and *o*-hydroxyacetanilide in about a 3:1 ratio were found in this extract, along with a small amount of additional benzyl *o*-hydroxycarbanilate. Conversion of the benzoxazolone weight to benzyl *o*-hydroxycarbanilate from which it was formed gave average material balances of 75%.

Isomers **1b** and **2b** were saponified by stirring 0.20-g samples with 10 mL of 2% NaOH. Solution was complete in about 15 min and the reaction mixtures were stirred for an additional 2 h before being acidified. The acid mixtures were evaporated to dryness, the residues were extracted with 15 mL of $CHCl_3$, and these extracts were filtered and diluted to 25 mL for HPLC analysis. The material balances in these saponifications averaged 65%.

Registry No.—Acetyl chloride, 75-36-5; benzyl chloroformate, 501-53-1; butyl chloroformate, 592-34-7.

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Styrene Bromination: Evidence for a Bridged Rate-Determining Transition State

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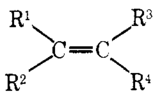
The mechanism of the bromination of styrene and its derivatives has been the subject of debate.[1] An open carbonium-ion-like rate-determining transition state has been proposed on the basis of stereochemical evidence[2] and the magnitude of the negative ρ values[3] for bromination of ring substituted styrenes. A bridged rate-determining transition state has been proposed, based upon the observation that the initial enthalpy difference between pairs of cis,trans isomeric alkenes was increased at the bromination transition state.[4]

One way of resolving this problem is to compare the structure-reactivity profiles of bromination with two model reactions: one involving a bridged, the other an open-ion-like rate-determining transition state. The following reactions have been chosen as models. Protonation of alkenes in acid-catalyzed hydrations has been established to proceed by an open ion through the entire range of reactivity.[1,5] The addition of arenesulfenyl halides to alkenes is a reaction which proceeds through a bridged rate-determining transition state for the entire range of reactivity.[1] The purpose of this note is to make such a comparison of the bromination, hydration, and addition of 4-chlorobenzenesulfenyl chloride to the following compounds. The rate data are collected in Table I.

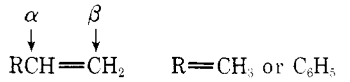
Table II. Ratios $k(\alpha\text{-CH}_3)/k(\text{H})$ and $k(\beta\text{-CH}_3)/k(\text{H})$

Compd	Br_2 in HOAc	Br_2 in CH_3OH	ArSCl in TCE	Hydration
2-Phenylpropene (**2**)/ styrene (**1**)	60.7		4.27	1070
cis-1-Phenylpropene (**3**)/styrene (**1**)	0.80		0.69	
trans-1-Phenylpropene (**4**)/styrene (**1**)	1.10		1.91	0.34
Methylpropene (**6**)/ propene (**5**)		89	2.7	7500
cis-2-Butene (**7**)/ propene (**5**)		43	6.5	1.68
trans-2-Butene (**8**)/ propene		28	2.1	0.71



	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
1	C_6H_5	H	H	H	5	CH_3	H	H	H
2	C_6H_5	CH_3	H	H	6	CH_3	CH_3	H	H
3	C_6H_5	H	CH_3	H	7	CH_3	H	CH_3	H
4	C_6H_5	H	H	CH_3	8	CH_3	H	H	CH_3

The effect of substituting a methyl group for a hydrogen on the rate of addition is used as the mechanistic probe. For purpose of comparison, the positions of the methyl groups which replace the olefinic hydrogens in styrene and propene can be designated α and β as follows:



$$\overset{\overset{\alpha}{\downarrow}}{\mathrm{RCH}}{=}\overset{\overset{\beta}{\downarrow}}{\mathrm{CH_2}} \qquad \mathrm{R{=}CH_3\ or\ C_6H_5}$$

The effect of substituting the olefinic hydrogens on styrene and propene by methyl groups on the rates of addition is different for the two limiting mechanisms. By expressing the rates as the ratios $k(\alpha\text{-CH}_3)/k(\text{H})$ and $k(\beta\text{-CH}_3)/k(\text{H})$, this fact is clearly demonstrated as shown in Table II.

Several points are evident from the data in Table II. As expected, substituting a methyl group in the α position has the greatest effect on hydration where an open ion is formed. The $k(\alpha\text{-CH}_3)/k(\text{H})$ ratio for the bromination of styrene is not unusually large. It is about the same as propene and much smaller than that for hydration.

The small variation in the ratio $k(\alpha\text{-CH}_3)/k(\text{H})$ and $k(\beta\text{-CH}_3)/k(\text{H})$ for additions of bromine and 4-chlorobenzenesulfenyl chloride in the propene series indicate a bridged rate-determining transition state in accordance with the accepted mechanisms of these additions.[1] The methyl substitutents affect the rates of bromination more than those of

Table I. Rates of Hydration, Bromination, and Addition of 4-Chlorobenzenesulfenyl Chloride at 25 °C

Compd	Registry no.	$k_2(Br_2)$,[a] $M^{-1}\,s^{-1}$	$k_g(Br_2)$,[b] $M^{-1}\,s^{-1}$	$k_2(\text{ArSCl})$, $M^{-1}\,s^{-1}$	$k_2(H^+)$,[e] $M^{-1}\,s^{-1}$
Styrene (**1**)	100-42-5	11.2		62.0[c]	0.326×10^{-6}
2-Phenylpropene (**2**)	98-83-9	680		265[c]	0.967×10^{-4}
cis-1-Phenylpropene (**3**)	766-90-5	8.89		43.0[c]	
trans-1-Phenylpropene (**4**)	873-66-5	12.3		118[c]	1.12×10^{-7}
Propene (**5**)	115-07-1		30.7	205[d]	0.495×10^{-7}
Methylpropene (**6**)	115-11-7		2730	550[d]	0.371×10^{-3}
cis-2-Butene (**7**)	590-18-1		1310	1340[d]	8.32×10^{-8}
trans-2-Butene (**8**)	624-646		847	434[d]	3.51×10^{-8}

[a] In acetic acid solvent, ref 6. [b] In methanol containing 0.2 M NaBr, ref 7. [c] In 1,1,2,2-tetrachloroethane, ref 8. [d] In 1,1,2,2-tetrachloroethane, ref 9. [e] The second-order rates of hydration were obtained by dividing the observed rates extrapolated to $H_0 = 0$ by the acidity function h_0 for that acidity, ref 10.

Table III. Ratios $k(\alpha\text{-CH}_3)/k(\text{t-}\beta\text{-CH}_3)$

Parent compd	$k(\alpha\text{-CH}_3)/k(t\text{-}\beta\text{-CH}_3)$ ArSCl	Br_2	Hydration
Styrene	2.24	55	3147
Propene	1.26	3.2	10563

addition of 4-chlorobenzenesulfenyl chloride. This indicates that more charge is developed on the ring carbons in the bridged rate-determining transition state in the addition of bromine than arenesulfenyl chlorides. This is consistent with the greater ability of sulfur to support a positive charge.

By comparing the effect of methyl groups in the α and β positions, in terms of the ratios $k(\alpha\text{-CH}_3)/k(t\text{-}\beta\text{-CH}_3)$, we can obtain an estimate of the symmetry of the rate-determining transition state. These data are presented in Table III. To eliminate any problems due to steric hindrance, the values of the trans-β isomers are used. The difference between addition of 4-chlorobenzenesulfenyl chloride and hydration is striking. For a bridged rate-determining transition state the ratio is small (1.3–2.2) while for an open-ion-like transition state the ratio is large (10^3–10^4).

Bromination in the propene series closely resembles the addition of 4-chlorobenzenesulfenyl chloride. Clearly the rate-determining transition state for these additions is quite symmetrical. The $k(\alpha\text{-CH}_3)/k(t\text{-}\beta\text{-CH}_3)$ ratio for the bromination in the styrene series more closely resembles that of the addition of 4-chlorobenzenesulfenyl chloride than hydration. Consequently, the data are best explained by proposing a weakly bridged rate-determining transition state. Thus the structures range from strongly bridged for arenesulfenyl chloride to weakly bridged for bromination to an open one for hydration.

These data indicate that the formation of nonstereospecific products in the bromination of styrene and its derivatives is due to the intervention of open ions *after* the rate-determining step.

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Reductive Alkylation of Phenazine. Electrochemical Preparation of 5,10-Dihydro-5,10-dimethyl and 5,10-Dihydro-5,10-diethyl Derivatives

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In conjunction with research on the chemical behavior of certain cation radical species and as part of a more general study of reductive alkylation initiated electrochemically, a method has been developed for the facile synthesis of 5,10-dialkyl-5,10-dihydrophenazine derivatives in high yield.

Previous methods for the synthesis of N,N'-dialkyldihydrophenazines consisted of chemical reduction of phenazine followed by treatment with the appropriate alkylating agent. For example, Gilman and Dietrich[1] prepared the dimethyl derivative in 1,2-dimethoxyethane (DME) by reduction of phenazine with potassium metal, followed by addition of methyl iodide. Only 62% yield was reported. In a more elaborate preparation, Mikhailov and Blokhina[2] synthesized the diethyl derivative by first isolating the disodium salt of reduced phenazine after treatment with sodium metal in DME for 30–35 h. The salt was then reacted with either ethyl chloride or ethyl iodide for an additional 40 h, resulting in only 40–44% yield.

More recently, reactions of this type have been carried out electrochemically.[3,4] This technique offers the advantage of a selective reduction potential such that the parent compound can be reduced at a potential where the alkylating agent is not. Thus both reagents can be present in solution simultaneously. The alkylating agent reacts with reduced parent compound as it is generated at the cathode eliminating the need for stepwise addition of reagents or isolation of reactive intermediates.

Results and Discussion

A cyclic voltammogram of phenazine in acetonitrile shows two reduction waves, a reversible one-electron reduction at −1.60 V (vs. $Ag|0.1\ M\ Ag^+$), and a second irreversible one-electron transfer at −2.41 V. The radical anion species is very stable showing completely reversible behavior at scan rates as slow as 20 mV/s. Also, controlled potential coulometry at the first reduction wave yields an n_{app} value of 1.0 (where n_{app} is the number of equivalents of electrons added per mole of substrate). The second wave exhibits irreversible behavior at scan rates as fast as 50 V/s indicating the presence of a fast following chemical reaction which is most likely protonation by solvent or trace impurities to produce the 5,10-dihydro derivative.[4]

In the presence of a fourfold excess of dimethyl sulfate, which is itself electroinactive, the first reduction wave of phenazine exhibits irreversible behavior at slow scan rates indicating a reaction between the phenazine anion radical and the added alkylating agent. Also, two new oxidation waves appear at −0.18 and +0.52 V on scan reversal. When the cyclic scan is allowed to include both reduction waves these same two oxidation waves appear in greater magnitude showing that the reaction of dimethyl sulfate with either the radical anion or dianion of phenazine yields the same product.

With diethyl sulfate as an alkylating agent, no change is observed in the first reduction wave indicating that the reaction between the phenazine radical anion and diethyl sulfate is very slow. With inclusion of the second reduction wave in the cyclic scan two new oxidation waves appear at −0.28 and +0.48 V and a third, smaller wave at −0.46 V, showing a rapid reaction does occur with the phenazine dianion.

Ethyl bromide is electrochemically reducible at a more negative potential than either reduction process exhibited by phenazine. Its effect on the phenazine reduction however is similar to that observed on addition of diethyl sulfate: slow reaction with the radical anion, and rapid reaction with the dianion species. The anodic portion of the scan includes the new oxidation waves at −0.28 and +0.48 V, the latter obscured by the oxidation of Br^-, a reaction by-product. A wave at +0.78 V corresponding to the oxidation of Br_3- is also observed.

Controlled potential coulometry at the first reduction wave of phenazine yields an n_{app} of 2.0 when any of the three alkylating agents is added in excess to the solution. Since an n_{app} value of 1.0 is observed in the absence of alkylating agent, the alkylating agents must react with the phenazine radical anion

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