were placed in a test tube with a diameter of 10 mm equipped with a Teflon-lined screw cap. The reaction mixture was handly shaked for 1 min and then kept at 50 °C for 18 h in a thermostat. After addition of 1 mL of 0.2 N aqueous HCl and extraction with $CHCl_3$ (3 × 10 mL), the organic layer was separated and analyzed by GLC. The reaction was repeated under identical conditions by using stoichiometric amounts of **2a** and **2b** (400 and 88 mg, respectively) and in the absence of catalyst. The data reported in the text are not corrected for the uncatalyzed reaction.

Kinetic Measurements. Kinetics were run in a cylindric 50-mL flask (internal diameter 3.0 cm) equipped with a Teflon-lined screw cap and thermostated at 55 °C with circulating butyl phthalate and a magnetic stirrer (2.5 cm long). The temperature was controlled to within ±0.02 °C by a Colora K-5 ultrathermostat. The stirring speed (1300 ± 50 rpm) was controlled by using a strobe light. A general example of the procedure employed follows. The flask was charged with 202 mg (1.4 mmol) of β-naphthol, 7 mL of 0.2 N aqueous sodium hydroxide, 20 mg (0.0786 mmol) of octadecane as an internal standard, 2 mL of toluene, and 80 mg (0.08 mequiv) of resin **3** (1 mequiv of Br^-/g, 25% ring substitution). The mixture was stirred at the reaction temperature for 3 h to condition the catalyst. Benzyl bromide (2 mL of a 0.4 M toluene solution) was added at zero time. The reaction was followed by GLC analysis up to about 40% conversion, after which a progressive deviation from the pseudo-first-order stright lines was observed both for products **6** and **7**. The pseudo-first-order rate constants (k_C and k_O) were obtained by following ln [**6**] and ln [**7**] vs. time and computed by the least-square method. The measurements were repeated at least twice, and their reproducibility was found to be ±10%.

Product Distribution in the Alkylation of β-Naphthoxide with Equimolecular Amounts of Polymer-Supported Quaternary Salts. A 50-mL flask was charged with 72 mg (0.5 mmol) of β-naphthol, 2.5 mL of aqueous 0.2 N sodium hydroxide (0.5 mmol), and 0.5 g of resin **3** (0.5 mequiv) and heated at 55 °C for 2 h with magnetic stirring. Benzyl bromide (2.5 mL) of a 0.2 M toluene solution) was added, and heating and stirring were continued for 18 h. The reaction mixture was acidified with 2 mL of 2 N aqueous hydrochloric acid, 5 mL of toluene was added, and the organic phase was analyzed by GLC in the presence of octadecane as an internal standard.

Hydration State of Polymeric Catalysts. The catalyst was stirred for 3 h at 90 °C in the presence of toluene and saturated aqueous solution of sodium or potassium halide; after filtration and being allowed to stand at room temperature, it reached a constant weight after 2–3 h for catalysts **2a,b** and **3** and after 72 h for catalyst **4**. Karl-Fisher and potentiometric titrations on weighed portions of catalyst, carried out as previously reported,[1] gave the amounts of absorbed water and halide ions, respectively. The H_2O/Br^- and H_2O/Cl^- ratios were 1.7 and 2.8–3.2 for catalysts **3**, and **2a,b**, and **4**, respectively.

Distribution of Benzyltributylphosphonium β-Naphthoxide in a Toluene-Water Two-Phase System. A solution of the quaternary salt (436 mg, 1 mmol) in 2 mL of toluene and 2 mL of water was stirred for 2 h at room temperature. A measured portion (1.0 mL) of the organic phase was added to 1.0 mL of water, 1.0 mL of 1 N HCl, and 1.0 mL of ethyl ether (solution A). A measured portion (1.0 mL) of the aqueous phase was added to 1.0 mL of toluene, 1.0 mL of 1 N HCl, and 1 mL of ethyl ether (solution B). Both solutions were shaken, and the amount of β-naphthol in the organic portions of A and B was determined by GLC (SE-30 on Varaport-5%, 180 °C). The A/B ratio was 120.

Acknowledgment. This paper was supported by a grant from the "Progetto Finalizzato di chimica fine e secondaria" of Consiglio Nazionale delle Ricerche (CNR) Roma.

Registry No. Dowex-1, 11138-21-9; sodium β-naphthoxide, 875-83-2; sodium phenoxide, 139-02-6; benzyl bromide, 100-39-0; benzyltributylphosphonium β-naphthoxide, 83746-97-8.

Multipathway Mechanism in Aryl Olefin Bromination: Competition between Tertiary and Secondary Carbocation Pathways

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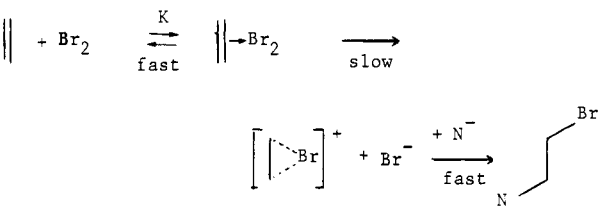
Received March 2, 1982

Rate constants, product stereochemistry, and regiochemistry of the bromination of 26 α-methylstilbenes $XC_6H_4C(Me)=CHC_6H_4Y$ have been measured in methanol at 25 °C. Kinetic substituent effects on the rate show the competitive formation of secondary and tertiary carbocations in the rate-determining step. The secondary pathway competes with the tertiary one only if Y is strongly electron donating and X electron accepting. The ρ values are all consistent with carbocationic transition states: in the tertiary pathway ρ_α for X is −4.59 and ρ_β for Y is −1.66, whereas in the secondary pathway ρ_β for X, which varies with Y from −1.95 (Y = 4-OMe) to −0.89 (Y = 4-NMe_2), is in the expected range for a β effect. Product analysis is in complete agreement with the kinetic results. The formation of dibromides and methoxy bromides is nonstereoselective as expected from the absence of bromine bridging in the transition states and the intermediates. The experimental regiochemistry is correctly predicted by the relative rates of formation of the secondary and tertiary carbocations. From this rate–product correlation, the first established for an addition reaction, the unambiguous conclusion is that the positive charge distribution does not change on going from the rate-determining to the product-determining transition state.

Though the general Ad_ECl mechanism for the electrophilic addition of bromine to double bonds, postulated by Dubois and Garnier[1] (Scheme I), is now well established, there is still controversy about the structure of the ionic intermediates and of the rate- and product-determining transition states.

This debate is based on the apparently contradictory results given by kinetics and product stereochemistry. Two different approaches have been used to interpret the data.

Scheme I

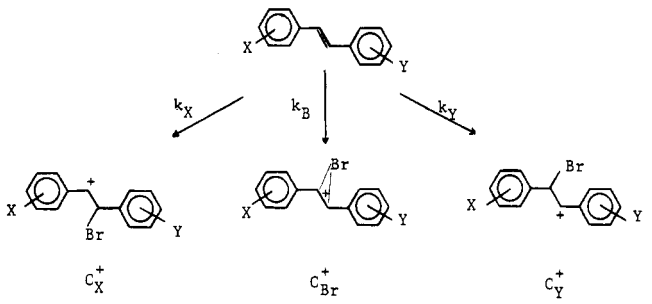


Schmid et al.[2] postulate that the structures of the transition states of the rate-determining electrophilic step

(1) Garnier, F.; Dubois, J. E. *Bull. Soc. Chim. Fr.* **1968**, 3797–3803.

0022-3263/83/1948-0202$01.50/0

Scheme II



and of the product-determining nucleophilic step are different. They suggest that the first is always a bridged, bromonium ion type, leading to a bridged intermediate, the second being open or bridged as evidenced by the stereochemistry of the addition. This hypothesis, which distinguishes two different types of transition state, allows separate interpretations of kinetic and stereochemical data since they deal with two completely different steps. However, it has been shown, first, that the rate-determining transition state is late on the reaction coordinate and therefore that its structure closely resembles that of the intermediate.[1,3] Second, the last step, nucleophilic attack of the intermediate, is very fast, the transition state being very near the reactants; it should then have a structure similar to the intermediate. It is therefore unlikely that the extent of bridging would be completely different in these two transition states.

The second approach, developed in this laboratory,[4] maintains that the two types of transition state, open or bridged, are formed competitively as early as the rate-determining step, leading to different intermediates depending upon the structure of the olefin. In this case, interpretations of kinetic and stereochemical data must be coherent since the former concerns the formation of the intermediate and the latter its destruction, both transition states closely resembling the intermediate. One should observe quantitative correlation between rates and products which, up to now, have not been obtained due to the complexity of the experimental systems studied.

Though the two approaches can explain all the experimental results, our multipathway mechanism, taking into account the competitive formation of several intermediates, is of wider interest since it permits quantitative analysis of the data. Successfully applied to styrene bromination,[5] the multipathway hypothesis was first used to explain substituent effects on the reactivity and the products of stilbene bromination[4] (Scheme II). Depending upon the substituents, open ions C_X^+ (when X is electron-donating) and C_Y^+ (when Y is electron-donating) or a bridged ion C_{Br}^+ (when X and Y are electron attractors) are the intermediates of the reaction. Quantitative interpretation of the data and measurement of the competition between the pathways are not precise due to the simultaneous occurrence of three intermediates. It was not possible to establish an accurate rate–product correlation which would test the multipathway scheme and confirm the similarity of charge distribution in the rate-determining and the product-determining transition states.

Therefore we attempted to simplify the general scheme by eliminating one pathway. In styrene bromination[5] there is competition between bromonium ion C_{Br}^+ and carbocation C_X^+ formation, and rough agreement between kinetics and stereochemistry was observed, but, since the regiochemistry of nucleophilic attack on a bromonium ion is unpredictable, no exact rate–product correlation could be established. We looked, therefore, for another example where only the two carbocations C_X^+ and C_Y^+ compete. To this end we have analyzed substituent effects on the bromination of α-methylstilbene for which it can be anticipated that bromine participation is negligible. We report here the first rate–product correlation for an addition reaction.

Table I. Experimental Rate Constant for Bromine Addition to α-Methylstilbenes in Methanol (0.2 M NaBr) at 25 °C

compd	X	Y	k_{exptl}[a]	method[b]
1	4-OH	H	1.22×10^5	A
2	4-OMe	H	2.48×10^4	A
3	4-Me	H	3.72×10^2	B
4	3-Me	H	4.68×10	B
5	4-F	H	1.91×10	B
6	H	H	1.66×10	B
7	4-Cl	H	4.27	B
8	3-Cl	H	3.32×10^{-1}	B
9	3-CF_3	H	1.27×10^{-1}	B
10	4-CF_3	H	4.75×10^{-2}	C
11	H	4-NMe_2	2.93×10^5	A
12	H	4-OH	1.62×10^3	C
13	H	4-OMe	1.41×10^2	B
14	H	4-Me	3.08×10	B
15	H	4-F	1.01×10	B
16	H	4-Cl	6.52	B
17	H	3-Cl	4.07	B
18	H	3-CF_3	2.28	B
19	3-Cl	4-NMe_2	1.54×10^5	A
20	3-CF_3	4-NMe_2	1.02×10^5	A
21	4-Me	4-OH	3.15×10^3	A
22	4-Cl	4-OH	4.45×10^2	C
23	4-CF_3	4-OH	2.0×10^2	B
24	4-Cl	4-OMe	6.27×10	B
25	3-Cl	4-OMe	3.13×10	B
26	3-CF_3	4-OMe	1.51×10	B

[a] k_{exptl} in M^{-1} s^{-1}. Reproducibility, generally in the range ± 2–3%, is always better than 5%. [b] Kinetic method: A, couloamperometry;[7] B, potentiometry;[6] C, UV spectroscopy.[8]

Results

Nomenclature. The substituents on the ring α and β to the methyl-substituted carbon are denoted X and Y, respectively.

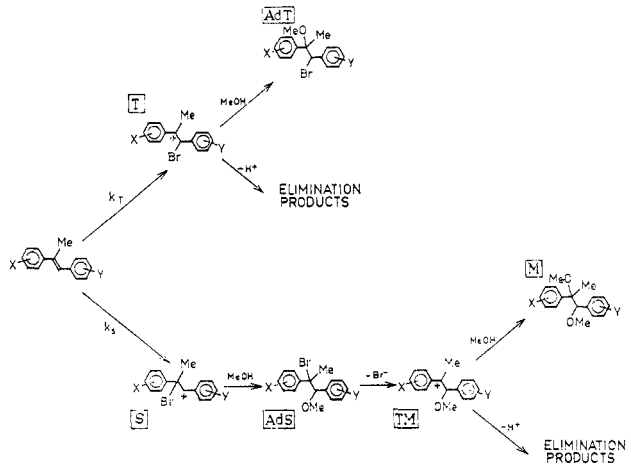
Kinetic Results. Experimental bromination rate constants k_{exptl} of 26 X,Y-substituted α-methylstilbenes listed in Table I were measured in methanol containing 0.2 M NaBr at 25 °C by various potentiometric,[6] couloamperometric,[7] and spectroscopic[8] methods.

In this medium two brominating agents, free bromine (Br_2) and tribromide ion (Br_3^-) formed in the equilibrium shown in eq 1, add to the olefin.[9] Owing to the complexity

$$Br_2 + Br^- \rightleftharpoons Br_3^- \quad (1)$$

(2) Schmid, G. H.; Garratt, D. G. "Chemistry of the Functional Groups, Double Bonded Functional Groups"; Patai, S., Ed.; Wiley: New York, 1977 Suppl. A, p 725.
(3) Ruasse, M. F.; Dubois, J. E. *J. Am. Chem. Soc.* **1975**, *97*, 1977–1979; *J. Org. Chem.* **1977**, *42*, 2689–2694.
(4) Ruasse, M. F.; Dubois, J. E. *J. Org. Chem.* **1972**, *37*, 1770–1778; **1973**, *38*, 493–499; **1974**, *39*, 2441–2444.
(5) Ruasse, M. F.; Argile, A.; Dubois, J. E. *J. Am. Chem. Soc.* **1978**, *100*, 7645–7652.
(6) Dubois, J. E.; Hegarty, A. F.; Bergmann, E. D. *J. Org. Chem.* **1972**, *37*, 2218–2221.
(7) Dubois, J. E.; Alcais, P.; Barbier, G. *J. Electroanal. Chem.* **1964**, *8*, 359–365.
(8) Dubois, J. E.; Garnier, F. *Spectrochim. Acta, Part A* **1967**, *23A*, 2279–2286.
(9) Bienvenue-Goetz, E.; Dubois, J. E. *Bull. Soc. Chim. Fr.* **1968**, 2089–2093.

Scheme III



of the $k_{Br_3^-}$ constant, only the structural effect on k_{Br_2} will be considered. It has been shown[10] that the variation of k_{exptl} closely parallels that of k_{Br_2} when the ratio Q of k_{Br_2} to $k_{Br_3^-}$ is greater than 16. For compounds **1**, **6**, **10**, and **19** this ratio was found to be in an acceptable range (107, 94, 36, and 103, respectively) even for the least reactive compound, **10**. The discussion will therefore be limited to the structural effect on the experimental constant, k_{exptl}.

Moreover, if necessary it is possible to obtain k_{Br_2} from k_{exptl} for any α-methylstilbene by means of eq 2, obtained by correlating k_{exptl} to k_{Br_2} for the compounds **1**, **6**, **10**, and **19**.

$$\log k_{Br_2} = 1.047 \log k_{exptl} + 1.346 \qquad R = 0.9994 \qquad (2)$$

Stereochemistry of Bromide Ion Attack on the Intermediate. The stereochemistry of the reaction of compounds **2**, **6**, **7**, **10**, **13**, and **24** has been investigated through the diasteroisomeric dibromides formed by addition of bromine to olefins in a nonnucleophilic solvent, dichloromethane. The two diastereoisomers are readily identified by the NMR chemical shifts of the methyl and methine protons. Integration of their signals leads to the erythro/threo[11] composition of the products. Addition is not completely stereoselective (70 ± 5% erythro), and the stereoselectivity does not depend on substituents. Even when X is an electron-attracting substituent (4-CF_3), the stereoselectivity of the addition does not increase, in contrast to what was observed in β-methylstyrene bromination.[5]

When X is a strongly electron-donating group such as 4-OMe, addition does not only lead to dibromide. Integration of the α-methyl group proton signals is 30% less than that of the ring methoxy group, and new signals, too small to be unambiguously identified, appear in the spectra. This decrease in the methyl group signal probably indicates that proton elimination followed by subsequent bromine addition occurs after formation of the ionic intermediate.

Regiochemistry of Methanol Attack. In hydroxylic solvents such as methanol, bromination of α-methylstilbenes leads only to solvent-incorporated products. Depending on X and Y, two regioisomers, AdT (1-bromo-2-methoxy-1,2-diarylpropanes) and AdS (2-bromo-1-methoxy-1,2-diarylpropanes), identified by their NMR spectra, are formed (Table II, Scheme III).

Table II. Regiochemistry[a] of α-Methylstilbene Bromination in Methanol

	distribution, %			
compd	AdT[b]	AdS[b]	M[b]	others[c]
2	65			35
32[d]	70			30
33[d]	80			20
3	100			
30[d]	100			
6	100			
7	100			
10	100			
14	100			
16	100			
13	35		40	25
24		20	60	20
26		100		
34[d]		100		
12		50	20	30
35[d]		100		
23		100		
11				100
19				100

[a] In percent. When no value is given, the corresponding product has not been detected in the NMR spectra; consequently they are present to the extent of no more than 2%. [b] AdT = 1-bromo-2-methoxy-1,2-diarylpropane; AdS = 2-bromo-1-methoxy-1,2-diarylpropane; M = 1,2-dimethoxy-1,2-diarylpropane. [c] Elimination. [d] **32** (X = 4-OMe, Y = 3-Cl), **33** (X = 4-OMe, Y = 3-CF_3), **30** (X = 4-Me, Y = 4-Cl), **34** (X = 4-CF_3, Y = 4-OMe), **35** (X = 3-CF_3, Y = 4-OH).

Methanol attacks either the tertiary or the secondary carbon. AdT regioisomers are the major products no matter what X is as long as Y is not strongly electron donating. On the other hand, AdS regioisomers are observed when Y is a strongly electron-donating substituent (4-OMe, 4-OH) and X strongly electron attracting (3-CF_3, 4-CF_3). When X is less electron-attracting, dimethoxy adducts M are formed (1,2-dimethoxy-1,2-diarylpropanes), or more complex products which we were not able to identify precisely but which involve proton elimination from the α-methyl group. Moreover, an AdS adduct (X = 3-CF_3, Y = 4-OMe) in methanol is completely converted in 8 days to a dimethoxy product, M, as shown by the NMR spectra. The M products are formed by methanolysis of tertiary bromides AdS.

The regiochemistry of the α-methylstilbenes not included in Table I has also been studied to determine the pathway by which elimination products are formed.

Stereochemistry of Methanol Attack. Identification of diastereoisomeric methoxy bromide adducts from NMR spectra is more complex than that of the corresponding dibromides. The difference in chemical shift of the aliphatic protons of the two diastereoisomers is markedly substituent dependent. The stronger the electron donor or electron attractor, X or Y, the greater this difference (and the easier the identification). While the chemical shifts of the methoxy protons of the erythro and threo products differ by 0.17 ppm when X and Y are 4-CF_3 and 4-OH, respectively, this difference is no more than 0.03 ppm when X and Y are hydrogens. Diastereoisomeric methoxy bromides were identified unambiguously by NMR spectra recorded either at 60 or at 200 MHz when required.

The stereoselectivity of methanol attack is the same as that of bromide ion attack and is constant (70 ± 5% erythro) whatever the regioisomer (AdS or AdT) or the ring substituents.

(10) Dubois, J. E.; Huynh, X. Q. *Tetrahedron Lett.* **1971**, 3369–3372. Dubois, J. E.; Huynh, X. Q. *Bull. Soc. Chim. Fr.* **1968**, 1436–1441.

(11) The nomenclature used is not strictly correct but is more convenient than the IUPAC recommendation: "erythro" = (*R*,*S*)-1,2-dibromo-1,2-diarylpropane; "threo" = (*S*,*S*)-1,2-dibromo-1,2-diarylpropane.

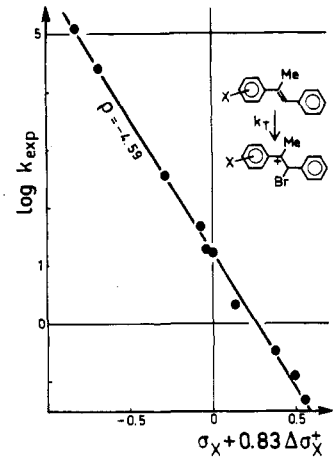
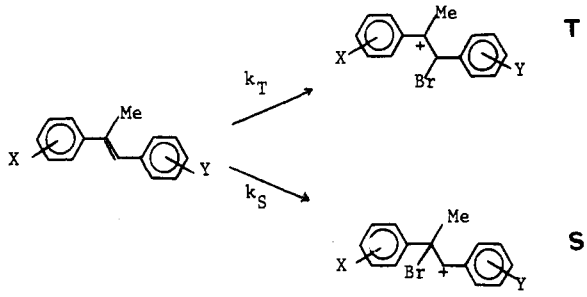


Figure 1. Yukawa–Tsuno plot for α-methylstilbene bromination. Evidence for an exclusive tertiary pathway when Y = H.

Scheme IV



Discussion

Dual Pathway Mechanism in α-Methylstilbene Bromination. Kinetic Evidence. Tertiary Pathway. The effect of X on α-methylstilbene reactivity can be analyzed by a free energy relationship. The Yukawa–Tsuno equation[12] is used to evaluate precisely the inductive substituent effect. The ρ value was established from the meta-substituted compounds (**4**, **6**, **8**, **9**) and the r^+ value[13] from the deviation of para-substituted ones (**1**, **2**, **3**, **5**, **7**, **10**). The correlation thus obtained (eq 3) shows that,

$$\log k_{XH} = -4.59(\sigma_X + 0.83\Delta\sigma_X^+) + 1.29$$
$$R = 0.994 \qquad s_\rho = 0.21 \qquad s_r^+ = 0.12 \qquad (3)$$

contrary to stilbene bromination, the Yukawa–Tsuno plot is linear (Figure 1) no matter what X is, even if it is as electron attracting as 4-CF_3. A unique ionic intermediate must be considered. The curvature of the $\rho\sigma^+$ plot observed when X is an electron-donating group ($r^+ < 1$) can be explained, as for α-methylstyrene[5] bromination, by geometrical factors. In the ground state, and in the transition state since the hybridization of the tertiary carbon remains sp^2, the two aromatic rings are rotated out of the plane of the double bond, thus limiting the resonance capacity of the substituents X. The large ρ value of −4.59, nearly identical with that measured in cumyl chloride methanolysis[14] (−4.82) and larger in absolute value than that observed in α-methylstyrene bromination[5] (−4.26), indicates extensive charge development on the carbon α to the substituted ring. Accordingly, this ρ value will be denoted as ρ_α. The tertiary carbocation T (Scheme IV) is therefore the most plausible intermediate. This result is confirmed by analysis of the effect of Y on the reactivity.

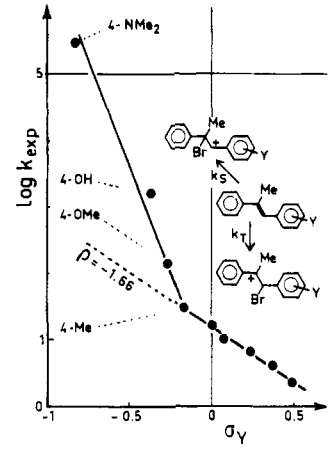


Figure 2. $\rho\sigma$ plot for α-methylstilbene bromination (Y variable, X = H). Competition between tertiary and secondary pathways for electron-donating Y substituents.

When Y is not strongly electron donating (Y ≠ 4-OMe, 4-OH, 4-NMe_2), there is a good linear correlation (Figure 2) between log k of compounds **6** and **14**–**18** and the Hammett substituent constant σ (eq 4). With Brown–

$$\log k_{HY} = -1.66\sigma_Y + 1.22 \qquad R = 0.994 \qquad s = 0.09 \qquad (4)$$

Okamoto's[15] σ^+, the correlation coefficient is smaller: 0.964. Moreover, the reactivity of the *p*-fluoro compound **15** is less than that of the unsubstituted α-methylstilbene, which indicates that σ constants are more appropriate than σ^+. Thus the Y-substituted ring is not directly conjugated with the charge. The small absolute value of ρ, denoted as ρ_β, suggests also that the charge is in the β-position relative to the substituted ring, consistent with the formation of the tertiary carbocation, T.

The similarity of the substituent effects observed in α-methylstilbene bromination with those measured in 1,2-diarylethanol dehydration[16] or in 2-chloro-2-arylpropane[14] and 1-aryl-2-chloro-2-methylpropane[17] solvolysis confirms the structure of the intermediate since for the latter reactions there is no ambiguity about the localization of the charge.

Limits of the Tertiary Pathway. Figure 2 shows that a marked increase in reactivity appears when Y is a strong conjugatively electron-donating group: 4-OMe, 4-OH, 4-NMe_2.

The sharp curvature in the $\rho\sigma$ relationship shows a change in the mechanism. This change is most likely due to the intervention of the secondary pathway where the Y-substituted ring is in the α position with respect to the charged carbon. Other competing mechanisms such as pathways involving bromonium or phenonium ion intermediates are highly improbable. Bromonium ions are not expected when an aromatic ring bears a strongly electron-donating group such as 4-NMe_2 or 4-OH, the substituents for which the greatest deviations are observed. Phenonium ions, where the charge on the C_X atom would be stabilized by delocalization in the Y-substituted ring, are also highly improbable since bromine can choose, in the rate-determining step, the olefinic carbon atom which

(12) Yukawa, Y.; Tsuno, Y.; Sawada, M. *Bull. Chem. Soc. Jpn.* **1966**, *39*, 2274–2286.
(13) r^+ is the Yukawa–Tsuno coefficient when σ^+ is used as the enhanced substituent constant; the correlation coefficient is denoted by *R*.
(14) Okamoto, Y.; Inukai, T.; Brown, H. C. *J. Am. Chem. Soc.* **1958**, *80*, 4972–4976.
(15) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1957**, *79*, 1913–1917.
(16) Noyce, D. S.; Hartrer, D.; Miles, F. B. *J. Am. Chem. Soc.* **1968**, *90*, 3794–3796.
(17) Landis, A; VanderWerf, C. A. *J. Am. Chem. Soc.* **1958**, *80*, 5277–5280.

Table III. Competition between Tertiary and Secondary Pathways in α-Methylstilbene Bromination (X = H, Y ≠ H)

Y	k_T[a]	k_{exptl}	k_S[b]	% k_S[c]
4-OMe	51.9	141	89.1	63
4-OH	76.5	1620	1540	95
4-NMe_2	812	2.93×10^5	2.92×10^5	100

[a] Tertiary rate constant in M^{-1} s^{-1} calculated by eq 4. [b] Secondary rate constant in M^{-1} s^{-1}; $k_S = k_{expt} - k_T$. [c] Percent secondary pathway: $100k_S/k_{expt}$.

gives the most stabilized carbocation directly.

Thus, in α-methylstilbene bromination, the increase in reactivity can be readily attributed to competitive formation of the secondary carbocation (S, Scheme IV). If this is so and if the charge is localized on the secondary carbon α to the Y-substituted ring when Y is electron donating, Y and X substituent effects on the reactivity should be quite different, symmetric with those observed when the intermediate is the tertiary carbocation. Y substituents capable of stabilizing the charge on the secondary carbon are too scarce (4-OMe, 4-OH, 4-NMe_2) for reliable measurement of their effect when they are on the ring α to the charged carbon. But it is possible to measure the effect of a sufficient number of X substituents when Y is 4-OMe, 4-OH, or 4-NMe_2 and to determine unambiguously whether their effect is of the α type (large $|\rho|$, use of σ^+) or rather of the β type (small $|\rho|$, use of σ) as required by the secondary ion pathway.

Secondary Pathway. For the charge to remain localized on the secondary carbon, X must be sufficiently electron attracting (at least not electron donating) to prevent competitive formation of the tertiary ion.

Linear correlations from **13** and **24-26** (eq 5), from **12** and **21-23** (eq 6), and from **11**, **19**, and **20** (eq 7) express satisfactorily the substituent effects when Y is 4-OMe, 4-OH, or 4-NMe_2, respectively.

$$\log k_{X,OMe} = -1.95\sigma_X + 2.19 \qquad R = 0.992 \qquad s_\rho = 0.10 \tag{5}$$

$$\log k_{X,OH} = -1.73\sigma_X + 4.95 \qquad R = 0.986 \qquad s_\rho = 0.20 \tag{6}$$

$$\log k_{X,NMe_2} = -0.89\sigma_X + 5.48 \qquad R = 0.986 \qquad s_\rho = 0.14 \tag{7}$$

When σ is replaced by σ^+ in eq 5 and 6 the correlation coefficients are smaller: 0.979 and 0.946, respectively.[18]

The fact that σ appears to be more appropriate than σ^+ is not rigorously significant since for the substituents used in these correlations σ does not differ greatly from σ^+. The substituent effect of X on the reactivity is small, indicating that the X-substituted ring is not directly conjugated with the carbon which bears the charge, and is consistent with the secondary intermediate S.

The ρ_β values found here are of the same order of magnitude as ρ_β values for the substituent effect of Y on the tertiary pathway. Therefore, the sharp break of the $\rho\sigma$ plot observed when Y varies (Figure 2) is due to the increasing importance of the secondary pathway as Y becomes more and more electron donating. The rate constant via the tertiary path (k_T) for the three compounds **11-13** can be calculated by relation 4. The secondary pathway rate constant (k_S) is obtained by subtraction of k_T from the experimental rate constant. Table III shows that the two pathways are of comparable importance when Y is 4-OMe but that compounds where Y is 4-OH or 4-NMe_2 react via the secondary pathway only.

Therefore, in the transition state the charge is very dissymmetrically distributed between the two carbon atoms. Values of ρ_α and ρ_β and use of σ or σ^+, depending upon the substitution pattern, cannot be interpreted by a bridged transition state for the rate-determining step. Such a dissymmetry argues in favor of a competitive scheme with two distinct pathways for α-methylstilbene bromination. If, as we believe, the transition states for both rate-determining and product-determining steps have the same structure, this competition must lead to different products when the reaction is carried out in nucleophilic solvents. Investigation of the regiochemistry and of the stereochemistry of the addition will confirm both the dual-pathway mechanism and the similarity of the transition states of the nucleophilic and electrophilic steps.

Dual-Pathway Mechanism in α-Methylstilbene Bromination. Product Evidence. The stereochemistry of bromide ion or methanol attack on the ionic intermediate does not vary with the ring substituents. Erythro dibromides from trans addition of bromine account for 70% of the dibromides formed. The same stereoselectivity (70%) is observed for the methoxy bromides. This stereoselectivity can be assumed to be that of the attack of the nucleophiles upon the carbocation, T or S, since Fahey et al.[19] showed that erythro dibromide formation (65%) in *trans*-anethole bromination corresponds to the stereoselectivity of the attack on the free carbocation. Even for a strong electron-attracting substituent such as 4-CF_3 the stereoselectivity does not increase significantly, contrary to β-methylstyrene bromination.[5] The addition is not stereoselective. Therefore, the reaction intermediate can be bridged neither by bromine (bromonium ion) nor by the Y-substituted aryl group (phenonium ion). This result implies that the ionic intermediates of the reaction are carbocations.

In methanol, a nucleophilic solvent, mixed adducts incorporating the solvent are obtained. No dibromide is detected even when the addition is carried out in methanol containing 0.5 M NaBr. The HSAB principle,[20] successfully applied to alkyl olefin bromination,[21] can interpret this observation: methanol, a harder nucleophile than bromide ion, adds preferentially, and the harder the electrophilic center the greater the difference. Since carbocations where the charge is localized are harder than bromonium ions where the charge is delocalized on bromine and two carbons, methanol addition will predominate. Therefore, in α-methylstilbene bromination via carbocations in methanol, only methoxy bromides are obtained whereas in alkene bromination via bromonium ions, the products are a mixture of dibromides and methoxy bromides.

The identification of the two regioisomers, AdT and AdS, resulting from methanol addition to secondary and tertiary ions, respectively, fully confirms the two-pathway scheme. AdT isomers are observed when Y is not a strong electron-donating group (**6**, **7**, **10**, **14**, **30**), elimination competing with nuleophilic addition only when X is electron donating (**2**, **32**, **33**). When Y is strongly electron donating, no AdT is detected, and AdS is generally but not systematically obtained. The secondary adduct is formed exclusively only when X is a strong electron attractor (**23**, **26**, **34**, **35**); when X is H, 4-Cl, or even 3-Cl, AdS is not the

(18) Such a comparison is worthless for the correlation in eq 7 since only meta-substituted compounds have been used.

(19) Fahey, R. C.; Schneider, H. J. *J. Am. Chem. Soc.* **1968**, *90*, 4429-4434.
(20) Pearson, R. G. "Hard and Soft Acids and Bases"; Dowden, Hutchinson, and Ross: Stroudsburgh, 1973.
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major product (12, 24) or is even absent (11, 13, 19). Instead, either a dimethoxy product, M, where a methoxy group replaces the bromine atom in AdS, or unidentified products resulting from hydrogen elimination from the α-methyl group are obtained. The formation of these products can be explained in the following way, which constitutes another argument in favor of the dual-pathway mechanism.

In AdS, bromine is on a tertiary carbon. In methanol, a strongly ionizing solvent, the bromine acts as a leaving group. The stability of the resulting cation, TM, increases with the electron-donor character of X which is directly bonded to the charged carbon. The tertiary carbocation TM can lead, as in any solvolysis,[22] either to the dimethoxy adduct M by addition of a second methoxy group or to an olefin formed by elimination of a hydrogen from the α-methyl group. The products depend upon the substituent X. When X is electron attracting (23, 26, 34, 35), the breaking of the C–Br bond is too slow to be observed before bromine addition ends, and normal secondary adducts AdS are obtained. But if these products are left several days in the reaction mixture, ionization occurs, and AdS reacts to give M. For example, when X = 3-CF_3 and Y = 4-OMe, AdS is completely transformed in 8 days. When X is less electron attracting (12, 24), methanolysis is fast enough to be observed by the end of the addition; the product is then a mixture of AdS, M, and products resulting from hydrogen elimination from TM. However, all these products are characteristic of the secondary pathway, since solvolysis is fast only if the bromine is at a tertiary carbon.

Consequently, the unidentified products observed in the reaction of 11–13, 19, and 24 are reasonably assumed to be derived from the secondary pathway. Conversely, analogous products in the reaction of 2, 32, and 33 where X is methoxy should result from the tertiary pathway since elimination is expected mainly when the intermediates are highly stabilized by electron-donating substituents.

Agreement between Kinetic Data and Product Formation. The stereochemistry of the bromination products shows that ionic intermediates are not bridged, and the regiochemistry shows that these intermediates are tertiary or secondary carbocations, depending on the substituents. Kinetic data lead to the same substituent–charge localization relationship. Thus when tertiary ion or secondary ion formation is predicted from kinetic substituent effects, only methoxy bromides, with the methoxy group on the tertiary or secondary carbon, are obtained. The only substrate where the two intermediates are formed competitively is 4′-methoxy-α-methylstilbene. From kinetic data a 63%/37% distribution between the secondary and tertiary pathways, respectively, is inferred. According to the products, 35% of the reaction goes via the tertiary pathway.

The overall results of the competition between both pathways obtained either from kinetics or product regiochemistry are given in Table IV: the agreement between the two sets of results is excellent.

The close coherence of the results of the kinetic and product studies suggests that the charge distributions in the rate-determining and product-determining transition states are the same. In particular, it appears that the charge distribution between the two carbons does not change from one transition state to the other.

In α-methylstilbene bromination, two arguments tend to discredit Schmid's postulate that there is a bridged rate-determining transition state and an open carbenium-ion-like product-determining transition state. First, the marked dissymmetry of α and β substituent effects on the reactivity and the high ρ_α value are hardly compatible with a bridged rate-determining transition state. They are better explained by a charge localized on one or the other of the olefinic carbons. Second, the kinetic results and the regiochemistry imply that the charge distributions in the transition states of the nucleophilic and electrophilic steps are closely similar. The same conclusion can be inferred from the very high solvent effect in bromination (m = 1.1),[1,3] typical of a late, intermediate-like, rate-determining transition state, and from the very fast addition of nucleophiles, indicative of an early product-determining transition state.

Table IV. Competition between Tertiary and Secondary Cations in α-Methylstilbene Bromination. Agreement between the Regiochemistry Predicted from Kinetic Data and That Observed in the Products

compd	X	Y	kinetics, % T	% products T	% products S
2	4-OMe	H	100	100[a]	0
32	4-OMe	3-Cl	100[b]	100[a]	0
33	4-OMe	3-CF_3	100[b]	100[a]	0
3	4-Me	H	100	100	0
30	4-Me	4-Cl	100[b]	100	0
6	H	H	100	100	0
7	4-Cl	H	100	100	0
10	4-CF_3	H	100	100	0
14	H	4-Me	100	100	0
16	H	4-Cl	100	100	0
13	H	4-OMe	37	35	65[c]
24	4-Cl	4-OMe	0	0	100[c]
26	3-CF_3	4-OMe	0	0	100
34	4-CF_3	4-OMe	0[d]	0	100
12	H	4-OH	0	0	100[c]
35	3-CF_3	4-OH	0[d]	0	100
23	4-CF_3	4-OH	0	0	100
11	H	4-NMe_2	0	0	100[c]
19	3-Cl	4-NMe_2	0	0	100[c]

[a] Elimination products have been attributed to the tertiary pathway (see text). [b] Estimated value; since 2 reacts via the tertiary pathway only, it is likely that when Y is more electron attracting than H, the intermediate will be the tertiary carbocation. [c] The observed elimination products have been attributed to the secondary pathway (see text). [d] These values are estimated from those of compounds 24 and 26 and compounds 12 and 23.

Conclusion

According to the results presented here, bromination of α-methylstilbenes is a dual-pathway addition where the two carbocations T and S can be formed competitively in the rate-determining step. We showed previously that in styrene bromination, a bromonium ion and a benzylic carbocation are implicated. For stilbene bromination we proposed that, depending on the substituents, all three pathways leading to bromonium ion and both carbocations may be followed. These three examples establish the multipathway scheme for electrophilic bromination of aryl olefins.

It is of great interest that the multipathway scheme is generally applicable because by these means the stereo- and the regiochemistry of electrophilic additions can be accurately predicted. This prediction is only subordinated to the knowledge of the ρ values of the corresponding free energy relationships. Unfortunately, we have observed that the ρ value in aryl olefin bromination depends markedly on the others substituents at the double bond.[4,5] In particular, for the secondary pathway of α-methylstilbene

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Table V. Free Bromide and Tribromide Ion Rate Constants in Bromination of α-Methylstilbenes

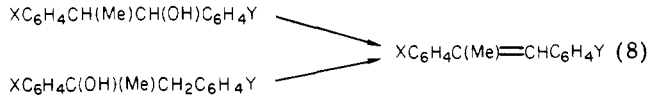
X	Y	k_{Br_2}[a]	$k_{Br_3^-}$[a]	Q[b]
4-OH	H	3.36×10^6	3.14×10^4	107
H	H	4.43×10^2	4.73	94
4-CF_3	H	0.89	2.49×10^{-2}	36
3-Cl	4-NMe_2	8.13×10^6	7.86×10^4	103

[a] In units of M^{-1} s^{-1}. [b] $Q = k_{Br_2}/k_{Br_3^-}$.

bromination, we found that ρ_β for X varies with Y. We must, therefore, consider that the cumulative effects of the substituents X and Y are not additive.[23] Consequently, as a preliminary to the prediction of the stereo- and regiochemistry in electrophilic additions, it is necessary to develop interactive free energy relationships which take into account the nonadditivity of multiple substituent effects. This is the subject of the companion paper.

Experimental Section

Synthesis of α-Methylstilbenes. The *trans*-α-methylstilbenes were prepared by dehydration of the corresponding secondary or tertiary alcohols (eq 8).



1,2-Diarylpropanols were obtained by condensation of an arylmagnesium halide with the appropriate ketone or aldehyde. Alcohols where Y = 4-NMe_2 or 4-OH were prepared by condensation of X-substituted arylmagnesium halides on Y-substituted benzyl methyl ketones. The alcohol (X = H, Y = 4-OMe) was prepared from hydratropaldehyde and anisylmagnesium bromide. The other alcohols were prepared by condensation of Y-substituted benzylmagnesium chlorides on X-substituted acetophenones. All halides and ketones or aldehydes used were commercial except for substituted benzyl methyl ketones. These were prepared from the corresponding benzaldehydes and nitroethane.[24]

Secondary alcohols were dehydrated either by P_2O_5 in benzene or by refluxing in HMPT when Y = 4-NMe_2. Tertiary alcohols were dehydrated by *p*-toluenesulfonic acid in benzene.[25]

α-Methylstilbenes were purified by preparative column chromatography on Al_2O_3 or preparative GLC. Their physical properties (melting points, analyses, and NMR spectra) are given in Tables VI and VII (supplementary material).

Kinetic Methods. Three kinetic methods were used to measure the experimental rate constants k_{exptl}: couloamperometry,[7] potentiometry,[6] and UV spectroscopy.[8]

Experimental k_{Br_2} Determination. Experimental rate constants k_{exptl} are measured at three bromide ion concentrations. As shown previously,[5] the bromide ion effect follows the equation $k_{exptl}(1 + K[Br^-]) = \alpha + \beta[Br^-]$. K is the equilibrium constant of the Br_2/Br_3^- equilibrium, α is the rate constant k_{Br_2}, and β is usually identified with $Kk_{Br_3^-}$ where $k_{Br_3^-}$ is the rate constant of tribromide addition. Thus the plot of $k_{exptl}(1 + K[Br^-])$ against $[Br^-]$ gives k_{Br_2} at $[Br^-] = 0$ and $k_{Br_3^-}$ from the slope (Table V).

Product Analysis. To a stirred solution (5×10^{-3} M) of α-methylstilbene in methanol or dichloromethane is added dropwise a slight excess (5%) of bromine diluted in the same solvent, so that only a pale yellow color is developed. When the addition is complete, the solvent is evaporated under vacuum at room temperature, and the residue analyzed by NMR spectroscopy. Complete NMR spectroscopic data of the products obtained are given in the supplementary material.

The diastereoisomeric dibromides are identified by comparison with literature data.[26] The structure of the "erythro" isomer, which can be isolated from the product mixture by fractional recrystallization in pentane, is obtained by stereospecific debromination with sodium iodide in ethanol.[27] Similarly, the "erythro" methoxy bromide (mp 67–69 °C. Anal. Found: C, 63.28; H, 5.57; Br, 26.22. Calcd: C, 62.95; H, 5.57; Br, 26.23) has been isolated from product mixture by fractional recrystallization from petroleum ether. Its structure has been attributed by stereospecific demethoxybromination with *n*-BuLi in diethyl ether.[28]

Dimethoxylated products formed by solvolysis of the secondary adduct AdS (X = 4-Cl and Y = 4-OMe) were identified from their NMR spectra and isolated by column chromatography. The product is probably a mixture of two diastereoisomers. NMR spectra show two signals for methyl group protons at δ 1.63 and 1.67, two for the hydrogen at δ 4.05 and 4.11, and four for the aliphatic methoxy groups at δ 2.98, 3.07, 3.19, and 3.25 (CCl_4, Me_4Si as an internal reference).

Acknowledgment. The authors are indebted to Professor J. E. Dubois for helpful discussion and encouragement.

Registry No. (*E*)-1, 58662-07-0; (*E*)-**2**, 5912-82-3; (*R**,*R**)-**2** Adt, 83832-10-4; (*R**,*S**)-**2** Adt, 83832-26-2; (*E*)-**3**, 58662-08-1; (*R**,*R**)-**3** Adt, 83832-13-7; (*R**,*S**)-**3** Adt, 83832-29-5; (*E*)-**4**, 58662-09-2; (*E*)-**5**, 58662-10-5; (*E*)-**6**, 833-81-8; (*R**,*R**)-**6** Adt, 83832-15-9; (*R**,*S**)-**6** Adt, 83832-31-9; (*E*)-**7**, 58662-11-6; (*R**,*R**)-**7** Adt, 83832-16-0; (*R**,*S**)-**7** Adt, 83832-32-0; (*E*)-**8**, 58662-12-7; (*E*)-**9**, 58662-13-8; (*E*)-**10**, 58662-14-9; (*R**,*R**)-**10** Adt, 83832-17-1; (*R**,*S**)-**10** Adt, 83832-33-1; (*E*)-**11**, 83832-02-4; (*E*)-**12**, 83832-03-5; (*R**,*R**)-**12**-AdS, 83832-23-9; (*R**,*S**)-**12**-AdS, 83832-39-7; (*E*)-**13**, 83832-04-6; (*R**,*R**)-**13**-AdT, 83844-79-5; (*R**,*S**)-**13**-AdT, 83844-80-8; (*E*)-**14**, 62924-88-3; (*R**,*R**)-**14**-AdT, 83832-18-2; (*R**,*S**)-**14**-AdT, 83832-34-2; (*E*)-**15**, 83832-05-7; (*E*)-**16**, 60753-98-2; (*R**,*R**)-**16**-AdT, 83832-19-3; (*R**,*S**)-**16**-AdT, 83832-35-3; (*E*)-**17**, 83832-06-8; (*E*)-**18**, 83832-07-9; (*E*)-**19**, 83816-17-5; (*E*)-**20**, 83830-92-6; (*E*)-**21**, 83816-18-6; (*E*)-**22**, 83816-19-7; (*E*)-**23**, 83816-20-0; (*R**,*R**)-**23**-AdS, 83832-25-1; (*R**,*S**)-**23**-AdS, 83832-41-1; (*E*)-**24**, 83816-21-1; (*R**,*R**)-**24**-AdS, 83832-20-6; (*R**,*S**)-**24**-AdS, 83832-36-4; (E)-**25**, 83816-22-2; (*E*)-**26**, 83816-23-3; (*R**,*R**)-**26**-AdS, 83832-21-7; (*R**,*S**)-**26**-AdS, 83832-37-5; (*E*)-**30**, 83816-26-6; (*R**,*R**)-**30**-AdT, 83832-14-8; (*R**,*S**)-**30**-AdT, 83832-30-8; (*E*)-**32**, 83816-28-8; (*R**,*R**)-**32**-AdT, 83832-11-5; (*R**,*S**)-**32**-AdT, 83832-27-3; (*E*)-**33**, 83816-29-9; (*R**,*R**)-**33**-AdT, 83832-12-6; (*R**,*S**)-**33**-AdT, 83832-28-4; (*E*)-**34**, 83832-08-0; (*R**,*R**)-**34** AdS, 83832-22-8; (*R**,*S**)-**34** AdS, 83832-38-6; (*E*)-**35**, 83832-09-1; (*R**,*R**)-**35** AdS, 83832-24-0; (*R**,*S**)-**35** AdS, 83832-40-0.

Supplementary Material Available: Tables VI–X giving the physical properties of α-methylstilbenes and their bromination products (5 pages). Ordering information is given on any current masthead page.

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