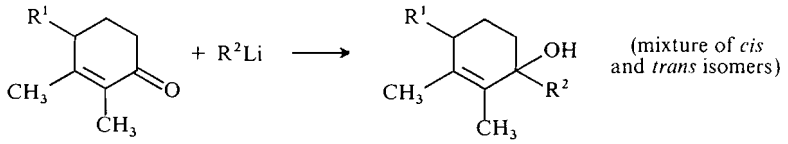
they would most certainly not be direct R^1–R^2 interactions, but in fact, differential interactions of R^1 and R^2 with two non-equivalent sites in the testing vehicle, the 2,3-dimethylcyclopentenyl cation substructure. In the cyclopentenyl system, the two sites are an sp^2 center containing an internal angle smaller than the normal 120° and an sp^3 center flanked by an sp^2 $\overset{\delta+}{C}$—CH_3 center and (assuming a planar molecule) eclipsing protons at C-5. In the corresponding cyclohexenyl ring there are slight differences. The sp^2 center can be substantially closer to 120° and the C-4 and C-5 centers probably involve pseudo axial and equatorial arrangements (2) so that the vicinal interactions are skew. The proposed experiments are not actually dependent on any assumed geometry and the essential point is simply the not unreasonable hope that the steric environment in the two cases will be different. If the various equilibrium constants are due to steric effects, then one would expect the equilibria to be rather sensitive to even small structural changes such as may be involved here. It was of interest therefore to determine whether the equilibrium constants for an analogous series of cyclohexenyl cations would match those of the cyclopentenyl series.

Results

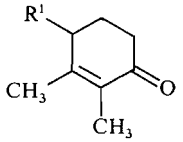
Only one of the cations involved in each equilibrium "pair" was synthesized and this was then allowed to reach an equilibrium with the other isomer. The ions were prepared by the addition of the appropriate allylic alcohol to the strong acid solvents, as described previously for

[1]



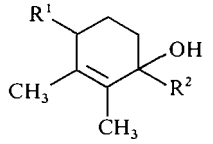
[2] 

the cyclopentenyl system (1, 3). The standard route to the allylic alcohol was as depicted by eq. 2. To prepare all of the possible combinations of R^1 and R^2 = methyl, ethyl, isopropyl, and *t*-butyl, where $R^1 \neq R^2$, requires the three ketones **1**, **2** and **3**. The trimethyl ketone **1** was known (4) and the synthesis of ketones **2** and **3**



1 $R^1 = CH_3$
2 $R^1 = CH_3CH_2$
3 $R^1 = (CH_3)_2CH$

proceeded in the same manner, starting with Hagemann's ester (see Scheme 1). The first step is well known but only methylation (4) has been tried in the second stage. For the base, the use of sodium hydride in toluene was superior to alkoxide–alcohol mixtures. More forcing conditions are required to introduce the ethyl and isopropyl groups and in all cases, the second alkylation produces mixtures of the 2,2- and the 2,4-dialkyl products. Only the 2,4 product (vinylogous β-keto acid) decarboxylates so the separation of the desired ketone is no problem. In preparing the alcohol, the usual problems were encountered with partial enolization of the ketone on R^2Li addition and with the very easy dehydration of the alcohol product (1, 2). The six alcohols **4**–**9** were prepared.

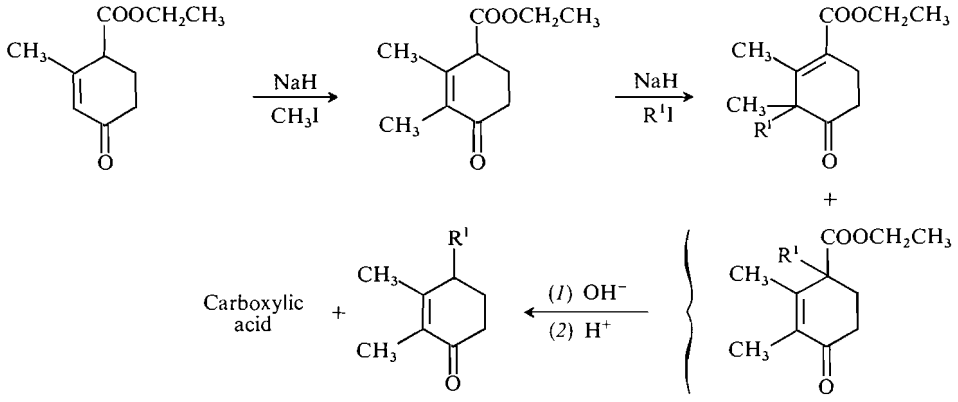


4 $R^1 = Me$; $R^2 = Et$
5 $R^1 = Me$; $R^2 = i$Pr
6 $R^1 = Me$; $R^2 = t$Bu
7 $R^1 = Et$; $R^2 = i$Pr
8 $R^1 = Et$; $R^2 = t$Bu
9 $R^1 = i$Pr; $R^2 = t$Bu

Measurement of the Ion Equilibria

For the equilibrium constant measurements the ions were initially prepared in 95% H_2SO_4 and then allowed to equilibrate at room temperature (< 1 h). As in the cyclopentenyl cation series (1), the analysis involved area measurements of peaks characteristic of each ion and the n.m.r. data for the 12 ions **10**–**21** and the peaks used in the area analyses are reported in Table 1.

Unexpected problems were encountered with all of the *t*-butyl substituted ions. It was anticipated that all of the tetraalkylcyclohexenyl cations would eventually ring-contract to a five-membered cation (2, 5, 6) but this process was

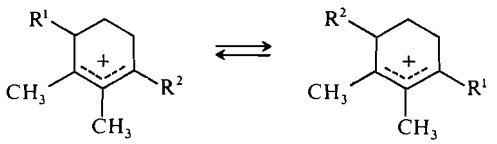


SCHEME 1

TABLE 1. The n.m.r. spectra of the cations*

Ion (Text no.)	CH_3 at C-2	CH_3 at C-4 (when present)	Other
10	7.82†	8.60 (d),‡ $J = 7.2$	CH_3 of ethyl 8.64 (t),‡ $J = 6.9$
11	7.82†		CH_3 of ethyl 8.89 (t),‡ $J = 7.2$
12	7.82†	8.59 (d),‡ $J = 7.2$	CH_3 of isopropyl 8.665 (d), $J = 6.9$
13	7.82†		CH_3 of isopropyl = two (d), 8.875‡ and 9.095,‡ $J = 6.9$ each
14	7.58	8.51 (d), $J = 7.2$	CH_3 of *t*-butyl 8.42‡
15	7.69		CH_3 of *t*-butyl 8.83‡
16	7.82†		CH_3 of isopropyl 8.68 (d),‡ $J = 6.6$ CH_3 of ethyl 8.89 (t),‡ $J = 6.6$
17	7.82†		CH_3 of isopropyl = two (d), 8.89‡ and 9.12,‡ $J = 6.6$ each CH_3 of ethyl 8.65 (t),‡ $J = 6.6$
18	7.65		CH_3 of *t*-butyl 8.49‡ CH_3 of ethyl 8.76–9.0§
19	7.77		CH_3 of *t*-butyl 8.89‡ CH_3 of ethyl 8.61 (t), $J = 7.2$
20	7.61		CH_3 of *t*-butyl 8.46‡ CH_3 of isopropyl = two (d), 8.745 and 9.035, $J = 6.9$ each
21	7.73		CH_3 of *t*-butyl 8.86‡ CH_3 of isopropyl = two (d), 8.585 and 8.625, $J = 6.9$ each
22	7.83	8.585, $J = 7$	
24	7.86		CH_3 of isopropyl 8.615 (d), $J = 7$
25	7.74	8.62	CH_3 of isopropyl = two (d), 8.90 and 9.08, $J = 6.6$ each
26	7.58		α,α-dimethyl 8.54, CH_3 of isopropyl 8.995 (d), $J = 6.6$

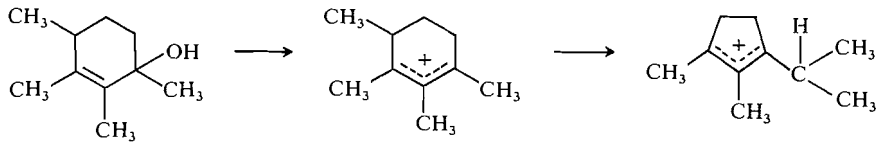
*Unless specified, centers of multiple peaks are quoted relative to internal tetramethylammonium cation = τ 6.90; J in Hz. The solvent is sulfuric acid except for cations **25** and **26** where the solvent was fluorosulfuric acid.
†Peaks overlap completely.
‡Indicates peak used for the area analysis.
§Partially buried.



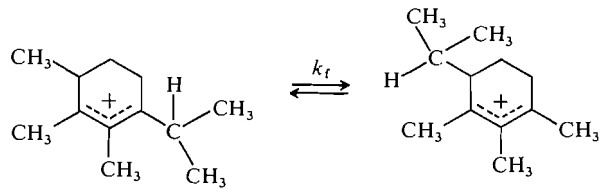
10 $R^1 = Me$; $R^2 = Et$ **11** $R^1 = Et$; $R^2 = Me$
12 $R^1 = Me$; $R^2 = iPr$ **13** $R^1 = iPr$; $R^2 = Me$
14 $R^1 = Me$; $R^2 = tBu$ **15** $R^1 = tBu$; $R^2 = Me$
16 $R^1 = Et$; $R^2 = iPr$ **17** $R^1 = iPr$; $R^2 = Et$
18 $R^1 = Et$; $R^2 = tBu$ **19** $R^2 = tBu$; $R^1 = Et$
20 $R^1 = iPr$; $R^2 = tBu$ **21** $R^1 = tBu$; $R^2 = iPr$

expected to be much slower than the equilibration reactions if sulfuric acid was used as the solvent. To make certain that this reaction was not responsible for the difficulties, we sought first to measure the rate of this reaction and for simplification chose the 1,2,3,4-tetramethyl system **22**, prepared from the allylic alcohol **23** (eq. 3).

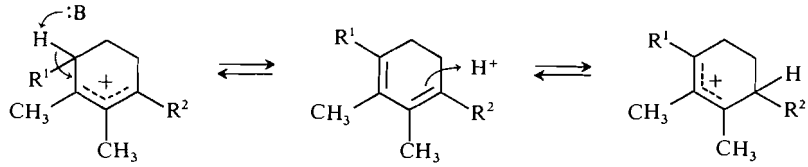
At 25.0°, the first order rate constant for **22** → **24** (also prepared unambiguously from 1-isopropyl-2,3-dimethylcyclopent-2-en-1-ol) was 9×10^{-6} s^{-1} in four different sulfuric acid concentrations (91–100%). The reaction is therefore not base-catalyzed. The rate of this reaction is unlikely to be very dependent on the nature of the R^1 and R^2 alkyl groups and where $R^1 \neq R^2$, two different cyclopentenyl cations would be

[3] 

23 22 24

[4] 

13 12

[5] 

expected under conditions where the equilibration reaction is rapid. Although the rate of the six–five reaction was not measured in the other cases, it was verified that the reaction was very slow on the time scale needed for the six–six equilibration. The rate of this latter equilibration reaction should be dependent on the basicity of the solvent system used (1) and it was desirable to have a rough measure of this. For this study, the rearrangement of ion **13** to the equilibrium mixture of **12** and **13** (eq. 4) was chosen as the representative example since the area analyses are particularly good in this case. The first order rate constants for the forward reaction are reported in Table 2. The results are only approximate for the two weaker acid solvents since substantial rearrangement occurred before the first area measurements could be made. The equilibration reaction is clearly base-catalyzed, thereby implying equilibration mechanism depicted by eq. 5, and in all cases, much faster than the six–five reaction.

TABLE 2. Kinetics of the equilibrium reaction of **13** ⇄ **12** in H_2SO_4 at 25°

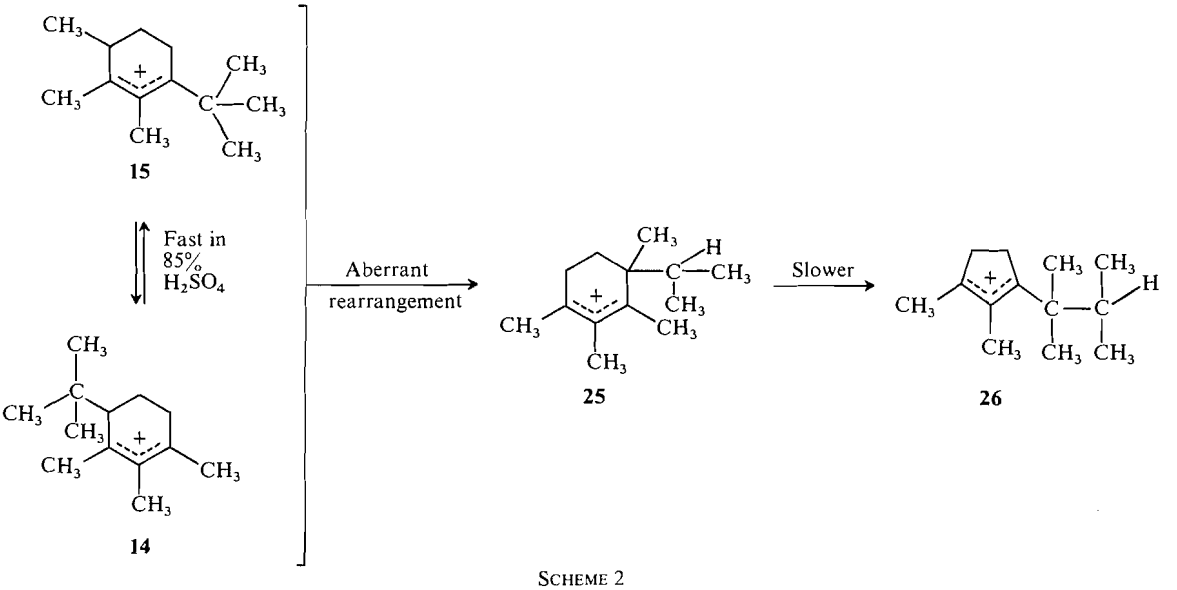
% acid	Actual acid concentration*	k_f (s^{-1})	k_f (s^{-1}) for analogous cyclopentenyl members†
100.0	99.4	1.5×10^{-3}	4.7×10^{-5}
97.1	96.5	5.0×10^{-3}	1.6×10^{-4}
95.3	94.7	*ca.* 6×10^{-3}	3.1×10^{-4}
93.8	93.2	*ca.* 7×10^{-3}	$4\text{–}6 \times 10^{-4}$

*Corrected to take into account the water produced during the ion preparation.
†Reference 1.

The fact that the equilibrations are 15–30 times faster in the cyclohexenyl series compared to the cyclopentenyl (Table 2) was expected from the prior results of Deno *et al.* (7) on the pK_a's and H–D substitution rates of both cyclohexenyl and cyclopentenyl cations.

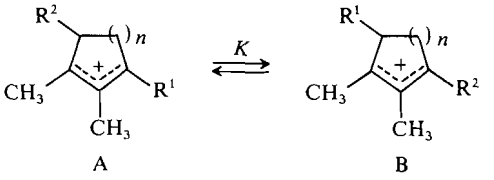
It was clear, therefore, that the problem observed with the *t*-butyl compounds was not due to a six–five reaction. However, this aberrant reaction of the *t*-butyl ions also appeared to be solvent-independent and it proved possible to obtain some equilibrium constant measurements by working in 85% H_2SO_4 at 0°. This percentage of acid is the lowest possible if one wishes to retain relatively sharp peaks for the ion n.m.r. spectra and from extrapolation of the results in Table 2, would be predicted to result in a rapid six–six equilibration, even at 0°. Even so, the aberrant *t*-butyl ion rearrangement eventually causes enough spurious peaks in the n.m.r. spectrum so that one becomes uncertain whether a given peak is in fact a peak of the minor isomer or some other ion peak. Thus, in Table 3, the equilibrium constant figures quoted are minimum values in the case of the *t*-butyl substituted ions.

The aberrant rearrangement was eventually



SCHEME 2

TABLE 3. Equilibrium constants for the cations



Cation	$K = [B]/[A]$ $n = 1$*	$n = 2$†
R^1 = ethyl; R^2 = methyl	1.6	1.35
R^1 = isopropyl; R^2 = methyl	2.6	2.0
R^1 = *t*-butyl; R^2 = methyl	18	≥6.1‡
R^1 = isopropyl; R^2 = ethyl	1.7	1.2
R^1 = *t*-butyl; R^2 = ethyl	11.4	≥5.3‡
R^1 = *t*-butyl; R^2 = isopropyl	5.5	≥3.4‡

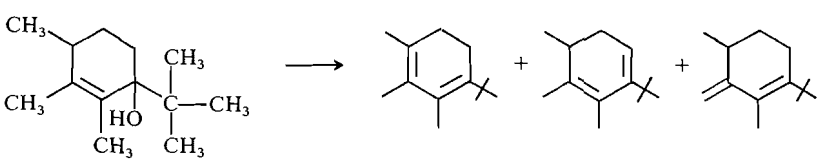
*Taken from ref. 1.
†The error is estimated as ±10% except for the *t*-butyl substituted cations.
‡Obtained in 85% H_2SO_4. The remainder were measured in 95% H_2SO_4.

shown to be as depicted in Scheme 2, using the methyl-*t*-butyl system **14**→**15** as an example. The structural assignments of ions **25** and **26** are based solely on the observed n.m.r. spectra but these are so distinctive that the assignments are unequivocal.

That it is isomer **15** which reacts was shown by dehydrating the alcohol **6** to give the three isomeric dienes **27**, **28**, and **29** (eq. 6), each separated by preparative g.l.c. When these dienes are added to the much stronger acid, FSO_3H, the allylic cations which are formed do not equilibrate with the other isomer. Dienes **28** and **29** produce only ion **15** while diene **27** gives a non-equilibrium mixture of both **15** and **14**. The ion **15** rearranges to the ion **25** with a first-order rate constant of 8.5×10^{-4} s^{-1} at 0°, while ion **14** much more slowly forms a different, unidentified, product, possibly the six–five rearrangement product analogous to ion **24**.

There appears to be an intermediate formed in the conversion of ion **15** to **25** but no definite structural assignment for this ion was possible. The rearrangement reactions in the ethyl–*t*-butyl and isopropyl–*t*-butyl ions are likely to be analogous to **15** but these were not investigated in detail. This rearrangement occurs, however, *only* in the *t*-butyl-substituted ions.

[6]



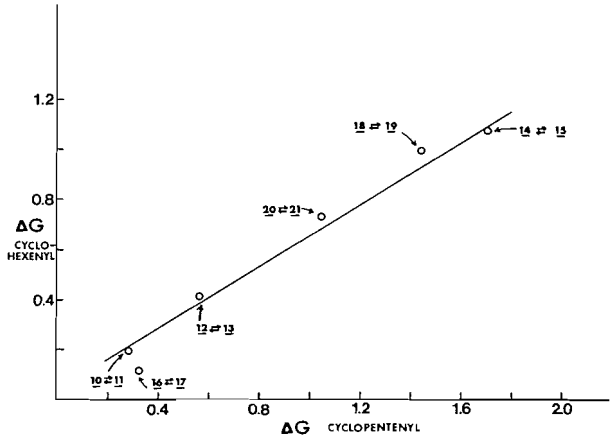


FIG. 1. Linear free energy plot of the related cyclopentenyl and cyclohexenyl cation equilibrium constants.

The aberrant ion **25** further rearranges to the cyclopentenyl cation **26** ($k = 2 \times 10^{-3}$ s^{-1} at 30°), but this process is entirely predictable, based on previous work on very similar systems (2).

Discussion

The equilibrium results for the cyclohexenyl and cyclopentenyl series are compared in Table 3. If one accepts the *t*-butyl-substituted cyclohexenyl ion equilibria as equal to the stated values, then one has an extremely close correlation between the two series and this is shown graphically in Fig. 1. The free energy difference, ΔG, between any two alkyl groups in a cyclohexenyl cation is only about 60% of the value for the corresponding cyclopentenyl series. If all of these equilibrium constants are the result of steric effects, they would have to have occurred because of slightly lower differential steric interactions of the larger alkyl group with the C-1 and -4 positions and to explain the numerical values in both series, the interaction with C-1 would, of necessity, have to be dominant. It is certainly possible that this interaction would be reduced in the cyclohexenyl cations because of the changed situation at C-6 (C-5 in the cyclopentenyl cations).

Simple cyclohexenyl cations are, however, less stable than cyclopentenyl cations for reasons which are not totally understood. One of us has suggested previously (2) that this may be the result of the cyclopentenyl cation possessing a quasi-6π-electron system *or* that direct 1,3 π-overlap stabilization, expected to be stronger in the cyclopentenyl cations, is involved. Paradoxically, if the results of this work are in fact due to differential C—H hyperconjugation, then the cyclohexenyl cations must be less stable because they are less efficient in delocalizing the charge out of the basic allyl cation system into the alkyl substituents, compared to a cyclopentenyl cation.

One has therefore two plausible explanations, admittedly of the assumed cause–expected effect type, each singly based on the effects one is trying to separate. We remain pessimistic that the problem of hyperconjugation can ever be "solved" by using the "big four" alkyl group series, even where the hyperconjugation order is observed.

Experimental

The various instruments and general procedures used in this work are described in the preceding paper (1) together with a description of the various abbreviations used in the text.

Preparation and Analysis of the Cations

The procedures were virtually identical to those used for the cyclopentenyl cations (1). The spectra are actually very similar in many ways and this has helped in assigning the n.m.r. peaks. In Table 1, we report those peaks in the n.m.r. spectrum which are distinctive for the particular cation. In general, the C-1 and -3 methyl groups, where present, absorb about τ 7.2, and since these are broad peaks, they overlap from both isomers of the equilibrium "pair". The same situation exists with the C-4 and -6 protons (*c.a.* 6.5–7.1) and the C-5 protons (*ca.* 8.0).

Kinetic Measurements

The first order cation **22**→ cation **24** rearrangement was

followed by periodically measuring the n.m.r. spectra of thermostated (25.0°) solutions. The area analysis is not very accurate since the rather broad C_1–C_3 methyl proton peaks had to be used; the cyclohexenyl cation peak coming at τ 7.25 (6H) and the cyclopentenyl at τ 7.09 (3H). The base-catalyzed equilibration reactions (cation **12** ⇄ cation **13**) were carried out at the same temperature and the data were analyzed for reversible first order kinetics. The area analyses used the high field isopropyl methyl peaks of **13** and the C-4 methyl and C-1 isopropyl methyl peaks of **12**. The first order cation **15** → cation **25** kinetics were measured in fluorosulfuric acid at 0° using the *t*-butyl peak in **15** and either the C-4 methyl or C-4 isopropyl methyl peaks in **25**. The first order cation **25** → cation **26** kinetics were measured in fluorosulfuric acid at 25° using the C-2 methyl peaks of each ion for the area analysis.

4-Carboethoxy-2,3-dimethylcyclohex-2-en-1-one

Hagemann's ester (91.8 g, 0.504 mol) was added with stirring to sodium hydride (28 g in 56% oil dispersion, 0.65 mol) in dry toluene solvent (300 ml) at room temperature. After stirring for 2 h, hydrogen evolution ceased and iodomethane (84.5 g, 0.595 mol) was added dropwise together with 2 drops of ethanol and the reaction mixture was refluxed for 8 h. Work-up in the usual way and distillation of the residue through an 18 in. spinning band column (18:1 reflux ratio) gave 87 g (88%) of the title compound, b.p. 139–140°/8 mm, reported (8), 144–146/13 mm. Partial n.m.r. spectrum: 8.74 (t) $J = 6.9$ Hz (3H); 8.26 (3H); 8.05 (3H); 6.77 (m) (1H); 5.85 (q) $J = 7$ Hz (2H).

*2,3,4-Trimethylcyclohex-2-en-1-one (**1**)*

A second methylation, using 51.0 g, 0.256 mol, of the above ester was carried out, as above, to yield a fraction, b.p. 136–155°, containing both the 2,2- and 2,4-dimethyl adduct. This fraction was hydrolyzed with a refluxing (10 h) 10% alcoholic sodium hydroxide solution, under nitrogen. The solvent was stripped off and the solution acidified with 6 *M* HCl at 0°. This mixture was refluxed until carbon dioxide evolution ceased and then cooled and extracted with ether (3 × 30 ml). The combined ether layers were washed twice with dilute sodium carbonate and then water and finally dried over anhydrous $MgSO_4$. Distillation of the residue through a spinning band column gave 6.2 g (18%) of the title compound, b.p. 93–98°/8 mm. N.m.r.: 8.79 (d) $J = 6.9$ Hz (3H); 8.30 (3H); 8.09 (3H); i.r.: 1675 and 1645 cm^{-1}; semicarbazone 208–210°, reported (4), 210°.

*4-Ethyl-2,3-dimethylcyclohex-2-en-1-one (**2**)*

The preparation of **1** was followed (except that a 36 h reflux was used) using iodoethane. The carboethoxy compound had b.p. 141–148°/8 mm and the title ketone b.p. 98–102°/8 mm. The overall yield was 19%. N.m.r.: 9.00 (t) $J = 7$ Hz (3H); 8.32 (3H); 8.10 (3H); i.r.: 1675 and 1635 cm^{-1}; semicarbazone had m.p. 192–194°.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.9; H, 10.59. Found: C, 79.02, H, 10.48.

*4-Isopropyl-2,3-dimethylcyclohex-2-en-1-one (**3**)*

The preparation of **1** was followed (72 h reflux) using isopropyl iodide. The carboethoxy compound had b.p. 137–147°/8 mm and the title compound b.p. 48.5–51°/0.05 mm. N.m.r.: 8.98 and 9.15, two (d), $J = 6.2$ Hz each (3H each); 8.28 (3H); 8.08 (3H); i.r. 1678, 1650, 1378, and 1372 cm^{-1}. In another preparation, a very impure product was obtained which necessitated a preparative g.l.c. separation to obtain the pure title compound.

The Allylic Alcohols

These were prepared in a manner similar to previous descriptions (1–3). The n.m.r. spectra of these indicate the presence of both *cis* and *trans* isomers and the n.m.r. spectra are therefore quite complex. Descriptions of the n.m.r. and i.r. spectra can be found in ref. 9.

*1,2,3,4-Tetramethylcyclohex-2-en-1-ol (**23**)*

The compound had b.p. 75–77°/0.5 mm, yield 85%.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 78.36; H, 11.73.

*1-Isopropyl-2,3,4-trimethylcyclohex-2-en-1-ol (**5**)*

The compound had b.p. 85–92°/0.35 mm, yield 86%.

Anal. Calcd. for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.79; H, 12.41.

*1-t-Butyl-2,3,4-trimethylcyclohex-2-en-1-ol (**6**)*

The compound had b.p. 75–82°/0.05 mm.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.25; H, 12.23.

*4-Ethyl-1,2,3-trimethylcyclohex-2-en-1-ol (**4**)*

The compound had b.p. 57–59°/0.15 mm.

Anal. Calcd. for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 76.17; H, 11.41.

*1-Isopropyl-2,3-dimethyl-4-ethylcyclohex-2-en-1-ol (**7**)*

The compound had b.p. 82–89°/0.2 mm.

Anal. Calcd. for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.88; H, 11.80.

*1-t-Butyl-2,3-dimethyl-4-ethylcyclohex-2-en-1-ol (**8**)*

The compound had b.p. 87–92°/0.1 mm.

Anal. Calcd. for $C_{14}H_{26}O$: C, 79.94; H, 12.46. Found: C, 80.85; H, 11.88.

*1-t-Butyl-2,3-dimethyl-4-isopropylcyclohex-2-en-1-ol (**9**)*

The compound had b.p. 124–127°/0.8 mm.

Anal. Calcd. for $C_{15}H_{28}O$: C, 80.29; H, 12.58. Found: C, 80.38; H, 12.46.

*Dehydration of Alcohol **6***

Alcohol **6** was dehydrated in the injection port (220°) of a g.l.c. column and the alkenes separated using a 6 ft × 1/4 in. column of 20% SE-30 on Chromosorb W at 124°. He flow 30 ml/min, employing sample sizes of 25 μl. The n.m.r. spectra are definitive in distinguishing the three isomers, one has =CH—, one has $=CH_2$, and the remaining one has no low field peaks.

*Low Retention Product (58 min, 37% of the total): 3-t-Butyl-1,2,6-trimethylcyclohexa-1,3-diene (**28**)*

Partial 100 MHz n.m.r.: 9.185 (d) $J = 6.5$ Hz (3H); 8.85 (9H); 8.24 (b) (3H); 8.12 (b) (3H); 4.5 (m) (1H).

*Middle Retention Product (73 min, 43% of the total): 1-t-Butyl-2,4-dimethyl-3-methylenecyclohex-1-ene (**29**)*

Partial 100 MHz n.m.r.: 8.965 (d) $J = 6.5$ Hz (3H); 8.79 (9H); 8.04–8.14 (b); 5.15 (b) and 5.35 (b) (2H).

*High Retention Product (85 min, 20% of the total): 4-t-Butyl-1,2,3-trimethylcyclohexa-1,3-diene (**27**)*

Partial 100 MHz n.m.r.: 8.81 (9H); 8.26, 8.15, 8.13 (9H).

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