R. S. Givens, and R. G. Carlson, *J. Am. Chem. Soc.*, **96**, 7554 (1974).

(10) The procedure utilized for this reaction modeled that of J. Broome, B. R. Brown, A. Roberts, and A. M. White, *J. Chem. Soc.*, 1406 (1960).

(11) Despite indications of homogeneity of this material using GLC, LC, and from its ^{1}H NMR and uv spectra, it appears to contain a trace impurity on the basis of exceptionally small spikes seen in its ^{13}C NMR spectrum. Since microanalysis of this material gave an atomic composition exceptionally close to calculated, we assume that the impurity present is a regioisomer of **6**, perhaps having the spiro-1,8-diene structure. This would derive from conjugate addition of hydride to the aluminum complexed allylic alcohol intermediate in the conversion of dienone to diene. Evidence for this type of reaction is present in the literature.[12]

(12) H. J. Williams, *Tetrahedron Lett.*, 1271 (1975), and references cited therein.

(13) Yield is based upon recovered **6**.

(14) By all estimates based upon energetic considerations of simpler transfused model systems, the tricyclic undecene **8** should be of excessively high energy: (a) K. B. Wiberg and A. de Meijere, *Tetrahedron Lett.*, 519 (1969); (b) J. V. Paukstelis and J. L. Kao, *J. Am. Chem. Soc.*, **94**, 4783 (1972).

(15) Energy transfer from both benzophenone (E_t, 68 kcal/mol) and acetophenone (E_T = 74 kcal/mol) triplet to **6**, having a styryl chromophore (E_T = 64 kcal/mol) is expected to occur with a diffusion-controlled rate.[16]

(16) N. J. Turro, "Molecular Photochemistry", W. A. Benjamin, New York, N.Y., 1967, p 95.

(17) G. S. Hammond, R. P. Foss, and W. M. Moore, *J. Am. Chem. Soc.*, **83**, 2789 (1961).

(18) The quantum efficiency for formation of the triplet product, 1-phenyl-5-methyl-6-*endo*-(*trans*-1-propenyl)bicyclo[3.1.0]hexane,[1b] was found to be 0.010 ± 0.001.

(19) In other investigations we have found that di-π-methane conformation is also influential in determining the singlet reaction stereochemistry: P. S. Mariano and D. G. Watson, *Tetrahedron Lett.*, 3439 (1975).

(20) Alternately, the conversion of **6** to **7** could follow a nonconcerted reaction pathway through both cyclopropyldicarbinyl and 2-vinyltrimethylene diradical intermediates. Although possible, this mechanism seems unlikely in view of previous observations,[19] which demonstrate that when concerted rearrangement via anti-disrotatory pathways are blocked, the reaction remains stereospecific. Thus, the concerted syn-disrotatory route appears to be the energetically next best mechanistic route for the singlet di-π-methane rearrangement.

(21) The spirodiene and propenylcyclohexene systems being compared have similar structures. Importantly, the two π moieties in each contain the same substitution patterns; one π moiety in each is of the α-alkylstyryl variety and the other of the *cis*-alkylvinyl variety. Indeed, Zimmerman and co-workers have found from single photon counting studies that substituents at C-1, C-3, and C-5 of the 1,4-diene grouping are very important in determining the singlet lifetime, i.e., rate of singlet decay, of di-π-methane systems. As a result of these considerations, it seems reasonable to expect that the spirodiene and propenylcyclohexene will have nearly the same rates of singlet excited-state decay. In that event, the ratio of the quantum yields for reaction would be equivalent to the ratio of rate constants for singlet reaction. H. E. Zimmerman, K. S. Kamm, and D. P. Werthemann, *J. Am. Chem. Soc.*, **96**, 439 (1974).

(22) H. E. Zimmerman and P. S. Mariano, *J. Am. Chem. Soc.*, **91**, 1718 (1969).

(23) See for example, (a) W. R. Roth and M. Martin, *Justus Liebigs Ann Chem.*, **702**, 1 (1967); *Tetrahedron Lett.*, 4695 (1967); (b) D. H. White, P. B. Condit, and R. G. Bergman, *J. Am. Chem. Soc.*, **94**, 7931 (1972).

(24) Earlier observations in the literature[24a] had shown that cyclopropyldicarbinyl diradical intermediates generated by photodecarbonylation of bicyclo[3.1.0]hexanones rearrange to vinylcyclopropanes. More recently, Zimmerman and co-workers[24b] have presented compelling evidence that triplet diradicals of this type, generated by sensitized photodecompositions of parent polycyclic diazenes, rearrange in a similar way as do the triplet states of hydrocarbon analogues having barrelene-like structures; (a) L. D. Hess and J. N. Pitts, *J. Am. Chem. Soc.*, **89**, 1973 (1967); (b) H. E. Zimmerman, R. J. Boettcher, N. E. Buehler, and G. Keck, *ibid.*, **97**, 5635 (1975).

(25) An accumulation of results[19,26] have sharpened the initial postulate to include structural constraints which limit free rotation about only the π moiety of lowest triplet energy.

(26) S. S. Hixson and J. C. Tausta, *Tetrahedron Lett.*, 2007 (1974).

(27) Another interesting conclusion derives from the postulate presented. The lack of triplet reactivity of **6** and the stereospecificity of the triplet rearrangement of **23** suggest that the conversions of initially formed triplet cyclopropyldicarbinyl diradicals to their corresponding vinylcyclopropanes do not proceed through intermediate 2-vinyltrimethylene diradicals.

(28) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).

Cyclohexadienyl Cations. 6. Methyl Group Isotope Effects in the Dienone–Phenol Rearrangement

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Abstract: Rates of rearrangement of 4,4-di(trideuteriomethyl)cyclohexadienone (**1-DD**) and 4-methyl-4-trideuteriomethylcyclohexadienone (**1-HD**) are compared with the unlabeled material (**1-HH**). The observed isotope effects are k_{HH}/k_{DD} = 1.149 ± 0.017 and k_{HH}/k_{HD} = 1.060 ± 0.012. The product isotope effect obtained from **1-HD** by converting the rearrangement product to 3,4-dimethyl-4-dichloromethylcyclohexadienone and NMR integration of the two methyl resonances is 1.36 ± 0.05. Suitable combination of these results give $\kappa_H{}^\alpha$ (methyl migrational isotope effect) = 1.25 and $\kappa_H{}^\beta$ (remnant methyl group isotope effect) = 0.92. The magnitude and direction of these isotope effects are compared with others in the literature.

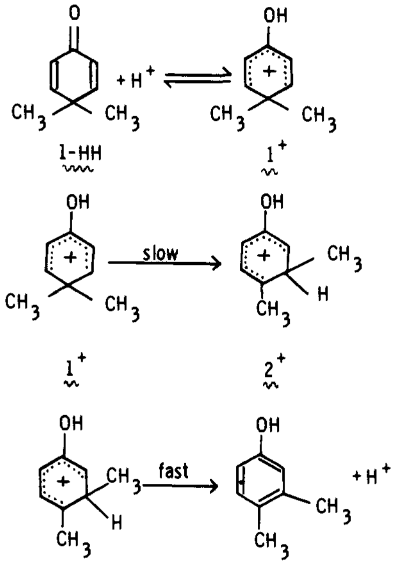
Introduction

One of the ultimate goals of physical organic chemistry is to obtain structural information for the transition state similar to that now available for stable molecules. However, the lifetime of the transition state prohibits all attempts at studying these high-energy species directly using presently available spectroscopic techniques and structural information must be obtained indirectly. Unfortunately, ordinary substituent effects which might be used to obtain charge distributions for the transition state are very likely to alter in some degree that property which is being determined. On the other hand, isotopic substitution is known[1] not to affect the potential energy surface of a given molecule or transition state. Thus a comparison of rates of reaction which differ only because of isotopic substitution constitutes very nearly a noninteracting probe.

Secondary deuterium isotope effects have been shown to be a powerful tool in the evaluation of force constant changes attending the formation of the transition state.[2,3] An interesting application of the use of secondary deuterium isotope effects has been achieved recently by Schubert and LeFevre.[4,5] They have shown that the secondary isotope effects in a characteristic 1,2-methyl migration (the pinacol rearrangement of 1,1-diphenyl-2-methyl-1,2-propanediol) are 1.205 for the migrating methyl group and 0.978 for the nonmigrating methyl group (remnant methyl group). In a related paper Schubert and Henson[6] have shown that the absence of an appreciable methyl group kinetic isotope effect in the solvolysis of a neopentyl arenesulfonate required that methyl migration was not coincident with ionization. Winnik, Stoute, and Fitzgerald[7] have determined the migrational ($C_6H_5CH_2$, migrating) and remnant (CH_3 group) isotope effects for the Baeyer–Villiger reaction of 1-phenyl-2-propanone. The migrational isotope effect was found to be substantially reduced (1.035 ± 0.014 per D) compared with Schubert's[4,5] result (1.064 per D). However, the remnant isotope effect observed by Winnik[7] et al. (1.052 ± 0.010 per D) was significantly larger than the analogous result in Schubert's system (0.995 per D). From these results a later transition state for benzyl migration in the Baeyer-Villiger reaction than for methyl migration in the pinacol rearrangement was inferred.

In previous work from this laboratory we have shown that the acid-catalyzed dienone-phenol rearrangement of 4,4-dimethylcyclohexadienone involves a simple rate-determining methyl migration[8] (Scheme I). Thus the evidence for Scheme I is: (1) **1**$^+$ is a readily observable intermediate;[9] (2) ring deuteration results in an inverse isotope effect[10] and (3) the acidity dependence of the reaction shows an inverse dependence on the water activity[11] and is understandable in terms of desolvation of the **1-OH** group[12] in forming the transition state. In addition, other published work is consistent with Scheme I and in turn provides corroborative evidence.[13-16] We were interested in the magnitude of the migrational and remnant CH_3-CD_3 isotope effects for this reaction as a possible probe for force constant changes and (inferentially) structural changes attending the formation of the transition state. The results of this investigation are reported in this paper.

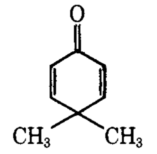
Scheme I



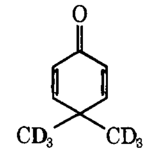
Results

The synthesis of 4,4-di(trideuteriomethyl)cyclohexadienone (**1-DD**) has been reported.[17] Oxidation of the resulting labeled enone to the dienone with DDQ in carbon tetrachloride followed that described earlier.[8] The synthesis of 4-methyl-4-trideuteriomethylcyclohexadienone (**1-HD**) proceeded in an analogous fashion. A sample of 4,4-dimethylcyclohexadienone (**1-HH**) was available from previous work.[8] All dienones were purified by GLC before use (Scheme II).

Table I. CH_3–CD_3 Isotope Effects in the Acid-Catalyzed Dienone–Phenol Rearrangement of 4,4-Dimethylcyclohexadienone



HH

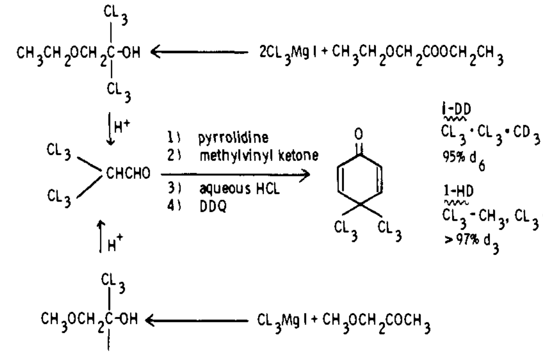


DD

Run no.	k_{HH}	k_{DD}	k_{HH}/k_{DD}
1[a]	8.40	7.29, 7.49	1.137
2[a]	8.14, 8.11	7.02	1.157
3[a]	8.16, 8.22	7.03	1.165
4[a]	8.32	7.14, 7.22	1.159
5[a]	8.09, 8.10	7.17	1.129
6[a]	8.35	7.16, 7.02	1.178
7[a]	8.24, 8.24	7.18	1.148
8[a]	8.02	7.00, 6.95	1.150
9[a]	8.02, 8.03	7.08	1.133
10[a]	8.07	6.86, 7.03	1.162
11[a]	7.92	7.08, 7.05	1.121
12[a]	8.06, 7.80	6.87	1.154
13[a]	8.11, 8.21	7.09	1.151
14[a]	7.78	6.76, 6.59	1.166
15[a]	8.02, 8.02	6.90	1.162
16[a]	8.14	7.16, 7.15	1.138
17[b]	5.02, 5.16	4.58	1.111
18[b]	5.21, 4.99	4.44	1.149
19[b]	5.05	4.38, 4.30	1.164
	$(k_{HH}/k_{DD})_{average} = 1.149 \pm 0.017$		

[a] Wt % $HClO_4$ = 62.70, $H_0 = -5.86$, $T = 25.0 \pm 0.15$ °C, $10^4 k_{obsd}$ (s^{-1}). [b] Wt % $HClO_4$ = 59.53, $H_0 = -5.16$, $T = 25.0 \pm 0.15$ °C, $10^4 k_{obsd}$ (s^{-1}).

Scheme II



Kinetic isotope effects were determined spectrophotometrically by monitoring the change in optical density at 260 nm for **1-HH** and **1-DD** or **1-HD** simultaneously (Tables I and II). Under the conditions of our experiments **1** is virtually completely protonated, i.e., $[1^+]/[1]$ is greater than 10. In this way k_{HH}/k_{DD} was found to be 1.149 ± 0.017 and k_{HH}/k_{HD} = 1.060 ± 0.012. In contrast, these isotope effects obtained from averaged k_{HH}, k_{DD}, and k_{HD} values are k_{HH}/k_{DD} = 1.150 ± 0.037 (62.70% $HClO_4$), 1.152 ± 0.037 (59.53% $HClO_4$), and k_{HH}/k_{HD} = 1.061 ± 0.029 (60.67% $HClO_4$). It is clear, therefore, that the isotope effects are known with greater precision than the individual rate constants. (All error estimates in this paper are standard deviations.) As expected, the isotope effects are independent of acid concentration.

Following Schubert,[4,5] we write:

$$k_{HH} = 2k_H{}^H \tag{1}$$

$$k_{HD} = k_D{}^H + k_H{}^D \tag{2}$$

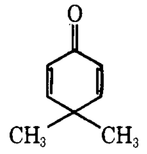
$$k_{DD} = 2k_D{}^D \tag{3}$$

where superscripts refer to the isotopic character of the migrating methyl group and subscripts refer to the isotopic character of the remnant methyl group. Thus

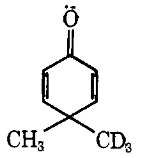
$$\frac{k_{HH}}{k_{DD}} = \left(\frac{k_H{}^H}{k_D{}^D}\right) = \frac{(k_H{}^H/k_H{}^D)}{(k_D{}^D/k_H{}^D)} = \kappa_H{}^\alpha \kappa_D{}^\beta \tag{4}$$

where κ^α and κ^β are migrational and remnant isotope effects, respectively. The subscripts for κ refer to the isotopic character of the remaining methyl group, i.e., $\kappa_H{}^\beta$ is the remnant group isotope effect when the migrating methyl group is undeuterated whereas $\kappa_D{}^\beta$ is the remnant group isotope effect when the mi-

Table II. CH_3–CD_3 Isotope Effects in the Acid-Catalyzed Dienone–Phenol Rearrangement of 4,4-Dimethylcyclohexadienone



HH



HD

Run no.	k_{HH}	k_{HD}	k_{HH}/k_{HD}
1^a	9.06, 9.00	8.37	1.079
2^a	8.95	8.32, 8.37	1.073
3^a	9.10, 9.03	8.50	1.067
4^a	8.65	8.27, 8.32	1.043
5^a	8.91, 8.83	8.31	1.067
6^a	9.15	8.86, 8.62	1.047
7^a	8.83, 8.66	8.31	1.052
8^a	8.91, 8.93	8.34	1.063
9^a	8.65	8.18, 8.17	1.058
10^a	8.86, 8.81	8.33	1.061
11^a	8.80	8.38, 8.35	1.052
12^a	8.78, 8.91	8.20	1.079
13^a	9.10	8.62	1.056
14^a	8.54	8.20, 8.27	1.037
15^a	8.78, 8.82	8.24	1.068
	$(k_{HH}/k_{HD})_{average} = 1.060 \pm 0.012$		

[a] Wt % $HClO_4 = 60.67$, $H_0 = -5.40$, $T = 25.0 \pm 0.15$ °C, $10^4 k_{obsd}$ (s^{-1}).

grating methyl group is deuterated.

Noting that

$$\frac{k_H{}^D}{k_D{}^D} = \frac{k_H{}^H}{k_D{}^H}, \text{ i.e., } \kappa_D{}^\beta = \kappa_H{}^\beta \tag{5}$$

equation 5 is simply an application of the "rule of the geometric mean" and states that the remnant isotope effect is independent of the isotopic character of the migrating methyl group. Thus

$$\frac{k_{HH}}{k_{DD}} = \kappa_H{}^\alpha \kappa_H{}^\beta \tag{6}$$

and

$$\frac{k_{HD}}{k_{DD}} = \frac{1}{2}\left[\frac{k_D{}^H}{k_D{}^D} + \frac{k_H{}^D}{k_D{}^D}\right] = \frac{1}{2}[\kappa_D{}^\alpha + \kappa_D{}^\beta] \tag{7}$$

Similar reasoning as (5) gives:

$$\frac{k_{HD}}{k_{DD}} = \frac{1}{2}[\kappa_H{}^\alpha + \kappa_H{}^\beta] \tag{8}$$

Equations 6 and 8 constitute two equations in two unknowns and therefore,

$$\kappa_H{}^\alpha \text{ or } \kappa_H{}^\beta = \left(\frac{k_{HD}}{k_{DD}}\right) \pm \left[\left(\frac{k_{HD}}{k_{DD}}\right)^2 - \left(\frac{k_{HH}}{k_{DD}}\right)\right]^{1/2} \tag{9}$$

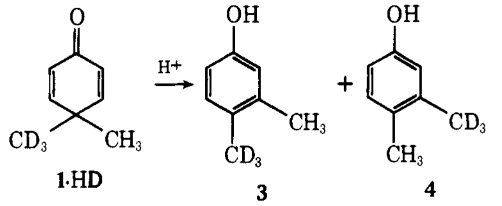
Since $k_{HH}/k_{DD} = 1.149 \pm 0.017$ and $k_{HD}/k_{DD} = 1.086 \pm 0.017$, both $\kappa_H{}^\alpha$ and $\kappa_H{}^\beta$ may be determined:

$$\kappa_H{}^\alpha \text{ or } \kappa_H{}^\beta = 1.260 \pm 0.18 \tag{10}$$

$$\kappa_H{}^\alpha \text{ or } \kappa_H{}^\beta = 0.912 \pm 0.15 \tag{11}$$

Unfortunately, $\kappa_H{}^\alpha$ and $\kappa_H{}^\beta$ are very sensitive functions of k_{HD}/k_{DD} and k_{HH}/k_{DD}, and for this reason our preliminary analysis[18] of these isotope effects assumed $\kappa_H{}^\beta \geq 1$. Since $\kappa_H{}^\beta$ measures the remnant isotope effect in the conversion of $\mathbf{1}^+$ to $\mathbf{2}^+$ it was felt that $\kappa_H{}^\beta$ should be greater than or equal to one in analogy to β-deuterium isotope effects in solvolysis.[19]

However, a measure of the amount of CH_3 vs. CD_3 migration in the phenol product coupled with the kinetic isotope effects previously discussed allows an unequivocal evaluation of $\kappa_H{}^\alpha$ and $\kappa_H{}^\beta$.

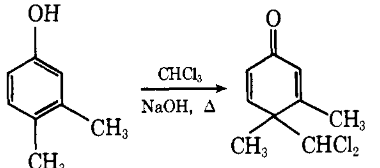


(12)

1-HD **3** **4**

$$R = \frac{[3]}{[4]} = \frac{k_D{}^H}{k_H{}^D} = \frac{(k_D{}^H/k_H{}^H)}{(k_H{}^D/k_H{}^H)} = \frac{(1/\kappa_H{}^\beta)}{(1/\kappa_H{}^\alpha)} = \frac{\kappa_H{}^\alpha}{\kappa_H{}^\beta}$$

We wished to use NMR spectroscopy as the analytical tool to estimate the relative amounts of CH_3 and CD_3 migration. However, the NMR spectrum of 3,4-dimethylphenol at 60 MHz reveals only a sharp singlet at δ 2.05 for both methyl groups. For this reason, the phenol product was converted to a suitable derivative for NMR analysis. It has been reported[20] that the methyl resonances of 3,4-dimethyl-4-dichloromethylcyclohexadienone (**5**) are widely separated: 3-methyl, δ 2.08 (d); 4-methyl, 1.46 (s). **5** is one of the products of the Reimer–Tieman reaction of **3**. A sample of **5** prepared in this way from unlabeled 3,4-dimethylphenol has as the ratio (*R*) of low-field to high-field methyl resonances, 1.01 ± 0.05. *R* from a sample of **5** obtained from the rearrangement product of **1-HD** in 60.7% $HClO_4$ is 1.36 ± 0.05. The fact that this ratio is greater than 1 indicates a clear migrational preference of CH_3 vs. CD_3.



5

With this estimate of *R*, it now becomes possible to evaluate each of these isotope effects. From eq 4 and 12 $\kappa_H{}^\alpha = 1.250 \pm 0.024$, $\kappa_H{}^\beta = 0.919 \pm 0.019$. These isotope effects derived from eq 8 and 12 are $\kappa_H{}^\alpha = 1.252 \pm 0.037$, $\kappa_H{}^\beta = 0.920 \pm 0.024$. The agreement between the isotope effects derived from either 4 and/or 8 and eq 12 show that methyl migration occurs in the rate-determining step and that the product-determining step and rate-determining steps are coincident.

It should be pointed out here that the possibility of an isotope effect in the Riemer–Tieman reaction used to obtain the isotopic composition of the product mixture from **1-HD** is such that the inverse nature of $\kappa_H{}^\beta$ is not completely unequivocal. All that can be said with certainty is that $\kappa_H{}^\beta$ is small.

Discussion

The product of methyl migration is $\mathbf{2}^+$ in which the nonmigrating methyl group is adjacent to a carbonium ion center. The isotope effect on a remnant methyl group freely conjugating with the carbonium ion center is expected to be analogous to a β-deuterium isotope effect in solvolysis; i.e., a normal isotope effect ($k_H/k_D > 1$). However, if only the inductive effect of a remnant methyl group is felt in the transition state, a 1–2% per D *inverse* isotope effect is expected.[21,22] This would be the case if certain geometric constraints were present which did not allow the isotopically substituted methyl group to be aligned with the developing vacant p orbital. There is some evidence[23] that very little conjugative interaction exists for the remnant 4-substituent in the dienone phenol rearrangement. A remnant methoxy group accelerates the dienone-phenol rearrangement of 4-methoxy-4-methylcyclohexadienone by a factor of only 2.4.[24] Such a modest rate enhancement for a methoxy group in a carbonium ion rearrangement is consistent with relatively weak conjugative interaction between the remnant 4-group and the positive charge in the transition state. Thus, a slightly inverse isotope effect for the remnant methyl

Table III

System	k_H^{α} per D	k_H^{β} per D
Dienone–phenol rearrangement (this work)	1.077	0.973
Pinacol rearrangement (ref 4, 5)	1.064	0.995
Baeyer–Villiger reaction (ref 7)	1.035	1.052

group in the dienone–phenol rearrangement is not unreasonable.

On the other hand κ_H^{α} is quite large and similar to that previously reported by Schubert,[4,5] reflecting the fact that a good deal of positive charge is born by the migrating group in these rearrangements. Increased positive charge in the migrating methyl group should result in decreased C–H stretching and bending force constants and larger isotope effects.

Table III summarizes the migrational and remnant isotope effects thus far observed.

It is quite clear that large values of κ_H^{α} are accompanied by much smaller (and perhaps even inverse) values of κ_H^{β}. The substantially reduced value of κ_H^{β} observed in the Baeyer–Villiger reaction[7] is attended by a substantially increased and normal value for κ_H^{β} consistent with the asymmetric product-like transition state postulated by Winnik.[7] Here hyperconjugation with the developing carbonyl group is responsible for the large, normal effect for κ_H^{β}.

Experimental Section

4,4-Dimethylcyclohexadienone (1-HH). This material was available from a previous investigation[8] and was purified by GLC before use.

4,4-Di(trideuteriomethyl)cyclohexadienone (1-DD). The precursor enone was prepared as described by Harris, Komitsky, and Djerassi.[17] The enone was oxidized with 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) as described earlier. An analysis (Scheme II) for deuterium (J. Nemeth, University of Illinois) indicated 95% $(CD_3)_2$. This material was purified by GLC before use.

4-Methyl-4-trideuteriomethylcyclohexadienone (1-HD). The precursor enone was prepared as in **1-DD**, the only difference being the use of methoxyacetone as the aldehyde precursor. The enone was oxidized to the dienone with DDQ (Scheme II). Analysis for deuterium by mass spectrometry indicated >97% CD_3 incorporation. This material was purified by GLC before use.

Rearrangement of 1-HD. 27.8 mg of **1-HD** was dissolved in 0.5 ml of 60.7% $HClO_4$ and allowed to stand at room temperature for 2.5 h. At the end of this time, the acid was extracted with 2 × 50-ml portions of ether. After washing with $NaHCO_3$ (10%), saturated NaCl, the ether solution was dried by passing it through $CaSO_4$. Removal of the ether afforded 26.1 mg (94%) of isotopically labeled 3,4-dimethylphenol.

Synthesis of Labeled 3,4-Dimethyl-4-dichloromethylcyclohexadienone from Labeled 3,4-Dimethylphenol. 26.1 mg of isotopically labeled 3,4-dimethylphenol was dissolved in 5 ml of 10% NaOH and placed in a round-bottom flask equipped with a reflux condenser. The solution was heated in an oil bath. As soon as the temperature reached 70 °C, 1.04 g of $CHCl_3$ was added. The mixture was allowed to reflux for 24 h. At the end of this time, the reaction mixture was cooled and extracted with 2 × 100-ml portions of ether. The ether solutions were combined and washed successively with 30 ml of 10% NaOH, 30 ml of water, 50 ml of saturated NaCl. After drying, the ether was removed. The crude product was purified by GLC (7 1/2% SE30 on Chromosorb W, 150 °C). In this way 7.0 mg (27%) of the title compound was obtained. The unlabeled material was prepared in a similar way, and there was obtained 13.5 mg of purified dienone. This material had the reported NMR spectrum.[20]

NMR Spectra. The NMR spectra were recorded on a Perkin Elmer Model R-20A NMR spectrometer equipped with a computer of average transients. Thirteen scans of the labeled dienone were stored in the memory. The average and standard deviation of seven integrations of the downfield and upfield resonances gave $R = 1.36 \pm 0.05$ for the labeled dienone and $R = 1.01 \pm 0.05$ for the unlabeled dienone. Similar results were obtained using a 100 MHz instrument.

Kinetics. The rate of decay of the 260-nm band of the protonated dienone was monitored with a Gilford 2400 spectrophotometer.[8] The three cuvettes filled with acid of the desired strength were allowed to equilibrate for ½ h before each run. Required stock solution (5–15 μl) was introduced and the absorbance monitored at 260 nm. For each run one H and two D's were done, followed by two H's and one **D**. The isotope effect per run was computed from the three rate constants determined in that run. The rate constants were computed from the absorbance-time trace using a nonlinear least-squares regression analysis. In all cases, the standard deviation of individual rate constants, calculated by computer, is less than 0.5%.

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References and Notes

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