

Polar Additions to the Styrene and 2-Butene Systems. II. Medium Dependence of Bromination Products

John H. Rolston and Keith Yates

Contribution from the Department of Chemistry, University of Toronto,
Toronto, Canada. Received October 5, 1968

Abstract: The product distribution and stereochemistry of bromine addition to several substituted styrenes has been investigated in acetic acid with added lithium bromide, sodium acetate, and lithium perchlorate. The presence of lithium bromide suppresses acetoxy bromide formation and increases the stereoselectivity of dibromide formation to give 95% *trans* addition. Both sodium acetate and lithium perchlorate increase acetoxy bromide formation. Lithium perchlorate markedly decreases the stereoselectivity of acetoxy bromide formation from *cis*- β -methylstyrene but has little effect on the stereochemistry of dibromide formation from either of the β -methylstyrenes or from the 2-phenyl-2-butenes. The stereochemistry of dibromide formation from *cis*- and *trans*- β -methylstyrenes was determined in six solvents varying in polarity from dioxane to nitrobenzene. The additions in all solvents were nonstereospecific. The stereoselectivity of addition to both olefins is solvent dependent, particularly for the *cis* olefin which ranges from 73% *trans* to 80% *cis* addition. Only in dioxane are the stereochemical results approximately independent of the starting olefin. The results are interpreted in terms of a mechanistic scheme involving both intimate and solvent-separated ion pairs, in which the cationic portions resemble weakly bridged, rather than open, benzylic carbonium ions. In marked contrast, additions to *cis*- and *trans*-2-butenes were found to give almost exclusively dibromides, which were formed completely stereospecifically and *trans*, under all conditions investigated. This is taken as evidence that the bridging interaction in the intermediates from these aliphatic olefins is distinctly different from any which may be present in the styrene intermediates, and that only the 2-butenes react by way of strongly bridged cyclic bromonium ions. The temperature dependence of some of these additions is discussed.

Polar additions of bromine to olefins have been studied in a wide variety of reaction media, ranging from the pure olefin itself to aqueous solution. Although the most commonly used solvent, particularly for rate studies, has been acetic acid, chlorinated hydrocarbons and polar hydroxylic solvents such as alcohols and water have also been frequently used. The latter are well known to give greatly enhanced rates of addition, as well as giving substantial amounts of solvent-incorporated products such as methoxy bromides and bromohydrins. Apart from the possible role of solvent in nucleophilic attack on the cationic intermediates in these reactions, the nature of the transition states, and presumably the subsequently formed intermediates themselves, also depends on the solvent. This is illustrated by the fact that the relative importance of the various kinetically significant processes in bromine addition has been found to depend on the polarity of the reaction medium.¹

Addition of salts, particularly halides, can also result in significant changes in the course of bromine additions, apart from any ability of these salts to act as nucleophiles and divert the cationic intermediates into the formation of mixed products such as bromo chlorides and bromo nitrates. However it is not clear whether added halide ions affect the nature of the brominating species itself, or act as catalysts in a termolecular addition process.^{1d,2}

Very few systematic studies of the influence of reaction medium on the course of bromine addition have been

carried out, particularly with respect to the stereochemistry of addition. Such investigations seem highly desirable in view of the emphasis usually placed on stereochemical results in describing the nature of the reaction intermediates. For example, although additions of bromine to maleic and fumaric acids, and to *cis*- and *trans*-2-butenes have been reported to be highly stereospecific, the former were investigated in aqueous solutions³ and the latter in the neat olefins.⁴ No attempt has been made to examine these reactions in different media to determine if this stereospecificity is independent of the medium. The stereoselectivity of bromine addition to *cis*- and *trans*-stilbenes on the other hand has been shown to depend markedly on solvent polarity,⁵ particularly for addition to the *cis* olefin. It would seem that valuable mechanistic information could be obtained from further studies of this type. We have therefore attempted to investigate both the product distribution and stereochemistry of bromine addition to typical styrene systems as a function of solvent polarity, added salts, and temperature. The corresponding reactions of *cis*- and *trans*-2-butenes have also been investigated for comparison purposes.

Results and Discussion

Effect of Added Salts. The products of bromine addition to a number of substituted styrenes were investigated in acetic acid in the presence of added salts. The salts used were lithium bromide, sodium acetate,

(3) A. McKenzie, *J. Chem. Soc.*, 1196 (1912); K. Nozaki and R. A. Ogg, Jr., *J. Am. Chem. Soc.*, **64**, 679 (1942).

(4) W. G. Young, R. T. Dillon, and H. J. Lucas, *ibid.*, **51**, 2528 (1929); R. T. Dillon, W. G. Young, and H. J. Lucas, *ibid.*, **52**, 1953 (1930).

(5) R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962); J. Heublein, *J. Prakt. Chem.*, **31**, 84 (1966).

(1) (a) P. D. Bartlett and D. S. Tarbell, *J. Am. Chem. Soc.*, **58**, 466 (1936); (b) I. K. Walker and P. W. Robertson, *J. Chem. Soc.*, 1515 (1939); (c) P. B. D. de la Mare, *Quart. Rev.* (London), **3**, 126 (1949); (d) N. Kanyaev, *J. Gen. Chem. USSR*, **29**, 825 (1959).

(2) J. R. Atkinson and R. P. Bell, *J. Chem. Soc.*, 3260 (1963); R. P. Bell and M. Pring, *ibid.*, **B**, 1119 (1966).

Table I. Dependence of Product Distribution^a on Added Salts

Substituted styrene	Addition procedure ^b	Added salt (0.1 M)	% acetoxy bromide ^c
Styrene	i, ii	...	32.4, 20.2
	i, ii	LiBr	16.0, 16.5
	i, ii	NaOAc	37.1, 27.8
3-Chloro	i, ii	LiClO ₄	44.3, 32.5
	i, ii	...	28.5, 22.6
	i	LiBr	6.5
	i	NaOAc	31.2
3-Nitro	i, ii	LiClO ₄	37.0, 31.8
	i	...	13.2
	i	LiBr	3.6
α -Methyl ^d	i	LiClO ₄	11.9
	i, ii	...	13.6, 2.0
	i, ii	LiClO ₄	14.0, 2.0
<i>cis</i> - β -Methyl	ii	...	19.6
<i>trans</i> - β -Methyl	ii	LiClO ₄	38.7
	ii	...	23.4
<i>cis</i> - α,β -Dimethyl ^d	ii	LiClO ₄	36.7
<i>trans</i> - α,β -Dimethyl ^d	ii	...	18
	ii	LiClO ₄	21
β,β -Dimethyl	ii	...	12
	ii	LiClO ₄	15
α,β,β -Triethyl ^d	ii	...	21
	ii	LiClO ₄	33
	ii	...	4
	ii	LiClO ₄	16

^a For brominations in acetic acid only. ^b Procedure i at high Br₂ concentration and procedure ii at low Br₂ concentration, see preceding paper for experimental details (J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469 (1969)). ^c Percentage of total isolated product as estimated from nmr spectrum. ^d Products include some bromohydrin formed during work-up.

and lithium perchlorate at concentrations of 0.1 M. This represents roughly a 20- to 100-fold excess over the other reagents present. The product distributions obtained both with and without added salt are shown in Table I. It is obvious that the ratio of dibromide to acetoxy bromide can be varied over a fairly wide range by addition of these salts, even for individual styrenes. For example, the ratio of dibromo to acetoxybromo adduct for styrene varies from 5.3 (LiBr) to 1.3 (LiClO₄), and for *m*-chlorostyrene from 14.3 (LiBr) to 1.7 (LiClO₄). The sensitivity of these bromine additions to the presence of even such moderate concentrations of added salt is quite different from that observed for analogous chlorine additions to styrenes,⁶ and also to pentenes.⁷ For these chlorinations the product distributions are virtually unaffected by the presence of similar salts (LiCl, LiOAc, LiClO₄) at concentrations comparable with those in Table I. Since these chlorine additions are most reasonably interpreted^{6,7} in terms of mechanisms involving intimate ion-pair intermediates, the greater sensitivity of the bromine additions to the presence of external ions (or ion pairs) makes it probable that solvent-separated ion pairs are involved as well.

As expected, the presence of lithium bromide suppresses acetoxy bromide formation, presumably by diverting the cationic reaction intermediate to give more dibromide.⁸ However, significant amounts of acetoxy

bromide are still found even in the presence of this large excess of bromide over both bromine and olefin. This indicates that acetoxy bromide is formed at least partly by direct solvent attack on an initially formed intimate ion pair. The addition of excess sodium acetate gives increased yields of acetoxy bromides. This is also as expected, but since the increases are only modest, it is a further indication that substantial acetoxy bromide formation can occur through direct solvent attack on an intimate ion pair. The most interesting effect of added salt is that produced by lithium perchlorate, where with one exception (*m*-nitrostyrene) increased yields of the acetoxybromo adduct result. In most cases the addition of LiClO₄ raised the yield of acetoxy bromide¹⁰ to 30–50% of total product, with the exception of the α -methyl-substituted styrenes.

Apart from any effect of increasing the ionic strength of the medium by adding the salt, it is known that solvent-separated ion pairs can interact specifically with LiClO₄ in acetic acid.¹¹ Thus it is reasonable to suggest that the observed increases in acetoxy bromide result from the ability of LiClO₄ to stabilize solvent-separated ion pairs and prevent return to the preceding intimate ion pairs, and also to increase the susceptibility of the cationic intermediates toward attack by the weakly nucleophilic solvent molecules. The formation of a more ionic¹² solvent-separated ion pair would require increased charge dispersal over that required in an intimate ion pair. Hence if formation of solvent-separated ion pairs is occurring, the results in the presence of LiClO₄ should be more sensitive to ring substituents. This is shown by the curves in Figure 1,

(10) The acetoxy bromides formed in the presence of LiClO₄ are the 1-acetoxy-2-bromo derivatives, with the exception previously noted (see Rolston and Yates, footnote b, Table I).

(11) A. H. Fainberg and S. Winstein, *J. Am. Chem. Soc.*, **78**, 2780 (1956).

(12) S. Winstein and G. C. Robinson, *ibid.*, **80**, 169 (1958).

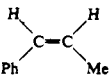
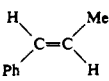
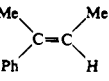
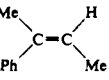
(6) K. Yates and E. Leung, unpublished results.

(7) M. L. Poutsma and J. L. Kartch, *J. Am. Chem. Soc.*, **89**, 6595 (1967).

(8) Another factor which may lead to increased dibromide formation is that in the presence of LiBr a substantial fraction of bromination could be proceeding by way of a termolecular mechanism involving a molecule of olefin, bromine, and a bromide ion. This process would give exclusively dibromide. However this would be kinetically indistinguishable from direct attack of Br₂ on the olefin, which would not necessarily give only dibromide, hence no definite conclusion can be drawn at present.⁹

(9) J. A. Pincock and K. Yates, *J. Am. Chem. Soc.*, **90**, 5643 (1968).

Table II. Dependence of Stereochemistry on Added Salts

Olefin	Added salt (0.1 M)	% erythro ^a dibromide	% trans addition	% erythro ^b acetoxy bromide	% trans addition
	...	27.9	72	5	95
	LiBr	5.1	95
	LiClO ₄	22.8	77	33	67
	...	83.3	83	95	95
	LiBr	94.7	95
	LiClO ₄	86.3	86	95	95
	...	31.9	68		
	LiClO ₄	28.8	71		
	...	62.9	63		
	LiClO ₄	55.9	56		

^a Percentage of total dibromo adduct. Results given are means of nmr and glpc analyses. ^b Percentage of total acetoxybromo adducts. Results based on nmr analysis only.

where the percentage of acetoxy bromide decreases more steeply with the electron-withdrawing ability of the substituent when LiClO₄ is added to the system. The convergence of these curves indicates that *m*-nitrostyrene only forms solvent separated ion pairs with great difficulty. The low yields of acetoxy bromide from the α -methyl-substituted styrenes on the other hand can probably be attributed to the greater steric effect of methyl to solvent approach at the cationic center than its effect on the rate of ion-pair collapse.

The stereochemical results of adding salts to the system are shown in Table II and provide support for the above working hypothesis. The presence of excess bromide increases the stereoselectivity of bromine addition to both *cis*- and *trans*- β -methylstyrenes to the extent that these additions become nearly stereospecific. This is presumably caused by rapid rear side attack of external bromide on the α -carbon, without the necessity for the initially formed bromide counterion to have to reorient and thus permit rotation about the C _{α} -C _{β} bond. However the presence of LiClO₄ alone has little effect on the stereochemistry of dibromide formation from either the β -methylstyrenes or the 2-phenyl-2-butenes. This suggests that dibromide is formed only from the intimate pairs (I) and that internal rotation within the solvent-separated ion pairs (II) can occur while the counterion is reorienting to the less hindered side, away from the first attached bromine. On the other hand, the stereoselectivity of acetoxy bromide formation, which is virtually all *trans* for both isomers in the absence of LiClO₄, is drastically reduced in the case of the *cis*- β -methylstyrene when LiClO₄ is present. This again indicates that the additional yield of acetoxy bromide (when LiClO₄ is present) arises from the solvent-separated ion pair (III) which in the presence of a substantial driving force for rotation (in the *cis* olefin only) takes place less stereospecifically than that arising by direct solvent attack on the intimate ion pair (I). The tendency for direct solvent attack to occur *trans* has been noted previously for chlorine additions,¹³ where it seems more probable that mainly intimate ion pairs are involved.^{6,7} The previous mechanistic considerations are

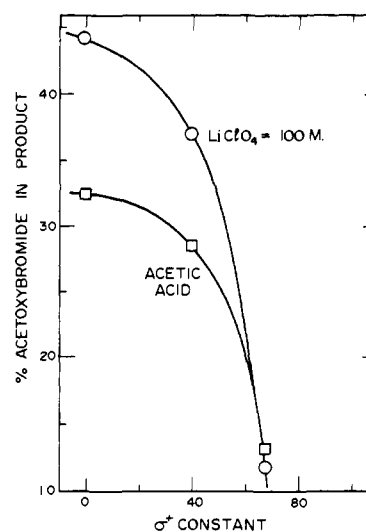


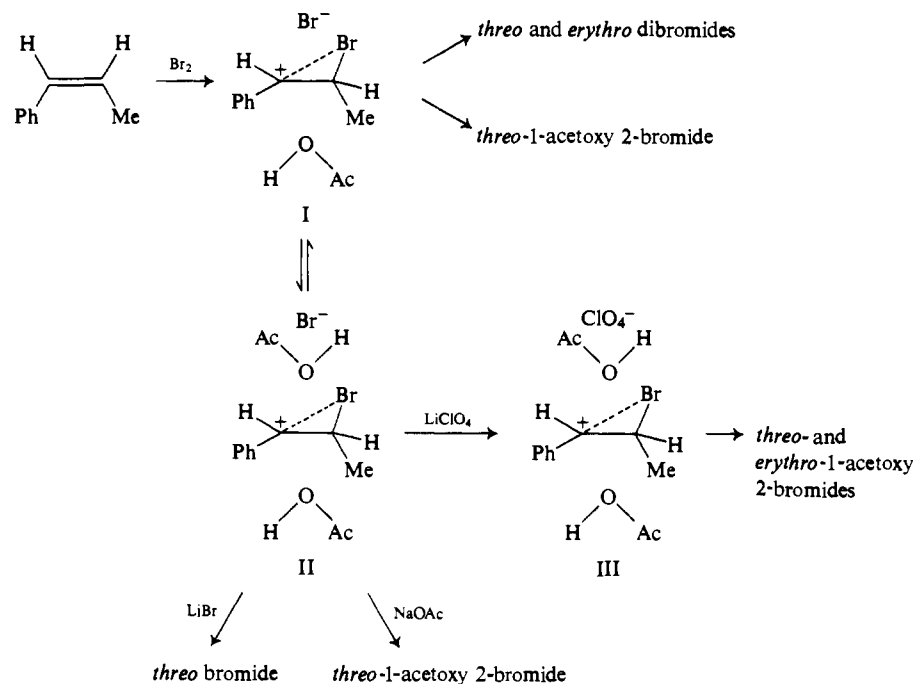
Figure 1. Product dependence on substituent constant for bromination of styrenes in acetic acid.

illustrated below for the case of *cis*- β -methylstyrene. The intermediates are represented as asymmetrically bridged structures, in which rotation is possible, rather than open benzylic cations, for reasons which are discussed later.

Medium Dependence of Stereochemistry of Addition.

The stereochemistry of bromine addition to *cis*- and *trans*- β -methylstyrenes has been investigated in six solvents of widely different polarity. Since the majority of the solvents used were nonnucleophilic, only the dibromide stereochemistry was studied. The results for *cis*- β -methylstyrene in Table III show that the stereochemistry of addition is markedly dependent on the nature of the solvent, the products ranging from predominantly *trans* to predominantly *cis* adducts. Apart from the results in dioxane, which will be discussed later, the most striking feature is the marked decrease in *trans* addition in the solvents of highest polarity, the additions in both acetic anhydride and nitrobenzene being virtually nonstereoselective. This type of result has been reported previously for additions to *cis*-stilbene.⁵ On the other hand, the results for the *trans*- β -methylstyrene in the same six solvents given in Table IV, show much less

(13) R. C. Fahey and C. Schubert, *J. Am. Chem. Soc.*, **87**, 5172 (1965).



dependence on the nature of the solvent, the additions in all cases being predominantly, though not exclusively, *trans*. This also resembles the reported behavior of *trans*-stilbene.⁵ The results in Tables III and IV were obtained using low Br_2 concentrations (*i.e.*, $< 10^{-3} M$). These were repeated in several of the solvents using much higher Br_2 concentrations ($\sim 0.3 M$) to investigate the possibility that olefin isomerization under the reaction conditions, followed by *trans* addition, was responsible for the observed *cis*-addition products. Examination of the unreacted olefins under these conditions showed that only 1–2% at most had isomerized, so that the *cis* adducts obtained are actually formed from a *cis*-addition mechanism. The net stereochemical results using high bromine concentrations do not differ significantly from those given in Tables III and IV. This is shown in Figure 2 where the results obtained using both addition procedures are plotted as a function of the solvent dielectric constant. This shows that the percentage of *trans* addition to the *cis* olefin is much more sensitive to solvent polarity than that for the *trans* olefin. This presumably reflects a greater driving force for rotation about the $\text{C}_\alpha\text{-C}_\beta$ bond in the intermediate from the *cis* olefin (IV) due to partial eclipsing of the adjacent methyl and phenyl groups. It is expected that most of

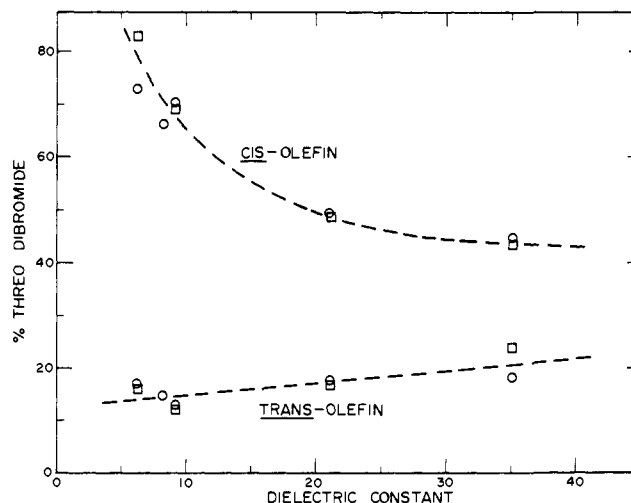
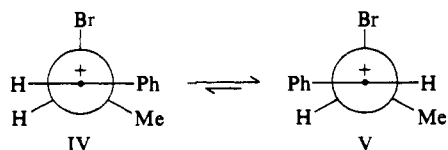


Figure 2. Dependence of stereochemistry of addition on solvent dielectric constant for β -methylstyrenes: \circ , additions at low $[\text{Br}_2]$; \square , additions at high $[\text{Br}_2]$.



the ground-state free energy difference between the *cis* and *trans* olefins would be retained in the carbonium ion intermediates IV and V, since although the groups are no longer fully eclipsed as in the olefins, one carbon is now sp^3 hybridized and the corresponding decreases in bond angle from 120 to 109° would bring adjacent groups closer together. This steric interaction would be made even more pronounced by any significant participation

by neighboring bromine since this would convert the sp^2 carbonium ion center into something resembling an sp^3 center. It seems clear from the stereochemical results in this and the preceding paper that the bromination intermediates from styrenes resemble benzylic carbonium ions more than they do cyclic bromonium ions of the Roberts and Kimball type.¹⁴ However, despite the nonstereospecific course of these additions, it is equally clear that *some* bridging interaction must be present in the intermediates, since open and freely rotating carbonium ion intermediates would be expected to give rise to the same product distribution from either a *cis* or *trans* starting material, particularly in strongly polar solvents. This is clearly never the case, as shown

(14) I. Roberts and G. E. Kimball, *J. Am. Chem. Soc.*, **59**, 947 (1937).

Table III. Solvent Dependence of Stereochemistry of Dibromo Adducts from *cis*- β -Methylstyrene

Solvent	Dielectric constant ^a	% <i>erythro</i> dibromide ^b Nmr	% <i>trans</i> ^c Glpc	% <i>trans</i> ^c addition
Dioxane	2.2	81.5	79.2	20
Acetic acid	6.2	27.9	26.3	73
Tetrachloroethane	8.2	34.4	33.4	66
Dichloromethane	9.1	29.8	29.5	70
Acetic anhydride	21	50.5	50.8	49
Nitrobenzene	35	54.8	55.7	45

^a Values for 20–25° taken from A. Weissberger, E. S. Proskauer, J. A. Riddick, and E. E. Troops, Ed., "Technique of Organic Chemistry," Vol. VII, 2nd ed, Interscience Publishers, New York, N. Y., 1955. ^b Percentage of total dibromides obtained by addition procedure ii (see Rolston and Yates, footnote b, Table I) using low Br₂ concentrations. ^c Based on average of glpc and nmr results.

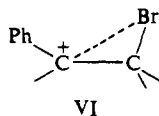
Table IV. Solvent Dependence Stereochemistry of Dibromo Adducts from *trans*- β -Methylstyrene

Solvent	Dielectric constant ^a	% <i>threo</i> dibromide ^b Nmr	% <i>trans</i> ^c Glpc	% <i>trans</i> ^c addition
Dioxane	2.2	27.6	30.6	71
Acetic acid	6.2	16.7	17.1	83
Tetrachloroethane	8.2	12.4	16.7	85
Dichloromethane	9.1	12.0	13.8	87
Acetic anhydride	21	16.4	18.1	83
Nitrobenzene	35	15.5	21.1	82

^a Values for 20–25° taken from Weissberger, *et al.*, footnote a, Table III. ^b Percentage of total dibromides obtained by addition procedure ii (see Rolston and Yates, footnote b, Table I) using low Br₂ concentrations. ^c Based on average of glpc and nmr results.

in Figure 1, and a crude extrapolation of these results suggests that a dielectric constant of greater than 100 would be required for this to occur. Similar but more limited studies on the 2-phenyl-2-butene system (in acetic acid, acetic acid–LiClO₄, and dichloromethane) also give stereochemical results which are not independent of the geometry of the starting olefin.

The present results are most consistent with an unsymmetrically bridged intermediate (VI) in which there



is a weak electrostatic interaction between the carbonium ion center and the negative end of the β -carbon–bromine dipole, which is sufficiently strong to prevent completely free rotation. This tends to result in stereoselective additions but the barrier to rotation can easily be overcome by steric effects, particularly in the more polar solvents where open charged species such as benzylic carbonium ions can be more effectively stabilized. This type of intermediate is more in accord with current views^{1c,15,16} than an open ion and explains equally well the almost exclusively Markovnikov orientation observed for the acetoxy bromides. There is however one case where the results point to an open intermediate cation. The results of addition to both *cis*- and *trans*- β -methylstyrenes in dioxane are anomalous in view of its very low

(15) R. E. Buckles, J. L. Miller, and R. J. Thurmaier, *J. Org. Chem.*, **32**, 888 (1967).

(16) J. E. Dubois and W. V. Wright, *Tetrahedron Letters*, 3101 (1967).

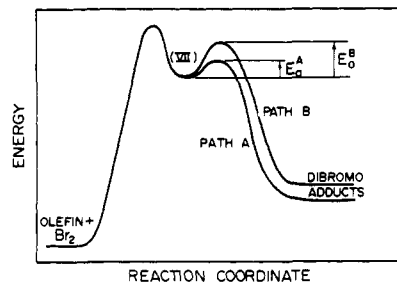
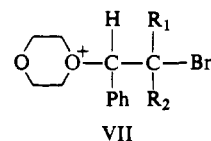


Figure 3. Reaction profile for bromine additions to *cis*- or *trans*- β -methylstyrene.

dielectric constant, since in this solvent each olefin gives the lowest yield of *trans* addition observed.¹⁷ This is particularly notable for the *cis* olefin which gives predominantly *cis* addition. The formation of crystalline 1:1 complexes between dioxane and halogens¹⁹ shows the unique ability of dioxane, among the solvents used, to coordinate effectively with a bromine molecule. Thus dioxane might be expected to provide specific solvation for the incipient carbonium ion center, giving an unstable oxonium ion intermediate such as VII.



The ability of dioxane to solvate cationic intermediates is supported by the observation that solvolysis reactions in this solvent show an unusually high degree of retention of configuration.^{20,21} Such coordination would reduce the necessity of bromine participation as in VI and hence permit greater freedom of rotation about the C _{α} –C _{β} bond as in VII. In the limit, with completely free rotation, ratio of *erythro* to *threo* dibromide would be independent of starting olefin. This is approximately the case for dioxane, the observed ratios being 80:20 (*cis* olefin) and 71:29 (*trans* olefin). It is interesting that if the difference in thermodynamic stability between the two olefins²² were exactly retained in the intermediates, the expected ratio would be 78:22.

Effect of Temperature. It was of interest to examine the effect of temperature on the ratio of *cis*- to *trans*-dibromo adducts from both *cis*- and *trans*- β -methylstyrenes. If the two diastereomeric dibromides (from either olefin) are pictured as arising from an intimate ion pair (VIII) formed in the rate-determining step of the addition, then the *cis*- and *trans*-dibromo adducts can be formed by partitioning of this intermediate be-

(17) The effectiveness of dioxane in decreasing the yield of *trans*-addition products has also been reported¹⁸ for the Prins reaction of these two olefins.

(18) L. J. Dolby, C. Wilkens, and T. G. Frey, *J. Org. Chem.*, **31**, 1110 (1966).

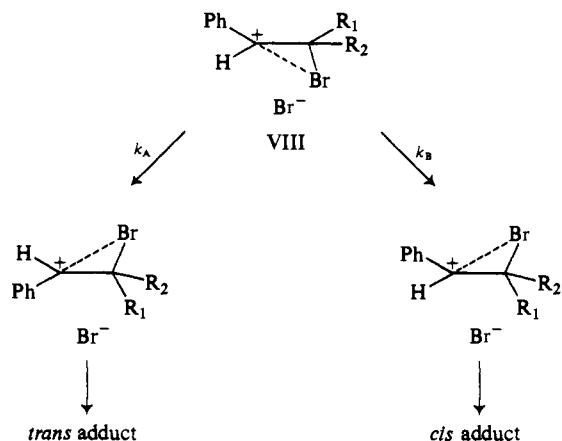
(19) L. J. Andrews and R. M. Keefer, "Molecular Complexes in Organic Chemistry," Holden-Day, Inc., San Francisco, Calif., 1964, p 50.

(20) A. Streitwieser, Jr., and S. Andreades, *J. Am. Chem. Soc.*, **80**, 6553 (1958); A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.*, **79**, 6233 (1957).

(21) H. A. Weiner and R. A. Sneed, *ibid.*, **84**, 3599 (1962); H. A. Weiner and R. A. Sneed, *Tetrahedron Letters*, 1309 (1963).

(22) J. E. Kilpatrick, K. S. Pitzer, and F. D. Rossini, *J. Res. Natl. Bur. Stand.*, **42**, 225 (1949).

tween two post transition-state paths. The electrostatic repulsion between the bromide ion and the polarized C-Br bond should cause reorganization of the intermediate so that the Br⁻ is more favorably oriented for attack on the electrophilic center. This could occur without internal rotation of the C_α-C_β bond (path A), giving net *trans* addition, or with rotation (path B), leading to net *cis* addition. It is assumed that the bulk of the first bonded bromine atom plus the ion-dipole repulsion will effectively prevent a direct collapse of VIII to a *cis* adduct.²³ If the two dibromides are formed



under kinetically controlled conditions, as seems reasonable,²⁴ then the ratio of *cis* to *trans* adduct will be simply equal to the ratio of rate constants k_B/k_A . By studying the temperature dependence of this ratio it should be possible to evaluate the difference in activation energies,²⁵ $\Delta E_a = E_a^A - E_a^B$ for the two paths as shown in Figure 3. Substitution for the rate constants using the Arrhenius equation gives

$$\log \frac{\text{cis}}{\text{trans}} = \log \frac{k_B}{k_A} = \log \frac{A_B}{A_A} + \frac{E_a^A - E_a^B}{2.3RT}$$

Thus the value of ΔE_a should be measurable from the slope of a plot of $\log \text{cis}/\text{trans}$ against $1/T$. The *cis/trans* ratios for bromine additions in tetrachloroethane were determined over a wide temperature range for both *cis* (-25 to +75°) and *trans* olefins (-35 to +105°) and were found to increase with temperature in each case. The variations observed were unfortunately not much larger than the experimental uncertainty, and yielded values of $\Delta E_a = -169 \pm 88$ cal/mol for the *cis* olefin and $\Delta E_a = -226 \pm 73$ cal/mol for the *trans* isomer. The standard deviations of the slopes indicate that these effects are real. Thus the difference in activation energy between path A (no internal rotation) and path B (internal rotation) is in the expected direction in that internal rotation accompanying reorientation requires more energy. Also the value of ΔE_a would be expected to be smaller starting from the *cis* olefin because of the unfavorable interaction between phenyl and methyl

(23) Although the formation of *cis* adducts in chlorine additions has been reasonably explained in terms of such a direct collapse, it seems much less probable on steric grounds for bromine additions. This is partly because of the greater size of bromine (and bromide ion) and partly because of the presence of a more effective halogen bridging interaction.

(24) R. C. Fahey and H.-J. Schneider, *J. Am. Chem. Soc.*, **90**, 4429 (1968).

(25) G. H. Schmid and V. M. Csizmadia, *Can. J. Chem.*, **44**, 1338 (1966).

already present in the initially formed intermediate VIII.

These differences can be regarded as lower limits, since increasing the temperature also lowers the dielectric constant of the solvent.²⁶ This superimposed effect would tend to increase the amount of *trans* adduct and hence lower the *cis/trans* ratio, partly offsetting the observed trend to higher *cis/trans* ratios at higher temperatures. This second factor is clearly more dominant in nitrobenzene as solvent, since for the temperature range studied (+10 to +75°) the observed variations in *cis/trans* ratio were found to be within the experimental uncertainty.

Since a change in dielectric constant is a necessary consequence of changing the reaction temperature, little quantitatively meaningful information or differences in activation energy between the various stereochemically possible paths can be obtained²⁷ unless, as a minimum requirement, the temperature dependence of solvent dielectric constant is negligible over the range studied. The above results, although disappointing, are valuable in that they demonstrate the differences in activation energy which control product stereochemistry are probably only of the order of a few hundred calories. Thus even small steric effects present in the starting olefin could cause facile rotation in the reaction intermediates, leading to nonstereospecific additions, as observed.

Studies on *cis*- and *trans*-2-Butene. The stereochemistry of the dibromides formed from *cis*- and *trans*-2-butenes was studied under a variety of reaction conditions as shown in Table V. In sharp contrast to the previous results on styrenes, the additions to both *cis*- and *trans*-2-butenes are virtually 100% *trans* in every case. This stereospecificity appears to be completely independent of both reaction medium and temperature.

Table V. Stereochemistry of Br₂ Addition to *cis*- and *trans*-2-Butenes

Solvent	Temp, °C	Olefin	% <i>trans</i> addition ^a
Acetic acid	25	<i>cis</i>	99.5
		<i>trans</i>	99.5
Acetic acid (0.1 M LiClO ₄)	25	<i>cis</i>	99.5
Dioxane	25	<i>cis</i>	99.7
Acetic anhydride	25	<i>cis</i>	99.8
Acetonitrile	25	<i>cis</i>	99.5
Nitrobenzene	10	<i>cis</i>	99.8
		<i>trans</i>	99.9
Nitrobenzene	65	<i>cis</i>	99.8
Nitrobenzene	90	<i>cis</i>	99.8
		<i>trans</i>	99.9

^a Based on calibrated glpc analysis. It was shown by this method that as little as 0.2% of one diastereomeric dibromide could be detected in the presence of the other.

The marked differences in the behavior of the 2-butene system compared with that of the styrene system, which were also noted on the previous paper,²⁸ leave little doubt that the nature of the reaction intermediates, and hence the mechanisms of bromine addition to these two systems, are quite different. Only the results from the

(26) E. W. Washburn, Ed., "International Critical Tables of Numerical Data, Physics, Chemistry and Technology," McGraw-Hill Book Co., Inc., New York, N.Y., 1962, pp 82-84.

(27) J. H. Beard and P. H. Plesch, *J. Chem. Soc.*, 3682 (1964).

(28) See Rolston and Yates, footnote b, Table I.

2-butenes are fully consistent with formation of strongly bridged bromonium ion intermediates of the type originally postulated by Roberts and Kimball.¹⁴ The nature of the bromine participation in such intermediates is clearly quite different from any participation which may be present in the intermediates formed by bromine addition to phenyl-substituted olefins such as styrenes or stilbenes.

Experimental Section

Materials. Lithium perchlorate, lithium bromide, and sodium acetate were the best commercial grades available and were dried before use over P_2O_5 at 140° (0.1 mm) for 48 hr. Acetic acid (C.I.L. Glacial) was purified by refluxing for 48 hr with a calculated 2% excess of acetic anhydride, followed by fractionation through a 75-cm column packed with glass helices. The fraction boiling at 118.1° was collected and stored in an automatic buret fitted with drying tube. Only samples with minimum melting point of 15.58° were used in reactions. The other solvents were purified by standard methods²⁹ and fractionally distilled before

(29) See Weissberger, *et al.*, footnote a, Table III.

use. Pure samples of the olefins were prepared or obtained as described previously.²⁸

Product Analysis. Details of the addition procedures used have also been given previously.²⁸ Products of reactions in acetic acid, acetic anhydride, and dioxane were isolated by the extraction procedure described previously.²⁸ Products of reactions in dichloromethane, tetrachloroethane, and nitrobenzene were obtained by direct evaporation of the solvent. Providing these evaporations were carried out at room temperature for a minimum length of time analysis of the concentrates gave results within 1–2% of those obtained by direct glpc analysis of the reaction solutions.

Determination of percentage compositions of product mixtures was carried out either by nmr analysis as described previously or by calibrated glpc analysis, or by both methods. The results obtained by each method were found to be in good agreement and were individually reproducible to within $\pm 1\%$ for most reaction mixtures. Product structures were determined as described previously.²⁸

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Polar Additions to the Styrene and 2-Butene Systems. III. Kinetics and Linear Free Energy Relationships

John H. Rolston and Keith Yates

Contribution from the Department of Chemistry, University of Toronto, Toronto, Canada. Received October 5, 1968

Abstract: The rates of bromination of styrene and its six side-chain methyl-substituted derivatives have been measured in acetic acid using a potentiometric method. The observed rate constants (which are composites of the molecular bromine and tribromide ion processes) show no simple dependence on the number of methyl groups attached to the double bond, unlike similar reactions of the ethylene system. This plus the fact that α -methyl substitution gives significant rate enhancements, whereas β substitution produces little or no effect, is taken as evidence for an unsymmetrical charge distribution at the transition state for bromine additions to styrene systems. The rates of bromination of eight *meta*- and *para*-substituted styrenes have also been investigated under similar conditions and the separated rate constants for bromine and tribromide ion attack have been obtained from a study of the dependence of k_{obsd} on added bromide, and measurement of the tribromide formation constant. Both sets of rate constants give better correlations against σ^+ than σ , with $\rho_{Br_2} = -4.21$ and $\rho_{Br_3^-} = -2.02$. The magnitude of the former ρ value is taken as evidence for a transition state in which a substantial charge is developed at C_α , similar to that expected for a benzylic type carbonium ion. The latter ρ value is interpreted in terms of an electrophilic attack by tribromide ion in which much less cationic charge is developed on C_α at the transition state, rather than in terms of a kinetically equivalent bromide ion catalyzed attack of molecular bromine. This conclusion is based on consideration of the relationship between the kinetics and observed product distribution. A simple mechanistic scheme is developed which is consistent with both the observed kinetics and product distribution.

Kinetic studies of the polar addition of bromine to olefins in both aqueous and organic solvents have shown that there are several paths available for the reaction.^{1,2} These include both first- and second-order bromine processes, as well as the kinetic equivalent of a bromide ion catalyzed addition of molecular bromine. It has been shown^{3,4} that high kinetic orders with respect

to bromine are generally confined to the more concentrated bromine solutions, and that these processes become less important kinetically as the temperature is raised and as the solvent becomes more polar, *e.g.*, as water is added to acetic acid.⁵

Additions of bromine to some unsaturated compounds, particularly vinyl and allyl halides, in the presence of halide ions follow a kinetic equation involving the concentration of olefins and bromine and halide ion.² The effectiveness of this "halide ion catalyzed process" appears to be sensitive to olefin structure

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 (2) K. Nozaki and R. A. Ogg, Jr., *J. Am. Chem. Soc.*, **64**, 697, 704, 709 (1942).
 (3) I. Ting and P. W. Robertson, *J. Chem. Soc.*, 628 (1947).
 (4) P. W. Robertson, N. T. Clare, K. J. McNaught, and G. W. Paul, *ibid.*, 335 (1937).

(5) I. K. Walker and P. W. Robertson, *ibid.*, 1515 (1939).