

Figure 5. Plot of $1/\lambda_{max}$ vs. $(n^2-1)/(2n^2+1)$ for a mixed solution of CV^+ and TPB^- in various solvents. Concentrations: CV^+ , $4.0 \times 10^{-6}M$; TPB^- , $4.0 \times 10^{-6}M$. The numbers correspond to the solvents in Table 1.

shown in Figure 5. The value for water is excluded because it lies far above the line. This plot shows a relatively good linear relationship of the observed solvent shift, which is somewhat different from the result with methylene blue.² The refractive index of a solvent probably plays an important role in the spectral variation of the present system. More experimental information using different types of dyes and a wide range of organic solvent should be accumulated to establish a firm conclusion on this complicated solvent polarity.

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Acid-Catalyzed Migration of the Methyl Substituent in the Dienone-Phenol Rearrangement of *p*-Quinol Ether

Young-Sook Paik Hahn

Department of Chemistry, Kyung Hee University, Suwon 449-900. Received November 14, 1988

4-Methoxy-4-methylcyclohexa-2,5-dienone **1** in aqueous sulfuric acid underwent the normal dienone-phenol rearrangement with methyl group migration. The fact that methyl is migrating group and methoxy is remaining group can be rationalized by the stabilization of positive charge at C-4 during the transition state. Methoxy methyl dienone **1** ($(H_0)_{1/2} = -4.6$) is less basic than 4,4-dimethylcyclohexa-2,5-dienone whose half protonation acidity is reported as -3.15 or -3.66 . This basicity difference comes from the unstabilization of the protonated methoxy methyl dienone **1** due to the electron withdrawing inductive effect of a methoxy group.

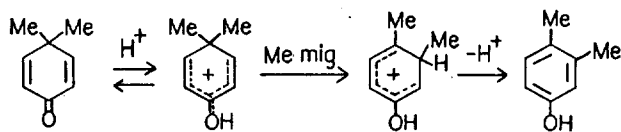
Introduction

The intramolecular 1,2-shift¹ of group R to a cationic

center has been studied extensively. The group R undergoing the rearrangement is commonly alkyl, aryl, or hydrogen. The order of relative migratory aptitude of the group R is

mainly related to the ability of the substituent to stabilize a positive charge in the migration reaction.

For the study of the intrinsic property of the migrating group R, several simple structural models have been used in the literatures.¹ Dienone-phenol rearrangement system is of particular interest because there is a large driving force (aromatization), and because potential migrating and remaining groups are in the same environment, and the migration step is rate determining and irreversible.^{2,3} The acid-catalyzed dienone-phenol rearrangement of 4,4-dimethylcyclohexadienone is known as A-1 mechanism.²⁻⁵ 4,4-Dimethylcyclohexadienone undergoes fast equilibrium with the conjugate acid. Unimolecular methyl group migration from C-4 to C-3 in the conjugate acid is the rate determining step. The rearranged cation rapidly deprotonates to give the stable aromatic product.



In this report, 4-methoxy-4-methylcyclohexa-2,5-dienone **1** was chosen and studied in various strengths of acidic media in order to evaluate the substituent effect of methoxy group in the rearrangement reaction.^{6,8}

Experimental

Instruments. Infrared spectra were obtained on a Nicolet MX-S FT-TR spectrophotometer. NMR spectra were run in CDCl₃ on a Varian EM-360A spectrophotometer. UV spectra were recorded on a Perkin-Elmer Lambda-5 UV-VIS spectrophotometer. Melting points were taken in open capillaries in a Mel-Temp apparatus and are uncorrected.

Procedure for Kinetic Runs. A 3.0 ml aliquot of a solution of the desired strength of acid was placed in a 1 cm cell in the thermostatted cell compartment of Perkin-Elmer Lambda-5 UV-VIS spectrophotometer. After the solution has come to 25 °C, the reaction was initiated by injecting 5 μl of 0.1M solution of dienone **1** in 95% ethanol and mixing it thoroughly with the acidic media in the cell. The decrease in the optical density of the solution at 240 nm with time was then followed. The rate of rearrangement was determined from the slope of a plot of $\ln A_t A_\infty / A_0 - A_\infty$ vs. time.

Preparation of 4-Methoxy-4-methylcyclohexa-2,5-dienone 1. Dienone **1** was prepared by the method of McKillop.⁹ Chromatography of the crude dienone **1** on silica gel with 5:95 ethyl acetate/petroleum ether afforded a white solid: mp 63.5-64 °C *R_f* 0.31 (silica gel, 5:95 ethyl acetate/petroleum ether); UV λ_{max} 229 nm (H₂O, log ϵ = 4.15); IR (CCl₄) 1705, 1676, 1637, 1608 cm⁻¹; NMR (CDCl₃) δ 1.46 (s, 3H), 3.23 (s, 3H), 6.35 (d, 2H, *J* = 10 Hz), 6.83 (d, 2H, *J* = 10Hz).

Results and Discussion

Vitullo⁷ reported that methoxy methyl dienone **1** undergoes the normal dienone-phenol rearrangement in conc-HCl with methyl group migration. The rearrangement product of **1** in aqueous sulfuric acid was found to be identical with that of Vitullo's result.

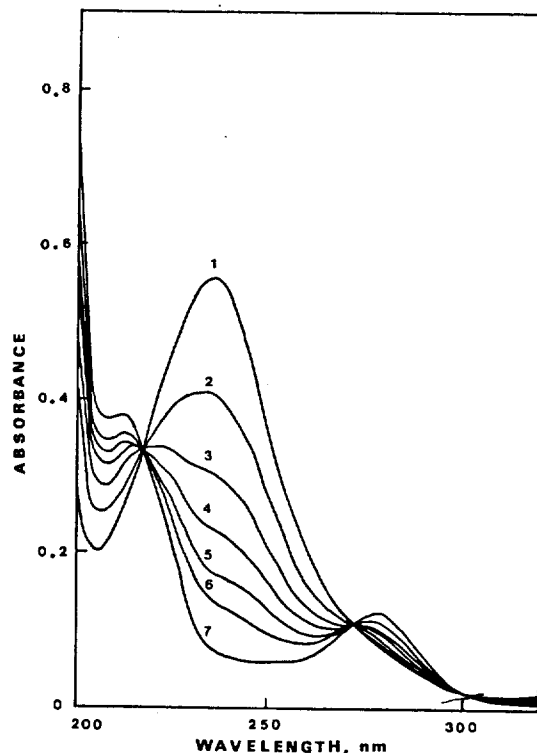


Figure 1. UV spectra for the rearrangement of methoxy methyl dienone **1** (6.7×10^{-5} M) in 67.6% aqueous sulfuric acid at 25 °C: 1; 10 sec; 2; 2 min; 3; 4 min; 4; 6 min; 5; 8 min; 6; 10 min; 7; 18 min.

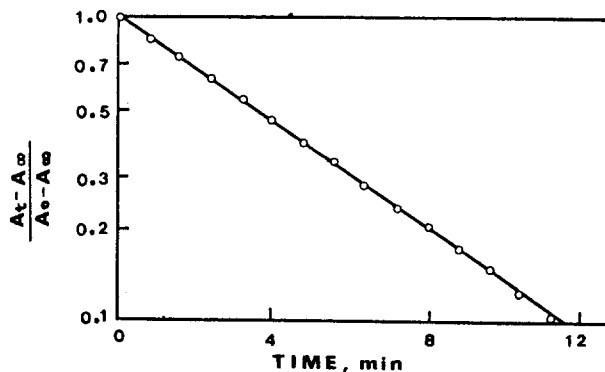


Figure 2. Kinetics of methoxy methyl dienone **1** (1.7×10^{-4} M) at 25 °C in 67.6% aqueous sulfuric acid. The rate constant was determined from the slope of $\ln A_t A_\infty / A_0 - A_\infty$ vs. time where A_0 is the initial absorbance of the dienone **1** in acidic condition at 240 nm, A_∞ is the final absorbance after 10 half lives and A_t is the absorbance at time *t*. Calculated k_{obs} was $3.38 \times 10^{-3} \text{s}^{-1}$ ($r = 0.9997$).

UV spectrum of unprotonated dienone **1** in water, or in 9.8% aqueous H₂SO₄ ($H_0 = -0.34$), or in 17.8% aqueous HClO₄ ($H_0 = -0.83$) showed the peak at 229 nm which is a characteristics of cyclohexa-2,5-dienones.^{1(d)} In 67.6% aqueous H₂SO₄ ($H_0 = -5.46$), partially protonated dienone **1** showed the peak at 235 nm. Figure 1 shows typical UV spectra for the rearrangement of **1** in 67.6% aqueous H₂SO₄. The rearranged product showed the peak at 275 nm. There are isosbestic points at 217 nm and 270 nm. Figure 2 shows a typical kinetic plot for the rearrangement of dienone **1** in 67.6% aqueous H₂SO₄. The rate constant was determined from the slope of a plot of $\ln A_t A_\infty / A_0 - A_\infty$ vs. time ($k_{obs} =$

Table 1. Equilibrium Protonation Data for Dienone 1 ($1.67 \times 10^{-4}M$) in Aqueous Sulfuric Acid at 25°C at 240 nm

Acid (wt. %)	$-H_0^a$	Absorbance	$[SH^+]/[S]^b$
43.8	2.75	1.71	
48.8	3.19	1.66	
51.3	3.42	1.72	
53.5	3.63	1.62	0.20
57.9	4.12	1.57	0.37
63.2	4.79	1.48	0.85
67.6	5.46	1.36	2.43
72.8	6.27	1.22	

^a H_0 acidity function; see ref. 10. ^b $[SH^+]/[S]$ ratio was obtained from the equation $\log [SH^+]/[S] = \log \epsilon_S - \epsilon/\epsilon - \epsilon_{SH^+}$ where $[S]$ is the concentration of dienone **1**, $[SH^+]$ is the concentration of protonated **1**, ϵ_S is the absorbance (average; 1.70) of the unprotonated **1**, ϵ_{SH^+} is the absorbance (1.22) of the protonated **1** and ϵ is the absorbance of **1** in intermediate acidity.

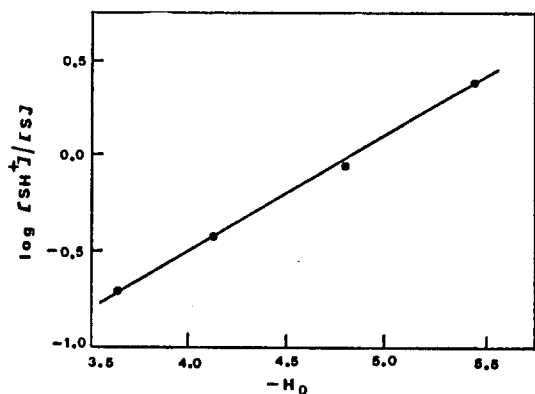


Figure 3. Plot of $\log [SH^+]/[S]$ vs. $-H_0$ for the protonation of dienone **1** in aqueous sulfuric acid: $\log [SH^+]/[S] = -0.59H_0 - 2.86$, $r = 0.998$. $[SH^+]/[S]$ ratio was obtained from the equation $\log [SH^+]/[S] = \log \epsilon_S - \epsilon/\epsilon - \epsilon_{SH^+}$; see Table 1.

$3.38 \times 10^{-3} s^{-1}$, $r = 0.9997$).

UV spectra of dienone **1** in conc-HCl showed the same pattern as in aqueous H_2SO_4 . However, UV spectra of **1** in strongly acidic 68.8% aqueous $HClO_4$ ($H_0 = -7.45$) showed different patterns from those in aqueous H_2SO_4 or in conc-HCl. The reaction in conc- $HClO_4$ has almost completed within 10 second by showing the peak at 255 nm (data not shown).

In order to estimate the basicity of dienone **1** in aqueous sulfuric acid, $[SH^+]/[S]$ ratio was checked spectrophotometrically where $[S]$ is the concentration of dienone **1** and $[SH^+]$ is the concentration of protonated dienone **1**. UV spectrum of unprotonated dienone **1** was obtained in dilute aqueous sulfuric acid with λ_{max} at 229 nm. The absorption spectra of partially protonated dienone **1** in 57.9% and in 67.6% aqueous sulfuric acid were obtained with λ_{max} at 232 nm and 235 nm, respectively. However, the absorption spectrum of the fully protonated dienone **1** could not be obtained because protonated dienone **1** rearranged very fast in the concentrated sulfuric acid. Therefore, in order to obtain $[SH^+]/[S]$ ratio, the initial absorptions of **1** in various strengths of sulfuric acid were checked at fixed wavelength. Table 1 shows the equilibrium protonation data for dienone **1** in various strengths of aqueous sulfuric acid. Figure 3 shows

Table 2. Kinetic Data for the Rearrangement of 4-Methoxy-4-methylcyclohexa-2,5-dienone 1 in Aqueous Sulfuric Acid at 25°C

Acid (wt. %)	$-H_0^a$	$k_{obs} \times 10^4 s^{-1}(r)^b$
48.8	3.19	0.36 (0.9971)
51.3	3.42	0.73 (0.9985)
53.5	3.63	1.24 (0.9978)
55.8	3.88	1.98 (0.9992)
57.9	4.12	3.30 (0.9992)
60.6	4.45	6.03 (0.9994)
63.2	4.79	10.7 (0.9998)
67.6	5.46	33.8 (0.9997)
72.8	6.27	98.8 (0.9999)
76.9	6.95	216 (0.9999)
79.4	7.36	311 (0.9999)

^a H_0 acidity function; see ref. 10. ^b Plot of $\log k_{obs}$ against H_0 for the rearrangement of **1** in aqueous sulfuric acid showed a linear relationship at low acidity or at high acidity; see Figure 4.

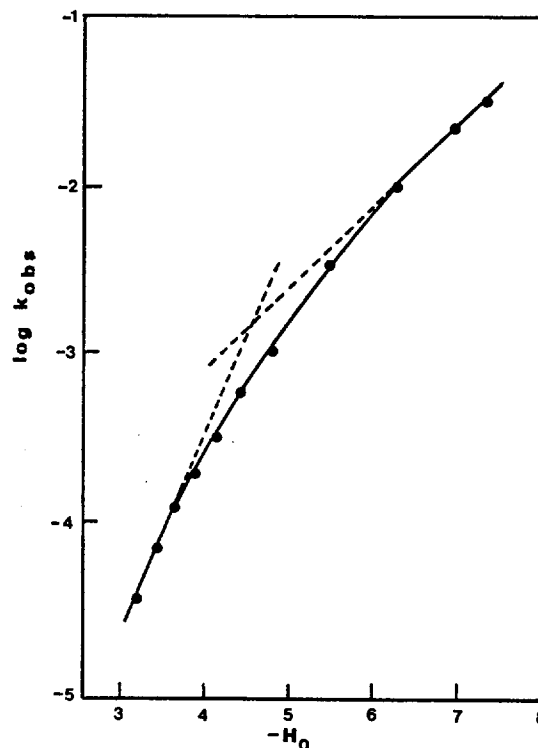


Figure 4. Plot of $\log k_{obs}$ against $-H_0$ for the rearrangement of **1** in the various strengths of aqueous sulfuric acid: Plot of $\log k_{obs}$ against H_0 at low acidity ($H_0 = -3.19 \sim -3.63$) showed a linear relationship (slope = -1.22 , $r = 0.998$); Plot of $\log k_{obs}$ against H_0 at high acidity ($H_0 = -6.27 \sim -7.36$) showed a linear relationship (slope = -0.46 , $r = 0.998$); There was a curved region at medium acidity ($H_0 = -3.88 \sim -5.46$).

the plot of $\log [SH^+]/[S]$ vs. Hammett acidity function, $-H_0$,¹⁰ for the protonation of dienone **1** in aqueous sulfuric acid. There is a linear relationship as shown in equation (1).

$$\log [SH^+]/[S] = -0.59H_0 - 2.86 \quad (r = 0.998) \quad (1)$$

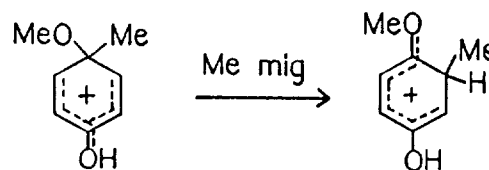
The slope of 0.59 is consistent to the values of 0.53¹¹ or 0.62¹² in 4,4-dimethylcyclohexadienone in the literatures. These values, rather than -1 , are presumably due to the fact

that dienones are not Hammett-type bases (*i.e.*, substituted anilines). The half protonation acidity, $(H_0)_{1/2}$ for **1** can be estimated as -4.8 as shown in Figure 3.

Total rate constants, k_{obs} , for the rearrangement of **1** in various strengths of aqueous sulfuric acid are shown in Table 2. Figure 4 shows plots of $\log k_{obs}$ against the Hammett acidity function, $-H_0$, for the rearrangement of **1**. Waring¹³ reported that basicity of the cyclohexadienones and the kinetic behavior of the corresponding cations can be calculated by the examination of $\log k_{obs}$ against Hammett acidity of 4-methyl-4-R-cyclohexadienones (R = Me, Et, *n*-Pr). He derived that half protonation acidity, $(H_0)_{1/2}$, of 4-methyl-4-R-cyclohexadienones are on a curved region joined by two straight lines at low and high acidity and, therefore, $(H_0)_{1/2}$ can be obtained from the intersection of the two extrapolated straight lines at low acidity and high acidity. Figure 4 which plots $\log k_{obs}$ vs. $-H_0$ for the rearrangement of dienone **1** shows the similar behavior with Waring's experiment.¹³ The three data points at low acidity ($H_0 = -3.19, -3.42, -3.63$), where the concentration of the protonated substrate is very low, gives a linear relationship with the slope of -1.22 ($r = 0.998$). Historically, Zuker and Hammett¹⁴ found that a number of reactions in strong acid showed a linear relationship between $\log k_{obs}$ and H_0 with gradient of -1 , which is to be expected if the reaction mechanism involves a first order rate determining step of the conjugate acid. At high acidity ($H_0 = -6.27, -6.95, -7.36$), where the substrate is fully protonated, the slope of the three data points is -0.46 ($r = 0.998$). There is a curved region between low and high acidity ($H_0 = -3.88 \sim -5.46$). Half protonation acidity, $(H_0)_{1/2}$, of dienone **1** can be obtained from the intersection of the two extrapolated straight lines at low and high acidity and estimated as -4.6 as shown in Figure 4. The value of -4.6 is similar with the result of -4.8 which was obtained from the previous basicity data in Table 1.

Methoxy methyl dienone **1** whose H_0 value at half protonation is -4.6 is less basic than 4,4-dimethylcyclohexadienone whose H_0 value at half protonation is -3.15 ¹¹ or -3.66 ¹². This basicity difference can be explained that electron withdrawing inductive effect by a methoxy group in **1** reduces its basicity presumably due to the unstabilization of the resulting protonated dienone **1**. Methoxy substituent at C-4 can only exert $-I$ effect since the resonance stabilization of the cation by methoxy substituent is not possible.

Product study of **1** in conc-HCl or in aqueous H_2SO_4 showed that dienone **1** undergoes the normal dienone-phenol rearrangement with the methyl group migration. The fact that methyl is migrating group and methoxy is remaining group can be rationalized by the stabilization of positive



charge at C-4 during the transition state. In the transition state, some positive charge develops at C-4 and the remaining methoxy substituent can stabilize the partial positive charge by resonance better than methyl group can.

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