(7) D. D. Tanner, D. Darwish, M. W. Mosher, and N. J. Bunce, *J. Am. Chem. Soc.*, **91**, 7398 (1969).

(8) (a) P. S. Skell and K. J. Shea, *J. Am. Chem. Soc.*, **94**, 6550 (1972); (b) J. G. Traynham, E. E. Green, Y.-S. Lee, F. Schweinsberg, and C. E. Low, *ibid.*, **94**, 6552 (1972); (c) P. S. Skell, R. R. Pavlis, D. C. Lewis, and K. J. Shea, *ibid.*, **95**, 6735 (1973); (d) K. J. Shea, D. C. Lewis, and P. S. Skell, *ibid.*, **95**, 7768 (1973); (e) D. D. Tanner, J. E. Rowe, T. Pace, and Y. Kosugi, *ibid.*, **95**, 4705 (1973); (f) J. G. Traynham and Y.-S. Lee, *ibid.*, **96**, 3590 (1974); (g) D. D. Tanner, Y. Kosugi, R. Arhart, N. Wada, T. Pace, and T. Ruo, *ibid.*, **98**, 6275 (1976).

(9) P. S. Skell, D. L. Tuleen, and P. D. Readio, *J. Am. Chem. Soc.*, **85**, 2849 (1963), reported the formation of optically active bromination product from optically active 1-chloro-2-methylbutane, data which indicate that a chlorine-bridged radical intermediate is formed before loss of chirality but do not reveal anything about the kinetic effect of the chloro substituent on the hydrogen-abstraction reaction.

(10) (a) J. G. Traynham and W. G. Hines, *J. Am. Chem. Soc.*, **90**, 5208 (1968); (b) J. H. B. Chenier, J. P.-A. Tremblay, and J. A. Howard, *ibid.*, **97**, 1618 (1975).

(11) The chloro substituent in radicals **6** and **7** must promote loss of bromine atom, because bromination of 2,3-dimethylbutane under the same conditions gave only 2,3-dibromo-2,3-dimethylbutane.

(12) A mixture of **8** and its isomer, 3-chloro-2,3-dimethyl-1-butene (3:2 by GC and NMR data), prepared by addition of hydrogen chloride to 2,3-dimethyl-1,3-butadiene at −30 °C [L. F. Hatch and G. E. Journey, *J. Am. Chem. Soc.*, **75**, 3712 (1953)] and dissolved in carbon tetrachloride, was rapidly converted by excess bromine to products identified by ^{1}H NMR (CCl_4) data as a 3:2 mixture of **5** and its isomer, 1,2-dibromo-3-chloro-2,3-dimethylbutane.

(13) If [Br·] is constant and selective reversal of hydrogen abstraction from isomeric positions is unimportant, the rate of disappearance of **1** can be represented by the pseudo-first order equation

$$-\frac{d[1]}{dt} = (k_2 + k_3) \qquad [1]$$

from which the integrated expression

$$\ln(1 - F) = -(k_2 + k_3)t$$

is obtained (F = fraction of reaction). By a nonlinear least-squares treatment, the slope of the linear plot was -2.90×10^{-4} s^{-1}.

(14) Analysis by GC was performed to determine the ratio of reactants relative to carbon tetrachloride in the unreacted starting mixture and in each sample. The relative rate was then calculated from the relationship

$$\frac{k_{\text{halide}}}{k_{\text{alkane}}} = \frac{\log \dfrac{(\text{halide}/CCl_4)_{\text{final}}}{(\text{halide}/CCl_4)_{\text{initial}}}}{\log \dfrac{(\text{alkane}/CCl_4)_{\text{final}}}{(\text{alkane}/CCl_4)_{\text{initial}}}}$$

For further discussion of this method, see ref 5.

(15) For the **11**:**12** competition, the rate ratio was not changed significantly by the addition of *N*-bromosuccinimide to the reaction mixture to remove hydrogen bromide and maintain bromine concentration.[8d] Earlier workers reported 0.4 for this rate ratio.[8d] Since our value of 3.6 is consistent with all the other competitions we measured between a vicinal tertiary position in RCl and a tertiary position in the alkane, we are not able to account for the lower value reported.

(16) P. S. Fredricks and J. M. Tedder, *J. Chem. Soc.*, 144 (1960).

(17) To a substantial degree, this argument is equivalent to proposing that neighboring halogen participation increases as the degree of C–H bond breaking increases (electron density between C and H decreases). Relative rates for some other radical halogenations are supportive of this point of view. Cyclohexane undergoes chlorination (little C–H bond breaking at the transition state) more rapidly than does toluene (electron withdrawal, rate retardation by phenyl substituent), but toluene undergoes bromination (more C–H bond breaking at transition state; phenyl participation by resonance) much faster than does cyclohexane.[18]

(18) G. A. Russell and H. C. Brown, *J. Am. Chem. Soc.*, **77**, 4578 (1955).

(19) J. H. Markgraf, *J. Chem. Eng. Data*, **13**, 447 (1968).

(20) M. Gaudry and A. Marquet, *Tetrahedron*, **26**, 5611 (1970), describe a procedure for preparation of bromomethyl ketones on which our procedure was based.

(21) M. S. Malinovskii and A. G. Yudasina, *Zh. Obshch. Khim.*, **29**, 1889 (1959); *Chem. Abstr.*, **54**, 8772*a* (1960).

(22) F. Schweinsberg and J. G. Traynham, *Tetrahedron Lett.*, 3809 (1970).

(23) M. Bartok, B. Kozma, and N. I. Shuikin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1241 (1966); *Chem. Abstr.*, **65**, 1854b (1966).

(24) E. Z. Said and A. E. Tipping, *J. Chem. Soc., Perkin Trans. 1*, 1986 (1972).

Cyclohexadienyl Cations. 7. Kinetics and Mechanism of the Acid-Catalyzed Dienol–Benzene Rearrangement

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Abstract: The rates of the acid-catalyzed dienol–benzene rearrangement for 4-trichloromethyl-4-methylcyclohexadienol (**3**) and 4,4-dimethylcyclohexadienol (**4**) are reported. While **3** undergoes the dienol–benzene rearrangement in concentrated mineral acids, **4** undergoes the same reaction in dilute buffers. Interestingly **4** also undergoes a concomitant allylic rearrangement not observed for **3**. Certain mechanistic conclusions for **3** and **4** are derived and compared. α-D effects are reported for both **3** and **4**. Stereochemical assignments for both isomers of **3** and of solvolysis products are made using NMR shift reagents.

For some time now we have been interested in the molecular details of the dienone–phenol and related rearrangements.[3-8] All of the results thus far obtained in our laboratory, as well as the work of Waring,[9] provide substantial support for the mechanism outlined in Scheme I for the dienone–phenol rearrangement.

In this paper we report results for the dienol–benzene rearrangement, a reaction which is formally similar to the dienone–phenol rearrangement but which provides several interesting differences. A representative scheme for this reaction is provided in Scheme II.

A notable difference between this reaction and the dienone–phenol rearrangement is the absence of a protonated carbonyl group as an intermediate. This is thought to seriously affect the kinetic acidity dependence of the dienone–phenol rearrangement because of strong intermolecular hydrogen bonding to neighboring water molecules. In the dienol–benzene rearrangement no such interaction is possible and it is of some significance to determine the kinetic acidity dependence for this reaction.

Although 4,4-dimethylcyclohexadienone (**1**) undergoes the dienone–phenol rearrangement readily,[3-9] 4-trichloromethyl-4-methylcyclohexadienone (**2**) protonates in acid, but does not rearrange unless very forcing conditions are used, where more complex reactions can occur.[10] In contrast, both of the corresponding dienols **3** and **4** do rearrange in acid,

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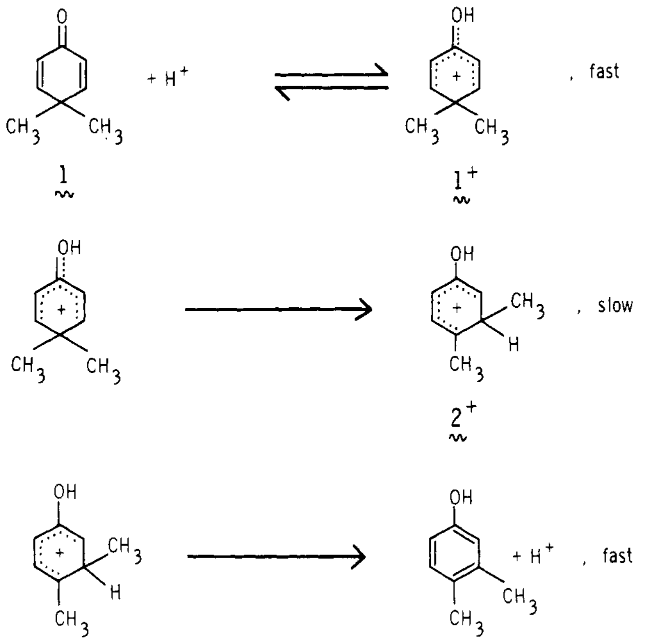
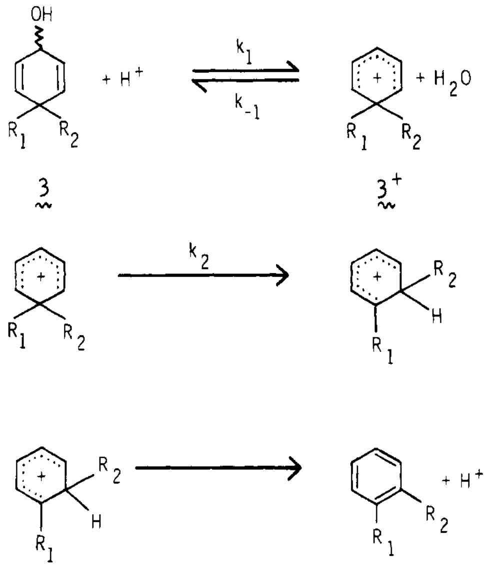
Scheme I



Scheme II

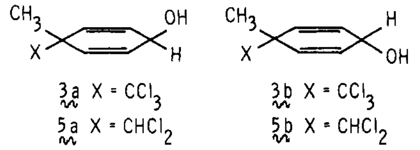


though **4** reacts 10^8 times faster than **3**.[7] Since there are also substantial other differences in the behavior of the two compounds, we shall discuss them separately.

Stereochemistry of 4-Trichloromethyl-4-methylcyclohexadienols 3a and 3b. Initially, the trichloromethyl dienone **2** was reduced to the dienol **3** by the Meerwein-Ponndorf-Verley method, as reported by Plieninger.[11] The dienol isolated after crystallization was a single isomer, mp 127-128 °C, characterized by the methyl peak at δ 1.54 in the NMR spectrum. In order to understand this apparent stereoselective reduction, a detailed study of the stereochemistry of reduction in this system was undertaken.

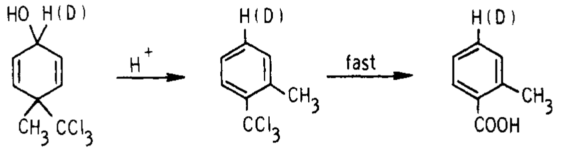
Reduction of the dienone **2** with $NaBH_4$ in ethanol gave 30% of the above dienol isomer and 70% of the other isomer with mp 68-69 °C, methyl signal at δ 1.50. The two could be separated by fractional crystallization, although the minor isomer crystallized preferentially. The minor isomer was assigned as the *E* isomer **3a**, since the methyl signal was shifted ca. 12% farther downfield than the *Z* isomer **3b** upon addition of the shift reagent, Eu(fod)$_3$.[12]

Reduction of the dienone with $LiAlH_4$ in ether was more complex and gave ratios of the dienols which varied with reduction time. In addition, two other products formed slowly, and were identifed as the dichlorodienols **5a** and **5b**. These were



independently synthesized by reduction of 4-dichloromethyl-4-methycyclohexadienone.[13] It was shown that the initial reduction of dienone **2** gave the 30:70 ratio of dienols **3a**:**3b** within 10 s. This result is reasonable assuming that initial attack on the dienone is slightly favored from the least hindered side. Moreover, we noted that reduction of the *Z* isomer **3b** to **5b** was substantially faster than the corresponding reduction of **3a**.

Rearrangement of 4-Trichloromethyl-4-methylcyclohexadienols 3a and 3b in Aqueous Acid. The trichloromethyldienol **3a** (or **3b**) rearranges smoothly in aqueous solutions of $HClO_4$ and H_2SO_4 to *o*-toluic acid (λ 277 nm) giving excellent first-order kinetics. It can be independently shown that the intermediate *o*-methylbenzotrichloride solvolyzes to *o*-toluic acid rapidly under the conditions of these kinetic determinations. Thus the overall scheme may be written in the following way.



The same product would of course result whether the methyl or the trichloromethyl group migrates. Methyl migrates in more complex systems;[14] we have proven conclusively that it does also in the present system. Thus, the deuterated analogue of **3** was synthesized by use of $LiAlD_4$ and the solvolysis carried out to *o*-toluic acid. This compound was over 95% monodeuterated as shown by mass spectrometry. The position of the deuterium was shown to be para to the carboxyl group by $LiAlH_4$ reduction to *o*-methylbenzyl alcohol and NMR analysis with the shift reagent, Eu(fod)$_3$.[12] The signal for the C-6 proton was shifted free of the other aromatic signals, and appeared as a clean doublet, $J = 9$ Hz, thus demonstrating that a hydrogen was at C-5 and a deuterium at C-4.

Tables I and II give the results of our kinetic investigations in $HClO_4$ and H_2SO_4. The kinetic data for the nucleophilic acid HCl are given in Table III. All of these results are shown graphically in Figure 1.

As can be seen, rates of rearrangement can only be measured conveniently at moderately high acidities, clearly in the acidity function range.[15] The response of the rate (k_{obsd}) to changes in acidity as measured by H_0 for both $HClO_4$ and H_2SO_4 is very steep.

$$HClO_4\text{: } \log k_{\mathrm{obsd}} = (-1.70 \pm 0.02)H_0 - (7.99 \pm 0.06) \quad (1)$$

$$H_2SO_4\text{: } \log k_{\mathrm{obsd}} = (-1.68 \pm 0.01)H_0 - (8.17 \pm 0.03) \quad (2)$$

That the slopes of these plots is substantially greater than unity suggests a carbonium ion intermediate[15] for this reaction as well as perhaps the choice of a "carbonium ion" acidity function such as H_R. The H_R acidity function is based on the ionization of triarylcarbinols, a process which more clearly resembles the dienol-benzene rearrangement.

$$H_R \text{ acidity function: } Ar_3COH + H^+ \rightleftharpoons Ar_3C^+ + H_2O$$

The H_R acidity function correlates the rate data equally well but with slopes closer to unity.

$$HClO_4\text{: } \log k_{\mathrm{obsd}} = (-0.82 \pm 0.01)H_R - (8.48 \pm 0.05)$$

$$H_2SO_4\text{: } \log k_{\mathrm{obsd}} = (-0.79 \pm 0.02)H_R - (8.17 \pm 0.03)$$

Table I. Rates of Rearrangement of 4-Trichloromethyl-4-methylcyclohexadienol in $HClO_4$ at 25 °C[a]

Wt % $HClO_4$	$-H_0$	10^5k_{obsd}
34.17	1.89	1.50
37.93	2.18	4.78
41.54	2.51	20.4
44.70	2.83	91.8
48.13	3.24	323.
52.83	3.92	4480.

[a] Log $k_{obsd} = (-1.70 \pm 0.02)H_0 - (7.99 \pm 0.06)$. Log $k_{obsd} = (-0.82 \pm 0.01)H_R - (8.48 \pm 0.05)$.

Table II. Rates of Rearrangement of 4-Trichloromethyl-4-methylcyclohexadienol in H_2SO_4 at 25 °C[a]

Wt % H_2SO_4	$-H_0$	10^5k_{obsd}
35.45	2.18	1.16
37.98	2.36	2.33
41.90	2.68	7.59
44.94	2.94	20.9
48.04	3.22	75.7
52.17	3.63	329.
54.33	3.86	746.
56.69	4.13	2010.
60.08	4.54	11 000.

[a] Log $k_{obsd} = (-1.68 \pm 0.01)H_0 - (8.60 \pm 0.02)$. Log $k_{obsd} = (-0.79 \pm 0.02)H_R - (8.17 \pm 0.03)$.

Table III. Rates of Rearrangement of 4-Trichloromethyl-4-methylcyclohexadienol in HCl at 25 °C

Wt % HCl	M HCl	$-H_0$	10^5k_{obsd}
20.78	6.29	2.26	1.13
25.41	7.83	2.80	5.51
28.77	9.04	3.23	10.1
32.60	10.39	3.74	17.5
35.86	11.60	4.25	27.8

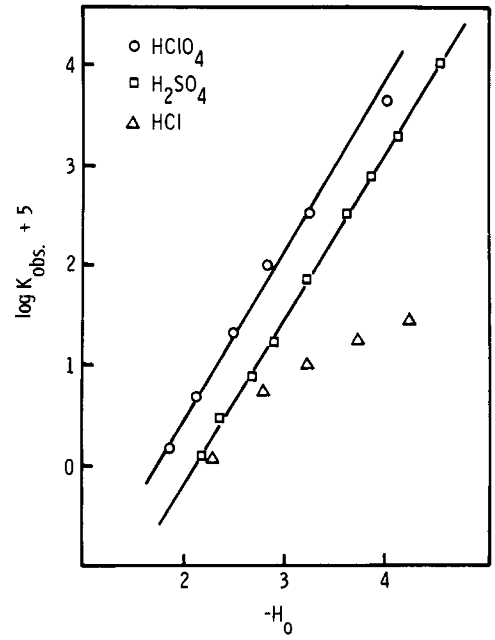


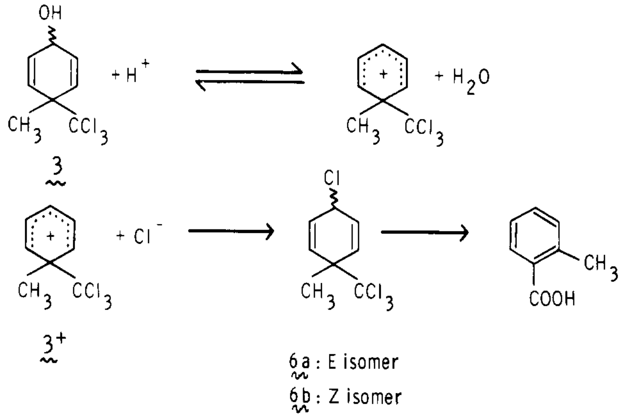
Figure 1. Plots of log k_{obsd} vs. $-H_0$ for the rearrangement of **3a** in $HClO_4$, H_2SO_4, and HCl at 25 °C.

It is clear from this analysis that the transition state in the dienol-benzene rearrangement has substantial carbonium ion character.

An examination of the data in both Table III and Figure 1 reveals that the acidity dependence for this reaction is quite different in HCl solutions. The much shallower acidity dependence at high HCl concentrations suggests a change in mechanism. That this is the case is shown by the following argument. A 95% yield of 4-trichloromethyl-4-methylcyclohexadienyl chloride, as a mixture of the *E* and *Z* isomers **6a** and **6b**, was isolated from a solution containing 10 mL of 35.86% HCl and 5 mL of dioxane after 3 min, during which time less than 5% conversion to *o*-toluic acid would have occurred. In addition, a sample of the authentic chloride mixture prepared as described below produces *o*-toluic acid with a first-order rate constant of 1.5×10^{-4} s^{-1} in 32.60% HCl whereas the rate constant for **3** in this solution is 1.8×10^{-4} s^{-1}.

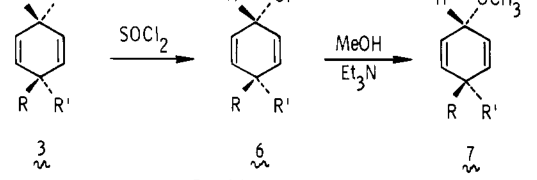
Thus it would appear that in concentrated HCl solutions $\mathbf{3}^+$ is rapidly captured by Cl^- and then undergoes solvolysis ultimately to *o*-toluic acid (Scheme III).

Scheme III



The Nature of the Rate-Determining Step for 3. It is clear from Scheme II that the step leading to $\mathbf{3}^+$ (k_1) or its rearrangement (k_2) would have transition states with substantial carbonium ion character. Therefore, generation of $\mathbf{3}^+$ in a nucleophilic solvent under nonequilibrating conditions and determination of the amount of rearrangement product gives a direct measure of k_{-1}/k_2 (see Scheme II) and thus the rate-limiting step may be deduced. Toward this end we studied the solvolysis of a mixture of isomers of **6** in methanol buffered with triethylamine. It has been shown that methanol is only two to three times more nucleophilic than water toward covalent[17,18] and carbonium ion[19] substrates.

The mixture of allylic chlorides **6a** and **6b** was best prepared by the reaction of the alcohols **3a** or **3b** with $SOCl_2$. However, the two alcohol isomers behaved differently toward this reagent. The *Z* isomer **3b** in CCl_4 gave a 48:52 ratio of the *Z* to *E* chlorides **6b**:**6a**, characterized by NMR methyl signals at δ 1.49 and 1.56, respectively. However, the *E* isomer **3a** gave mainly the *E* isomer **6a** (81% in $CHCl_3$ and greater than 98% in CCl_4). These differences presumably reflect conformational differences in the alcohols **3a** and **3b**.[16]



a. R = CCl_3, R' = CH_3
b. R = CH_3, R' = CCl_3

Upon storage, one or both of these chlorides is converted slowly to *o*-methylbenzotrichloride. Solvolysis of a freshly

Table IV. α-Deuterium Isotope Effects in the Acid-Catalyzed Rearrangement of **3a**

% $HClO_4$	$-H_0$	k_H/k_D[a]
34.17	1.89	1.122 ± 0.003
37.93	2.18	1.110 ± 0.006
41.68	2.51	1.110 ± 0.007
44.82	2.84	1.123 ± 0.008

[a] Average $k_H/k_D = 1.118 \pm 0.009$.

Table VI. Rates of Isomerization of 4,4-Dimethylcyclohexa-2,5-dienol in Phosphate Buffers at 26 °C ($\mu = 0.32$, NaCl)[a]

$[NaH_2PO_4]$	$[Na_2HPO_4]$	pH	$10^5 k_i$, s^{-1}	$k_i/[H^+]$, $M^{-1} s^{-1}$
0.010	0.0020	5.990	3.01	29.5
0.025	0.0050	6.002	2.90	29.2
0.050	0.0100	6.017	2.93	30.5
0.080	0.0320	6.031	2.93	31.5
0.100	0.0200	6.041	2.62	28.9

[a] $k_i = 30.0 \pm 1.1$.

Table VII. Rates of Rearrangement of 4,4-Dimethylcyclohexa-2,5-dienol in Aqueous Buffers at 25 °C ($\mu = 0.1$, NaCl)[a]

HX	[HX]	[NaX]	pH	$10^5 k_r$, s^{-1}	k_r, M^{-1} s^{-1}
HOAc	0.025	0.025	4.602	3.56	1.42
HOAc	0.050	0.050	4.590	3.48	1.35
HOAc	0.096	0.020	3.855	18.7	1.35
HOAc	0.480	0.100	3.898	16.4	1.30
HCOOH	0.020	0.020	3.583	38.5	1.19
HCOOH	0.100	0.100	3.603	39.8	1.21
HCl			3.490	43.7	1.35
DCl			3.483	152	4.63

[a] $k_r = 1.31 \pm 0.08$ $M^{-1} s^{-1}$. $k_{D_2O}/k_{H_2O} = 3.4$.

prepared sample of **6** in methanol with or without triethylamine buffer afforded *solely* a mixture of the methyl ethers **7a** or **7b**, characterized by NMR peaks at δ 1.53 and 1.47, respectively. The stereochemistry was determined by use of $Eu(fod)_3$ and by converting the *Z* isomer of the alcohol (δ 1.50) into the *Z* ether (δ 1.47) by methylation with dimethyl sulfate and base.

Importantly, in the solvolysis, there was no detectable amount by GLC (1% could easily have been detected) of the rearrangement product, methyl *o*-toluate. Using pure **6a**, the reaction was found to proceed with 60% inversion. This is not a surprising result for a stabilized secondary system.[10] Solvolysis of the chlorides in aqueous acetone gave the alcohols **3a** and **3b** with similar stereochemistry. Thus, 3^+ is preferentially captured by the solvent rather than undergoing rearrangement. Extrapolating these results to water, this observation demands that k_{-1}/k_2 (Scheme II) is greater than 100. This, of course, means that k_2 in the acid-catalyzed dienol-benzene rearrangement of **3** is rate determining. An analogous rate-determining methyl migration has also been postulated for the dienone-phenol rearrangement.

In an effort to gain supporting information concerning the mechanism of the acid-catalyzed rearrangement of **3** we have determined the α-deuterium isotope effect for this reaction. These results are reported in Table IV. As expected for a carbonium ion process[21] the α-D effect is substantially greater than unity although less than the maximum value of 1.22 suggested by Shiner for oxygen leaving groups[22] provided that there is no covalent attachment of the leaving group to the potential carbonium ion center. This should be the case for the acid-catalyzed rearrangement of **3** (vide supra) even though the α-D effect is approximately one-half this maximum value. It has been suggested[22] that even limiting α-D effects may depend on the detailed structure of the carbonium ions involved and since this bis-allylic cation (3^+) is quite different in structure from Shiner's systems this apparent discrepancy may be explained using Schleyer's interpretation. Regardless of the detailed interpretation of the magnitude of the α-D effect observed for the rearrangement of **3** this α-D effect is clearly consistent with the formation of a carbonium ion intermediate.

Rearrangement of 4,4-Dimethylcyclohexadienol (4) in Aqueous Acid. In contrast to the high acidities required for the rearrangement of **3**, **4** rearranges at convenient rates in acetate buffers! Moreover, when **4** is dissolved in dilute acid there is observed the formation of a new species (λ_{max} 259 nm, ϵ 1600). This intermediate forms *o*-xylene 20 times slower than it is formed. Monitoring this reaction by NMR spectroscopy in 80% CD_3COCD_3 and 20% D_2O containing 0.01 M DCl indicates that this new species is very similar to **4**. For example, the slightly broadened singlet for the vinyl hydrogens in **4** at δ 5.63 is replaced by a complex multiplet centered at δ 5.96. The methyl resonances are significantly broadened and shifted upfield slightly: δ 1.08 and 1.02 to δ 0.99 and 0.94, respectively. Eventually the spectrum decays to that of *o*-xylene: δ 7.03 (4 H) and 2.17 (CH_3, 6 H). These results indicate that in acid solution **4** undergoes isomerization to 6,6-dimethylcyclohexa-2,4-dienol (**8**) in an equilibrium reaction followed by a slower reaction leading to *o*-xylene. From the spectral parameters published[23] for 5,5-dimethyl-1,3-cyclohexadiene (λ_{max} 257 nm, ϵ_{max} 4300) we estimate the equilibrium constant (**8**/**4**) to be 0.6 independent of pH.

The kinetic data obtained for the isomerization reaction are recorded in Tables V and VI. This reaction is clearly catalyzed only by H^+ in acetate, formate, and phosphate buffers. In dilute solutions of HCl/DCl the reaction shows an inverse solvent deuterium isotope, $k_{D_2O}/k_{H_2O} = 2.8$. Thus, the reaction involves initial preequilibrium protonation of oxygen.

The kinetic data obtained for the isomerization reaction are recorded in Table VII. Once again, this reaction appears to be clearly only hydrogen ion catalyzed in acetate and formate buffers. Again the solvent deuterium isotope effect is inverse

Table V. Rates of Isomerization of 4,4-Dimethylcyclohexa-2,4-dienol in Aqueous Buffers at 25 °C ($\mu = 0.1$, NaCl)

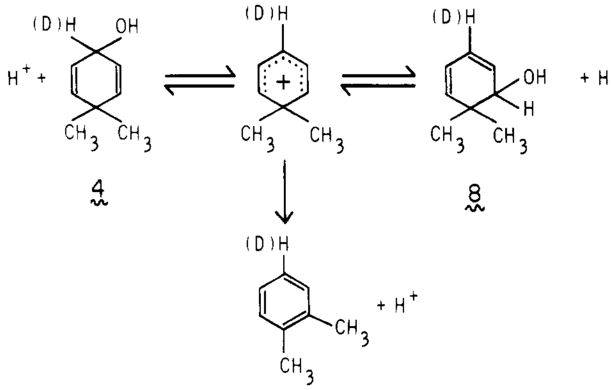
HX	[HX]	[NaX]	pH	$10^4 k_i$, s^{-1}	$k_i/[H^+]$, $M^{-1} s^{-1}$
HOAc	0.025	0.025	4.602	6.86	27.4
HOAc	0.050	0.050	4.590	6.72	26.1
HOAc	0.096	0.020	3.855	36.3	26.1
HOAc	0.480	0.100	3.898	33.7	26.7
HOAc	1.00	1.00[a]	4.650	5.63	25.2
HCOOH	0.020	0.020	3.583	71.9	27.5
HCOOH	0.100	0.100	3.603	68.6	27.6
HCl			3.490	86.9	26.9
DCl			3.483	247]	75.3

[a] $\mu = 1.00$. $k_i = 26.7 \pm 0.8$ $M^{-1} s^{-1}$. $k_{D_2O}/k_{H_2O} = 2.8$.

and of approximately the same magnitude as that observed in the isomerization reaction, $k_{D_2O}/k_{H_2O} = 3.4$.

The data for both reactions are incorporated in Scheme IV.

Scheme IV



α-Deuterium isotope effects were determined for both the isomerization and rearrangement reactions of **4**. Although clouded somewhat by the complexity of Scheme IV (e.g., $k_{\text{isomerization}} = k_{\text{forward}} + k_{\text{reverse}}$), certain approximate conclusions can be reached. Since the conversion **4** → **8** involves the hybridization change $sp^3 \rightarrow sp^2$ at the position of isotopic substitution, a normal α-D effect is expected. Indeed, $k_H/k_D = 1.10 \pm 0.01$ for the isomerization reaction, very close to the observed isotope effect for the dienol-benzene rearrangement of **3**. On the other hand, if the rearrangement of **8** to product represents the principal pathway for $k_{\text{rearrangement}}$, then a much reduced α-D effect might be expected since the hybridization change observed in this conversion is $sp^2 \rightarrow sp^2$. The observed α-D effect for the rearrangement reaction is 1.00 ± 0.03, providing some evidence in support of this assumption.

A Comparison of 3 and 4. Either isomer of **3** undergoes the acid-catalyzed dienol-benzene rearrangement in concentrated mineral acids and from the evidence cited above appears to involve rate-determining methyl migration (see Scheme II). We could see no evidence for an isomerization analogous to that found for **4** in which substantial amounts of the conjugated isomer are formed. Moreover, **4** undergoes both the isomerization and rearrangement reactions in dilute buffer solutions. No evidence supporting general acid catalysis was found in dilute formate, acetate, or phosphate buffers. Ritchie has shown[24] that certain resonance-stabilized carbonium ions react with water in a general-base-catalyzed reaction. This is clearly not the case for 4^+ (cf. Scheme IV). Fife[25] has shown that such general catalysis is to be expected only for highly resonance-stabilized carbonium ions.

Finally, **4** and/or **8** undergo the isomerization reaction some 10^8 times as fast as **3**. No doubt, this is at least in part due to the relative stability of the rearranged carbonium ions, 3^+ and 4^+, respectively.

Experimental Section

Synthesis of Dienols 3a and 3b. A. NaBH$_4$. To a solution of 1.00 g of dienone **2** in 25 mL of ethanol at 0 °C the product was recovered by acidification, removal of the ethanol, and ether extraction. The resulting oil showed NMR peaks at 1.54 and 1.50 ppm in a 30:70 ratio. Crystallization from petroleum ether gave in the first crop 150 mg of pure **3a**: mp 127–128 °C; NMR ($CDCl_3$) δ 1.54 (3 H, s, Me), 1.7 (1 H, OH), 4.52 (1 H, br, C*H*OH), 6.17 (4 H, br s, vinyl). Either isomer, upon oxidation with Jones reagent, gave only the dienone **2**.

B. Al(OPr-*i*)$_3$. The procedure of Plieninger[11] gave a mixture of **3a** and **3b**. The melting point reported (141–142 °C) could not be duplicated, but some fractions of mixtures had melting points which were sharp and above that of either pure compound.

C. LiAlH$_4$. Reduction of the dienone **2** with excess $LiAlH_4$ in slightly wet ether was monitored by removing aliquots by syringe, acidifying and extracting with ether, and analyzing by NMR spectroscopy. Within 10 s, the dienols **3a** and **3b** were formed as the only products, in a 30:70 ratio. Within 1 min, the δ 1.50 peak of **3b** was being replaced by one at δ 1.28. Within 1 h, most of **3b** was gone and a detectable amount of the δ 1.54 peak of **3a** was converted into one at δ 1.35. After 2 days at room temperature none of **3a** was detectable and the only products were the dichlorodienols, **5b** and **5a**. Compound **5b** had NMR ($CDCl_3$) δ 1.28 (3 H, s, Me), 4.4 (1 H, br, C*H*OH), 5.53 (1 H, s, $CHCl_2$), 5.95 (4 H, br, vinyl), and **5a**, δ 1.28 (3 H, s, Me), 4.4 (1 H, s, C*H*OH), 5.53 (1 H, s, $CHCl_2$), 5.95 (4 H, br, vinyl). The mixture was not separated, but was identical by NMR, IR, and mass spectrum with a mixture prepared by reduction of 4-dichloromethyl-4-methylcyclohexadienone.

Reduction of **2** with excess $LiAlH_4$ in very dry THF (from Na-K) gave complete reduction to the dichlormethyl dienols **6a** and **6b** within 10 min. In dry ether ($LiAlH_4$) the reaction required ca. 4 h for completion.

Proof of Methyl Migration in Dienols 3a and 3b. A sample of deuterated dienols (200 mg, 30:70 ratio of **3a**:**3b**), prepared by $LiAlD_4$ reduction of **2**, was treated with 1 mL of concentrated H_2SO_4 at 0 °C for 25 min. Addition of ice gave *o*-toluic acid, mp 96–100 °C, *m*/*e* 137, which was reduced directly with excess $LiAlH_4$ in ether. The resulting *o*-methylbenzyl alcohol-*d* was analyzed using Eu(fod)$_3$ in $CDCl_3$. At one concentration, the spectrum (100 MHz) showed the following changes: Me, δ 2.37 to 5.73; C*H*$_2$OH, 4.72 to 15.45; H_3, 7.3 m to 8.92 s; H_5, 7.3 m to 8.85, d, J = 9 Hz; H_6, 7.3 m to 13.28, d, J = 9 Hz. The H_6 signal in the undeuterated compound appeared as a doublet of doublets in the shifted spectrum, J = 9 and 2 Hz.

Synthesis of Chlorides 6a and 6b. To a suspension of 50 mg of the *Z* dienol **3b** in CCl_4 in an NMR tube was added 3 drops of $SOCl_2$. The reaction was complete within 15 s to give a 52:48 ratio of the chlorides **6a** and **6b**. Compound **6a** had NMR spectrum δ 1.56 (3 H, s, Me), 5.04 (1 H, br s, CHCl), 6.24 (4 H, s, vinyl). Compound **6b** had δ 1.49 (Me), other peaks same as **6a**. On a larger scale, the mixture was isolated as a wide-melting white solid, which could be sublimed at 50 °C at 0.01 mm, but which slowly decomposed on storage.

Treatment of the *E* dienol **3a** with $SOCl_2$ in $CDCl_3$ gave **6a** and **6b** in an 87:13 ratio. When the reaction was carried out on a suspension of dienol **3a** in CCl_4, only **6a** was detectable by NMR.

Solvolysis of Chlorides 6a and 6b to Methyl Ether 7a and 7b. A solution of the *E* chloride **6a** was allowed to stand in anhydrous methanol for 2 h at room temperature. Removal of the solvent gave a 40:60 ratio of the *E* to *Z* methyl ethers **7a** and **7b**. Compound **7a** had NMR δ (CCl_4) 1.54 (3 H, s, Me), 3.36 (3 H, s, OMe), 4.45 (1 H, br, CH*O*Me), 6.15 (4 H, br s, vinyl); and **7b** had NMR δ 1.47 (3 H, s, Me), 3.33 (3 H, s, OMe), 4.45 (1 H, br, C*H*OMe), 6.15 (4 H, br s, vinyl). Addition of a quantity of Eu(fod)$_3$ in $CDCl_3$ shifted the methyl peaks for **7a** as follows: Me, 1.47 to 2.02 and OMe, 3.33 to 8.06.

To a solution of NaOMe, prepared by dissolving 60 mg of Na in 5 mL of absolute MeOH, was added 42 mg of the *E* chloride **6a**. After 2 h, NMR analysis showed an 82:18 ratio of **7a** to **7b**.

To a solution of 50 mg of alcohol **3a** in 2 mL of anhydrous DMF was added ca. 20 mg of NaH and 100 mg of Me_2SO_4. After 12 h at room temperature the reaction mixture was poured into H_2O, acidified, and extracted with ether. The product was only the *E* ether **7a** by NMR.

Synthesis of 4. Reduction of 4,4-dimethylcyclohexadienone, available from a previous study,[4] afforded **4** in high yield: NMR analysis δ 5.63 (4 H, vinyl), 4.32 (1 H, C*H*OH), 2.63 (1 H, OH), 1.08 (3 H, CH_3), 1.02 (3 H, CH_3). Reduction with $LiAlD_4$ produced the same spectrum except that the δ 4.32 signal was absent, indicating greater than 98% deuteration. Attempted purification of **3b** or its deuterated analogue resulted in extensive decomposition to *o*-xylene. For this reason this material was used immediately after its preparation.

Kinetics. The rearrangement of **3a** was determined by monitoring the increase in UV absorption at λ 277 nm due to the formation of *o*-toluic acid. A small volume (5–20 μL) of a stock solution of **3a** in dioxane was rapidly added to a previously temperature-equilibrated cuvette. The absorbance–time data obtained from these tracings were fitted to a nonlinear least-squares regression analysis from which the first-order rate constant was extracted. Monitoring **4** at λ 259 nm shows evidence of a biphasic reaction, i.e., the absorbance increases (due to the formation of the conjugated isomer) followed by a decrease in OD due to the formation of *o*-xylene. Since the isomerization reaction was some 20 times as fast as the rearrangement these data were treated as separable consecutive first-order reactions and treated as above for the simpler case. Because of the fact that $k_{\mathrm{rearrangement}} \approx \frac{1}{20} k_{\mathrm{isomerization}}$ very little error will be introduced by treating the data in this fashion.

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References and Notes

(1) (a) University of Maryland Baltimore County; (b) Texas Tech University.
(2) Project CATALYST Student, sponsored by the American Chemical Society, summer 1975.
(3) Part 6: V. P. Vitullo and E. A. Logue, *J. Am. Chem. Soc.*, **98**, 5906 (1976).
(4) V. P. Vitullo and N. R. Gossman, *J. Am. Chem. Soc.*, **94**, 3844 (1972).
(5) V. P. Vitullo and E. A. Logue, *J. Org. Chem.*, **37**, 3339 (1972).
(6) V. P. Vitullo and E. A. Logue, *J. Org. Chem.*, **38**, 2265 (1973).
(7) V. P. Vitullo and M. J. Cashen, *Tetrahedron Lett.*, 4823 (1973).
(8) J. N. Marx, J. C. Argyle, and L. R. Norman, *J. Am. Chem. Soc.*, **96**, 2121 (1974).
(9) K. L. Cook and A. J. Waring, *J. Chem. Soc., Perkin Trans. 2*, 84, 88 (1973).
(10) M. S. Newman and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 6450 (1959); T. G. Miller, *J. Org. Chem.*, **27**, 1549 (1962).
(11) H. Plieninger and G. Keilich, *Ber.*, **91**, 1891 (1958).
(12) R. E. Rondeau and R. E. Sievers, *J. Am. Chem. Soc.*, **93**, 1522 (1971).
(13) K. Von Auwers and G. Keil, *Ber.*, **35**, 4207 (1902). See also A. J. Waring, *Adv. Alicyclic Chem.*, **1**, 146 (1966); H. Wynberg, *Chem. Rev.*, **60**, 169 (1960).
(14) M. S. Newman, J. Eberwien, and L. L. Wood, Jr., *J. Am. Chem. Soc.*, **81**, 6454 (1959).
(15) C. H. Rochester, "Acidity Functions", Academic Press, New York, N.Y., 1970, pp 109–187.
(16) For conformational studies of dihydrobenzenes, see P. W. Rabideau, E. G. Burkkolder, M. J. Yates, and J. W. Paschal, *J. Am. Chem. Soc.*, **99**, 3596 (1977). Conformational studies in the present system will be published later.
(17) P. E. Peterson and F. J. Waller, *J. Am. Chem. Soc.*, **94**, 991 (1972).
(18) T. W. Bentley, F. L. Schadt, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **94**, 992 (1972).
(19) C. D. Ritchie, *Acc. Chem. Res.*, **5**, 348 (1972).
(20) M. Sczwarc, Ed., "Ions and Ion Pairs in Organic Reactions", Vol. 2, Wiley, New York, N.Y., 1974, p 322 ff.
(21) C. J. Collins and N. Bowman, Ed., "Isotope Effects in Chemical Reactions", Van Nostrand-Reinhold, Princeton, N.J., 1970, p 90.
(22) T. W. Bentley, S. H. Liggero, M. A. Imhoff, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, **96**, 1970 (1974).
(23) C. W. Spangler and P. L. Boles, *J. Org. Chem.*, **37**, 1070 (1972).
(24) C. D. Ritchie, *J. Am. Chem. Soc.*, **94**, 3275 (1972).
(25) T. H. Fife, *Acc. Chem. Res.*, **5**, 264 (1972).

Molecular Orbital Theory of the Electronic Structure of Molecules. 38. Flexible Olefins Preferring Nonplanar Puckered Structures

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Abstract: Ab initio molecular orbital calculations indicate that a number of strained olefins prefer nonplanar structures. These include bicyclobutene-$\Delta^{1,3}$, bicyclopentene-$\Delta^{1,4}$, and bicyclohexene-$\Delta^{1,5}$. In addition, bicyclohexene-$\Delta^{1,4}$, although planar, is indicated to have a very weak out-of-plane bending force constant. Model calculations from ethylenes distorted to represent these olefins demonstrate the generality of this behavior and provide a theoretical explanation.

Unless dictated by geometrical constraints (e.g., I)[2a,b] or by the lack of the appropriate symmetry,[2c] olefins are planar entities. Remarkably, Hehre and Pople's ab initio calculations on bicyclobutene-$\Delta^{1,3}$ (II)[3] indicated preference for a nonplanar structure even though nothing would seem to preclude planarity. As possible reasons for this behavior were not analyzed,[3] a more extensive molecular orbital investigation of II and other olefins (III, IV, V, and VI (R = H)) which might also be nonplanar has now been undertaken. IV[4] and VI (R = CH_3)[5] are known, but no experimental structural studies have been reported. Very recently, a tricyclic derivative of II has been implicated as a reaction intermediate.[6] A platinum

Table I. Relative Energies of Distorted Ethylene Models[a] for II and IV (RHF/STO-3G), kcal/mol

∠HCC, deg	Planar (VIIA) D_{2h}	Nonplanar (VIIB)[c] C_{2v}
120	0.0 (−77.071 21)[b]	11.1
110	0.0 (−77.034 59)	7.3
100	0.0 (−76.944 19)	2.1
90	0.0 (−76.786 88)	−5.5
80	0.0 (−76.518 85)	−17.3
70	0.0 (−75.981 37)	−37.9

[a] Assumed geometrical parameters: r(C═H) = 1.34, r(C–H) = 1.08 Å. [b] Total energy (au) of planar form in parentheses. [c] ϕ(H_aCCH_c) = ϕ(H_bCCH_d) = 0°, ϕ(H_aCCH_d) = 150°.

Table II. Relative Energies of Distorted Ethylene Models[a] for III, V, and VI (RHF/STO-3G), kcal/mol

θ,[c] deg	Planar (XIA) C_{2v}	Nonplanar (XIB)[c] C_s
150	0.0 (−76.608 67)[b]	2.5
120	0.0 (−76.590 17)	−1.1
100	0.0 (−76.501 03)	−6.5

[a] Assumed geometrical parameters: r(C═C) = 1.34, r(C–H) = 1.08 Å. [b] Total energy (au) of planar form in parentheses. [c] ∠H_aCC = ∠H_cCC = 70°, ϕ(H_aCCH_c) = 0°, ∠H_bCC = ∠H_dCC = θ, ϕ(H_aCCH_d) = 150°.

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