monia liberated from the reaction with H_2O.[16] The amount of sodium amide, indicated in moles, was corrected for active amide present. The purity (55–64%) varied according to source and handling conditions. The equilibrium composition of the rearranged products was invariant to the amine or base used.

Reaction of Lithium and Sodium with EDA.—EDA (50 ml, 0.83 mol) and lithium wire (0.5 g, 0.07 mol) were allowed to react using the procedure described by Wender and coworkers.[9] The mixture immediately turned dark blue. It was refluxed and stirred for 30 min, after which the color discharged to cloudy white. On cooling, the condenser was replaced by a rubber stopper. Immediately, the solution turned light blue (different from the dissolved metal color) and on stirring, turned blue-purple.[7] Upon heating, the blue-purple color discharged and reappeared on cooling.

Sodium metal, when treated with EDA in a similar manner, gave a dark, viscous mixture. Numerous higher molecular weight amines were identified by vpc analysis.[7]

Preparation of Ethylenediamine-d_4 (94% N–D).—EDA (10 g, 0.17 mol) was stirred with D_2O (75 g, 3.7 mol) for 2 hr. The solution, cooled in a Dry Ice–acetone bath, was treated with sodium metal until the diamine layered out. The diamine (top layer) was separated in the same manner and was dried over sodium metal for 24 hr. Vacuum transfer gave 6.0 ml, nmr (CCl_4) δ 2.62 (s, 17, methylene), 0.99 (s, 1, NH).

Reaction of Sodium Amide with EDA.—EDA (78.3 mmol) was vacuum transferred into an evacuated flask containing sodium

amide (5.7 mmol). The stirred mixture evolved ammonia (4.0 mmol), which was identified by ir and mass spectrometry. Quantitative data was obtained by using a volume calibrated vacuum manifold and a mercury manometer.

3-Hexyne and Pyrazine Radical Anion.[8]—The pyrazine radical anion was prepared by vacuum transferring 15 ml of 10^{-2} M pyrazine in THF to 0.015 mol of n-butyllithium.[7] 3-Hexyne was vacuum transferred and the mixture was stirred for 100 hr. No rearranged hexyne was found.

Reactions of Deuterated Ethylenediamine. A.—EDA-d_4 (2.0 ml, 28 mmol), BuLi (2.0 ml, 3.2 mmol), and 3-hexyne (2.0 ml, 18 mmol) were allowed to react. The reaction was sampled by vacuum transfer. The vpc and mass spectral results are found in Table V.

B.—EDA-d_4 (0.8 ml, 11 mmol), BuLi (1.0 ml, 1.6 mmol), and 1-hexyne (1.0 ml, 8.8 mmol) were mixed. A sample was vacuum transferred 5 min after thawing: nmr (CCl_4) δ 2.12 (m, 1.6, propargylic), 1.86 (t, 0.3, acetylenic), 1.47 (m, 4.0, methylene), 0.91 (m, 3.0, methyl); mass spectrum m/e (rel intensity) 81 (55.3), 82 (100), 83 (7.2). A second sample was taken after 18 hr, mass spectrum m/e (rel intensity) 81 (36.5), 82 (100), 83 (7.9). Neither sample showed any rearrangement (vpc).

C.—EDA-d_4 (0.5 ml, 7 mmol) and 3-hexyne (0.5 ml, 4 mmol) were stirred for 20 hr. The 3-hexyne did not rearrange (vpc) or incorporate any deuterium (mass spectrum).

Registry No.—3-Hexyne, 928-49-4; EDA, 107-15-3; 1-hexyne, 693-02-7; EDA-d_4, 37164-19-5; BuLi, 109-72-8.

(16) D. A. Skoog and D. M. West, "Analytical Chemistry," Holt, Rinehart, and Winston, New York, N. Y., 1965, p 308.

Electrophilic Bromination of Aromatic Conjugated Olefins. II. The Mechanism of the Dual-Path Additions in Stilbene Bromination. Evidence from Multiple Substituent Effects for Carbonium Ion Intermediates[1]

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Kinetic data for the bromination of disubstituted stilbenes, $XC_6H_4C_xH{=}C_yHC_6H_4Y$, in methanol are interpreted in terms of the dual-path addition mechanism in which two pathways (with rate constants k_x and k_y, respectively), leading to discrete carbonium ions, C_x^+ and C_y^+, are involved. The nonlinear free energy relationship corresponding to this scheme is $\log (k/k_0) = \log [(k_x + k_y)/k_0] = \log [10^{\rho_\alpha \sigma_X^+ + \rho_\beta \sigma_Y} + 10^{\rho_\alpha \sigma_Y^+ + \rho_\beta \sigma_X}]$, where ρ_α and ρ_β are the reaction constants for aryl substituents α and β to the charged center, respectively. Values of ρ_α (−5.07) and ρ_β (−1.40) are obtained by simplification of the above equation using sets of compounds for which k_x or k_y can be neglected. These values are found to be applicable, in a reactivity range of six powers of ten, to compounds for which k_x and k_y are of comparable magnitude. However, substituent effects are only approximately additive; i.e., substituents do not act wholly independently, and agreement between calculated and experimental reactivities is occasionally unsatisfactory. Nevertheless, it is possible to exclude any significant contribution from a bromonium ion pathway for this reaction. The bromination of the same stilbenes in carbon tetrachloride, where intermediates are bromonium-ion-like, reveals a dramatically different situation, there being an additive linear free-energy relationship, $\log (k/k_0) = \rho \Sigma \sigma$, which shows that in this solvent the structures of the transition states are symmetrical, whereas, in methanol, the transition states are carbonium-ion-like.

For electrophilic additions involving carbonium ion intermediates, a dual-path mechanism is postulated since the attacking electrophile can, in principle, choose for σ bonding either one of the two olefinic carbon atoms in the rate-determining step. The feasibility of this mechanism has been evaluated by studying the bromination of the monosubstituted trans stilbenes, $XC_6H_4C_xH{=}C_yHC_6H_5$, whose bromination is assumed to lead to two discrete intermediates, the carbonium ions C_x^+ and C_y^+ (1 and 2; Y = H), by competitive pathways, referred to as the C_x and C_y paths. The kinetic data have been

interpreted in terms of a nonlinear free-energy relationship derived from this mechanism by application of the Hammett equation to each pathway. Circumstantial evidence for the validity of this scheme is provided by the agreement between the regioselectivity of attack by methanol and the calculated relative importance of each pathway. However, the assumption regarding the structures of the intermediates cannot be verified beyond doubt. Only for the C_x path can it be stated with certainty that the intermediate is a carbonium ion; the effect of the substituent X in this path is expressed by ρ_α, whose value is closely related to those obtained for reactions with benzylic cationic intermediates. For the intermediate of the C_y path, the value of ρ_β requires only that the

(1) M. F. Ruasse and J. E. Dubois, *J. Org. Chem.*, **37**, 1770 (1972). Also regarded as Part XXXV of the series "Reactivity of Unsaturated Compounds: Bromination." Part XXXIV: J. E. Dubois, J. Guillo, and X. Q. Huynh, *J. Chim. Phys.*, in press.

1

C_x path intermediate

2   **3**

C_y path intermediate
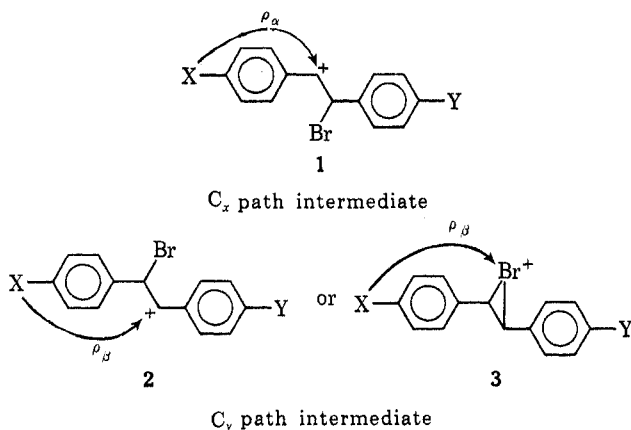
charge be in the β position, so that the intermediate of this path could be the bromonium ion **3** or the carbonium ion **2**.

The bromination of the X,Y-disubstituted stilbenes, which we report now, was undertaken with two objectives in view: firstly, the generalization of the kinetic treatment of the dual-path additions to include polysubstituted compounds and, secondly, the determination of the real structure of the second intermediate. The distinction between the two possible structures can be tackled, in principle, by measurement of the effect of the substituent Y in the second aromatic ring. If the bromine atom bears the charge in the transition state, the effect of Y must equal the effect of the first substituent X in the C_y path. On the other hand, if the carbon atom bears the charge, the effect of Y must equal the effect of X in the C_x path.

However, nonadditivity of multiple substituent effects has been observed in electrophilic reactions, in the bromination of the 1,1-diarylethylenes in particular.[2a] It is possible that in stilbenes also the introduction of a second substituent modifies the effect of the first one, because of interactions between the charge and the substituents. The kinetic data for the bromination of disubstituted trans stilbenes must be examined with this problem in mind before we attempt to draw any conclusion regarding the structures of the intermediates.

Results and Discussion

The rate constants for the bromination of 21 trans-disubstituted stilbenes have been measured under the same conditions as those of the monosubstituted stilbenes,[1] i.e., in methanol, 0.2 M NaBr added, at 25°, and are listed in Table I.

In this solvent, the brominating agents are molecular bromine and tribromide ion, the latter being formed in equilibrium by reaction of bromide ion with bromine. Strictly speaking, analysis of structural effects should be based on the elementary rate constant, k_{Br_2}, and not on the composite rate constant,[2b] k_{exp}. However, during the study of the bromination of the monosubstituted stilbenes, we established that there exists a linear relationship between the elementary rate constant and k_{exp}, $\log k_{exp} = 0.99 \log k_{Br_2} - 1.16$, in a

(2) (a) E. D. Bergmann, A. F. Hegarty, and J. E. Dubois, *Chem. Commun.*, 1616 (1968); A. F. Hegarty, J. S. Lomas, V. W. Wright, E. D. Bergmann, and J. E. Dubois, *J. Org. Chem.*, **37**, 2218, 2222 (1972). (b) J. E. Dubois and X. Q. Huynh, *Bull. Soc. Chim., Fr.*, 1436 (1968); P. Alcais, J. J. Aaron, R. Uzan, F. Rothenberg, and J. E. Dubois, *ibid.*, 612 (1971).

TABLE I
EXPERIMENTAL RATE CONSTANTS OF STILBENE BROMINATION IN METHANOL

X	Y	k^a	Kinetic method[b]
p-OH	p-OH	3.40×10^6	A
p-OH	p-OMe	2.40×10^6	A
p-OH	p-Me	1.27×10^6	A
p-OH	p-Cl	3.37×10^5	B
p-OH	p-NO$_2$	8.40×10^4	B
p-OMe	p-OMe	2.20×10^5	C
p-OMe	p-Me	1.14×10^5	C
p-OMe	m-Me	9.53×10^4	C
p-OMe	p-Cl	4.50×10^4	D
p-OMe	m-Cl	3.39×10^4	D
p-OMe	p-NO$_2$	5.22×10^3	C
p-Me	p-Me	6.10×10^2	C
p-Me	m-Me	4.09×10^2	B
p-Me	p-Cl	1.04×10^2	D
p-Me	m-Cl	6.6×10	D
p-Me	p-NO$_2$	9.9	E
p-iPr	p-iPr	7.0×10^2	C
m-Me	p-NO$_2$	1.92	E
p-Cl	p-Cl	3.67	E
p-Cl	m-Cl	1.80	E
p-Br	p-Br	2.50	E

^{a} k in l. mol^{-1} min^{-1} in methanol-0.2 M NaBr at 25°; average error 2.5%. ^{b} A, couloamperometry: J. E. Dubois, P. Alcais, and G. Barbier, *J. Electroanal. Chem.*, **8**, 359 (1964). B, potentiometry: R. P. Bell and E. N. Ramsden, *J. Chem. Soc.*, 161 (1958). C, coulometric concentrostat: J. E. Dubois and G. Mouvier, *C. R. Acad. Sci.*, **255**, 1104 (1962). D, spectrometry: J. E. Dubois and F. Garnier, *Spectrochim. Acta*, **28A**, 2279 (1967). E, amperometric titrations: J. E. Dubois and E. Bienvenüe-Goetz, *Bull. Soc. Chim. Fr.*, 2086 (1968).

reactivity range varying from 1 to 10^8 l. mol^{-1} min^{-1}. The disubstituted stilbenes investigated here are in this reactivity range. It can, therefore, be reasonably assumed that the same relationship is valid here and structural effects and ρ values can be discussed in terms of experimental rate constants alone. To analyze these rate constants, it is convenient to classify the compounds in subpopulations in which a substituent X is held constant and the other one, Y, varied. In Table II, the relative rates, $k_{X,Y}/k_{X,H}$, are given

TABLE II
KINETIC EFFECTS, $k_{X,Y}/k_{X,H}$, OF THE VARIABLE SUBSTITUENT Y AS A FUNCTION OF THE CONSTANT SUBSTITUENT X IN THE BROMINATION OF THE X,Y-DISUBSTITUTED STILBENES

Y	X				
	p-OH	p-OMe	p-Me	p-Cl	p-NO$_2$
p-OH	4.00	30	4,230	43,000	80,000
p-OMe	2.80	2.80	380	5,800	5,000
p-Me	1.50	1.46	2.03	13.3	9.4
m-Me		1.22	1.37		1.80
H	1.00	1.00	1.00	1.00	1.00
p-Cl	0.39	0.58	0.35	0.47	
m-Cl		0.43	0.22	0.23	
p-NO$_2$	0.10	0.07	0.03		

for the subpopulations where X is *p*-hydroxy, *p*-methoxy, *p*-methyl, *p*-chloro, and *p*-nitro. Inspection of Table II reveals that, when a strong electron-releasing group is attached to the first ring, the introduction of a second substituent alters the rate very slightly. However, if the first substituent is electron attracting, the rate is considerably affected by the second one. A horizontal comparison (Y constant,

X variable) also shows that the effect of an electron-releasing group depends essentially on the electronic character of the other substituent, while the effect of an electron-withdrawing one is only slightly influenced by the other. We shall now analyze the data in more detail in terms of the dual-path mechanism.
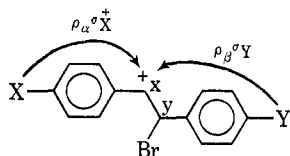
Extension of the Free-Energy Relationship for Dual-Path Additions to the Bromination of Disubstituted Stilbenes.—By analogy with the bromination of monosubstituted stilbenes[1] and if, as a first approximation, bromine participation is neglected, the mechanistic scheme for addition to a trans-disubstituted stilbene can be taken to involve two competitive pathways leading to two discrete intermediates, with rate constants k_x and k_y, respectively.
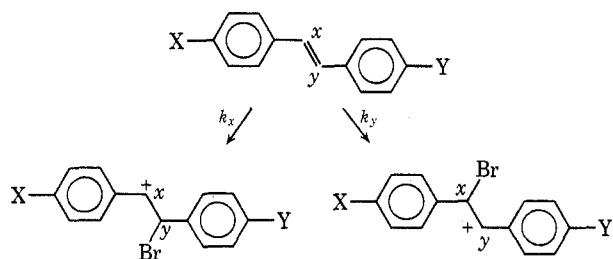
The measured rate constant is then the sum of the two partial rate constants

$$k_{exp} = k_x + k_y \tag{1}$$

Let us assume that each partial rate constant obeys the Hammett equation:[3] in the C_x intermediate, the effect of the substituent X, which is directly conjugated to the incipient carbonium center, is expressed by $\rho_\alpha \sigma_X^+$ and that of Y, transmitted by CHBr, is given by $\rho_\beta \sigma_Y$; ρ_α and ρ_β are the reaction constants for substituents in the aryl ring α and β with respect to the charge.[4] The σ^+ constant is used when the substituent is able to interact resonantly with the charged center and σ when it cannot do so.

To write the Hammett equation for the C_x path, it is necessary to assume the independence of the effect of X and Y. With this assumption,[5] we can write

$$\log (k_x/k_0) = \rho_\alpha \sigma_X^+ + \rho_\beta \sigma_Y \tag{2}$$

In the same way, for the C_y path

$$\log (k_y/k_0) = \rho_\alpha \sigma_Y^+ + \rho_\beta \sigma_X \tag{3}$$

Then the general free-energy relationship for electrophilic addition on trans-disubstituted stilbenes is

$$\log (k_{exp}/k_0) = \log [10^{\rho_\alpha \sigma_X^+ + \rho_\beta \sigma_Y} + 10^{\rho_\alpha \sigma_Y^+ + \rho_\beta \sigma_X}] \tag{4}$$

Reaction Constants, ρ_α and ρ_β.—From the rate constants of particular compounds for which the general

(3) J. E. Leffler and E. Grunwald, "Rates and Equilibria in Organic Reactions," Wiley, New York, N. Y., 1963, p 171.

(4) The indexes x and y refer to the positions of the charge in α to the substituent X and Y, respectively. The indexes α and β refer to the position of the substituent α and β with respect to the charge.

(5) In this way, we postulate that the introduction of Y does not modify the effect of X, so that we can consider the kinetic effects of X and Y as additive. This assumption will be discussed in more detail later.

X	$\rho_\beta^{X\,a}$	$\rho_\alpha^{X\,a}$	n^b
p-OH	-1.25 ± 0.4	c	3
p-OMe	-1.52 ± 0.6	c	4
p-Me	-1.88 ± 0.3	c	3
H	-1.53 ± 0.2	-5.05 ± 0.7	5
p-Cl	c	-5.71 ± 0.4	3
m-Cl	c	-4.97 ± 0.7	3
p-NO₂	c	-5.25 ± 0.8	5

^{a} For precisions, see footnote 7. ^{b} Number of compounds from which ρ_α^X and ρ_β^X have been determined. ^{c} The values of ρ_α^X and ρ_β^X corresponding to these substituents X cannot be calculated since their evaluation requires several substituents more electron-donating than p-hydroxy for $\rho_\alpha^{p\text{-OH}}$ or more withdrawing than p-nitro for $\rho_\beta^{p\text{-NO}_2}$.

free-energy relationship 4 could be simplified, two simple approaches, A and B, have been developed to obtain the values of the reaction constants, ρ_α and ρ_β.

A. Reaction Constants ρ_α^X and ρ_β^X for Defined Subpopulations (X Constant, Y Variable).—In subpopulations so arranged that one substituent, X, is constant and only Y varies (Table III), are chosen the stilbenes for which it can be reasonably assumed from previous results[1] that only one pathway contributes. In these cases, the free-energy relationship 4 simplifies to

$$\log (k_{X,Y}/k_{X,H}) = \rho_\alpha^X \sigma_Y^+ \tag{5}$$

if the preferred pathway leads to the intermediate **4** and

$$\log (k_{X,Y}/k_{X,H}) = \rho_\beta^X \sigma_Y \tag{6}$$

if the intermediate is **5**.
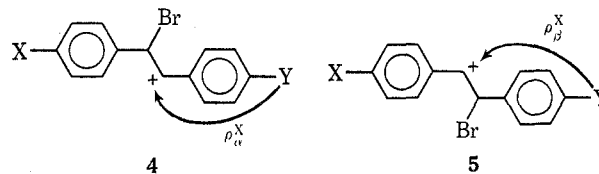
The application of eq 5 and 6 to stilbenes[6] where X = p-OH, p-OMe, p-Me, p-Cl, m-Cl, and p-NO₂ leads to the ρ_α^X and ρ_β^X values collected[7] in Table III. No significant variation of these values as a function of X appears.

B. General Reaction Constants, ρ_α and ρ_β.—Since the values of ρ seem to be independent of the substituent, general values of ρ_α^X and ρ_β^X must be valid for all the stilbenes. Average values of ρ_α^X and ρ_β^X (-5.08 and -1.53) are first used to calculate the partial rate constants k_x and k_y for all the stilbenes. From this calculation, we find that, for the compounds

(6) For instance, we showed previously[1] that, for the p-methoxystilbene (X = p-OMe, Y = H), only the C_x path leading to **5** contributes. When Y is more electron attracting than H, there is all the more reason for only this path to contribute. Therefore, when X = p-OMe and Y = H, p-Cl, m-Cl and p-NO₂, the free-energy relationship is $\log k_{X,Y} = \rho_\beta^{p\text{-OMe}} \sigma_Y + \log k_{p\text{-MeO,H}}$. In the same way, $\rho_\alpha^{p\text{-NO}_2}$ is calculated from stilbenes where X = p-NO₂ and Y = p-OH, p-OMe, p-Me, m-Me and H by means of the equation $\log k_{X,Y} = \rho_\alpha^{p\text{-NO}_2} \sigma_Y^+ + \log k_{p\text{-NO}_2,H}$.

(7) In preference to the correlation coefficients (ca. 0.99) and to the standard deviations (ca. 0.08), which are not very significant for calculations on rather few data, we give here the absolute errors on ρ for a confidence level of 95%.
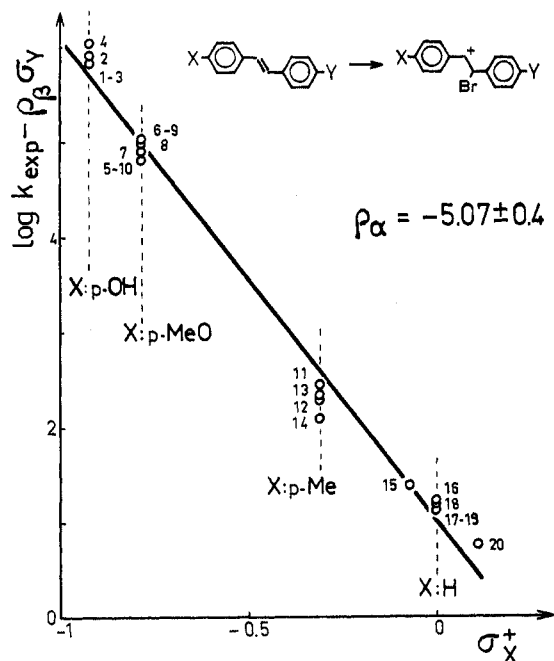
Figure 1.—Evaluation of ρ_α from disubstituted stilbenes whose bromination leads to a single intermediate (data of Table V); $\log k_{exp} - \rho_\beta \sigma_Y = \rho_\alpha \sigma_X^+$.

of Table IV, one of these rate constants is negligible[8] with respect to the other. We can, then, include in the subsequent calculations a number of additional compounds not used in the determination of the particular reaction constants. For the 20 mono- and disubstituted stilbenes where bromination occurs via a single pathway, the general relationship 4 simplifies to

$$\log (k_{X,Y}/k_0) = \rho_\alpha \sigma_X^+ + \rho_\beta \sigma_Y \qquad (7)$$

if the substituent X is always chosen so as to be more electron donating than Y.

General values of ρ_α, ρ_β, and $\log k_0$ are thus obtained by multiple regression: $\rho_\alpha = -5.07 \pm 0.4$; $\rho_\beta = -1.41 \pm 0.4$; $\log k_0 = 1.04$ (correlation coefficient $R = 0.995$).

These values of ρ_α and ρ_β allow the calculation of k_x and k_y and therefore the overall rate constant for any stilbene. These overall rate constants for the stilbenes of Table V,[9a] compounds which have not been used in the calculation of general ρ_α and ρ_β values, are

(8) For some compounds of Table IV, it can be remarked that the other path is not entirely negligible. For example, for the *p*-methylstilbene, the calculated reactivity, log *k*, of the C_x path is 2.60 whereas that of the C_y path is 1.24. The neglect of the C_y path leads therefore to an error on the overall reactivity of 1%, an error which is effectively negligible compared to the experimental errors (about 2%) and on the ρ values.

(9) (a) Seven stilbenes of this Table V are symmetrical compounds for which k_x equals k_y. Then for these, the general free energy relationship 4 simplifies to

$$\log (k/k_0) = \log (2k_x/k_0) = \rho_\alpha \sigma_X^+ + \rho_\beta \sigma_X + \log 2$$

This treatment for the symmetrical compounds provides the familiar value of ρ_α (-5.06 ± 0.5) but gives an abnormal and very imprecise ρ_β (-0.88 ± 1.5), although the coefficient correlation, 0.998, and the standard deviation, 0.004, are satisfactory. This result is probably due to the fact that $\rho_\alpha \sigma^+$ is very much greater than $\rho_\beta \sigma$ for electron-donating substituents, which predominate in this sample. (b) One of the referees suggested that the agreement between calculated and experimental reactivities might be the result of using a multiparameter calculation. The most striking argument in favor of our treatment is that the various methods of calculating the two ρ values lead to closely similar values. It might appear that simpler interpretations with fewer adjustable parameters could fit the data as well, but such interpretations are only valid for restricted sets of substituents chosen intuitively. To take into account all the data, this unifying treatment based on the dual-path mechanism is actually the most logical.

TABLE IV
CALCULATED RATE CONSTANTS FOR METHANOLIC BROMINATION OF STILBENES BY ONE PATHWAY: $\log k/k_0 = \rho_\alpha \sigma_X^+ + \rho_\beta \sigma_Y$
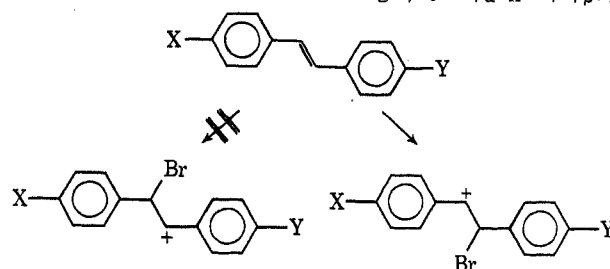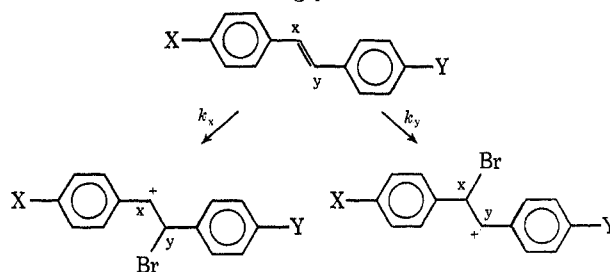

Registry no.[d]	No.	X	Y	Log k_{calcd}[a]	Log k_{exp}[b]	Δ[c]
18951-45-6	1	*p*-OH	*p*-Me	5.95 ± 0.6	6.10	−0.15
6554-98-9	2	*p*-OH	H	5.71 ± 0.4	5.93	−0.22
18951-46-7	3	*p*-OH	*p*-Cl	5.39 ± 0.4	5.53	−0.14
14064-83-6	4	*p*-OH	*p*-NO₂	4.61 ± 0.7	4.92	−0.31
37163-68-1	5	*p*-OMe	*p*-Me	5.24 ± 0.4	5.05	0.19
23940-93-4	6	*p*-OMe	*m*-Me	5.09 ± 0.3	4.98	0.11
1694-19-5	7	*p*-OMe	H	5.00 ± 0.3	4.89	0.11
18878-89-2	8	*p*-OMe	*p*-Cl	4.68 ± 0.3	4.65	0.03
37163-71-6	9	*p*-OMe	*m*-Cl	4.48 ± 0.4	4.53	−0.05
4648-33-3	10	*p*-OMe	*p*-NO₂	3.90 ± 0.6	3.72	0.18
1860-17-9	11	*p*-Me	H	2.61 ± 0.1	2.46	0.15
3041-83-6	12	*p*-Me	*p*-Cl	2.29 ± 0.2	2.02	0.27
37163-72-7	13	*p*-Me	*m*-Cl	2.09 ± 0.2	1.82	0.27
24325-70-0	14	*p*-Me	*p*-NO₂	1.50 ± 0.4	1.00	0.50
37163-74-9	15	*m*-Me	*p*-NO₂	0.29 ± 0.3	0.28	0.01
14064-43-8	16	H	*m*-Cl	0.52 ± 0.1	0.71	−0.19
891-70-3	17	H	*m*-CF₃	0.45 ± 0.1	0.53	−0.08
1149-56-0	18	H	*p*-CF₃	0.28 ± 0.2	0.40	−0.12
16194-20-8	19	H	*p*-NO₂	−0.06 ± 0.3	0.02	−0.08
25144-36-3	20	*p*-Cl	*m*-Cl	−0.06 ± 0.2	0.25	−0.31

[a] Log k_{calcd} calculated from eq 7. [b] *k* in l. mol⁻¹ min⁻¹ in methanol, 0.2 *M* NaBr at 25°. [c] Δ = log k_{calcd} − log k_{exp}. [d] Registry numbers apply to the *trans*-stilbenes.

TABLE V
CALCULATED PARTIAL AND OVERALL RATE CONSTANTS FOR BROMINATION OF STILBENES BY TWO COMPETITIVE PATHWAYS
$\log k/k_0 = \log [(k_x + k_y)/k_0] =$

$$\log [10^{\rho_\alpha \sigma_X^+ + \rho_\beta \sigma_Y} + 10^{\rho_\alpha \sigma_Y^+ + \rho_\beta \sigma_X}]$$

Registry no.[d]	No.	X	Y	Log k_x[a]	Log k_y[a]	Log k_{calcd}[b]	Δ[c]
15058-36-3	21	*p*-OH	*p*-OH	6.23	6.23	6.53	0.00
18951-44-5	22	*p*-OH	*p*-OMe	6.09	5.53	6.20	−0.18
15638-14-9	23	*p*-OMe	*p*-OMe	5.38	5.38	5.68	0.34
18869-29-9	24	*p*-Me	*p*-Me	2.85	2.85	3.15	0.37
37163-81-8	25	*p*-Me	*m*-Me	2.71	1.63	2.74	0.13
37163-82-9	26	*p*-iPr	*p*-iPr	2.67	2.67	2.97	0.13
14064-48-3	27	*m*-Me	H	1.39	1.14	1.58	−0.22
103-30-0	28	H	H	1.04	1.04	1.34	−0.16
1657-50-7	29	H	*p*-Cl	0.72	0.46	0.91	0.02
13041-70-8	30	H	*p*-Br	0.72	0.28	0.85	−0.06
1657-56-3	31	*p*-Cl	*p*-Cl	0.14	0.14	0.44	−0.12
18869-30-2	32	*p*-Br	*p*-Br	−0.04	−0.04	0.26	−0.14

[a] k_x and k_y calculated from eq 2 and 3. [b] $k_{calcd} = k_x + k_y$. [c] Δ = log k_{calcd} − log k_{exp}. [d] Registry numbers apply to the *trans*-stilbenes.

in good agreement with the experimental rate constants.[9b] This is the first evidence from kinetics in support of the initial assumption regarding the competition between two pathways for stilbene bromination in methanol.

TABLE VI

VARIATION, ρ^X/ρ^H, OF THE REACTION CONSTANT AS A
FUNCTION OF THE SUBSTITUENT X, IN REACTIONS OF
X,Y-DISUBSTITUTED AROMATIC COMPOUNDS
(X CONSTANT, Y VARIABLE)

X	Benzenes[a]	Benzhydryl chlorides[b]	1,1-Diarylethylenes[c]	Stilbenes[e] ρ_α	ρ_β
p-NMe₂	0.19				
p-OH			(0.54)[d]		0.82
p-OMe	0.62	0.60	0.63		0.99
p-Me	0.92	0.85	0.80		1.23
H	1.00	1.00	1.00	1.00	1.00
p-Cl		1.01	1.04		1.13
p-NO₂			(1.30)[d]		1.04

[a] Electrophilic substitution by bromine in water: R. Uzan and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 598 (1971); J. E. Dubois and J. J. Aaron, *J. Chim. Phys.*, 66, 1122 (1969); and ref 10 and 14. [b] Solvolysis of benzhydryl chlorides in ethanol: S. Nishida, *J. Org. Chem.*, 32, 2697 (1967); E. Berliner and M. Q. Malter, *ibid.*, 33, 2595 (1968). [c] Bromination of 1,1-diarylethylenes in methanol, ref 2. [d] Extrapolated value. [e] This work.

In Tables IV and V, differences >0.3 logarithmic units between calculated and experimental values can be observed for 4 of the 32 compounds investigated. In view of the imprecision of the calculated reactivities, these deviations may be taken as insignificant. Comparison of Figures 1 and 2 shows dramatically that ρ_β is subject to a much greater uncertainty than ρ_α: in the former case, log k_{exp} − $\rho_\alpha\sigma_X^+$ for a constant Y depends markedly on the identity of X. This could indicate that the additivity assumption used in the general free-energy relationship 4 is not valid. A dependence on the constant substituent X of the reaction constant ρ for another variable substituent Y has been demonstrated in the bromination of 1,1-diarylethylenes[2] and benzenes.[10] It was proposed "that the presence of a substituent, particularly one capable of electron donation by resonance, in the aromatic ring so alters the charge distribution in the transition state that the second substituent in the other ring, then, interacts with a different charge." Examining in detail the two intermediates in the bromination of stilbenes,[11] we see that $\rho_\alpha{}^X$, which measures the effect of the variable Y, can only be weakly affected by the remote X which is isolated from the charge by the bromomethylene group. On the other hand, $\rho_\beta{}^X$ can be modified rather more by X interacting with the charge. However, since ρ_β is inherently small, the differences will also be small.

In Table VI, we show the variation, ρ^X/ρ^H, of the reaction constant for a variable substituent Y as a function of the constant substituent X for various reactions of disubstituted aromatic conjugated systems. Compared to the other reactions considered in Table VI, the variation of ρ_α for the stilbene bromination can be considered as insignificant, on account of the uncertainty involved in calculations on rather
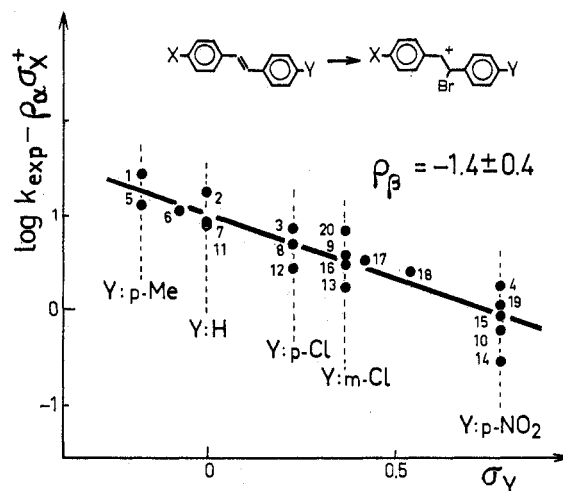

Figure 2.—Evaluation of ρ_β from disubstituted stilbenes whose bromination leads to a single intermediate (data of Table V); log k_{exp} − $\rho_\alpha\sigma_X^+$ = $\rho_\beta\sigma_Y$. For a same Y, a considerable scatter is observed when X varies. In addition to a normal dispersion (as in Figure 1) due to the imprecise evaluations of ρ^X, this is to be related to a poor additivity of substituent effects for the reaction constant ρ_β; *i.e.*, ρ_β varies really as a function of X (Table III).

few points (Table III). In the same way, the variations of ρ_β, although somewhat larger than those of ρ_α, are too small and too imprecise[13] to allow us to infer the existence or the magnitude of any interaction between substituents. However, from Figure 2, the existence of a weak interaction modifying ρ_β might be inferred. Unfortunately, no quantitative estimation can be deduced, since deviations must be attributed in part to errors on ρ.

For stilbenes brominated *via* a single intermediate, another way of measuring the importance of substituent interaction is, in principle, possible. In this series, we had applied the free-energy relationship log $(k_{X,Y}/k_0)$ = $\rho_\alpha{}^H\sigma_X^+$ + $\rho_\beta{}^H\sigma_Y$. To take into account any nonadditivity of substituent effects, we should have to write log $(k_{X,Y}/k_0)$ = $\rho_\alpha{}^Y\sigma_X^+$ + $\rho_\beta{}^X\sigma_Y$. It has been shown[2] that the reaction constant ρ^H is modified by a substituent X in proportion to the value of its σ^+, so that ρ^X = $a\sigma_X^+$ + ρ^H. Therefore, this relationship becomes

$$\log (k_{X,Y}/k_0) = \rho_\alpha{}^H\sigma_X^+ + \rho_\beta{}^H\sigma_Y + a_\alpha\sigma_X^+\sigma_Y^+ + a_\beta\sigma_X^+\sigma_Y \quad (8)$$

Applying this equation to the stilbenes of Table IV, we find the familiar values for $\rho_\alpha{}^H$ and $\rho_\beta{}^H$ (−5.05 and −1.42) and for the a_α and a_β coefficients, the small and highly uncertain values of −0.33 ± 3.2 and 0.29 ± 3.0, respectively. Therefore, no conclusion on additivity can be obtained from this treatment. The a coefficients, measuring the interaction causing the nonadditivity, are −6.2 for benzenes and −1.8 for 1,1-diarylethylenes. For stilbenes, estimated from the variations of ρ_β (Table III), this

(10) J. E. Dubois, J. J. Aaron, P. Alcais, J. P. Doucet, F. Rothenberg, and R. Uzan, *J. Amer. Chem. Soc.*, **94**, 6823 (1972).

(11) Additivity of substituent effects assumes no variation of interaction between substituents in the transition state and also in the ground state. For stilbenes, it has been shown[12] from measurements of polar moments that the interaction moments, defined as $\mu_m = \mu_{XY}{}^{exp} - (\mu_X + \mu_Y)$, are weak and approximately independent of the nature of X and Y. Interaction in the ground state seems insensitive to the variation of the electronic character of the substituents. Therefore nonadditivity will be discussed only in terms of the structures of the transition states.

(12) K. B. Everard and L. E. Sutton, *J. Chem. Soc.*, 2826 (1951).

(13) The variation of ρ_β for the p-methyl substituent (Table VI) is particularly conspicuous. Obviously, its value is weak since its σ^+ is rather weak (−0.31). However, in 1,1-diarylethylenes, p-methyl diminishes the reaction constant by 20%, in benzenes it modifies it only slightly, and in stilbenes it seems to increase it. For 1,1-diarylethylenes[2] and stilbenes, the corresponding ρ values have been established only from a few compounds (**4** and **3**, respectively), whereas, for benzenes,[14] it was evaluated accurately over a large range of reactivity using numerous compounds. Therefore, the variation of ρ_β for the p-methylstilbenes would reflect only the uncertainty on ρ.

(14) F. Rothenberg, P. Alcais, and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 592 (1971).

coefficient could be of the order of -0.5. Therefore, if this interaction exists in stilbene bromination, it cannot be very important and the previous analysis of the kinetic data which neglects interaction can be considered adequate.

Carbonium or Bromonium Ion Intermediates in Stilbene Bromination.—The kinetic scheme involving two pathways is based on two assumptions: the first one supposes the additivity of the substituent effects (we have already discussed this hypothesis and concluded to its validity) and the second one excludes the participation of bromine in stabilizing the charge in the transition state. The agreement between the kinetic results and the reactivities calculated from this scheme tends to confirm the validity of the second assumption. In fact, a more detailed examination of the results is necessary to demonstrate the absence of bromonium ions in stilbene bromination in methanol.

From the analysis of the data for the monosubstituted stilbenes alone, it was not possible to determine the structure of the C_y path intermediate. For the strongly electron-attracting compounds (p-nitrostilbene, for instance), it was only established, from the value of ρ_β, that the charge of the transition state was on an atom β to the substituted ring, i.e., on the β carbon or on the bromine atom. To distinguish between these two possibilities, it was proposed to measure the effect of a substituent on the second ring, since, if the charge is on the carbon atom β to the first substituent, the effect of the second must be expressed by ρ_α, whereas if the charge is on the bromine atom, the effect of this second substituent must be weaker.
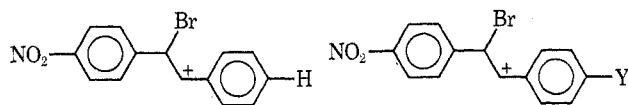
In the analysis of the disubstituted stilbenes, it appears that, if the effect of one substituent is expressed by ρ_β, the effect of the other is always given by ρ_α and vice versa. These results are only consistent with a structure for the intermediate in which there is always one substituent directly conjugated to the charge; i.e., this charge can only be on an olefinic carbon atom α to this substituent. Therefore, for the stilbenes investigated here, it can be affirmed that the bromine atom bears no significant charge.

This result is not unexpected for the stilbenes where one substituent at least is strongly electron donating, since the charge will be better stabilized by this electron-donating ring than by bromine, as is shown by the stereochemical results of Fahey[15] on the *trans*-β-methylstyrene and *trans*-anethole. However, bromine participation might be expected when both substituents are electron attractors, such as in the cases of the di-p,p'-chloro-, di-p,p'-bromo-, and di-p,m'-chlorostilbenes. These compounds do not deviate from the general correlation and we can deduce that bromine participation is unimportant also in these cases. In fact, the electron-attracting character of these substituents is rather weak, and it is possible that, when stronger electron attractors, such as in di-p,p'-nitrostilbene, are involved, bromine participation becomes important and, therefore, devia-

(15) R. C. Fahey, *J. Amer. Chem. Soc.*, **88**, 4681, 1966.

TABLE VII

COMPARISON OF THE KINETIC SUBSTITUENT EFFECTS IN BROMINATION OF STILBENES IN CARBON TETRACHLORIDE AND IN METHANOL

X	Y	CCl₄, log k/k_0	MeOH, log k/k_0
p-OMe	H	3.72[a]	3.38[a]
p-Me	H	0.47	0.95
p-Cl	H	0.25	-0.62
p-NO₂	H	-0.21	-1.49
p-NO₂	p-OMe	2.01[a]	2.21[a]
p-NO₂	p-Me	0.00	-0.51
p-Me	p-Me	0.72	1.27

[a] For the p-methoxystilbenes, the similarity of the kinetic effect seems to show that the transition state structures are identical in both solvents: carbonium-like.[19]

tions from the correlation might be observed. Investigations on such compounds, which are in progress and which will be the subject of a forthcoming paper, are possible only if the kinetic parameters of the carbonium ion mechanism are known precisely.

Another argument against bromonium ion intermediates in methanol for the stilbenes so far examined can be found in a comparison of our data with the results of a recent kinetic investigation[16] on bromination of the same stilbenes in carbon tetrachloride.[17] There is no correlation of the form log $k_{MeOH} = a$ log $k_{CCl_4} + b$, which would reveal an analogy between the two sets of data (Table VII) and therefore some similarity between the transition-state structures.

In carbon tetrachloride, the intermediate is bromonium-like[18] (10% only of syn adduct). Setting aside the p-methoxy compounds,[19] the relationship between the reactivities of mono- and disubstituted stilbenes in carbon tetrachloride and the sum of their σ constants is linear.

$$\log (k/k_0)_{CCl_4} = -0.65 \, \Sigma\sigma \qquad (9)$$

A relationship in terms of $\Sigma\sigma^+$ is also linear, since σ and σ^+ are rather similar for the compounds included in this correlation. The inequality of the ρ values in methanol and in carbon tetrachloride indicates differences in the magnitude of the developing charge in the transition states. Comparison of the effects of X and Y, which are identical in carbon tetrachloride but different in methanol, underlines the fact that the charge distribution in the transition states are very different: bromonium-like in the first solvent, carbonium-like in the second. In fact, as shown here, the mechanisms of stilbene bromination in carbon tetrachloride and in methanol are very

(16) G. Heublein and E. Schutz, *Z. Chem.*, **9**, 147 (1969).

(17) In carbon tetrachloride, the bromination is a third-order reaction: first order in stilbene and second order in bromine. The first molecule of bromine forms with a molecule of stilbene a π-complex whose ionization is assisted by the second molecule of bromine.[22]

(18) (a) R. E. Buckles, J. L. Forrester, R. L. Burham, and T. W. McGee, *J. Org. Chem.*, **25**, 24 (1960); (b) G. Heublein, *J. Prakt. Chem.*, **31**, 84 (1966).

(19) Deviations in the linear relationship observed for the p-methoxystilbenes in carbon tetrachloride may be due to a decrease in bromine participation. From differences between the rate constants experimentally measured and calculated from eq 9, for the p-methoxystilbene (1762 $-$ 1.1 M^{-2} sec⁻¹) and for the p-methoxy-p'-nitro compound (31.8 $-$ 0.34 M^{-2} sec⁻¹), it can be assumed that in carbon tetrachloride the transition state is free from bromine bridging and resembles a carbonium ion. This result is confirmed by the stereochemical results of Fahey.[15] If a double bond is substituted by a p-anisyl group, the intermediate is preferentially a benzylic carbonium ion, even in apolar solvents.

different. In the apolar carbon tetrachloride,[20] the rate-determining step[22] is the bimolecular ionization of the CTC (charge transfer complex), with a symmetrical transition state leading to a bromonium intermediate. In polar solvents such as methanol, the reaction involves an unimolecular ionization[23] with a carbonium-ion-like transition state.

Conclusion

In short, the initial hypothesis of a dual-path mechanism for additions with carbonium ion intermediates is confirmed for stilbene bromination by the kinetic substituent effects, by the regiochemistry of the reaction, by the analogy with the kinetics of dehydration of 1,2-diarylethanols,[1] and by the differences between the results in methanol and in carbon tetrachloride.

Until now, the structure of the bromination intermediates has been determined by essentially stereochemical methods. In stereospecific brominations, it is evident that bromonium intermediates are involved. However, from reactions which are only *stereoselective*, no clear conclusion can be drawn regarding the magnitude of bromine participation, since stereoselectivity could be the result of several factors:[24] bromine bridging but also ion pairing or competition between rotation and nucleophilic attack. Our kinetic treatment based on the dual-path addition mechanism represents a new approach to the determination of the structure of intermediates in electrophilic addition. Now that the kinetic parameters for addition *via* carbonium intermediates are known, it should be possible to measure the extent of any bromine bridging, if it occurs, by observation of deviations from the general kinetic relationship.

Experimental Section

Synthesis of Stilbenes.—The disubstituted stilbenes are prepared by methods F, G, H, J, and K (Table VIII) described below.

Method F.—The demethylation by pyridine hydrochloride of di-*p,p'*-methoxystilbene leads to the di-*p,p'*-hydroxystilbene.[25]

Method G.—The condensation of the appropriately substituted benzaldehydes with the appropriate phenylacetic acid in the presence of piperidine leads to the substituted stilbenes.[26]

Method H.—The condensation of anisole and diethyl bromo acetal in acetic acid in the presence of hydrochloric acid[27] leads to the di-α,α'-*p*-anisyl-β-bromoethane. This compound, dehydrobrominated in pyridine, affords the di-*p,p'*-methoxystilbene in a yield of 55%.

Method J.—Substituted benzaldehydes are condensed with benzylmagnesium chlorides as described by House.[28] The result-

TABLE VIII
Synthesis of Disubstituted Stilbenes

X	Y	Synthesis method	Mp, °C	Ref
p-OH	*p*-OH	F	278	25
p-OH	*p*-OMe	G	203–204	26
p-OH	*p*-Me	G	208–209	26
p-OH	*p*-Cl	G	186–187	26
p-OH	*p*-NO₂	G	204	26
p-OMe	*p*-OMe	H	214–215	25
p-OMe	*p*-Me	J	166–167	a
p-OMe	*m*-Me	J	98	b
p-OMe	*p*-Cl	J	196	c
p-OMe	*m*-Cl	J	96	d
p-OMe	*p*-NO₂	G	133–134	26
p-Me	*p*-Me	K	180	e
p-Me	*m*-Me	J	101–102	b
p-Me	*p*-Cl	J	203–204	f
p-Me	*m*-Cl	J	119	b
p-Me	*p*-NO₂	G	150	26
m-Me	*p*-NO₂	G	112–113	b
p-iPr	*p*-iPr	K	130–131	b
p-Cl	*p*-Cl	K	177–178	g
p-Cl	*m*-Cl	J	75	b
p-Br	*p*-Br	K	208–210	g

^{a} D. Y. Curtin, A. Bradley, and Y. G. Hendrickson, *J. Amer. Chem. Soc.*, **78**, 4064 (1956). ^{b} New compound. ^{c} L. Horner, H. Hoffman, W. Klinl, H. Ertel, and V. G. Toscano, *Chem. Ber.*, **95**, 581 (1962). ^{d} S. S. Jenkins and E. M. Richardson, *J. Amer. Chem. Soc.*, **55**, 3874 (1933). ^{e} G. Drehafl and G. Plottner, *Chem. Ber.*, **91**, 1274 (1958). ^{f} W. J. Linn, *J. Amer. Chem. Soc.*, **87**, 3665 (1965). ^{g} J. A. Stanfield and L. B. Reynolds, *ibid.*, **74**, 2878 (1952).

ing alcohols are dehydrated in cold benzene by phosphoric anhydride.

Method K.—To prepare symmetrical stilbenes, azines obtained from benzaldehydes and hydrazine are pyrolyzed by the method described by Buu-Hoi and Saint-Ruff.[29]

For the kinetic measurements, the stilbenes are purified by column chromatography on alumina or silica gel and further by recrystallizations from suitable solvents. The purity is checked by thin layer chromatography.

Among the stilbenes of Table VIII, the compounds listed in Table IX have not been described in the literature. All their

TABLE IX
Elemental Analysis of New Stilbenes

Stilbene X	Y	Calcd, % C	H	X	N	Found, % C	H	X	N
p-OMe	*m*-Me	85.68	7.19			86.25	7.74		
p-Me	*m*-Me	92.26	7.74			92.50	7.23		
p-Me	*m*-Cl	78.76	5.68	15.52		78.56	5.60	15.62	
m-Me	*p*-NO₂	75.30	5.48		5.85	75.47	5.87		5.50
p-iPr	*p*-iPr	90.85	9.15			90.02	8.88		
p-Cl	*m*-Cl	67.46	4.01	28.51		67.14	4.68	28.21	

spectra show the strong characteristic band at 960 cm⁻¹, due to the out-of-plane in-phase vibration of the olefinic hydrogen atoms.[30] In their nmr spectra, described and interpreted by Doucet, *et al.*,[31] the signals for the ethylenic protons are not readily distinguishable from the signals of the aromatic protons.

Kinetic Measurements.—Previous treatment of methanol and sodium bromide and the kinetic methods are already described in the references of Table I.

(20) Bromination of stilbenes in carbon tetrachloride is more closely related to epoxidation,[21] reaction in which the symmetry of the starting olefin is preserved in the transition state and even in the products, and linear relationships are obtained with Σσ⁺, including the *p*-methoxy- and the *p,p'*-dimethoxystilbenes.

(21) (a) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955); (b) M. A. Hoefnagel, A. VanVeen, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **88**, 569 (1969).

(22) G. Heublein and P. Umbreit, *Tetrahedron*, **24**, 4733 (1968).

(23) F. Garnier and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 3797 (1969).

(24) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 2944 (1970).

(25) W. H. Laarhoven, R. J. F. Nivard, and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **80**, 775 (1961).

(26) H. Veschambre and A. Kergomard, *Bull. Soc. Chim. Fr.*, 336 (1966); 2846 (1967).

(27) R. Quelet, C. Broquet, and M. F. Ruasse-Touré, *C. R. Acad. Sci.*, *Ser. C*, **254**, 1811, 1962.

(28) H. O. House, *J. Amer. Chem. Soc.*, **77**, 3070 (1955).

(29) N. P. Buu-Hoi and G. Saint-Ruff, *Bull. Soc. Chim. Fr.*, 955 (1967).

(30) S. F. D. Orr, *Spectrochim. Acta*, **8**, 218 (1956).

(31) J. P. Doucet, B. Ancian, and J. E. Dubois, *J. Chim. Phys.*, in press.