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THE NATURE OF THE INTERMEDIATE FORMED IN THE METHOXYMERCURATION OF P-SUBSTITUTED STYRENES

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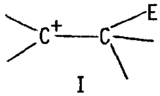
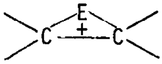
ABSTRACT - The logarithms of the rates of methoxymercuration of p-substituted styrenes give excellent correlations with, both, σ and σ^+. Based on the values of ρ and ρ^+ obtained, an unsymmetric bridged ion is proposed as the intermediate formed in these reactions.

The nature of the intermediate formed during electrophilic addition reactions has been the subject of numerous studies. Based on the evidence — stereochemical, kinetic, spectroscopic, and theoretical — currently, available, three different structures, I - III, for these intermediates have been proposed by various workers in the field (1), where E, I, II, and III represent the


I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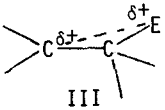
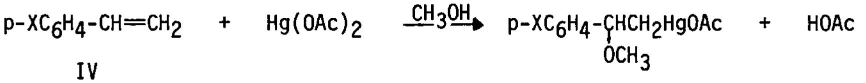

III

electrophile, an open α-substituted carbocation, a symmetric bridged or cyclic ion, and an unsymmetric bridged or cyclic ion, respectively.

In recent years it has become increasingly evident that the nature of the intermediate formed during an electrophilic addition reaction is dependent on various factors: (i) the nature of the electrophilic atom, (ii) the solvent, and (iii) the structure of the alkene (1,2). In regards to the nature of the electrophilic atom, it appears that if it is not highly electronegative and possesses easily polarizable nonbonding p- or d-electrons, then bridging of the electrophilic atom should be important and the reaction should proceed through a cyclic intermediate ion, II or III. On the other hand, if the electrophilic atom is highly electronegative and/or does not possess any nonbonding p- nor d-electrons, then bridging of the electrophilic atom should not be important and the reaction should proceed through an open intermediate ion, I. Solvent effect studies indicate that symmetric bridged or cyclic intermediate ions, II, are more likely to be formed in nonpolar solvents. The available evidence concerning the structure of the alkene suggests that if the alkene is conjugated, hence, capable of forming a resonance-stabilized allylic or benzylic type of cation, then the need for stabilization by bridging of the electrophilic atom is small and the reaction should proceed by way of an open intermediate ion, I. On the other hand, if the alkene is unconjugated or the formation of a resonance-stabilized cation is not possible, then stabilization of the ion by bridging of the electrophilic atom should be important and the reaction should proceed through a bridged or cyclic intermediate ion, II or III.

We have tested these ideas – (i) and (iii) – by determining the effects of substituents on the rates of methoxymercuration of a series of p-substituted styrenes, IVA - F, in anhydrous methanol at 25°C, eq 1. In these reactions, bridging of the mercury atom is possible because of its



$$p\text{-}XC_6H_4\text{-}CH{=}CH_2 \quad + \quad Hg(OAc)_2 \quad \xrightarrow{CH_3OH} \quad p\text{-}XC_6H_4\text{-}\underset{OCH_3}{CH}CH_2HgOAc \quad + \quad HOAc \qquad (1)$$

IV

A. $X = CH_3$; B. $X = H$; C. $X = F$; D. $X = Br$; E. $X = CN$; F. $X = NO_2$

nonbonding d-electrons. Further, for the styrenes, changing the substituent on the ring effectively changes the structure of the alkene. Thus, depending on which factor is dominant, one might expect this reaction to show a change in the nature of the intermediate formed as the structure of the alkene is changed.

The reactions were carried out under pseudo first order conditions, with the mercuric acetate being present in excess. The rates were determined spectrophotometrically by monitoring the decrease in the absorbances of IV at their longest wavelength absorption band. With the exception of IVF, which has only one intense absorption band, all of these compounds have several weak absorption bands around 290 nm. All reactions exhibited clean first order kinetic behavior, as shown by excellent linear plots of log $(A_t - A_\infty)$ versus time, over more than four half-lives. The pseudo first order rates were determined by least squares analyses of Kézdy-Jaz-Bruylants plots (3) of the data. All such plots had correlations coefficients of 0.998 or better. The data are summarized in Table I.

Plots of log k_X vs. σ and σ^+ are shown in Figures 1 and 2. The lines drawn in these Figures correspond to the least squares correlation lines. The correlation data are summarized in Table II. Both of the correlations are excellent.

Since the plots show no signs of curvature, changes in the structure of the transition states, hence, intermediates formed during these reactions can be ruled out (4). If the structure of the alkene were important in determining the nature of the intermediate formed, the plot in Figure 1 should have been curved, being concave upward. This is the expected behavior since the need for stabilization of the ion by bridging of the mercury would have increased as the ability of the aryl group to stabilize the ion decreased.

TABLE I

Rates[a] of Methoxymercuration of IV by $Hg(OAc)_2$[b] in CH_3OH at 25°C

IV	$10^5\{IV\}_o$	Ratio[c]	$10^4 k_{obs}$, sec^{-1} [d,e]
A	178.	9.79	3280. ± 61
B	164.	10.6	665. ± 19
C	185.	9.38	584. ± 17
D	133.	13.1	162. ± 5
E	140.	12.5	5.93 ± 0.33
F	8.02	217.	3.42 ± 0.07

[a] All rates were determined a minimum of three times. [b] The initial concentration of the $Hg(OAc)_2$, as determined by titration of the stock solution with standard KSCN, was 0.0174 M. The same $Hg(OAc)_2$ stock solution was used throughout this study. [c] Ratio refers to $\{Hg(OAc)_2\}_o/\{IV\}_o$. [d] The average pseudo first order rates. [e] The uncertainty is the standard deviation.

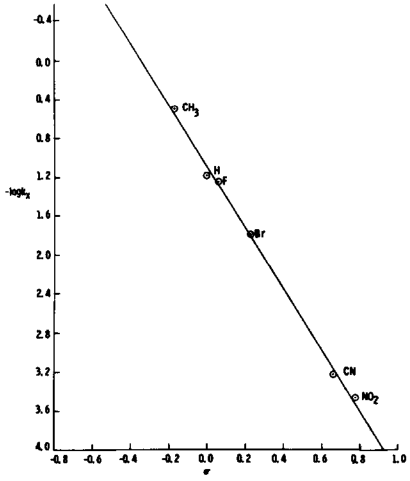


Figure 1. Plot of log k_X vs. σ. The σ-values were taken from ref. 5.

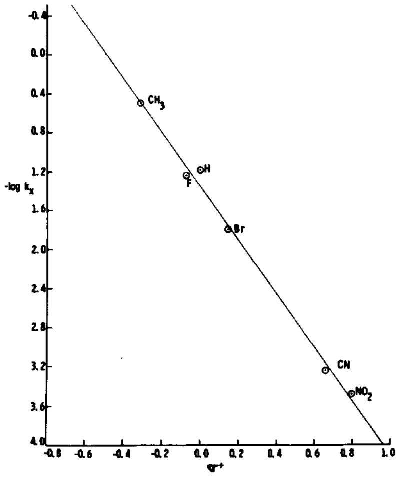


Figure 2. Plot of log k_X vs. σ^+. The σ^+-values were taken from ref. 6.

The value of ρ suggests that a large amount of positive charge is developed on the benzylic carbon in the transition states for these reactions. Thus, structure II, the symmetric bridged or cyclic mercurinium ion, can be ruled out. Our value of ρ is identical with that (-3.3) found by Halpern and Tinker (7) for the hydroxymercuration of a series of aliphatic olefins. Based on the identities of these ρ-values; the excellent correlations with both σ and σ^+; and the fact that ρ^+ is too low to be consistent with structure I (8), the open α-mercuriocarbocation, we propose

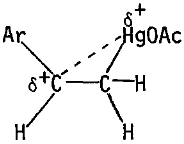
TABLE II

Correlations of log k_X with the Substituent Constants

Subst. Const.	ρ^a	log $k_H^{a,b}$	r^c
σ	-3.16 ± 0.09	-1.08 ± 0.04	0.998
σ^+	-2.76 ± 0.11	-1.34 ± 0.05	0.997

[a] The uncertainty is the standard deviation. [b] The Y-intercept. The experimental value is -1.18 ± 0.03. [c] The correlation coefficient.

that the intermediate formed in these reactions is of structure IIIA, the unsymmetric bridged or cyclic mercurinium ion.



IIIA

Further studies of these reactions are in progress.

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