trum, *m/e* 334 (parent ion); high-resolution mass spectrum, calcd for $C_{21}H_{34}O_3$ 334.25080, found 334.25041.

(1*R*)-1-Cyclohexyl-2-hydroxyethyl 5β-(2-Propyl)-2,3,3aβ,4,5,7aα-hexahydroindene-4β-carboxylate (3a). Data obtained on a 2:1 mixture of diastereomers[31] obtained from the $MeNbCl_4$-promoted cyclization of triene **1a**[12] (TLC for the mixture, R_f 0.7, two developments in 2:1 hexane–ether): NMR (250 MHz, $CDCl_3$) δ 5.97 (br d, J = 10.3 Hz, 1 H), 5.56 (dt, J = 10.3, 3.3 Hz, 1 H), 4.78 (m, this signal integrates for only 0.33 protons), 4.70 (m, this signal integrates for 0.67 protons), 3.72 (m, 2 H; the signals at 4.78 and 4.70 each collapse to broad doublets (J = 6.2 Hz) when this multiplet is saturated by double irradiation); 2.76 (dd, J = 11.2, 7.7 Hz, H_4-major diastereomer), 2.75 (dd, J = 11.5, 7.7 Hz, H_4-minor diastereomer), 2.63 (m, 1 H), the isopropyl signals of the major diastereomer (0.96 (d, J = 7.0 Hz, 0.85 (d, J = 7.0 Hz)), and of the minor diastereomer (0.97 (d, J = 7.0 Hz), 0.85 (d, J = 7.0 Hz)); IR (CH_2Cl_2) cm^{-1} 3600, 3475, 2924, 1717, 1643, 1432, 1372, 1325, 1244, 1182, 1141; the low-resolution mass spectrum shows a parent ion at *m/e* 334; high-resolution mass spectrum, calcd for $C_{21}H_{34}O_3$ 334.25080, found 334.25394.

(2*R*)-2-Cyclohexyl-2-hydroxyethyl 6β-(2-Propyl)-1,2,3,4,4aβ,5,6,8aα-octahydronaphthalene-5β-carboxylate (52b). This mixture of diastereomers[31] was isolated in 53% yield from the cyclization of triene **22**: TLC, R_f 0.7 (1:1 hexane–ether); NMR (250 MHz, $CDCl_3$) δ 5.56 (s, 2 H), 4.13 (m, 2 H), 3.57 (m, 1 H), 2.63 (dd, J = 11.8, 7.4 Hz, H_5), 2.44 (m, 1 H), 0.94 (d, J = 7.0 Hz, 3 H), 0.85 (d, J = 7.0 Hz, 3 H); IR (neat) cm^{-1} 3475, 2922, 1716, 1651, 1447, 1369, 1252, 1160, 1131; mass spectrum, *m/e* 348 (parent ion); high-resolution mass spectrum, calcd for $C_{22}H_{36}O_3$ 348.26645, found 348.27063.

5β-(Hydroxymethyl)-6β-(2-propyl)-1,2,3,4,4aβ,5,6,8aα-octahydronaphthalene (24). Obtained in 76% overall yield as a 96:4 mixture with the isomeric alcohol **25** by reduction of the crude product mixture from the hydrofluoric acid catalyzed cyclization of triene **22**: TLC of the mixture, R_f 0.5 (1:1 hexane–ether); NMR (250 MHz, $CDCl_3$) δ 5.64 (ddd, J = 10.2, 1.6, 2.6 Hz, 1 H), 5.54 (br d, J = 10.2 Hz, 1 H), 3.85 (d br d, J = 10.3, 5.2 Hz, 1 H), 3.65 (br t, J = 10.1 Hz, 1 H), 2.26 (m, 1 H), 1.98 (m, 1 H), 1.77 (m, 5 H), 0.98 (d, J = 7.0 Hz, 3 H), 0.84 (d, J = 7.0 Hz, 3 H); IR (neat) cm^{-1} 3335, 2925, 1649, 1464, 1447, 1376, 1081, 1042, 1008; mass spectrum, *m/e* 208 (parent ion). Anal. Calcd for $C_{14}H_{24}O$: C, 80.70; H, 11.62. Found: C, 80.92; H, 12.01.

One of the isopropyl doublets (J = 7.0 Hz) from the minor isomer **25** in the NMR spectrum of this mixture appeared at δ 0.77. The ratios **24** and **25** in such mixtures were determined by integration of the isopropyl signals.

***threo*-1,2-Dimethyl-2-hydroxyethyl 2,3,3aβ,4,5,7aα-hexahydroindene-4β-carboxylate (28):** TLC, R_f 0.7 (2:1 hexane–ether; two developments); NMR (250 MHz, $CDCl_3$) δ 5.81 (br d, J = 10.2 Hz, 1 H), 5.56 (dq, J = 9.9, 3.3 Hz, 1 H), 4.88 (m, 1 H), 3.86 (m, 1 H), 2.50 (dt, J = 7.0, 10.3 Hz, H_4), 2.36 (m, 2 H), the methyl signals of the major diastereomer[31] (1.19 (d, J = 6.2 Hz), 1.15 (d, J = 6.2 Hz)) and the minor diastereomer (1.18 (d, J = 6.2 Hz), 1.15 (d, J = 6.2 Hz)), this region of the spectrum integrates for a total of 6 H; IR (CH_2Cl_2) cm^{-1} 3590, 2940, 1718, 1638, 1417, 1372, 1243, 1170, 1082; mass spectrum, *m/e* 238 (parent ion); high-resolution mass spectrum, calcd for $C_{14}H_{22}O_3$ 238.15690, found 238.15216.

$LiAlH_4$ reduction of **28** afforded alcohol **29**[5b] in 89% yield.

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Registry No. (+)-**1a**, 92126-38-0; **1b**, 92126-39-1; **11**, 92126-40-4; **22**, 92126-41-5; **23**, 92126-42-6; (±)-**26**, 92126-43-7; (±)-**27**, 92126-44-8; **30**, 92126-45-9; **31**, 92126-46-0; **33**, 92126-47-1; **34**, 92126-48-2; **39**, 92126-49-3; **41**, 92126-50-6; **49**, 92126-51-7; *dl*-**50**, 92126-52-8; HF, 7664-39-3.

Solvent Effects on the Rates and the Activation Parameters for the Methoxymercuration of *p*-Substituted Styrenes

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The second-order rate constants and the activation parameters for the methoxymercuration of a series of para-substituted styrenes have been determined in four methanol/*p*-dioxane mixtures—X_{MeOH} varied from 1.00 to 0.791. For each styrene log k is a linear function of X_{MeOH}. The average value of the slopes of the correlation lines is 8.25 ± 0.32 which suggests the involvement of eight–nine MeOH molecules in the rate-determining transition state. For each solvent identical linear plots of log k vs. σ and σ^+ are obtained. At 25 °C, the values of ρ (av -3.26 ± 0.05) and ρ^+ (av -2.86 ± 0.05) are independent of the solvent's composition. For each styrene ΔG^* increases as the methanol concentration deceases; however, $\delta\Delta G^*$ is constant. While $\delta\Delta G^*$ varies linearly with σ and σ^+, in no case is $\delta\Delta H^*$ linearly related to $\delta\Delta S^*$. In anhydrous methanol this reaction series is isoenthalpic; however, this is not the case for either of the methanol/*p*-dioxane mixtures. On the basis of the ΔS^* values, the reaction series approaches an isoentropic state as the methanol concentration decreases.

Introduction

In our last report[1] on the methoxymercuration of para-substituted styrenes, because of the trend in the large negative values of ΔS^* found in anhydrous methanol and the rate reductions obtained upon adding *p*-dioxane to the kinetic mixture, in the case of *p*-bromostyrene, we proposed that solvents affect the rates of this reaction by altering either the concentration of the "reactive" mercury species and/or the stability of the rate-determining transition state. To better understand the role of the solvent, we studied the solvent effects on both the second-order rate constants and the activation parameters for this reaction.

The most widely accepted mechanism for this reaction is the Ad_E2 mechanism.[2-10] According to it, the rate-de-

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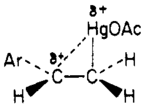
termining step involves the attack of an electrophilic mercury species—formulated as an ion pair below—on the alkene's double bond to form cation 1. This ion rapidly undergoes nucleophilic attack by solvent to form the observed product(s), eq 1-3. Our studies[1,11] support an unsymmetric bridged ion of structure 2 for 1.

$$Hg(OAc)_2 \rightleftharpoons HgOAc^{+}{}^{-}OAc \quad (fast) \tag{1}$$

$$>C{=}C< \; + \; HgOAc^{+}{}^{-}OAc \rightarrow [>C{=}C<{\cdot}HgOAc]^{+} + {}^{-}OAc \quad (slow) \tag{2}$$

$$MeOH + 1 \rightleftharpoons\; >(MeO)C{-}C(HgOAc)< \; + H^{+} \; (fast) \tag{3}$$



2

On the basis of this mechanism, the observed second-order rate constant, k, is a composite of the three specific rate constants given in eq 4, where k_2 is the specific rate

$$k = k_2k_1/k_{-1} = k_2K_{eq} \tag{4}$$

constant for step 2, k_1 and k_{-1} are those for the forward and reverse of step 1, respectively, and K_{eq} is the equilibrium constant for step 1. Thus solvents may influence the rates of this reaction by either shifting the position of the initial ion pair equilibrium as their polarities change or altering the energy of the transition state formed in step 2 as their abilities to solvate this polar species change. Solvents will affect both of these steps and because of the charge separation that occurs in them, they will be affected in the same way. However, the magnitudes of the effects need not be the same. One of the aims of this study was to determine which, if either, of these steps is the more sensitive to solvents.

Since k depends on both k_2 and K_{eq}, the observed values of the activation parameters are the sums of the two terms given in eq 5, where Y represents either H, S, or G and the

$$\Delta Y^{*}_{obsd_X} = \Delta Y^{0}_{1} + \Delta Y^{*}_{2_X} \tag{5}$$

subscripts 1 and 2 refer to steps 1 and 2, respectively. In a given solvent ΔY^{0}_{1} is the same for each styrene. Therefore what happens to the values[12] of $\Delta Y^{*}_{obsd_X}$, as the solvents and substitutents are varied, depends on which step is the more sensitive to these changes and on which term in eq 5 is the larger. A brief discussion of the two extreme possibilities is given below.

p-Dioxane is an essentially nonpolar aprotic solvent. As its concentration in the kinetic mixture is increased the overall polarity of the reaction medium is decreased, therefore ion aggregation is increased.[13] Accordingly, when solvents affect step 1 more than step 2 and $\Delta Y^{0}_{1} >> \Delta Y^{*}_{2_X}$ (case 1), eq 5 reduces to eq 6. Under these conditions

$$\Delta Y^{*}_{obsd_X} \simeq \Delta Y^{0}_{1} \tag{6}$$

there would be essentially no substituent effect on the activation parameters. Further, a change from one solvent to another (e.g., A to B) would cause the values of $\Delta\Delta Y^{*}_{obsd_X}$ to increase by approximately the same amount for each styrene, as shown in eq 7. On the other hand, when

$$\Delta\Delta Y^{*}_{obsd_X} = \Delta Y^{*}_{obsd_X}(B) - \Delta Y^{*}_{obsd_X}(A) \simeq \Delta Y^{0}_{1}(B) - \Delta Y^{0}_{1}(A) \tag{7}$$

solvents affect step 2 more than step 1 and $\Delta Y^{*}_{2_X} >> \Delta Y^{0}_{1}$ (case 2), eq 5 reduces to eq 8 and, as shown in eq 9, under

$$\Delta Y^{*}_{obsd_X} \simeq \Delta Y^{*}_{2_X} \tag{8}$$

$$\delta\Delta Y^{*}_{obsd_X} = \Delta Y^{*}_{obsd_X} - \Delta Y^{*}_{obsd_H} \simeq \Delta Y^{*}_{2_X} - \Delta Y^{*}_{2_H} \tag{9}$$

these conditions the values of $\delta\Delta Y^{*}_{obsd_X}$ would vary with the substituent. Further, a change from one solvent to another would, again, cause the values of $\Delta\Delta Y^{*}_{obsd_X}$ to increase. However, in this case the amount of the increase would be a function of the substituent, as shown in eq 10.

$$\Delta\Delta Y^{*}_{obsd_X} = \Delta Y^{*}_{obsd_X}(B) - \Delta Y^{*}_{obsd_X}(A) \simeq \Delta Y^{*}_{2_X}(B) - \Delta Y^{*}_{2_X}(A) \tag{10}$$

As the data which we report here will show, the effects of solvents on neither step 1 nor step 2 are completely dominant.

Results[14] and Discussion

The methanol and p-dioxane concentrations were varied by placing the required volume of p-dioxane into a volumetric flask and then diluting up to the mark with methanol. The compositions of the four solvents used were (vol % and mole fraction of MeOH) A (100, 1), B (85.7, 0.926), C (71.4, 0.840), and D (64.3, 0.791). The second-order rate constants, shown in Table I, and the activation parameters, shown in Table II, for the reaction of 3 with mercuric acetate were determined as previously described by us.[1]

$$\mathbf{3} = p\text{-}XC_6H_4CH{=}CH_2$$

a, X = MeO; **b**, X = Me; **c**, X = H; **d**, X = F;
e, X = Br; **f**, X = CN; **g**, X = NO$_2$

Substituent Effects on Rates.[15] The data in Table I clearly show that the reaction rates vary with the substituent. Excellent linear plots of log k, at 25 °C, vs. σ and σ^{+}, which are identical with those previously reported by us[1,11] for solvent A, are obtained for the other three solvents as well. The average value of ρ is -3.26 ± 0.05, while that for ρ^{+} is -2.86 ± 0.05.

The results of the analyses of log k vs. σ plots at all temperatures where three or more rate constants were measured are given in Table III. These data show[16] that at each temperature ρ is essentially the same in each

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(14) 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.

(15) Unless otherwise state, the data for p-methoxystyrene were not included in any of the plots involving the use of σ nor σ^{+}.

(16) The data from log k vs. σ^{+} plots show the same trends. However, as we noted in our initial publication on this reaction (ref 11), we feel that the correlations with σ are better than those with σ^{+}. The problems with the correlations with σ^{+} are (1) the reactivity of p-fluorostyrene is incorrectly predicted and (2) the correlation lines do not pass through the origin as required by theory. In all cases, the point for styrene lies above the line derived by the other members of this series.

Table I. Second-Order Rate Constants for the Reaction of 3 with $Hg(OAc)_2$[a] in Various Solvents

		10^3k,[b] $M^{-1}s^{-1}$			
solv	X	8 °C	15 °C	25 °C	35 °C
A[c]	MeO	104000 ± 1800[d]	116000 ± 2300[e]	146000 ± 600[f]	158000 ± 2300[g]
A[c]	Me	9010 ± 290	12900 ± 700	19800 ± 300	
A[c]	H	1850 ± 20	2700 ± 90	4170 ± 230	
A[c]	F	1410 ± 10	2070 ± 130	3360 ± 100	
A[c]	Br		577 ± 16	931 ± 29	1490 ± 70
A[c]	CN		22.2 ± 0.4	34.1 ± 1.9	57.3 ± 1.6
A[c]	NO_2	50.0 ± 2.4[h]		19.7 ± 0.4	34.0 ± 1.6
B	MeO	19000 ± 680	23200 ± 1130	2800 ± 170	
B	Me	1850 ± 20	2570 ± 30	3480 ± 110	
B	H	372 ± 2	550 ± 3	888 ± 6	1530 ± 40
B	F	335 ± 8	460 ± 32	706 ± 85	1110 ± 90
B	Br		100 ± 1	190 ± 6	328 ± 2
B	CN	19.4 ± 0.2[h]		5.38 ± 0.08	12.4 ± 0.1
B	NO_2	11.6 ± 0.1[h]		3.03 ± 0.01	7.57 ± 0.01
C	MeO	3060 ± 90	4030 ± 236	5790 ± 169	
C	Me	1930 ± 130[h]		931 ± 3	1390 ± 50
C	H	441 ± 25[h]		189 ± 3	297 ± 3
C	F	349 ± 6[h]		148 ± 5	232 ± 3
C	Br	91.0 ± 1.1[h]	25.0 ± 0.5	35.2 ± 1.0	63.5 ± 4.5
C	CN	3.24 ± 0.09[h]		1.17 ± 0.04	2.10 ± 0.10
C	NO_2	1.95 ± 0.04[h]		0.705 ± 0.015	1.24 ± 0.01
D	MeO	1680 ± 11	2340 ± 11	3180 ± 11	
D	Me	158 ± 8	234 ± 23	320 ± 18	463 ± 3
D	H		51.7 ± 0.5	81.1 ± 1.1	115 ± 1
D	F		38.5 ± 0.3	61.7 ± 0.6	85.7 ± 1.7
D	Br		10.5 ± 0.1	17.4 ± 0.2	23.8 ± 0.4
D	CN	1.53 ± 0.01[h]		0.555 ± 0.010	0.926 ± 0.011
D	NO_2	0.800 ± 0.040[h]		0.287 ± 0.009	0.491 ± 0.005

[a] The initial concentrations of the $Hg(OAc)_2$ solutions, as determined by titrations of the stock solutions with KSCN, ranged from 1.75×10^{-2} to 1.78×10^{-2} M. [b] The average of three or more determinations plus or minus the standard deviations. [c] Taken from ref 1. [d] 21 °C. [e] 26 °C. [f] 41 °C. [g] 47 °C. [h] 45 °C.

Table II. Activation Parameters for the Reaction of 3 with $Hg(OAc)_2$ in Various Solvents

solv	X	ΔH^*, kcal/mol	$-\Delta S^*$, eu	$-T\Delta S^*$[a]	ΔG^*[a]	$\delta\Delta H^*$[b]	$\delta\Delta S^*$, eu	$\delta\Delta G^*$[a]
A[c]	MeO	2.36 ± 0.11	41.2 ± 0.4	12.28	14.64	−5.00	−10.2	−1.96
A[c]	Me	7.12 ± 0.34	28.7 ± 1.2	8.56	15.68	−0.24	2.3	−0.92
A[c]	H	7.36 ± 0.38	31.0 ± 1.3	9.24	16.60	0.00	0.0	0.00
A[c]	F	7.93 ± 0.24	29.5 ± 0.8	8.80	16.73	0.57	1.5	0.13
A[c]	Br	7.81 ± 0.15	32.5 ± 0.5	9.69	17.50	0.45	−1.5	0.90
A[c]	CN	7.78 ± 0.63	39.1 ± 2.1	11.66	19.44	0.42	−8.1	2.84
A[c]	NO_2	8.17 ± 0.62	38.9 ± 2.0	11.60	19.77	0.81	−7.9	3.17
B	MeO	3.15 ± 0.38	41.3 ± 1.3	12.33	15.48	−5.10	−10.3	−2.03
B	Me	5.49 ± 0.66	37.6 ± 2.3	11.22	16.71	−2.76	−6.6	−0.80
B	H	8.25 ± 0.25	31.0 ± 0.8	9.26	17.51	0.00	0.0	0.00
B	F	6.95 ± 0.16	35.9 ± 0.6	10.70	17.65	−1.30	−4.9	0.14
B	Br	9.80 ± 0.29	29.0 ± 1.0	8.65	18.46	1.55	2.0	0.95
B	CN	11.48 ± 1.84	30.4 ± 6.0	9.05	20.53	3.23	0.6	3.02
B	NO_2	12.05 ± 2.38	29.5 ± 7.7	8.81	20.86	3.80	1.5	3.35
C	MeO	5.60 ± 0.04	36.3 ± 0.1	10.81	16.42	−1.78	0.8	−2.02
C	Me	6.26 ± 0.27	37.7 ± 0.9	11.23	17.49	−1.12	−0.6	−0.95
C	H	7.38 ± 0.16	37.1 ± 0.5	11.06	18.44	0.00	0.0	0.00
C	F	7.48 ± 0.08	37.3 ± 0.2	11.11	18.58	0.10	−0.2	0.14
C	Br	7.48 ± 0.65	39.9 ± 2.2	11.91	19.39	0.10	−2.8	0.95
C	CN	8.97 ± 0.62	41.9 ± 2.0	12.48	21.45	1.59	−4.8	3.01
C	NO_2	8.95 ± 0.41	42.9 ± 1.3	12.80	21.75	1.57	−5.8	3.31
D	MeO	5.55 ± 0.66	37.6 ± 2.3	11.21	16.76	−0.86	4.5	−2.20
D	Me	6.00 ± 0.45	40.7 ± 1.5	12.12	18.13	−0.41	1.4	−0.83
D	H	6.41 ± 0.38	42.1 ± 1.3	12.55	18.96	0.00	0.0	0.00
D	F	6.42 ± 0.59	42.6 ± 2.0	12.71	19.13	0.01	−0.5	0.17
D	Br	6.58 ± 0.83	44.6 ± 2.8	13.31	19.89	0.17	−2.5	0.93
D	CN	8.91 ± 0.15	43.6 ± 0.5	12.99	21.90	2.50	−1.5	2.94
D	NO_2	9.02 ± 0.06	44.5 ± 0.2	13.27	22.29	2.61	−2.4	3.33

[a] At 298 °K in kcal/mol. [b] In kcal/mol. [c] Taken from ref 1.

solvent. Thus, over the range investigated, solvent has no effect on the value of ρ. This result is suprising since other studies[17] of this type have routinely shown and theory predicts that ρ varies with the solvent's composition (polarity). Such variations are interpreted as being due to changes in the electronic demands being placed on the substituent as the solvent's ability to solvate the rate-determining transition state varies. Clearly, this is not the case here.

We interpret the constancy of ρ to mean (1) that the mechanism by which the substitutents operate is the same in each solvent and (2) that the structures of both the rate-determining transition state and intermediate are the

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Table III. Temperature and Solvent Effects on the Values of ρ

	$-\rho$			
solv	8 °C	15 °C	25 °C	35 °C
A	3.59 ± 0.45[a]	3.28 ± 0.08	3.18 ± 0.08	3.09 ± 0.24
B	3.39 ± 0.71[a]	3.46 ± 0.24	3.30 ± 0.08	3.08 ± 0.09
C	3.20 ± 0.08[b]		3.32 ± 0.09	3.24 ± 0.08
D		3.32 ± 0.18	3.26 ± 0.06	3.16 ± 0.05

[a] This value is considered high since the analysis was based on the data for the Me, H, and F derivatives of **3**, only. [b] 45 °C.

same in each solvent. Accordingly, we believe that these data reflect an increasing importance of bridging of the Hg as the methanol concentration decreases. That is, as the solvent's polarity decreases the Hg, rather than the substituent, assumes a larger share of the developing positive charge through more effective bridging. These data, therefore, lend support to our proposed structure **2**, for the cation, **1**.

Further inspection of the data in Table III, also reveals that in each solvent the value of $-\rho$ varies inversely with the temperature. We should point out, however, that because the values of ρ are not all based on the same set of data points, we do not believe that the variations are as large nor as real as the data suggest and that we do not attach any physical significance to them. However, as required by theory,[18] plots of $-\rho$ vs. $1/T$ are reasonably linear with correlation coefficients ranging from a high of 1.00, for solvent A, to a low of 0.976, for solvent C.

As noted above, the data for *p*-methoxystyrene was not included in any of the correlations involving the use of σ or σ^+. The point for this compound falls off the correlation lines made by the other members of this series. It lies above and below the σ and σ^+ correlation lines, respectively. Such deviations indicate the operation of both a resonance-stabilizing interaction between the *p*-MeO group and the developing positive charge on the benzylic carbon and a pseudosaturation effect—the offsetting stabilizing contributions made by the Hg through bridging. As reported by us for solvent A,[1] use of the Yukawa-Tsuno equation[19] to analyze the substituent effects on the second-order rate constants requires values of 0.37 ± 0.01 for the *r* parameter for the other three solvents as well.

Solvent Effects on Rates. The data in Table I clearly show that the addition of *p*-dioxane to the kinetic mixture causes a dramatic decrease in the reaction rates. Analyses of the data show that for each styrene excellent linear plots of log *k* vs. X_{MeOH} are obtained. The average value of the slopes of the correlation lines, at 25 °C, is 8.25 ± 0.32. The analogous plots of log *k* vs. log [MeOH] are identical with these. The average value of the slopes of the correlation lines, however, is 8.98 ± 0.35. Since methanol is not a reactant in either step 1 or 2, this value does not represent the kinetic order of these reactions in methanol. It suggests, instead, that eight–nine methanol molecules are involved in the solvation shell during the activation process.

The *y* intercept in the log *k* vs. X_{MeOH} plots correspond to the values of log *k* in pure dioxane. If the data for *p*-methoxystyrene is omitted, plots of the *y* intercept vs. σ and σ^+ give excellent straight lines with slopes of −3.62 ($r = 0.999$) and −3.15 ($r = 0.992$), respectively. These values are 14% and 13% larger than the values of ρ and ρ^+, respectively, obtained in anhydrous methanol.

For a reaction of this type a decrease in the solvent's polarity is expected to cause an increase in the value of $-\rho$ ($-\rho^+$). However, when one considers the large change in the dielectric constant of the medium that occurs on going from pure methanol (32.6) to pure *p*-dioxane (2.21) and if one assumes that the 14% increase in the value of $-\rho$ ($-\rho^+$) is real, the overall effect of the solvent's polarity on them is seen to be small. Experimentally, it is impractical for us to test this finding because (1) at high *p*-dioxane concentrations the reaction rates become immeasurably slow and (2) $\mathrm{Hg(OAc)_2}$ dissolves in pure *p*-dioxane to give, after a few minutes, a gel. Other researchers have also found relatively small changes in the value of ρ (ρ^+) for a reaction carried out in solvents of widely differing dielectric constants. For example, Kemp and Paul[20] studied the decarboxylation of a series of 5- and 6-substituted 3-carboxybenzisoxazoles in a series of solvents ranging in dielectric constant from 20.7 to 110 and found that the value of ρ only changed by 23%.

Because of the uncertainties in the values of the *y* intercepts, the values of ρ and ρ^+ obtained above have relatively large uncertainties in them. However, an error as large as 25% would not change the conclusions suggested by these data, namely, that for a transfer from pure methanol to pure *p*-dioxane (1) the structure of the transition state and the intermediate formed in the rate-determining step would remain unchanged and (2) the Hg, rather than the substituent, would assume a larger share of the developing positive charge.

Dubois and Ruasse[21] studied the analogous bromination of a series of disubstituted stilbenes in both methanol and $\mathrm{CCl_4}$. They found that two different modified forms of the Hammett equation—one linear and the other nonlinear—were required to correlate the substituent effects on the reaction rates in these solvents. Thus they proposed that the structure of the rate-determining transition state—indeed, the mechanism—changed in going from methanol to $\mathrm{CCl_4}$. This finding is signifcant since the difference in the dielectric constants of methanol and $\mathrm{CCl_4}$ is the same as that of methanol and *p*-dioxane. The differences between our findings and these can be rationalized in terms of two facts: (1) the dielectric constant is a macroscopic property of the solvent which is not, in all cases, the best parameter to use as a measure of the solvent's polarity and (2) Hg is a more effective bridging atom than Br; it does so at all times, while Br bridges only upon heavy demand.

For each styrene excellent linear plots of log *k* vs. log [*p*-dioxane] are also obtained. The average value of the slopes of the correlation lines is −2.48 ± 0.07. Collectively, the data suggest that an increase in the *p*-dioxane concentration results in a decrease in the reaction rate by causing a decrease in the number of methanol molecules present in the solvation shell.

As methanol molecules are replaced by those of *p*-dioxane, a number of solvent–solute interactions change. The most important of these are the following:

(1) Solvation of the developing positively charged centers becomes less effective. That is, because of both a smaller net dipole moment at each of its ends and its greater steric bulk, the attraction between the negative end of *p*-dioxane's dipole and the positively charged ends of the transient species involved in both steps 1 and 2 is less than that between methanol's negative dipole and these same cationic centers.

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(2) Solvation of the developing anion also becomes less effective. Unlike methanol, *p*-dioxane is not a hydrogen bond donor. This type of solvation is important in stabilizing the developing negative charge on the "incipient" acetate anion formed in both steps 1 and 2. Because the positive ends of *p*-dioxane's C–O bond moments are embedded in the molecule's nonpolar hydrocarbon portion, the attractive force between them and the developing negative charge is much smaller than the corresponding force between methanol and these same charges.

(3) While the forces of attraction would be weak, *p*-dioxane can form a complex with the reactive Hg^{2+} species present in solution. Thus, unlike methanol, it can play two different roles—those of both a solvating agent and a complexing agent. The role it plays is a function of its conformation. In the chair conformation it acts as a solvating agent, while in the bond conformation it acts as a complexing agent. The complex would be less reactive than any other Hg^{2+} species present.

Our studies (work in progress) on the effects of other solvents—of essentially the same dielectric constant as *p*-dioxane—on the rates of this reaction support these suggestions since the rate reductions observed in these cases are not as large as those reported here.

Solvent Effects on ΔG^*. Inspection of the data in Table II reveals that, while the values of ΔG^* for each styrene vary inversely with the methanol concentration, the corresponding values of $\delta\Delta G^*$ are the same in each solvent. In going from methanol to solvents B, C, and D, ΔG^* for each styrene increases by 0.98 ± 0.09 kcal/mol, 1.88 ± 0.08 kcal/mol, and 2.39 ± 0.12 kcal/mol, respectively. Thus, while the solvent's composition affects the overall stabilities of the transition states formed by each styrene, it does not affect their relative stabilities. These results are consistent with case 1, hence, they indicate the importance of solvent effects on step 1.

Solvent Effects on ΔH^*. Inspection of the data in Table II reveals that, except for *p*-methoxystyrene, no obvious relationship exists between the values of ΔH^* and the solvent's composition. For *p*-methoxystyrene it appears that ΔH^* increases as the methanol concentration decreases. This is the trend that one might have anticipated for each styrene, since ΔH^* measures changes in the extent of bonding that occur during activation. Thus the amount of bond making that attends the formation of the rate-determining transition state should decrease with both the solvent's polarity and its ability to solvate the developing positive charge. Accordingly, ΔH^* should increase as the methanol concentration decreases. The deviations probably reflect the composite nature of ΔH^* and show that solvent effects on both steps 1 and 2 are important.

Substituent Effects on ΔH^*. The data in Table II also show that for each solvent (with the exception of A, where the reaction series is isoenthalpic[1]), in general, the value of ΔH^* increases with the substituent's electron-withdrawing ability. This is the expected trend, since the amount of bond making that occurs on going to the rate-determining transition state also decreases with the substituent's ability to stabilize the developing positive charge. However, in all but solvent D, the relationships are only qualitative, since $\delta\Delta H^*$ is not a linear function of σ or σ^+. For solvent D plots of $\delta\Delta H^*$ vs. σ and σ^+ are fairly linear ($r = 0.974$, in both cases). Analyses of the data give values of ρ (−2.56) and ρ^+ (−2.25) which are 21% smaller than their corresponding standard values for this solvent. The differences are probably due mainly to the errors in the $\delta\Delta H^*$ values.

Further examination of the data in Table II and analyses of plots of $\delta\Delta H^*$ vs. $\delta\Delta S^*$ reveal that, in no case, is $\delta\Delta H^*$ a linear function of $\delta\Delta S^*$. Thus, while substituents have quantitative effects on the values of ΔG^*, they do not have, in all cases, the same effects on the values of ΔH^*. As suggested by Dubois and de Ficquelmont-Loizos[23] from their studies of the bromination of substituted styrenes, when this situation is found if the reaction series is neither isoentropic, isoenthalpic, nor isokinetic and ΔS^* (see below) is also not a linear function of σ (σ^+), then ΔH^* and ΔS^* may contain a common term which vanishes for ΔG^*.

Solvent Effects on ΔS^*. From the data in Table II it is seen, in almost all cases, that $-T\Delta S^*$ is larger than ΔH^*, hence, the reaction rates are more sensitive to the change in ΔS^* than to those in ΔH^*. In general, as the methanol concentration decreases, the average value of $-\Delta S^*$ increases (33.3 ± 4.2 eu, 32.2 ± 3.3 eu, 39.5 ± 2.3 eu, and 43.0 ± 1.4 eu, for solvents A to D, respectively). This increase may be ascribed to several factors, the more important of which are (1) an increase in the extent of bridging of the Hg as both the solvent's polarity and its ability to solvate the transition state decrease and (2) a loss in some of the solvent's degrees of freedom during the activation process. This loss results from the greater organization of *p*-dioxane's molecules in the transition state than in the ground state. When the standard deviation is used as an indicator, it appears that the reaction series is approaching an isoentropic state as the methanol concentration decreases.

Analyses of the data reveal that, with the exception of that for *p*-methoxystyrene, while in most solvents the value of $-\Delta S^*$ is largest for those styrenes which have a powerful electron-withdrawing susbtituent, the change in $-\Delta S^*$ in going from methanol to one of the other solvents (B, C, and D) is less for them. The average values of $\Delta\Delta S^*$ for *p*-methylstyrene through *p*-bromostyrene are −3.0 ± 4.9 eu, −7.6 ± 1.0 eu, and −12.1 ± 0.7 eu, respectively. Those for *p*-cyanostyrene and *p*-nitrostyrene are +9.0 ± 0.4 eu, −3.4 ± 0.6 eu, and −5.0 ± 0.6 eu, respectively. Since less positive charge is developed in the transition state for those styrenes which have an electron-withdrawing substituent than for those which do not, we believe that this finding reflects the greater need for solvation of the more polar transition states formed in the cases of *p*-methylstyrene through *p*-bromostyrene than for those formed from *p*-cyanostyrene and *p*-nitrostyrene.

The data for *p*-methoxystyrene appear to support this conclusion, since, in general, the value of $-\Delta S^*$ for it decreases with the solvent's polarity. This trend is consistent with a decreasing need for solvation of *p*-methoxystyrene's transition state as the solvent's polarity decreases because of (1) a decrease in the amount of positive charge developed of the benzylic carbon and (2) an increase in the extent of briding of the Hg. That is, as the solvent's polarity decreases, the structure of *p*-methoxystyrene's transition state changes from being highly open in nature to being more unsymmetrically bridged in nature. Thus its need for solvation decreases and ΔS^* increases.

Substituent Effects on ΔS^*. A survey of the data in Table II shows that, with the exception of solvent B and excluding the data for *p*-methoxystyrene, in general, the value of $-\Delta S^*$ increases with the substituent's electron-withdrawing ability. Since, as mentioned above, less positive charge is developed on the benzylic carbon in the transition state when the substituent is highly electron withdrawing, we attribute a large part of this increase to

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an increase in the extent of bridging of the Hg rather than to an increase in the extent of solvation.

Analyses of plots of $\delta\Delta S^*$ vs. σ and σ^+ reveal that in addition to the linear relationships found for solvent A^1, fairly linear ones also exist for solvent C ($r = 0.956$ and 0.947, respectively). The values of ρ (−1.38) and ρ^+ (−1.21) obtained from the correlation lines are 58% smaller than their corresponding standard values for this solvent. In this solvent, $\delta\Delta H^*$ is not a linear function of $\delta\Delta S^*$ nor σ (σ^+), thus these deviations probably indicate that the linearity of these plots are not significant.

In conclusion, these results show that the rates and the activation parameters for this reaction are functions of both the substituent and the solvent. The fact that ΔG^* for each styrene increases as the methanol concentration decreases reflects the destabilizing effect that a reduction in the solvent's polarity has on the polar transition state formed in step 2. However, the fact that ΔG^* for each styrene increases by the same amount in going from one solvent to another reflects the destabilizing effect that a reduction in the solvent's polarity has on the ion pair formed in step 1. Thus solvent effects on both steps are important. Unfortunately, it is not clear which, if either, step is the more sensitive to these effects. A part of the ambiguity arises from the fact that *p*-dioxane plays dual and competing roles—complexing agent vs. solvating agent—in this reaction. It is our hope that studies in progress, using solvents of the same dielectric constant as *p*-dioxane which cannot form a complex with the reactive Hg^{+2} species present in solution, will resolve this matter.

Experimental Section

Materials. All of the styrenes used in this study were prepared as previously described.[1] The mercuric acetate, methanol, and *p*-dioxane used were high grade commercial products which were purified as previously described.[1]

Kinetic Procedure. The rates of reaction were determined as previously described.[1]

Registry No. **3** (X = MeO), 637-69-4; **3** (X = Me), 622-97-9; **3** (X = H), 100-42-5; **3** (X = F), 405-99-2; **3** (X = Br), 2039-82-9; **3** (X = CN), 3435-51-6; **3** (X = NO_2), 100-13-0; $Hg(OAc)_2$, 1600-27-7; MeOH, 67-56-1.

Regioselective Halo- and Carbodesilylation of (Trimethylsilyl)-1-methylpyrazoles[1]

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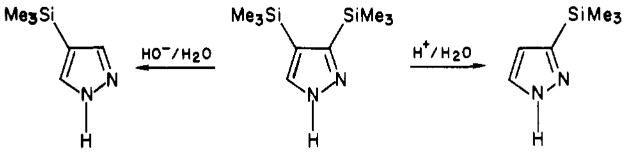
The isomeric 3-, 4-, and 5-(trimethylsilyl)- as well as the 3,4-, 3,5-, and 4,5-bis(trimethylsilyl)-1-methylpyrazoles (**2**, **7**, **3**, **5**, **9**, and **10**, respectively) are obtained by methylation of the corresponding (trimethylsilyl)-1*H*-pyrazoles or by silylation of Grignard or lithio derivatives of appropriate 1-methylpyrazoles with chlorotrimethylsilane. **5** and **10** are halodesilylated regioselectively by Br_2 or ICl in the 4-position, yielding **13** and **15**. With additional bromine, these monobromo compounds suffer exclusively bromodesilylation to give 3,4- and 4,5-dibromo-1-methylpyrazole (**14** and **16**, respectively). These findings are in accord with the electrophilic substitution reactivity indices for 1-methylpyrazole (**8**) and with ipso-directing influence of the Me_3Si group. The reaction of **5** with I_2, unexpectedly, attacks preferentially at the 3-position. Regioselective carbodesilylation in the 5-position is observed in the fluoride-catalyzed reactions of **3**, **9**, and **10** with carbon electrophiles. The high regiospecificity of this reaction is rationalized in terms of carbanion stabilization at the individual pyrazole positions.

Introduction

It has been recognized only in the last decade that the versatility of ipso reactions can be of preparative importance in electrophilic aromatic substitution.[3] Desilylation reactions, for instance, which have especially high ipso rate factors,[3,4] were used for the regioselective synthesis of some interesting disubstituted benzene derivatives.[5] Since, as a rule, the cleavage of the aryl silicon bond in such ipso reactions is believed to proceed as in normal electrophilic substitution, reactivity and orientation should be controlled by the well-established rule of aromatic substitution.[4a] For activated arenes, this has been verified in many cases.[4b,5] Acceptor-substituted aryltrimethylsilanes, on the other hand, react much faster in the presence of nucleophilic catalysts and thence must follow a different mechanistic route.[6]

Scheme I



It should be possible, therefore, to direct desilylation reactions of heteroaryltrimethylsilanes to different positions by adjusting the reaction conditions accordingly. Under regular Friedel–Crafts catalysis, the orientation should be governed by the relative stability of the re-

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