

THE NATURE OF THE RATE-DETERMINING STEP IN THE  
DIENONE-PHENOL REARRANGEMENT

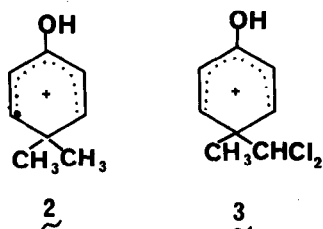
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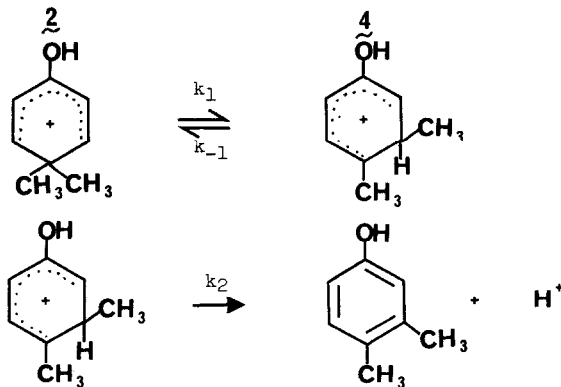
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We wish to report several experiments which unequivocally establish the nature of the rate determining step in the dienone-phenol rearrangement.<sup>1</sup>

In concentrated acid solutions a significant fraction of 4,4-dimethylcyclohexadienone (1)<sup>2</sup> exists as its oxygen protonated conjugate acid (2). In water 1 has an absorption spectrum characteristic of a cross conjugated dienone<sup>3</sup>;  $\lambda$  238 nm ( $\log \epsilon$  4.15). However, in 71% perchloric acid or 94.7% sulfuric acid the absorption spectrum of 1 is radically different. In these acid solutions two new bands appear;  $\lambda$  260 nm ( $\log \epsilon$  4.12),  $\lambda$  295 nm ( $\log \epsilon$  3.57). These bands are characteristic of oxygen-protonated dienones as evidenced by a comparison of these results with the uv spectrum of the stable ion 3;  $\lambda$  267 nm ( $\log \epsilon$  4.12),  $\lambda$  295 nm ( $\log \epsilon$  3.56). The structure of 3 has been fully confirmed by nmr spectroscopy.<sup>1,4</sup>



In concentrated acid solutions 1 rearranges smoothly to 3,4-dimethylphenol<sup>5</sup> in a first order process ( $k_{\text{obs}}$ ). The dependence of  $k_{\text{obs}}$  on acidity<sup>6</sup> is consistent with a mechanism in which 2 is formed rapidly and reversibly followed by its rate-determining isomerization. According to the commonly-accepted mechanism<sup>7</sup> of the dienone-phenol rearrangement, there are two possible rate-determining steps. One of these



involves rate determining methyl group migration ( $k_1$ ) while the other requires base catalyzed deprotonation of 3 ( $k_2$ ). A clear distinction between these possibilities is possible through the use of kinetic deuterium isotope effects. If the rate determining step involves base catalyzed deprotonation of 2, a primary isotope effect of  $>2$  is expected. On the other hand, rate determining methyl group migration should be accompanied by a small inverse isotope effect.

Accordingly, we have prepared 3-deuterio-4,4-dimethylcyclohexadienone (1d) and compared its rate of isomerization to that of 1. The results are collected in Table I.

Our results indicate that 1d isomerizes slightly faster than 1; a result consistent only with  $k_1$  rate determining at all acidities.

Some time ago Streitweiser *et. al.*<sup>8</sup> suggested that  $\alpha$ -deuterium isotope effects in solvolysis reactions ( $k_{\text{H}}/k_{\text{D}} \approx 1.15$ ) resulted from a decrease in the out-of-plane bending frequency of the  $\alpha$ -hydrogen caused by rehybridization at the isotopic position attending the

Table I. Deuterium Isotope Effects in the Dienone-Phenol Rearrangement.

Substrate	T (°C)	Wt % H <sub>2</sub> SO <sub>4</sub>	10 <sup>3</sup> k <sub>obs</sub> (min <sup>-1</sup> )	k <sub>H</sub> /k <sub>D</sub> <sup>c</sup>
<u>1</u>	25.2	97.29%	54.36 ± 0.85 <sup>a</sup>	
<u>1d</u>	25.2	97.29%	58.58 ± 1.17 <sup>a</sup>	0.866 ± 0.041
<u>1</u>	25.8°	55.24%	3.908 ± 0.049 <sup>b</sup>	
<u>1d</u>	25.8	55.24%	4.206 ± 0.041 <sup>b</sup>	0.868 ± 0.039

<sup>a</sup> Average and standard deviation of four runs

<sup>b</sup> Average and standard deviation of three runs

<sup>c</sup> Calculated from  $k_H/k_D = \frac{k_{HH}/k_{HD}}{2 - (k_{HH}/k_{HD})}$  where  $k_{HH} = k_{obs}(\underline{1})$  and  $k_{HD} = k_{obs}(\underline{1d})$

formation of the carbonium ion intermediate. The transformation of 2 to 4 is accompanied by the reverse hybridization change and should, therefore, proceed with an inverse isotope effect.<sup>9</sup>

It is interesting to note that the migration step remains wholly rate-determining even at very high acid concentrations where the water activity is low. The formation of the stable aromatic product probably provides the driving force which allows  $k_2$  to exceed  $k_{-1}$  even at low water activities.

#### References

1. For paper I in this series see V. P. Vitullo, *J. Org. Chem.*, 34, 224 (1969).
2. The last step in the synthesis of 1 was kindly provided by Dr. J. Swenton, Ohio State University.
3. A. J. Waring, *Adv. Alicyclic Chem.*, 1, 188 (1968).
4. E. C. Friedrich, *J. Org. Chem.*, 33, 413 (1968).
5. In sulfuric acid, the product is that derived from sulfonation of 3,4-dimethylphenol.
6. A detailed discussion of the acidity dependence for this reaction will be given at a later date.
7. Ref. 3, p. 207.

8. A. Streitwieser, Jr., R. H. Jagow, R. C. Fahey and S. Susuki, J. Am. Chem. Soc., 80, 2326 (1958).
9. For a similar inverse isotope effect in the  $\text{SCN}^-$  catalyzed isomerization of maleic acid see S. Seltzer, ibid., 83, 1861 (1961).