

namic NMR spectra were analyzed by using a modified version of the computer program DNMR3.<sup>23</sup> Chemical shifts of the nuclei participating in the exchange were obtained initially from slow-exchange spectra. The shifts of some nuclei varied slightly (and monotonically) with temperature, and over the region where peaks coalesced the shifts were extrapolated from slow- and fast-exchange spectra. For the purpose of analysis, proton-proton coupling constants for all compounds were taken to be the same as those in fluorene,<sup>24</sup> and these values provided good matches between simulated and experimental spectra.

**Bifluorenyls.** 9,9'-Bifluorenyl (**3a**) was available commercially (Aldrich) and was used without further purifications.

9,9'-Dimethyl-9,9'-bifluorenyl (**3b**) was prepared according to the procedure of Murahashi and Moritani<sup>25</sup> from bifluorenylidene (**4**).<sup>26</sup>

9,9'-Dichloro-9,9'-bifluorenyl (**3c**). Chlorine was bubbled through a solution of **4** (0.5 g) in carbon tetrachloride (50 mL) at 10 °C until the orange/red color of **4** disappeared. The solvent

was removed, and a sample of the crude product was recrystallized from heptane/toluene to yield **3c** as a colorless crystalline solid, mp 245.1 °C (lit.<sup>27</sup> mp 237-240 °C).

9,9'-Dibromo-9,9'-bifluorenyl (**3d**). Bromine (0.3 g, 1.9 mmol) was added dropwise to a stirred solution of **4** (0.5 g, 1.5 mmol) in carbon tetrachloride (50 mL) at 0 °C. The solution was allowed to warm to ambient temperature, and stirring was continued for 1 h. The solvent was removed under reduced pressure and a sample of the crude product was recrystallized from carbon tetrachloride to yield **3d** as a colorless, crystalline solid, mp 245.4 °C (lit.<sup>25</sup> mp 237-238 °C).

9-*tert*-Butyl-9,9'-bifluorenyl (**3e**) was prepared from **4** according to the procedure of Fuson and Porter.<sup>28</sup>

9-Phenyl-9,9'-bifluorenyl (**3f**) was prepared according to the procedure of Ziegler and Schafer.<sup>28</sup>

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**Registry No.** **3a**, 1530-12-7; **3b**, 15300-82-0; **3c**, 37167-64-9; **3d**, 15300-79-5; **3e**, 26456-16-6; **3f**, 76756-37-1; **4**, 746-47-4.

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## Substituent Effects on the Activation Parameters for the Methoxymercuration of *p*-Substituted Styrenes

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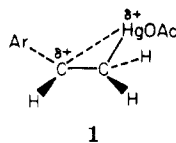
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The activation parameters for the methoxymercuration of a series of *p*-substituted styrenes in anhydrous methanol have been determined. The values of  $\Delta H^*$  and  $\Delta S^*$  are consistent with the formation of bridged activated complexes in the rate-determining step of these reactions. Analysis of the substituent effects on the values of  $\delta\Delta G^*$  for these reactions using the Yukawa-Tsuno equation required the use of small values for the  $r$  parameter. This finding is also consistent with the formation of bridged activated complexes in the rate-determining step. Variations of the substituents have small effects on  $\Delta H^*$  but large effects on  $\Delta S^*$ .  $\delta\Delta H^*$  is not linearly related to either  $\delta\Delta S^*$  or  $\delta\Delta G^*$ . However,  $\delta\Delta G^*$ —as expected for a reaction series in which the values of  $\delta\Delta H^*$  are small and/or constant—is a linear function of  $\delta\Delta S^*$ . Product studies on styrene and its *p*-MeO and *p*-NO<sub>2</sub> derivatives show that these reactions are clean and that they occur regiospecifically, giving the expected Markovnikov addition product in each case.

### Introduction

In our initial study of the methoxymercuration of a series of *p*-substituted styrenes, based on the values of  $\rho$  and  $\rho^+$  obtained from excellent linear Hammett plots, we<sup>1</sup> proposed that these reactions involve the formation of an unsymmetric bridged intermediate (**1**) in their rate-de-



terminating step. As a part of our continuing investigations into the nature of this intermediate, we have extended our initial study to include several additional styrenes (the *p*-MeO, *p*-Ac, and *p*-COOMe derivatives) and we have examined the substituent effects on both the activation

parameters and the products of these reactions. It was our aim, therefore, to obtain additional supporting information on this proposed structure and to evaluate the substituent effects on the activation parameters for this reaction in order to determine which, if any, relationships exist among  $\Delta G^*$ ,  $\Delta H^*$ , and  $\Delta S^*$ .

Electrophilic addition reactions involving styrenes usually exhibit small positive values of  $\Delta H^*$  and large negative values of  $\Delta S^*$ .<sup>2</sup> In most cases the values of these parameters, in particular  $\Delta S^*$ , have been used to argue for the formation of bridged or cyclic activated complexes, hence intermediates in the rate-determining steps of these reactions. In the case of the bromination of substituted styrenes, however, it has been suggested by some investigators<sup>2c,3</sup> that the values of  $\Delta S^*$  merely reflect greater

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Table I. Second-Order Rates of Reaction of *p*-XC<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub> with Hg(OAc)<sub>2</sub><sup>a</sup> in Anhydrous Methanol

X	10k <sub>2</sub> , <sup>b</sup> M <sup>-1</sup> s <sup>-1</sup> at temp, °C			
	8	15	25	35
MeO	1040.0 ± 18.0 <sup>c</sup>	1160.0 ± 23.0 <sup>d</sup>	1460.0 ± 6.0 <sup>e</sup>	1580.0 ± 23.0 <sup>f</sup>
Me	90.1 ± 2.9	129.0 ± 7.0	198.0 ± 3.0 <sup>g</sup>	
H	18.5 ± 0.2	27.0 ± 0.9	41.7 ± 2.3 <sup>g</sup>	
F	14.1 ± 0.1	20.7 ± 1.3	33.6 ± 1.0	
Br		5.77 ± 0.16	9.31 ± 0.29	14.9 ± 0.7
COOMe			2.01 ± 0.09 <sup>h</sup>	
Ac		1.06 ± 0.01	1.87 ± 0.05	2.73 ± 0.08
CN		0.222 ± 0.004	0.341 ± 0.019	0.573 ± 0.016
NO <sub>2</sub>	0.500 ± 0.024 <sup>i</sup>		0.197 ± 0.004	0.340 ± 0.016

<sup>a</sup> Initial concentrations of the various Hg(OAc)<sub>2</sub> solutions used, as determined by titrations of the stock solutions with standard KSCN, ranged from 1.71 × 10<sup>-2</sup> to 1.74 × 10<sup>-2</sup> M. <sup>b</sup> The average of three or more determinations plus or minus the standard deviations. <sup>c</sup> 21 °C. <sup>d</sup> 26 °C. <sup>e</sup> 41 °C. <sup>f</sup> 47 °C. <sup>g</sup> Reevaluations of the data from ref 1 and additional measurements of *k*<sub>obsd</sub> gave higher values in these cases—0.345 ± 0.005 for the *p*-Me derivative and 0.0725 ± 0.0040 s<sup>-1</sup> for styrene. <sup>h</sup> Measured at 25 °C only, see text. <sup>i</sup> 45 °C.

Table II. Activation Parameters for Reactions of *p*-XC<sub>6</sub>H<sub>4</sub>CH=CH<sub>2</sub> with Hg(OAc)<sub>2</sub> in Anhydrous Methanol

X	ΔH*, kcal/mol	-ΔS*, eu	-TΔS* <sup>a</sup>	ΔG* <sup>a</sup>	δΔH* <sup>b</sup>	δΔS*, eu	δΔG* <sup>a</sup>
MeO	2.36 ± 0.11	41.2 ± 0.4	12.28	14.64	-5.00	-10.2	-1.96
Me	7.12 ± 0.34	28.7 ± 1.2	8.56	15.68	-0.24	2.3	-0.92
H	7.36 ± 0.38	31.0 ± 1.3	9.24	16.60	0.00	0.0	0.00
F	7.93 ± 0.24	29.5 ± 0.8	8.80	16.73	0.57	1.5	0.13
Br	7.81 ± 0.15	32.5 ± 0.5	9.69	17.50	0.45	-1.5	0.90
COOMe				18.40 <sup>c</sup>			1.80 <sup>c</sup>
Ac	7.78 ± 0.78	35.9 ± 2.6	10.70	18.48	0.42	-4.9	1.88
CN	7.78 ± 0.63	39.1 ± 2.1	11.66	19.44	0.42	-8.1	2.84
NO <sub>2</sub>	8.17 ± 0.62	38.9 ± 2.0	11.60	19.77	0.81	-7.9	3.17

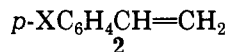
<sup>a</sup> At 298 K, in kcal/mol. <sup>b</sup> In kcal/mol. <sup>c</sup> Calculated values, see text.

organization in the transition state than in the ground state as a result of greater solvation of an open α-bromocarbo-cationic activated complex.

While numerous exceptions are now known, it was originally generally accepted that the existence of a linear Hammett plot required that the reaction series under study be either isoentropic or isokinetic.<sup>4</sup> Recently, Dubois and de Ficquelmont-Loizos<sup>3</sup> found that for the bromination of *p*-substituted styrenes in anhydrous methanol an excellent linear relationship exists between either log *k* or Δ*G*\* and σ<sup>+</sup>. However, the reaction series was neither isoentropic, isoenthalpic, nor isokinetic and neither Δ*H*\* nor Δ*S*\* was a linear function of σ<sup>+</sup>. By assuming that both Δ*H*\* and *T*Δ*S*\* include a common term that vanishes for Δ*G*\*, they justified these nonlinear relationships and suggested that they might be general phenomena. As the data which we report here will show, however, this is not the case for the related methoxymercuration reaction.

### Results<sup>5</sup> and Discussion

The activation parameters were determined by measuring the temperature dependence of the rates of reaction of 2 with mercuric acetate in anhydrous methanol. The



a, X = MeO; b, X = Me; c, X = H; d, X = F;  
e, X = Br; f, X = Ac; g, X = CN; h, X = NO<sub>2</sub>  
pseudo-first-order rate constants, *k*<sub>obs</sub> were determined

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(5) All of the results reported herein were obtained by using a linear least-squares program on a computer. Unless otherwise indicated, the corresponding correlation coefficient was 0.993 or better.

spectrophotometrically by monitoring the decrease in the absorbance of 2 at their longest wavelength absorption band.<sup>1</sup> These reactions obey the second-order rate law given in eq 1. The order in Hg(OAc)<sub>2</sub> was determined

$$-d[\text{ArCH}=\text{CH}_2]/dt = k_2[\text{ArCH}=\text{CH}_2][\text{Hg}(\text{OAc})_2] \quad (1)$$

by measuring *k*<sub>obsd</sub> for 2c and 2e at 25 °C as a function of the Hg(OAc)<sub>2</sub> concentration. Plots of log *k*<sub>obsd</sub> vs. log [Hg(OAc)<sub>2</sub>]<sub>0</sub> gave lines with slopes of 1.09 ± 0.04 and 1.01 ± 0.02, respectively. Thus the second-order rate constants, *k*<sub>2</sub>, were determined by dividing *k*<sub>obsd</sub> by the initial Hg(OAc)<sub>2</sub> concentration. These data are summarized in Table I. Table I also includes the rate of reaction at 25 °C for the COOMe derivative of 2. We found that this compound undergoes extensive polymerization if not used immediately after purification; therefore, its rate of reaction was measured at this temperature only.

The values of Δ*H*\* and Δ*S*\* were obtained from the slopes and intercepts, respectively, of the lines obtained from Eyring plots of ln *k*<sub>2</sub>/*T* vs. 1/*T*. The uncertainties in Δ*H*\* and Δ*S*\* were determined from the standard deviations in the slopes and intercepts, respectively, of these lines. These data along with the values of Δ*G*\* and the values of δΔ*Y*\* (eq 2, where *Y* represents either *G*, *H*, or

$$\delta\Delta Y^* = \Delta Y^*_X - \Delta Y^*_H \quad (2)$$

*S*, while *X* and *H* denote the substituted and the unsubstituted reactants, respectively) are listed in Table II. Table II also includes the calculated values of δΔ*G*\* and Δ*G*\* for the COOMe derivative of 2. δΔ*G*\* was calculated from eq 3, which was obtained from a plot of log *k*<sub>X</sub>/*k*<sub>H</sub>

$$\log k_X/k_H = -(0.734 \pm 0.003)\delta\Delta G^* + (0.003 \pm 0.005) \quad (3)$$

vs. δΔ*G*\* at 25 °C for the other eight styrenes. Δ*G*\* was then obtained by using eq 2.

Table III. Effect of Added *p*-Dioxane on the Rate of Reaction of *p*-Bromostyrene<sup>a</sup> with Hg(OAc)<sub>2</sub><sup>b</sup> in MeOH at 25 °C

% <sup>c</sup> <i>p</i> -dioxane	10 <sup>2</sup> <i>k</i> <sub>2</sub> , <sup>d</sup> M <sup>-1</sup> s <sup>-1</sup>
0.00	95.5 ± 5.1
3.54	30.6 ± 2.0
7.34	24.9 ± 0.3
11.5	12.0 ± 0.1
16.0	4.25 ± 0.11

<sup>a</sup> Initial concentration = 1.62 × 10<sup>-3</sup> M. <sup>b</sup> Initial concentration = 1.77 × 10<sup>-2</sup> M. <sup>c</sup> Molar percentages. <sup>d</sup> Average of two or more determinations plus or minus the standard deviation.

The magnitudes of the values of  $\Delta H^*$  and  $\Delta S^*$  listed in Table II are in agreement with those found previously for most other electrophilic additions to styrenes.<sup>2</sup> The relatively small positive values of  $\Delta H^*$  and the large negative values of  $\Delta S^*$  are consistent with reactions which pass through highly organized rate-determining transition states, in which bond formations are well advanced. Since the values of  $-\Delta S^*$  (average 33.7 eu) found in this study are much larger than those (average 17.6 eu) found by Dubois and de Ficquelmont-Loizos<sup>3</sup> for the bromination of *p*-substituted styrenes, we believe that they reflect contributions made by factors other than those due to increased solvation of the transition state. One of these other factors which we believe to be important is partial bridging between the mercury and the benzylic carbon. Accordingly, we believe that the activation parameters listed in Table II are consistent with the formation of an activated complex and intermediate of structure 1.

As the data in Table II show, varying the substituent has little, if any, effect on the values of  $\Delta H^*$ —the average value of  $\Delta H^*$  is 7.71 ± 0.33 kcal/mol. The standard deviation in this value is well within the limits of the experimental uncertainties in most of the values of  $\Delta H^*$  listed in Table II. The average value of  $\delta\Delta H^*$  is 0.35 ± 0.33 kcal/mol. Thus this reaction series appears to be isoenthalpic. If, however, the small variations in the values of  $\Delta H^*$  are real, then the general trend in these values is in qualitative accord with the ability of the substituent on the ring to interact with a developing positive charge on the benzylic carbon in the transition state.

Inspection of the data in Table II also reveals that varying the substituent has a large effect on the values of  $\Delta S^*$  and that, in general, the value of  $-\Delta S^*$  increases as the electron-withdrawing ability of the substituent increases. This trend is consistent with an increasing need for stabilization of the transition state by solvation<sup>7</sup> as a result of the increasing destabilization of the developing charge by the substituent.

The importance of solvation of the transition state in these reactions is shown by the data in Table III. From these data it is clear that the addition of *p*-dioxane to the kinetic mixture has a pronounced rate-retarding effect on these reactions. Romeyn and Wright<sup>8</sup> reported a similar finding from their studies of the methoxymercuration of cyclohexene. The net effect of the added *p*-dioxane is to reduce the polarity of the reaction medium. Accordingly, these rate-reductions are due, in large part, to a decrease in the ability of the solvent to solvate the polar transition

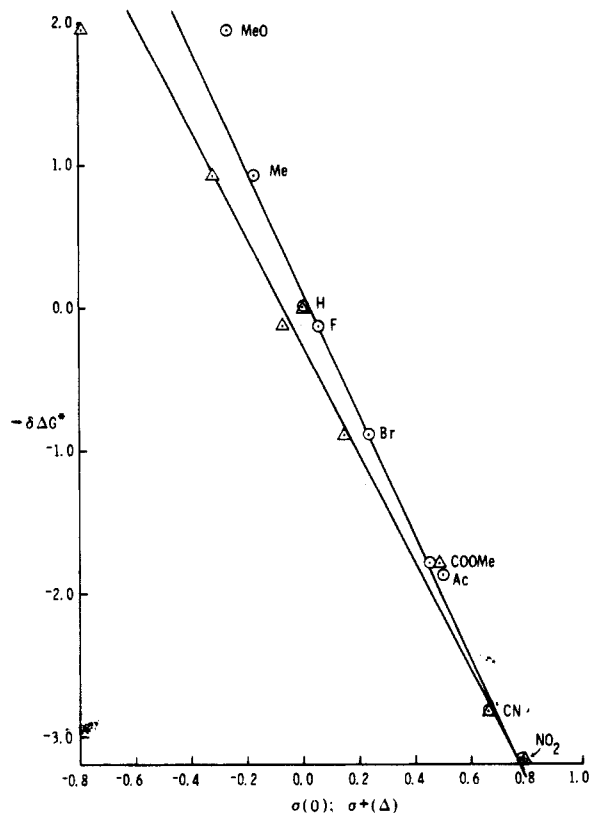
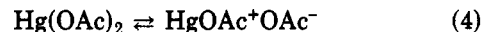


Figure 1. Plots of  $\delta\Delta G^*$  vs.  $\sigma$  and  $\sigma^+$ .

state formed in the rate-determining step. It should be pointed out, however, that a part of these rate reductions may also be due to a shift to the left in the initial ion-pair equilibrium step (eq 4) of these reactions as the polarity



of the solvent decreases. Further, as the data in Table II show,  $-\Delta S^*$  is larger than  $\Delta H^*$  for each of the styrenes; therefore,  $\Delta G^*$  and the rates of these reactions are controlled by  $\Delta S^*$ . This situation is generally found when solvent effects are very important.<sup>9,10</sup>

As shown in Figure 1 (if the points for *p*-methoxystyrene are omitted), plots<sup>11</sup> of  $\delta\Delta G^*$  vs.  $\sigma$  and  $\sigma^+$  give excellent linear correlations with values of  $-3.14$  for  $\rho$  and  $-2.73$  for  $\rho^+$  which are in excellent agreement with those ( $-3.16$  and  $-2.76$ , respectively) previously reported by us.<sup>1</sup> The deviations of the points for *p*-methoxystyrene from the correlation lines in Figure 1 may be the result of a change in the nature of the intermediate formed in the rate-determining step<sup>12</sup> and/or a change in the rate-determining step, itself. However, deviations of this sort for the *p*-MeO derivative in Hammett plots—for reactions involving the generation of a positive charge on the benzylic carbon—are quite often found,<sup>13</sup> even in those cases where no change in the rate-determining step occurs. The upward deviation of the point for the *p*-MeO derivative from the  $\sigma$  correlation line is generally attributed to direct resonance in-

(6) Because of the deviations shown by the data for *p*-methoxystyrene in Table II, this compound was not included in any of the discussions or correlations which involve  $\Delta H^*$  and/or  $\Delta S^*$ .

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(11) The  $\sigma$  and  $\sigma^+$  values were taken from: Ritchie, C. D.; Sager, W. F. *Prog. Phys. Org. Chem.* 1964, 2, 323. A reliable  $\sigma^+$  value for the *p*-Ac substituent could not be found; therefore, *p*-acetylstyrene was not included in any of the correlations involving the use of  $\sigma^+$ .

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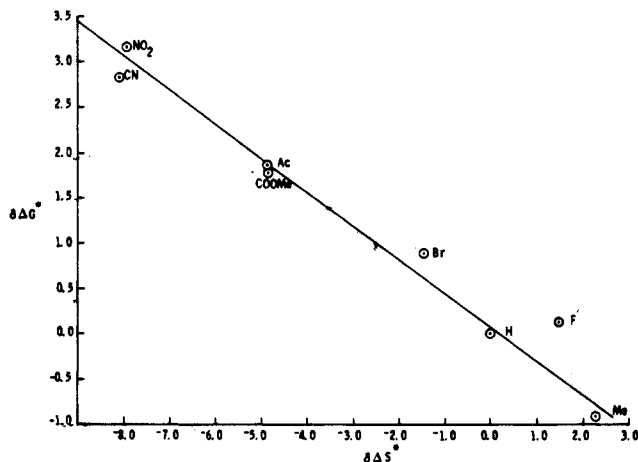


Figure 2. Plot of  $\delta\Delta G^*$  vs.  $\delta\Delta S^*$ .

interactions between the *p*-MeO substituent and the benzylic carbon, while the downward deviation of the point for this derivative from the  $\sigma^+$  correlation line has been considered, in some cases,<sup>13</sup> to be indicative of the operation of a saturation effect.<sup>14</sup> The deviations shown by the data for *p*-methoxystyrene in Figure 1 may be rationalized in similar fashions, hence without postulating either of the changes mentioned above. The intermediacy of a structure such as 1 is consistent with the operation of a saturation effect, of sorts. In 1 a portion of the charge developed on the benzylic carbon is delocalized onto the mercury; thus the need for resonance stabilization of the charge by the aryl substituent is reduced. Accordingly, the effect of the *p*-MeO substituent on the rate of reaction ( $\Delta G^*$ ) for *p*-methoxystyrene is smaller than one would expect based on the value of  $\sigma^+$  for this substituent.

Use of the Yukawa-Tsuno equation<sup>15</sup> (eq 5) to analyze

$$\log k_X/k_H = -\delta\Delta G^*/2.303RT = \rho[\sigma + r(\sigma^+ - \sigma)] \quad (5)$$

the substituent effects on the values of  $\delta\Delta G^*$  required values of  $0.37 \pm 0.01$  for  $r$ . The correlation lines thus obtained pass through the origin as required by eq 5. Small values of  $r$  have been used in correlating substituent effect data by eq 5 for reactions—e.g., the hydrolysis of  $\alpha$ -methoxystyrenes<sup>13</sup>—where direct resonance interactions between the substituent on the ring and benzylic carbon are small due to partial stabilization of the charge by some other means. Thus the small values of  $r$  required to correlate the data in this case are consistent with our proposal of the formation of an activated complex and intermediate such as 1 in the rate-determining step of these reactions.

By definition  $\delta\Delta G^*$  is related to  $\delta\Delta H^*$  and  $\delta\Delta S^*$  by eq 6. As mentioned above, this reaction series appears to be

$$\delta\Delta G^* = \delta\Delta H^* - T\delta\Delta S^* \quad (6)$$

isoenthalpic; that is,  $\delta\Delta H^* \approx 0$ . Accordingly,  $\delta\Delta G^*$  should be linearly related to  $\delta\Delta S^*$  and  $\delta\Delta S^*$  should be linearly related to both  $\sigma$  and  $\sigma^+$ . As shown in Figure 2, excluding the point for *p*-fluorostyrene, an excellent linear relationship does exist between  $\delta\Delta G^*$  and  $\delta\Delta S^*$ . A point for the COOMe derivative of 2 is also shown in Figure 2. The value of  $\delta\Delta S^*$  ( $-4.9$  eu) for this compound was calculated by using eq 6, the extrapolated (see above) value of  $\delta\Delta G^*$  for this compound, and the average value of  $\delta\Delta H^*$  for the other styrenes. The fact that the point for this compound falls on the correlation line supports the idea that this

reaction series is isoenthalpic. The value of  $T$  derived from the slope of the correlation line in Figure 2 (the point for the COOMe derivative was omitted in the analysis of the data) is  $373 \pm 22$  K. If the points for *p*-fluorostyrene are omitted, plots of  $\delta\Delta S^*$  vs.  $\sigma$  and  $\sigma^+$  are also highly linear ( $r = 0.988$  and  $0.990$ , respectively). These plots are essentially identical with that shown in Figure 2, with the exception that the slopes of the lines are reversed. Analyses of the data give values of  $-2.47$  for  $\rho$  and  $-2.23$  for  $\rho^+$ . The 25% difference between the extrapolated and experimental temperatures and the 21% difference in the values of  $\rho$  and  $\rho^+$  obtained here and above may be ascribed to the errors mainly in the values of  $\delta\Delta S^*$  and to the deviations of this reaction series from being completely isoenthalpic.

Inspection of the data in Table II and examinations of Figure 2 and plots of  $\delta\Delta S^*$  vs.  $\rho$  and  $\rho^+$  reveal that the value of  $-\Delta S^*$  for *p*-fluorostyrene (and to a lesser extent, *p*-bromostyrene) is smaller than expected based on the trend established by the other members of this series. As suggested by Kharasch<sup>16</sup> from studies of the addition of 2,4-dinitrobenzenesulfonyl chloride to *p*-chlorostyrene in acetic acid, this deviation may be due to greater solvation of the ground state, through hydrogen bonding (MeOH...FAr), than the transition state. On going to the transition state this interaction would be reduced due to partial delocalization of fluorine's nonbonding p electrons into the developing empty p orbital on the benzylic cation.

In conclusion, the activation parameters, in particular  $\Delta S^*$ , and the small values of  $r$  used in correlating the substituent effect data by the Yukawa-Tsuno equation are consistent with our originally proposed structure (1) for the intermediate formed in the rate-determining step of these reactions. While this reaction series exhibits the behavior expected of an isoenthalpic reaction series, the deviations shown by some of the members of this series may be real. The dominance of the entropy term in these reactions is consistent with the important role that the solvent plays. In order to better understand this role, we are currently engaged in a study of the effects of solvents on the rates of these reactions.

## Experimental Section

**General Procedures.** Melting points were determined on a Thomas-Hoover melting-point apparatus and are uncorrected. All boiling points were recorded under atmospheric pressure. Routine <sup>1</sup>H NMR spectra were obtained on either a Varian EM-360 or a Hitachi Perkin-Elmer R-600 spectrometer. The more detailed spectra required in the cases of the 2-methoxy-2-arylethylmercuric chlorides were obtained on a Nicolet NT-200 FT NMR instrument. GC-MS analyses were performed on a Finnigan 3200 automated gas chromatograph-mass spectrometer.

**Materials.** All styrenes used in this study were prepared by standard literature procedures—dehydrobrominations<sup>17</sup> of the appropriate 2-arylethyl bromides, dehydrations<sup>18</sup> of the corresponding 1-arylethanol, and/or decarboxylations<sup>19</sup> of the corresponding cinnamic acids. Purifications were accomplished by several vacuum fractional distillations and/or column chromatography on Florisil using low-boiling petroleum ether as the eluent. All of the styrenes, except *p*-(carbomethoxy)styrene, had physical properties that agreed with those reported in the literature. *p*-(Carbomethoxy)styrene is a low-melting solid which polymerizes readily in the absence of solvent. All attempts at distillation of this compound resulted in its polymerization. Thus

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(17) (a) DePuy, C. H.; Froemsdorf, D. H. *J. Am. Chem. Soc.* **1957**, *79*, 3710. (b) Saunders, W. H.; Williams, R. A. *Ibid.* **1957**, *79*, 3712.

(18) Berstein, I. A.; Bennett, W.; Fields, M. *J. Am. Chem. Soc.* **74**, 5763. (b) Wilkins, C. L.; Regulski, T. W. *Ibid.* **1972**, *94*, 6016.

(19) Walling, C.; Wolfstirn, K. B. *J. Am. Chem. Soc.* **1947**, *69*, 852.

(14) Hine, J. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1962; pp 101-102.

(15) Yukawa, Y.; Tsuno, T. *Bull. Chem. Soc. Jpn.* **1959**, *32*, 965, 971.

Table IV. FT 200-MHz <sup>1</sup>H NMR Spectral Data<sup>a</sup> of the Isolated β-Methoxyalkylmercuric Chlorides

X		peak no.					
		1	2	3	4	5	6
MeO	δ	7.24/6.90	4.58	3.82	3.22	2.47	2.25
	multiplicity	d/d	t	s	s	q	q
	no. of H's	2/2	1	3	3	1	1
	J, <sup>b</sup> Hz	c	5.6/5.9			5.4/6.3/5.4	5.9 <sup>d</sup>
H	δ	7.32	4.64		3.25	2.49	2.26
	multiplicity	m <sup>e</sup>	t		s	q	q
	no. of H's	5	1		3	1	1
	J, <sup>b</sup> Hz	c	5.6 <sup>d</sup>			5.6/6.1/5.6	5.9/6.1/5.6
NO <sub>2</sub>	δ	8.25/7.50	4.73		3.30	2.48	2.20
	multiplicity	d/d	t		s	q	q
	no. of H's	2/2	1		3	1	1
	J, <sup>b</sup> Hz	c	6.0/6.2			5.3/6.8/5.3	6.5/5.6/6.5

<sup>a</sup> In CDCl<sub>3</sub> containing 1% Me<sub>4</sub>Si. <sup>b</sup> The uncertainty in these values is ±0.2. <sup>c</sup> Not measured. <sup>d</sup> All coupling constants are the same. <sup>e</sup> An unresolved symmetrical multiplet which appears as a singlet at 60 MHz.

it was purified by column chromatography (twice) and used immediately. All of the styrenes had <sup>1</sup>H NMR spectra (CCl<sub>4</sub> or CDCl<sub>3</sub>) that were consistent with their structures. GC-MS analyses showed that each of them was, at least, 99% pure.

**Mercuric acetate** (B & A, AR) was purified according to the procedure of Allen et al.<sup>20</sup> It was stored in vacuo, in the dark, over KOH pellets. Periodic titrations with standard KSCN showed that it did not undergo decomposition and that it was better than 99% pure.

**Methanol** (MCB, AR) was refluxed over and distilled from NaOMe (2.5%, w/v) onto anhydrous K<sub>2</sub>CO<sub>3</sub> (1.0%, w/v), three times. The fraction distilling at 64.8 °C was collected in each case. It was stored in an all-glass (Teflon stopcocks) storage-dispensing bottle under a dry nitrogen atmosphere.

**p-Dioxane** (MCB, Scintillation Grade) was predried over CaH<sub>2</sub> and twice distilled from Na metal. The fraction distilling at 101 °C was collected in each case. This material was used immediately.

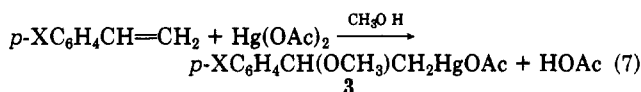
**Kinetic Procedure.** With the exception of *p*-methoxystyrene, all rates were determined spectrophotometrically in a 10-mm thermal-jacketed cell on a Cary 14 spectrophotometer. The temperatures of both the cell and the stock solutions were controlled to within ±0.02 °C, using a Forma Scientific Model 2095 refrigerated and heated bath and circulator. For experiments carried out below 25 °C, the sample compartment of the spectrophotometer was continuously flushed with dry N<sub>2</sub> in order to prevent moisture from condensing on the cell. The general procedure was as follows. Stock solutions, with less than the required amounts of anhydrous methanol, of the styrenes (2.8–56 × 10<sup>-4</sup>M) and mercuric acetate (~2.5 × 10<sup>-2</sup>M) in tightly stoppered volumetric flasks were placed in the constant-temperature bath at the desired temperature. After thermal equilibrium was achieved, the stock solutions were diluted up to the marks with anhydrous methanol, at the same temperature, and 750 μL of the Hg(OAc)<sub>2</sub> solution was pipetted into the thermal cell mounted in the sample compartment of the spectrophotometer, set at the desired wavelength and chart speed. To initiate the reaction, 300 μL of the appropriate styrene solution was rapidly and forcefully injected into the cell and the decrease in the absorbance of the styrene as a function of time was recorded.

The rates for *p*-methoxystyrene were determined on a Durrum Gibson stopped-flow spectrophotometer. The rates for styrene and *p*-methylstyrene were also measured on this instrument at 25 °C in order to determine whether the two instruments and procedures gave comparable results—they agreed to within ±2%.

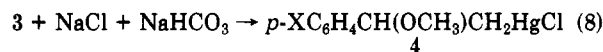
In carrying out the solvent effect studies, the initial concentrations of the *p*-bromostyrene and the Hg(OAc)<sub>2</sub> were held constant, while those of the *p*-dioxane and the methanol were varied by mixing varying volumes of two equimolar solutions of the styrene in *p*-dioxane and the styrene in methanol.

**Product Studies.** In order to determine the structures of the products formed under the pseudo-first-order conditions—

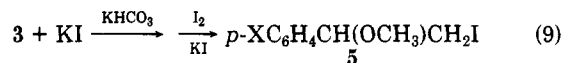
[Hg(OAc)<sub>2</sub>]/[styrene]<sub>0</sub> ≥ 10—of our kinetic experiments, product studies on the reaction of Hg(OAc)<sub>2</sub> with several of the styrenes at 25 °C were carried out (eq 7, where X = MeO, H, and NO<sub>2</sub>).



These styrenes were selected because they cover the entire range of reactivities investigated; therefore, the products of these reactions should be typical of those to be expected for the entire series. The structures of the mercurials, **3**, were determined by <sup>1</sup>H NMR analyses of the isolated β-methoxyalkylmercuric chlorides, **4** (eq 8), and by GC-MS analyses of the iododemercuration



products, **5** (eq 9). These reactions (eq 8 and 9) were selected



because they are known<sup>21</sup> to be essentially quantitative and free of side reactions.<sup>22</sup>

These studies showed that the methoxymercurations (i) occur cleanly, (ii) are essentially quantitative, and (iii) give only the expected Markovnikov addition product.

**Methoxymercurations.** The appropriate styrene solution (1 mL, 0.2–0.6M) was injected into an accurately measured volume (25–80 mL) of the Hg(OAc)<sub>2</sub> stock solution (7.6–8.8 × 10<sup>-2</sup>M) at 25 °C with vigorous shaking. After the desired length of time, the reactions were quenched.

**Isolation of 2-Methoxy-2-arylethylmercuric Chlorides, **4**.** The reaction mixtures were quenched in an excess volume of an ice-cold saturated aqueous solution of NaCl and NaHCO<sub>3</sub>. Each of the resulting mixtures was diluted with 50 mL of water and extracted with three 5-mL portions of CH<sub>2</sub>Cl<sub>2</sub>. The combined extracts were washed with water and the CH<sub>2</sub>Cl<sub>2</sub> was evaporated. The reaction times used, the isolated yield, and the melting points of the products were as follows: MeO (10 min; 87% 95–97 °C); H (20 min; 89%; 73–75 °C; lit.<sup>21b</sup> mp 65–70 °C); and NO<sub>2</sub> (6 h; 90%; 119–121 °C, softens at 110 °C).

(21) (a) Sayre, L. M.; Jensen, F. R. *J. Am. Chem. Soc.* **1979**, *101*, 6001. (b) Spengler, G.; Weber, A. *Brennst. Chem.* **1959**, *40*, 22; *Chem. Abstr.* **1959**, *53*, 19938a. (c) Chatt, J. *Chem. Rev.* **1951**, *48*, 7.

(22) Product studies involving the NaBH<sub>4</sub> reduction of **3** to the corresponding 1-methoxy-1-arylethanes were inconclusive since side reactions—demethoxymercuration (Bordwell, F. R.; Douglass, M. L. *J. Am. Chem. Soc.* **1966**, *88*, 993) and possibly rearrangements (Pasto, D. J.; Gontarz, J. A. *Ibid.* **1969**, *91*, 719)—are important for these compounds. Demethoxymercuration was found to be important in all cases, since GC-MS analyses of the reaction mixtures revealed the presence of from 8–74% of the corresponding styrenes. The possibility of a rearrangement was indicated in the case of the NO<sub>2</sub> derivatives of **3**, where from 0–17% of the unexpected 2-methoxy-1-(*p*-nitrophenyl)ethane was identified by GC-MS analyses of the reaction mixtures.

(20) Allen, E. R.; Cartledge, J.; Taylor, M. M.; Tipper, C. F. H. *J. Phys. Chem.* **1959**, *63*, 1437.

The FT 200-MHz  $^1\text{H}$  NMR spectral data of these compounds are given in Table IV. Inspection of the data in this table reveals that the three spectra are identical and—like the melting points—indicative of a single compound in each case. Thus these three compounds have the same basic structure, which—based on the analysis below—is consistent with that of the Markovnikov addition product, 4. The assignments of the signals (all sharp and well-defined) given in Table IV are as follows. Peaks number 1 are assigned to the aromatic protons. Peaks number 2 are attributed to the benzylic proton. The signal given by this proton appears as a triplet, rather than a quartet, because the coupling constants between this proton and the two adjacent diastereotopic protons,  $\text{H}_5$  and  $\text{H}_6$ , are very similar. Peak number 3 is due to the protons on the *p*-MeO group of that particular derivative. Peaks number 4 are assigned to the protons on the  $\alpha$ -MeO group. Peaks numbers 5 and 6 are ascribed to the two diastereotopic methylene protons. The resonances of these protons occur in the region where protons  $\alpha$  to mercury are expected.<sup>23</sup> Protons  $\text{H}_2$ ,  $\text{H}_5$ , and  $\text{H}_6$  from an ABX system; therefore,  $\text{H}_5$  and  $\text{H}_6$  experience both geminal and vicinal couplings and should appear as quartets. The only other signals present in these spectra were the low-intensity  $^{199}\text{Hg}$  satellites of peaks number 2, 5, and 6. In all cases,  $J_{^{199}\text{Hg}-\text{H}_2} \gg J_{^{199}\text{Hg}-\text{H}_5} > J_{^{199}\text{Hg}-\text{H}_6}$ , with the average values (hertz) being  $266.1 \pm 7.7$ ,  $202.6 \pm 0.9$ , and  $192.3 \pm 2.1$ , respectively.

**Iododemercurations.** The methoxymercuriation reactions were quenched by the addition of an excess volume of an ice-cold saturated aqueous solution of KI and  $\text{KHCO}_3$  to the reaction flasks. Within a few minutes, a slight excess of an aqueous solution

of  $\text{I}_2$  and KI was added. After at least 1 h, each reaction mixture was diluted with 50 mL of water; the excess  $\text{I}_2$  was destroyed by the dropwise addition of a dilute  $\text{Na}_2\text{S}_2\text{O}_3$  solution, and then the solution was extracted with one 10-mL portion of  $\text{CH}_2\text{Cl}_2$  followed by one 15-mL portion of pentane. The combined extracts were washed with water and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . GC-MS analyses of these extracts showed that only one product—the expected 2-methoxy-2-arylethyl iodide, 5—was formed in each case. The mass spectrum of each of these products showed a weak (0.2–3%)  $\text{M}^+$  peak at the correct *m/e* and a weak (2%, in all cases) peak at *m/e* 141 ( $\text{ICH}_2^+$ ). The other major distinguishing peaks—at *m/e* corresponding to the indicated losses (abundances are given in parentheses)—appeared at  $\text{M} - \text{CH}_3\text{O}$  (0.2%, in all cases),  $\text{M} - \text{Ar}$  (0.2–20%),  $\text{M} - \text{I}$  (15–30%), and  $\text{M} - \text{CH}_2\text{I}$  (100%, in all cases). Below the base peak, the spectra of these compounds were almost identical with those (below  $\text{M} - 15$ ) of the corresponding 1-methoxy-1-arylethanes. Evaporation of the extracts gave essentially quantitative yields of 5. The MeO and H derivatives of 5 are liquids, while the  $\text{NO}_2$  derivative is a white solid, mp 69.5–70 °C.

**Acknowledgment.** We are deeply indebted to Professors Peter Hambright and Carlyle B. Storm of this Department for both the loan of some of their equipment and their assistance in carrying out this work.

**Registry No.** 2 (X = MeO), 637-69-4; 2 (X = Me), 622-97-9; 2 (X = H), 100-42-5; 2 (X = F), 405-99-2; 2 (X = Br), 2039-82-9; 2 (X = COOMe), 1076-96-6; 2 (X = Ac), 10537-63-0; 2 (X = CN), 3435-51-6; 2 (X =  $\text{NO}_2$ ), 100-13-0; 4 (X = MeO), 76584-15-1; 4 (X = H), 72887-18-4; 4 (X =  $\text{NO}_2$ ), 67083-12-9; 5 (X =  $\text{NO}_2$ ), 76584-16-2;  $\text{Hg}(\text{OAc})_2$ , 1600-27-7.

(23) Brownstein, S. *Discuss. Faraday Soc.* 1962, 34, 25.

## Photochemistry of 2,3,6-Trialkyl-4-pyrimidinones in Liquid Ammonia-Ether Solution. Chemistry of Dewar 4-Pyrimidinones

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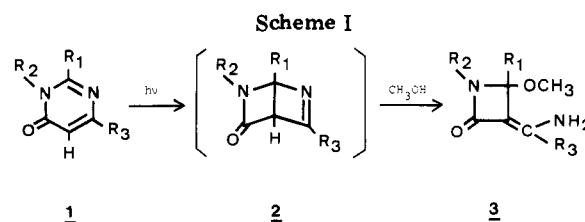
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Irradiation of the 2,3,6-trialkyl-4-pyrimidinones 4 and 18 in liquid ammonia-ether (7:3) solution at  $-40$  °C gave the corresponding Dewar 4-pyrimidinones, 5 and 19, which decomposed in inert solvents at room temperature and did not revert to the corresponding 4-pyrimidinones. The first-order rate constants for disappearance of 5 and 19 were measured at 10–54 °C. The solvolysis reactions of 5 and 19 occur in methanol to give the  $\alpha$ -(aminoethylidene)- $\beta$ -methoxy- $\beta$ -lactams 6 and 20, respectively, whereas treatment of 5 and 19 in methanol containing sodium methoxide gave the imino ether 7 and the ketal 23, respectively. The reactions of 5 and 19 in methylamine-ether (1:4) solution afforded the imine derivatives 9 and 24, respectively. Furthermore, treatment of 5 in methanol-*d* containing sodium methoxide gave *N*-methyl-3-[(methoxyethylidene)amino]-2-butenamide-2-*d* ( $7\text{D}_1$ ) and *N*-methyl-3-[(methoxyethylidene)amino]-2-butenamide-2,4-*d}\_2 ( $7\text{D}_2$ ) as the major components. The imino ether 7 did not give the deuterated imino ether under similar conditions. The products (7, 9, 23, 24, and 27) formed in basic solutions are discussed in terms of abstraction of the methine proton by base from the Dewar 4-pyrimidinone or in terms of addition of nucleophile to the imino group of Dewar 4-pyrimidinone.*

In the previous papers,<sup>1</sup> we reported the photochemical reactions of 4-pyrimidinones in alcoholic solution and in methylamine-ether solution. Irradiation of 2,3,6-trialkyl-4-pyrimidinone 1 in methanol gave the corresponding  $\alpha$ -(aminoalkylidene)- $\beta$ -methoxy- $\beta$ -lactam 3 (see Scheme I).

A Dewar 4-pyrimidinone intermediate 2 was postulated for the formation of 3, but no decisive evidence for this intermediate was available. A preliminary experiment



$\text{R}_1, \text{R}_2, \text{R}_3 = \text{alkyl}$

(1) (a) Yamazaki, T.; Nagata, M.; Hirokami, S.; Hirai, Y.; Date, T. *Heterocycles* 1978, 9, 505. (b) Hirokami, S.; Hirai, Y.; Nagata, M.; Yamazaki, T.; Date, T. *J. Org. Chem.* 1979, 44, 2083. (c) Hirai, Y.; Yamazaki, T.; Hirokami, S.; Nagata, M. *Tetrahedron Lett.* 1980, 21, 3067.

showed that the assumed Dewar 4-pyrimidinone was unstable at room temperature. Then, we undertook the