C(1). Further attempts to explain the differences between the bond lengths will be made.

Registry No.—(+)-*R*-Spiro[3.3]heptane-2,6-dicarboxylic acid, 27259-78-5.

Acknowledgment.—The authors are greatly indebted to Mr. J. F. Kleibeuker of the Department of Physical Chemistry, Rijksuniversiteit, Groningen, for the CD measurements, Dr. D. Kracht for his contribution to the CNDO calculations, Dr. J. L. de Boer for his valuable comments, Dr. J. P. M. Houbiers of the Department of Organic Chemistry, Rijksuniversiteit, Groningen, for the preparation of the *d*-Fecht acid used in this work, and Dr. G. J. Visser for his considerable contribution to this work.

Electrophilic Bromination of Aromatic Conjugated Olefins. I. Evaluation of a Competitive Path Mechanism in Bromination of Trans-Monosubstituted Stilbenes[1a]

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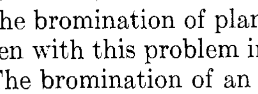
The bromine addition to monosubstituted stilbenes, $XC_6H_4C_xH{=}C_yHC_6H_5$, is treated as a reaction that can take place at two discrete centers C_x and C_y passing *via* C_x^+ and C_y^+ carbonium ion intermediates. The free-energy relationship for stilbenes whose substituents vary from *p*-hydroxy to *p*-nitro, and whose rate constants cover six powers of ten, is markedly curved. It corresponds to the equation, $\log (k/k_0) = \log [(k_x + k_y)/k_0] = \log (10^{\rho_\alpha \sigma^+} + 10^{\rho_\beta \sigma})$, where ρ_α is the reaction constant when the incipient carbonium center is C_x in the α position with respect to the substituted ring and ρ_β for the C_y center and where ρ_α and ρ_β are -5.0 and -1.5, respectively. It is shown that the bromination of *p*-methoxy- and *p*-hydroxystilbenes proceeds exclusively *via* the C_x path, whereas *p*-methyl, *m*-methyl, and *p*-chloro compounds involve this path only to the extent of 95, 65, and 35%, respectively. For *m*-chloro to *p*-nitro derivatives, only the C_y path is significant. These results are consistent with the regioselectivity of the nucleophilic attack of the solvent on the intermediates. The intermediate of the C_x path is clearly the free carbonium ion C_x^+, whereas in the intermediate of the C_y path, bromine participation cannot be excluded on the basis of kinetic data alone. The stereochemical and regiochemical analysis does not provide conclusive evidence either. Nevertheless, these latter data suggest that a free carbonium ion structure is the more likely.

For the bromination of styrenes, linear free-energy relationships, $\log k/k_0 = \rho\sigma^+$, were reported by Dubois, *et al.*, for electron-releasing substituents[1b,c] and by Yates, *et al.*, for electron attractors.[2] The value of ρ, -4.3 in methanol, -4.5 in acetic acid, compared with that of *tert*-cumyl chlorides,[3] -4.8, indicates that the benzylic carbon atom bears the charge in the transition state and neither the β carbon nor the bromine is concerned in the delocalization of the charge. The absence of bromine bridging in the transition state and consequently in the intermediate would lead to the absence of stereoselectivity in these solvents. However, in acetic acid, some stereoselectivity is observed in the bromination of the *cis*- and *trans*-β-methylstyrenes. This was explained[2] not by bromine bridging but by hindrance to free rotation in the carbonium ion, due to association with a bromine anion in an intimate ion pair. Thus, even when the ring bears a strongly electron-withdrawing substituent, the intermediate is an α-arylcarbonium ion, rather than a β-arylcarbonium or a bromonium ion where the destabilizing influence of the substituent would be minimized.[4]

It was, therefore, interesting to examine a system in which any carbonium ion formed would necessarily have both α- and β-aryl substituents. The charge distribution might then be expected to depend markedly on the electron-donating or electron-attracting character of the substituent. The present kinetic analysis[6] of the bromination of planar trans stilbenes was undertaken with this problem in mind.

The bromination of an unsymmetrical trans stilbene could generate three limiting intermediates, **1**, **2**, and **3**,



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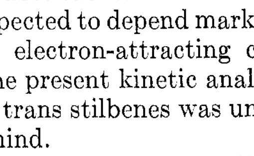

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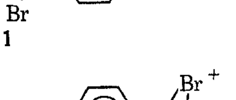

3

in which the charge is located on the α-aryl, the β-aryl carbon, or the bromine, respectively. For each one, there is a corresponding transition state, resembling each intermediate rather closely, since for bromination[7], the transition state structure has been shown to be nearer the intermediate than the ground state. Then the kinetic effect of X would be expected to be

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[1] (a) Also regarded as part XXX of "Reactivity of Ethylenic Compounds: Bromination." Part XXIX: E. Bienvenue-Goetz, J. E. Dubois, D. W. Pearson, and D. L. H. Williams, *J. Chem. Soc. B*, 1275 (1970). (b) J. E. Dubois and A. Schwarcz, *Tetrahedron Lett.*, 2167 (1964). (c) M. Ropars, Ph.D. Thesis, CNRS, No. AO 2640, 1968, Paris.

[2] J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469 (1969); J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 2944 (1970).

[3] Y. Okamoto, T. Inukai, and H. C. Brown, *J. Amer. Chem. Soc.*, **80**, 4972 (1958).

[4] In bromination of nonplanar 1,1-diphenylethylenes,[5] where two rings exert their influence on the same olefinic carbon, a dependence between the ring orientation and the electronic character of the substituent is observed; the more electron-releasing ring lies preferentially in the plane of the incipient carbonium ion, the other being turned out of this plane.

[5] E. D. Bergmann, J. E. Dubois, and A. F. Hegarty, *Chem. Commun.*, 1616 (1968).

[6] Preliminary communication: M. F. Ruasse and J. E. Dubois, *Tetrahedron Lett.*, 1163 (1970).

[7] F. Garnier, R. H. Donnay, and J. E. Dubois, *J. Chem. Soc. D*, 829 (1971).

different for each structure. The relative stabilities and the relative importance of these intermediates will depend on the electronic character of the substituent. In cases where the three intermediates contribute, the relationship $\log k/k_0 = f(\sigma)$ would not be linear. However, we expected that, by choosing conditions where one intermediate is overwhelmingly predominant, the substituent effects on each can be defined separately. It will then be possible to determine the contribution of each structure in the bromination of any stilbene.

The intermediate bromonium ion **3** is not expected to play a major role if the brominations are carried out in methanol. In fact the stereoselectivity, and therefore the bromonium character of the intermediate, depends on solvent polarity.[8] In nitrobenzene, whose dielectric constant is similar to that of methanol, the observed stereoselectivity is probably due to a competition between the rotation of the free carbonium ion and the nucleophilic attack of the counterion rather than to rotational hindrance by bromine bridging. It is reasonable, therefore, to discuss the kinetic results, first of all, without considering bromine participation in our model.

Kinetic Results.—The rate constants for the bromination of 12 trans-monosubstituted stilbenes, measured in methanol (0.2 *M* NaBr) at 25°, are given in Table I.[9–13] Depending on the substituent, the rate constants vary over about eight powers of ten. As expected for an electrophilic reaction, the electron-releasing groups accelerate the bromination and the electron-attracting groups slow it. However, the rate is much more affected by electron donors than by electron attractors. For instance, the acceleration by the *p*-methoxy susbstituent is a factor of 2000, and the retardation by the *p*-nitro group, whose absolute value of σ^+ equals that of *p*-methoxy, is only 30. Thus no linear relationship of the type $\log k/k_0 = \rho\sigma$ exists, neither with Brown's σ^+ nor with Hammett's σ constants.[14] In Figure 1, log k is plotted against σ^+ for the electron-donating substituents and against σ for the electron attractors. The free-energy relationship is markedly curved. The choice of the substituent constants will be justified later: we shall show that the reactivity depends predominantly on σ^+ for strong electron-donating substituents and on σ for strong electron attractors.

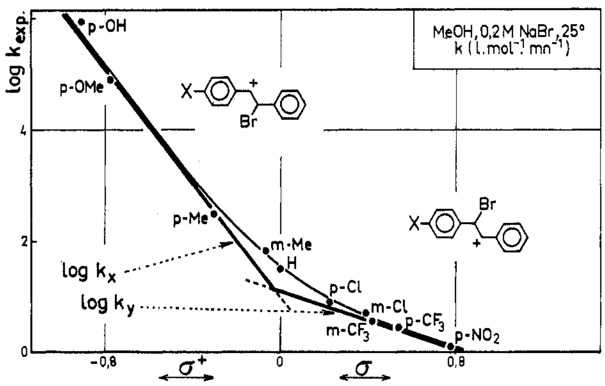

Figure 1.—Reactivity–structure relationship for monosubstituted stilbenes. The linear correlations of log k_x and log k_y corresponding to the C_x and C_y paths, are the tangents to the curved relationship for the overall reactivities.

In methanol, two brominating species, Br_2 and Br_3^-, act, making composite the overall rate constant. Owing to the complexity and uncertainty of the "Br_3^- mechanism,"[2,18] an exact assessment of structural effects can only be made from k_{Br_2}. Dubois and Huynh[19] have demonstrated that the overall rate constants can be used in free-energy relationships when Q, the $k_{Br_2}/k_{Br_3^-}$ ratio, in methanol is greater than or equal to 16. This ratio, measured by the usual method[13,23] for the most reactive compound **1**, for the unsubstituted stilbene **6**, and for the least reactive one **12** (see Table I), has values equal to 20, 43, and 17, respectively[19b] and is therefore in the acceptable range. Moreover, $\log k_g = 0.99 \log k_{Br_2} - 1.16$ (see Table VI).

Thus the curvature of the $\rho\sigma$ relationship can be attributed neither to peculiar resonance effects nor to competition between the bromine and "tribromide ion" attack. Another special feature of the mechanism of the stilbene bromination must be sought to elucidate these kinetic data.

Free-Energy Relationships for Electrophilic Reactions at Two-Carbon Centers.—In protic solvents, the bromination of unsaturated compounds proceeds *via* an $AdEC_1$ mechanism[20] whose rate-determining step is the transformation of the π complex into an ionic intermediate by Br–Br bond rupture and carbon-bromine σ-bond formation.

In brominations where the intermediate is a bro-

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(8) (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).

(9) J. E. Dubois, P. Alcais, and G. Barbier, *J. Electroanal. Chem.*, **8**, 359 (1964).

(10) J. E. Dubois and G. Mouvier, *C. R. Acad. Sci.*, **255**, 1104 (1962).

(11) J. E. Dubois and F. Garnier, *Spectrochim. Acta*, **23A**, 2279 (1967).

(12) R. P. Bell and E. N. Ramsden, *J. Chem. Soc.*, 161 (1958).

(13) J. E. Dubois and E. Bienvenue-Goetz, *Bull. Soc. Chim. Fr.*, 2086 (1968).

(14) The nonlinearity of the $\rho\sigma$ relationship could be the result of different resonance effects in stilbene bromination and in solvolysis, the defining reaction of σ^+ constants.[15] It should be possible, then, to correlate the reactivities using the Yukawa–Tsuno equation,[16] $\log k/k_0 = \rho(\sigma + R\Delta\sigma^+)$, where ρ is the usual reaction constant and R is a constant which measures the resonance effects. The application of this relationship to our data leads to a rather poor correlation (correlation coefficient, $r = 0.975$) and provides very improbable parameters, $\rho = -1.94$ and $R = 3.05$. For comparison, styrene bromination[1,2] gives $\rho = -4.30$ and $R = 1.00$. If the lessening of the ρ value, -4.3 to -1.9, could be interpreted in terms of a greater charge delocalization in stilbenes than in styrenes, the R value of 3.05 would be far and away the highest known value for reactions involving analogous benzylic cations.[16,17] Clearly two parameters give a better correlation than one, but the results of applying the Yukawa–Tsuno correlation to our data are ludicrous in terms of the values of ρ and R. Such multiparameter correlations can be very misleading if the apparent ρ and R values are not examined critically.

(15) H. C. Brown and Y. Okamoto, *J. Amer. Chem. Soc.*, **80**, 4979 (1958).

(16) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Jap.*, **32**, 965 (1959).

(17) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, 1963, p 211; Y. Yukawa, Y. Tsuno, and M. Sawada, *Bull. Chem. Soc. Jap.*, **39**, 2274 (1966); A. P. G. Kieboom and H. Van Bekkum, *Recl. Trav. Chim. Pays-Bas*, **88**, 1424 (1969).

(18) X. Q. Huynh, Ph.D. Thesis, CNRS, no. AO 5884, Paris, June 1971, and references cited therein.

(19) (a) X. Q. Huynh and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 1436 (1968). (b) As seen here, there is no monotonic relationship between the Q ratio and the reactivity. This is additional evidence for the complexity of the mechanism of the attack by "tribromide ion." Detailed investigations of this problem have been published.[19c] For alkenes and allylic compounds, Dubois and Huynh show that a plot of reactivity $\log k_{Br_2}$ against the "catalytic coefficient B" ($B = a + 1/Q$, a being the additional term accounting for the medium salt effects) leads to a curve with inversion of slope. We have concluded that the term "$k_{Br_3^-}$" involves at least two competing mechanisms: electrophilic attack by Br_3^- on the substrate and nucleophilic assistance by Br^- of the dissociation of the charge transfer complex between bromine and olefin, the former mechanism acting predominantly at high olefin reactivity and the latter at low reactivity. (c) J. E. Dubois and X. Q. Huynh, *Tetrahedron Lett.*, 3369 (1971).

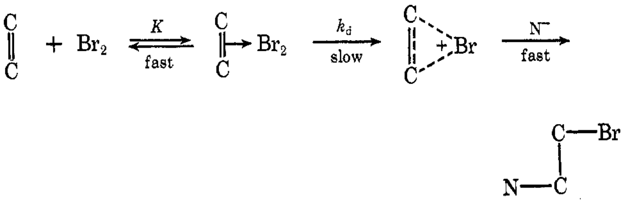
(20) F. Garnier and J. E. Dubois, *Bull. Soc. Chim. Fr.*, 3797 (1968).

TABLE I

RATE CONSTANTS FOR THE BROMINATION OF MONOSUBSTITUTED TRANS STILBENES

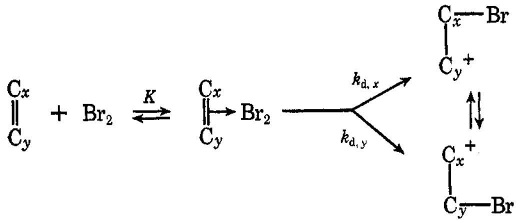
Registry no.	No.	X	k_2, M^{-1} min^{-1} [a]	Relative rates	Kinetic method[b]
838-95-9	**1**	p-NMe$_2$	2.2×10^8	6,850,000	A
6554-98-9	**2**	p-OH	8.5×10^5	26,000	B
1694-19-5	**3**	p-MeO	7.8×10^4	2,390	B
1860-17-9	**4**	p-Me	2.9×10^2	8.9	C
14064-48-3	**5**	m-Me	63	1.9	C
103-30-0	**6**	H	32.7	1.00	D
1657-50-7	**7**	p-Cl	7.8	0.23	E
13041-70-8	**8**	p-Br	8.2	0.25	E
14064-43-8	**9**	m-Cl	5.2	0.16	E
891-70-3	**10**	m-CF$_3$	3.4	0.104	E
1149-56-0	**11**	p-CF$_3$	2.5	0.076	E
1694-20-8	**12**	p-NO$_2$	1.05	0.032	E

[a] All rate constants measured in methanol (0.2 M NaBr) at 25° are averages of at least three determinations, with agreement between runs usually within 2%. [b] A, couloamperometry (ref 9); B, coulometric concentrostat (ref 10); C, potentiometry (ref 12); D, spectrometry (ref 11); E, amperometric titrations (ref 13).

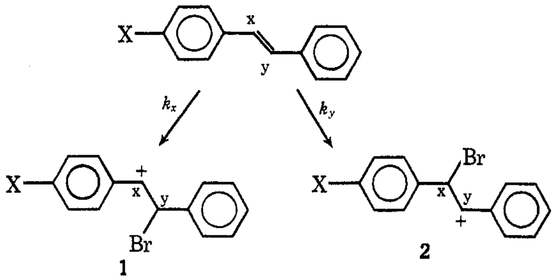


monium ion, the absence of accurate data[21] on the geometry and on the bond hybridization does not allow us to predict to what extent the entering bromine chooses between the two olefinic carbons. Kinetic results for such brominations, that of alkenes for instance,[22] have been interpreted without distinguishing the two carbons which act, to all intents and purposes, as a single center.

In brominations where the intermediate is postulated as a carbonium ion, the entering bromine must choose either one of two olefinic carbons for σ bonding. There exists, then, two modes of dissociation of the initial π complex, leading to two discrete intermediates. The occurrence of an equilibrium between the C_x^+ and C_y^+ ions cannot be deduced from the kinetic data, since this equilibrium modifies only the third step: fast nucleophilic attack of the solvent or the bromide anion.



For the interpretation of the structural effects, the simplified scheme is sufficient if the rate-determining step is not reversible. The irreversibility of this step has been shown by the effect of added bromide ion on the rate.[23] The rate dependence on bromide ion concentration is consistent with the formation of the less reactive Br$_3^-$, and it follows the usual equation: $k_g(1 + K[Br^-]) = a + b[Br^-]$.



$$k = k_x + k_y \qquad (1)$$

For a reaction at two independent centers,[24] the measured rate constant is the sum of two partial rate constants, k_x and k_y (k_x is the rate constant of the C_x path leading to the carbonium ion C_x^+). We assume[28] that each partial rate constant obeys the Hammett equation. Then, the effect of X, which may be directly conjugated to the incipient carbonium ion **1**, is expressed as $\rho_\alpha\sigma^+$; the effect of X on **2**, transmitted by CHBr, will be given by $\rho_\beta\sigma$. The reaction constant ρ_α represents the effect of the substituent on the ring in the α position with respect to the charged center, *i.e.*, the C_x atom in this case of monosubstituted stilbenes, and ρ_β for substituents in the β position. For the C_x path,

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(21) R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589 (1970).

(22) (a) J. E. Dubois and G. Mouvier, *Bull. Soc. Chim. Fr.*, 1441 (1968); (b) J. E. Dubois and E. Bienvenue-Goetz, *ibid.*, 2094 (1968).

(23) (a) P. D. Bartlett and D. S. Tarbell, *J. Amer. Chem. Soc.*, **58**, 466 (1936); (b) J. E. Dubois and F. Garnier, *Bull. Soc. Chim. Fr.*, 4512 (1967).

(24) Some examples of this type of reaction at two centers have been investigated; in particular, the protonation of azobenzenes,[25] examined by Jaffé and Wepster, where the difference between the two ρ values is so small that the $\rho\sigma$ relationship is approximately linear, and the reactions of N-phenylglycines[26] and 2,2′-bipyridyls[27] that their authors have not recognized as such.

(25) (a) H. H. Jaffé and R. W. Gardner, *J. Amer. Chem. Soc.*, **80**, 319 (1958); (b) M. A. Hoefnagel, A. Van Been, and B. M. Wepster, *Recl. Trav. Chim. Pays-Bas*, **88**, 569 (1969).

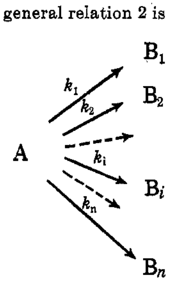
(26) A. Bryson, N. R. Davies, and E. P. Serjeant, *J. Amer. Chem. Soc.*, **85**, 1933 (1963).

(27) R. A. Jones, B. D. Roney, W. H. F. Sasse, and K. O. Wade, *J. Chem. Soc. B*, 106 (1967).

(28) This mechanistic scheme corresponds to a particular case of n competitive reactions whose rate constants, k_i for the ith reaction, depend on structural parameters p_i. The free-energy relationship which relates the overall reactivity, log k to the different structural parameters p_i, is a function such as

$$\log k = f(p_1, \ldots\ldots, p_n) \text{ with } k = \sum_{i=1}^{n} k_i \qquad (1)$$

If the partial reactivity for the ith reaction depends on the parameters p_i, $\log k_i = f_i(p_1, \ldots\ldots, p_n)$, the general relation 2 is inextricable.



$$\log k = \log \left[\sum_{i=1}^{n} \exp f_i(p_1, \ldots\ldots, p_n) \right] \qquad (2)$$

However, given, as is possible for the stilbene bromination, that the ith reaction depends on a single parameter, $\log k_i = f_i(p_i)$ (3), *i.e.*, postulating the structural independence of the reaction paths, the relation 2 becomes

$$\log k = \log[\exp f_1(p_1) + \exp f_2(p_2) + \ldots + \exp f_n(p_n)] \qquad (4)$$

Making the limits apparent, this equation is to be written

$$\log k = \sum \log k_i + \varphi(p_1, \ldots, p_n)$$

where φ is a nonlinear term which equals 0 when one of the partial rate constants predominates overwhelmingly.

$$\log (k_x/k_0) = \rho_\alpha \sigma^+ \quad (2)$$

$$\log (k_y/k_0) = \rho_\beta \sigma \quad (3)$$

the proper substituent constant is the Brown's σ^+, while for the C_y path, the substituent constant is the Hammett's σ. In the latter case, the substituted ring is insulated from the carbonium ion center by the bromomethylene group, hindering the transmission of most of the resonance effects. In the same way, it can be assumed that ρ_α is greater than ρ_β since the substituents are nearer the ionic center in the intermediate **1** than in the intermediate **2**.

With these assumptions, substituting 2 and 3 in eq 1, we developed the following relationship.

$$\log (k/k_0) = \log [(k_x + k_y)/k_0] = \log (10^{\rho_\alpha \sigma^+} + 10^{\rho_\beta \sigma}) \quad (4)$$

The solution of this equation, which relates nonlinearly the overall reactivities to the two structural parameters σ and σ^+, cannot be obtained directly. When $k_x \gg k_y$ or $k_y \gg k_x$, *i.e.*, when one of the exponential terms of the relationship 4 is negligible with respect to the other one, the reactivity becomes a linear function of a single parameter. Thus we can write the free-energy relationship in the form

$$\log (k/k_0) = \rho_\alpha \sigma^+ + \rho_\beta \sigma + \varphi(\sigma, \sigma^+)$$

where $\varphi = 0$ when one of the linear term $\rho_i \sigma_i$ predominates overwhelmingly. This nonlinear term does not express an interaction between k_x and k_y, but the fact that the partial rate constants are additive and not the free energies ($\log k \neq \log k_x + \log k_y$). This mathematical treatment of electrophilic additions with two carbonium ion intermediates requires two distinct transition states[29] for each path C_x and C_y. In extreme cases where $k_x \gg k_y$ or $k_y \gg k_x$, the reaction passes through a unique transition state since the other one is strongly disfavored, but, when k_x and k_y are in the same range, the two transition states coexist and there is not a single transition state whose charge would be distributed between the carbon centers. Thus this model for addition reactions is very similar to the electrophilic aromatic substitution[30] where partial rate constants for the ortho, meta, and para centers are derived from the overall rate constants, $k_g = 2k_o + 2k_m + k_p$. In these reactions, partial rate constants are measured from the overall rate constants and from the ratio of substitution products. Here we shall propose for addition reactions a treatment which makes possible the direct evaluation of partial rate constants from the overall rate constant only.

With a general relationship such as eq 4, the usual reactivity–structure diagram, $\log k = f(\sigma)$, is not really meaningful, since only for extreme cases does the reactivity depend on a single constant. In Figure 1, the reactivities of electron-releasing substituted stilbenes are plotted against σ^+ and that of electron-withdrawing ones against σ. The curve obtained in this way tends asymptotically to the straight lines log k_x and log k_y when σ^+ and σ are remote from zero. These asymptotes represent the partial free energies for each pathway C_x and C_y. At $\sigma = 0$, they intersect, while the experimental curve passes 0.3 l.u. beyond the intersection point, since at this point $10^{\rho_\alpha \sigma^+} = 10^{\rho_\beta \sigma} = 1$.

Reaction Constants, ρ_α and ρ_β, for the Bromination of Stilbenes.—In order to determine if the general free-energy relationship (eq 4) for the two-center reactions is suitable to the stilbene bromination in methanol, we must firstly evaluate the parameters ρ_α and ρ_β. ρ_α can be calculated from compounds for which k_x is the preponderant partial rate constant, *i.e.*, $\rho_\alpha \sigma^+ \gg \rho_\beta \sigma$ according to eq 2 and 3. This condition can be realized for strongly electron-releasing substituents where $\sigma^+ \gg \sigma$, if $\rho_\alpha - \rho_\beta$ is not very large. Conversely, ρ_β could be obtained from strongly electron-attracting substituents but only if $\rho_\alpha - \rho_\beta$ is sufficiently large, since for these $\sigma \simeq \sigma^+$. Then we have to determine for what substituents it is reasonable to assume the neglect of one of the two partial rate constants.

When the *trans*-β-methylstyrene is substituted by a *p*-methoxy group, the stereoselectivity, which measures the extent of bromine bridging, is entirely destroyed, even for the bromination in the apolar methylene chloride.[31] The intermediate is then a free benzylic carbonium ion. The similarity of the kinetic effect of this *p*-methoxy substituent on styrene, *trans*-β-methylstyrene, and stilbene (Table II) shows that the charges in the transition state are similar for the three compounds, *i.e.*, on the carbon atom in the α position with respect to the substituted ring. Therefore, when X = *p*-MeO and even more for *p*-hydroxy and *p*-dimethylamino, k_x is much greater than k_y and the experimental rate constant equals directly k_x so that the free-energy relationship becomes linear: $\log k_{exp} = \rho_\alpha \sigma^+ + \log k_0$. The σ^+ value for the *p*-dimethylamino group being uncertain,[15] ρ_α is only evaluated from compounds **2**, **3**, and **6**$_{corr}$. **6**$_{corr}$ corresponds to the unsubstituted stilbene (**6**) whose rate constant is corrected as follows. For this compound, k_x equals k_y. Then from eq 4, $k_0 = 0.5k_6 = k_{6corr}$. ρ_α obtained from these three compounds is in the range of -5.

TABLE II

IDENTITY OF THE KINETIC EFFECT OF THE *p*-METHOXY SUBSTITUENT ON THE BROMINATION OF AROMATIC OLEFINS, IN METHANOL (0.2 *M* NaBr) AT 25°

Compd	$\log (k_{MeO\text{-}4}/k_H)$
Styrene	3.20
trans-β-Methylstyrene	3.48
Stilbene	3.38

An estimation of ρ_β could be possible from ρ_α if the transmission factor for the bromomethylene group, CHBr, were known. In the bromination of alkenes[32] in methanol, the transmission factor of inductive effects

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(29) Another explanation for the nonlinearity of the free-energy relationship can be a continuous change in the structure of a single transition state rather than two discrete alternatives. In the latter case, for all the compounds the complete charge is localized on a unique atom and the substituent makes variable the relative importance of the C_x and C_y intermediates. If the reaction proceeds through a single transition state, the charge is distributed among the C_x and C_y atoms, the fraction of charge on each depending on the substituent. Such a situation would be different from a bromoniumlike transition state by the absence of charge on the bromine atom. At present, it is not possible either kinetically or by product analysis to distinguish between these possibilities: one or two transition states. It has turned out that the treatment in terms of competitive paths provides a satisfactory understanding of kinetics and product data, and we have preferred it on account of its simplicity.

(30) H. C. Brown and L. Stock, "Advances in Physical Organic Chemistry," V. Gold, Ed., Academic Press, New York, N. Y., 1963, p 55.

(31) R. C. Fahey and H. J. Schneider, *J. Amer. Chem. Soc.*, **90**, 4429 (1968).

(32) E. Bienvenue-Goetz, J. E. Dubois, D. W. Pearson, and D. H. Williams, *J. Chem. Soc. B*, 1275 (1970).

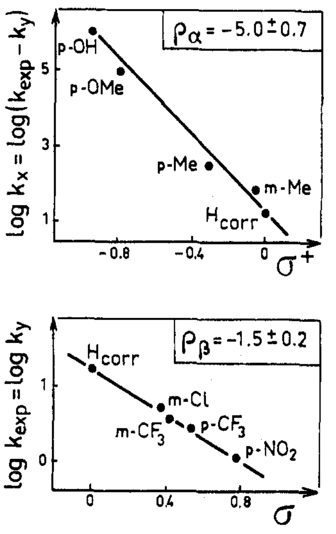

Figure 2.—Determination of the reaction constants.

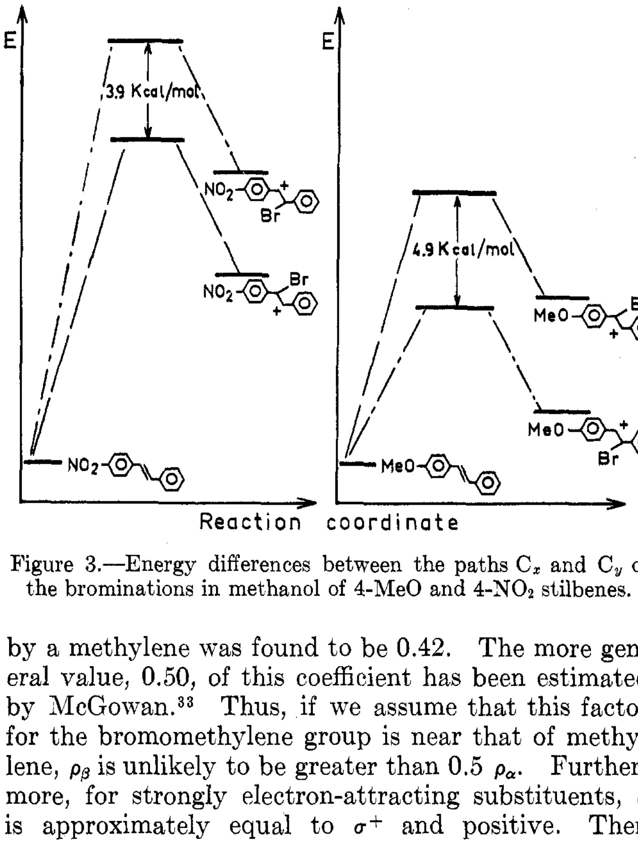

Figure 3.—Energy differences between the paths C_x and C_y of the brominations in methanol of 4-MeO and 4-NO$_2$ stilbenes.

by a methylene was found to be 0.42. The more general value, 0.50, of this coefficient has been estimated by McGowan.[33] Thus, if we assume that this factor for the bromomethylene group is near that of methylene, ρ_β is unlikely to be greater than 0.5 ρ_α. Furthermore, for strongly electron-attracting substituents, σ is approximately equal to σ^+ and positive. Then $\rho_\beta\sigma$, which is $\log k_y/k_0$, will not exceed the half value of $\rho_\alpha\sigma^+$, which is $\log k_x/k_0$. Since these logarithmic values are both negative, k_x can be neglected. For instance, if $\rho_\alpha = -5$, $\rho_\beta = -2.5$, for the *p*-trifluoromethyl stilbene, $k_x = 0.009$ and $k_y = 0.7$. From the compounds **9**, **10**, **11**, **12**, and $\mathbf{6}_{corr}$ (Figure 2), a precise value[34] of ρ_β (-1.5) is obtained by application of the equation $\log k_{exp} = \rho_\beta\sigma + \log k_0$. This value of ρ_β allows the calculation of k_y and $k_{x\ calcd} = k_{exp} - k_y$ for all the compounds; ρ_α is obtained[34] from compounds **2**, **3**, **4**, **5**, and $\mathbf{6}_{corr}$ using $\log k_{x\ calcd} = \rho_\alpha\sigma^+ + \log k_0$ (2′), $\rho_\alpha = 5.0$.

From these values of the two reaction constants ρ_α and ρ_β of each pathway, the partial rate constants k_x and k_y can be calculated from the general relationship, for all the stilbenes (Table III). The energy differences between the paths C_x and C_y, calculated from the equation $\Delta\Delta G^\ddagger = RT(\ln k_x - \ln k_y)$, give an approximate evaluation of the energy differences between the ions C_x^+ and C_y^+. The value obtained in this way is slightly underestimated, since the transition state is near the intermediate but not identical. For the ions derived from the *p*-methoxystilbene, the C_x^+ intermediate is favored by approximately 5 kcal/mol over the C_y^+ one in methanol. Conversely, for the *p*-nitrostilbene, the C_y^+ is more stable than the C_x^+ by about 4 kcal/mol (Figure 3). In another way, the respective values of k_x and k_y indicate the importance of paths C_x and C_y followed by each stilbene. Figure 4 shows how the importance of C_x and C_y depends on the value of σ_X^+ and σ_X, chosen as a convenient structure index.

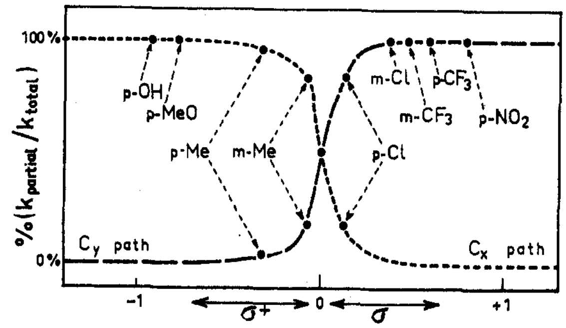

Figure 4.—Respective contribution of the C_x and C_y paths in the stilbene bromination.

TABLE III

CALCULATED OVERALL AND PARTIAL RATE CONSTANTS OF THE BROMINATION OF MONOSUBSTITUTED STILBENES

X	$\log k_x$[a]	$\log k_y$[a]	$\log k_{calcd}$[b]	Δ[c]
4-OH	5.78+	1.80	5.78 ± 0.6	−0.15
4-OMe	5.06+	1.65	5.06 ± 0.5	0.17
4-Me	2.69	1.50	2.73 ± 0.2	0.26
3-Me	1.48	1.35	1.72 ± 0.04	−0.08
H	1.13	1.24	1.49 ± 0.12	−0.02
4-Cl	0.55	0.87	1.05 ± 0.06	0.16
4-Br	0.37	0.87	1.00 ± 0.05	0.09
3-Cl	−0.90	0.67+	0.68 ± 0.07	−0.04
3-CF$_3$	−1.49	0.58+	0.58 ± 0.08	0.04
4-CF$_3$	−1.95	0.41+	0.41 ± 0.12	−0.02
4-NO$_2$	−2.81	0.05+	0.05 ± 0.16	0.02

[a] $\log k_x$ and $\log k_y$ calculated from eq 2 and 3. + This path predominates. [b] $k_{calcd} = k_x + k_y$. [c] Average $\Delta = \log k_{calcd} - \log k_{exp}$.

Partial Rate Constants and Regioselectivity Analysis.—Although the evaluation of ρ_α and ρ_β allows for accurate calculation of the overall rate constants, this agreement alone would not verify our initial hypothesis, since ρ_α is obtained from ρ_β, so that the linearity of eq 2′, $\log(k_x/k_0) = \rho_\alpha\sigma^+$, might only be due to the optimization of successive calculations. Thus a verification, independent of the kinetic data, must be found. As a consequence of the mathematical treatment, the relative importance of the C_x and C_y paths has been calculated (Figure 4). The reaction products derived from the nucleophilic attack of the solvent on the intermediates of each path must be different, since C_x leads to the carbonium ion **1** which, when trapped by methanol, is converted into a methoxybromo compound, a positional isomer of the other compound obtained by the C_y path. The regioselectivity, $\gg C_x$-OMe/

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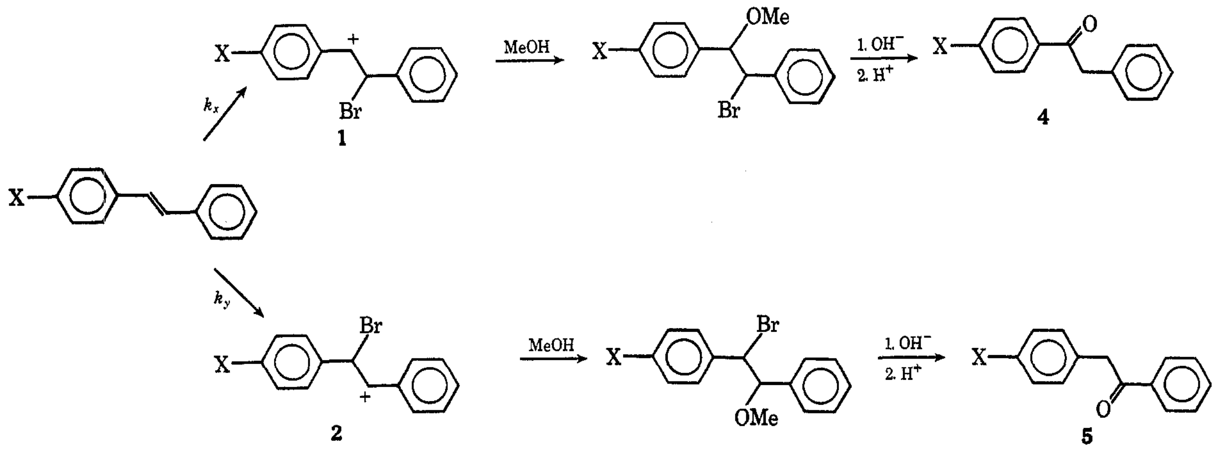
[33] J. C. McGowan, *J. Appl. Chem.*, **10**, 312 (1960).

[34] The correlation coefficients are 0.995 for ρ_α as well as for ρ_β. The absolute errors (t test) for a 95% confidence level are ±0.7 and ±0.2 for ρ_α and ρ_β, respectively.



$\gg C_y$-OMe, must be equal to the ratio k_x/k_y, provided that the ratio of methoxy bromides to dibromide is the same for C_x and C_y paths.[35a]

The regioselectivity was measured by chromatographic analysis of the two stable and known isomeric ketones **4** and **5**, derived from the methoxy bromides by successive treatment in basic and acidic media. The dibromide, which represents approximately 20 to 25% of the products,[23a] leads under these conditions to three compounds (tolane and dibromo olefins) whose retention times differ sufficiently from those of the ketones to produce no difficulty in the analysis.

The agreement between the ratio $k_x/(k_y + k_x)$ and the percentage of the C_x attack (Table IV) tends to confirm the validity of the initial hypothesis on two competitive paths in the rate-determining step. Moreover, since k_x and k_y measure directly the regioselectivity, either no equilibrium exists between the C_x and C_y intermediates, or the equilibrium constant is equal to k_x/k_y. Thus, from the regiochemical results, the question of the presence or the absence of an equilibrium between the two intermediates in the kinetic scheme can only be answered partially.

TABLE IV
AGREEMENT BETWEEN THE REGIOSELECTIVITY OF THE NUCLEOPHILIC ATTACK OF THE SOLVENT ON THE INTERMEDIATES AND THE RELATIVE IMPORTANCE OF THE C_x AND C_y PATHS

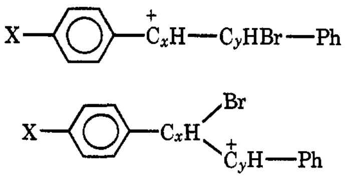
Stilbene	MeOH attack[a] on C_x, %	MeOH attack[a] on C_y, %	Partial rate constants[b] $k_x/(k_x + k_y)$, %	Partial rate constants[b] $k_y/(k_y + k_x)$, %
p-Me	97	3	95	5
p-Cl	34	66	35	65
m-Cl	0	100	0	100
m-CF_3	0	100	0	100

[a] Ratio of the ketones 4 and 5, measured by CPV after treatment of the bromination products; % C_x is measured to 2%. [b] Calculated from the results of Table III.

The regiochemistry also seems to confirm the carbonium ion structure of the intermediates. However, if the site of nucleophilic attack of the solvent on a carbonium ion is obvious, it is not possible to predict the regioselectivity of this attack on a bromonium ion which depends on the polar and steric effects of the substituents.[35b] Thus the agreement between the regioselectivity and the kinetic scheme does not necessarily imply the carbonium ion structure of the intermediates.

Structure of the Intermediates.—As a first approximation and to simplify the kinetic model, we have assumed that the intermediates of each pathway were carbonium ions. This assumption provides an accurate mathematical treatment of the kinetic data, but a more elaborate analysis must be carried out in order to determine the real structure of each intermediate, *i.e.*, to determine whether the bromine does or does not participate in the stabilization of the transition states and the intermediates.

The value of ρ_α, -5.0, is the same as that of many other reactions with benzylic carbonium ion intermediates: for example, methanolysis of *tert*-cumyl chlorides,[3] -4.8; bromination of styrenes, -4.3 in methanol,[1] -4.5 in acetic acid;[2] bromination of phenyl acetylenes,[36] -5.0. ρ_α tends to be reasonably accepted as the reaction constant for a bromination *via* an α-C_6H_4X carbonium ion intermediate. Concerning the value of ρ_β, -1.5, much lower than that of ρ_α, not enough is yet known to decide with the same certainty whether the intermediate of the C_y path is a β-aryl carbonium or bromonium ion, since the attenuation of the ρ value means mainly that the substituent and the charged center are more removed in the C_y path intermediate than in the C_x one.



In order to distinguish between the two possible structures of the C_y path intermediate, a comparison of these results on stilbene bromination with those obtained from reactions whose intermediate is a bromo-

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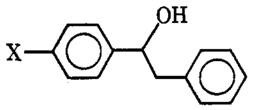
(35) (a) Obviously for a given pathway, if both intermediates are free carbonium ions, bromide ion attacks at the same site as methanol, independently of the magnitude of the ratio dibromide/methoxy bromide. However, if these ratios are different in each pathway, the overall regioselectivity would not be in agreement with the ratio k_x/k_y. The competition between bromide ion and methanol in attack of the bromination intermediate depends qualitatively[35b] on steric and inductive effects. Between attack on intermediate **1** or **2**, there is no difference in steric hindrance. Differences in inductive effects would be important only if the substituent is a strong electron donor or attractor. Since competition between intermediates **1** and **2** is possible only if the substituent is of weak electronic character (4-Me or 4-Cl), there are only small differences between inductive effects governing the competitive attack of bromide ion and methanol. This argument seems to be justified by the results (Table IV). (b) J. M. Chrétien, Ph.D. Thesis, CNRS, No. AO 5748, 1971, Orléans, France.

(36) J. A. Pincock and K. Yates, *Can. J. Chem.*, **48**, 3332 (1970).

nium or a β-aryl carbonium ion should be sought for more informations.

For the bromination of alkenes where a bromonium intermediate is strongly established,[35,37] a reaction constant ρ^* is reported:[20] ρ^* (bromonium) = -3.05. An analogous correlation between the reactivities of the stilbenes from which ρ_β has been obtained and the Taft's σ^* of the aryl groups[38] gives a $\rho_\beta^* = -2.63$, a value fairly near this ρ^* (bromonium). This agreement only confirms that the charge and the substituent are in the same relative position, *i.e.*, in β position, in the bromination of alkenes and in that of stilbenes substituted by strongly electron-attracting groups.

For anchimerically unassisted reactions whose intermediates are β-aryl carbonium ions, reaction constants are found to be near -1.00: *e.g.*, acetolysis of 1-aryl 2-propyl tosylates,[39] -0.71; solvolysis in aqueous ethanol of benzyl dimethyl carbinyl chlorides,[40] -1.11. A better analogy for stilbene bromination is to be found in the acid-catalyzed dehydration of 1,2-diaryl ethanols[41] where the rate-determining step is the formation of the olefin from carbonium ions derived from 1-aryl 2-phenyl ethanols **7** and 1-phenyl 2-aryl ethanols **8**.



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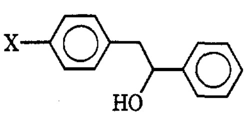

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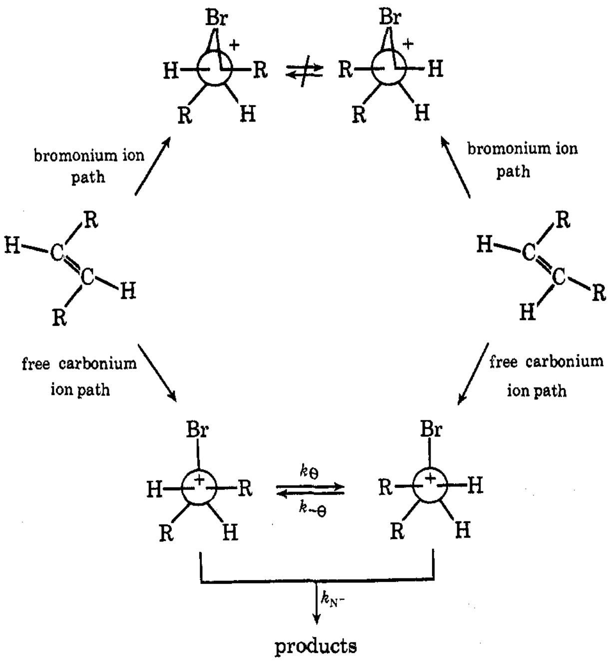
Thus in dehydration the two ions, α-aryl and β-aryl carbonium ions, are generated in independent reactions and there does not exist any ambiguity regarding the significance of the structural effects. The rate constants for the reaction of the alcohols **7** are correlated by σ^+ ($\rho_7^\alpha = -3.77$) and these for the alcohols **8** by σ ($\rho_8^\beta = -1.00$). The similarity of the transmission factors $\rho_8^\beta/\rho_7^\alpha = 0.27$ for dehydration and $\rho_\beta/\rho_\alpha = 0.30$ for bromination could provide support for a free carbonium structure in the C_y path of the bromination, as in dehydration of alcohols **8**. However, since numerous parameters of the two reactions are very different,[42] this agreement may be fortuitous and may signify only that the charge is localized on the β atom with respect to the substituted ring.

It is evident that, with ρ values alone, it is impossible to argue conclusively that bromine bridging is absent in the transition state leading to the C_y intermediate.

However, in methanol, as we have already noted, a carbonium structure is to be preferred, owing to the stereochemical results.[8] Moreover, the regiospecificity of the 3-CF_3 stilbene, which reacts only *via* the C_y path, cannot be clearly understood in terms of a bromonium ion. Regiospecificity is observed for a bromonium ion[33] only when bulky groups bounded to an olefinic carbon atom prevent the nucleophilic attack on this site. In stilbenes, the steric hindrance does not vary, and it is unlikely that polar effects alone could be so powerful as to direct entirely the opening of a bridged ion.

The stereoselectivity of the reaction provides generally better evidence for intermediate structure. A bromination *via* a bromonium ion must be stereospecific (100% anti adduct), but *via* a free carbonium ion the syn/anti adduct ratio depends on the relative rates of rotation of the ion, k_θ, and of the attack of the nucleophile, k_{N^-}, or on the conformational equilibrium if $k_\theta \gg k_{N^-}$. Approximate measurements of this dependence can be obtained from the ratio of syn/anti products derived from the pair of cis and trans olefins which lead to the same intermediate when free from bromine bridging.[2] For the unsubstituted cis and trans stilbenes, this measure has been carried out in several solvents.[8] It appears that, for the trans stilbene, the syn adduct goes from 5% when the intermediate is nearest the bromonium (in carbon disulfide) to 20% only for the nearest free carbonium ion (in methyl trichloroacetate). The relative rates, k_θ and k_{N^-}, or the equilibrium constant, $K_\theta = k_\theta/k_{-\theta}$, are such that the form **9**, which would be also the locked conformation of the bromonium ion, is preferred. The stereoselectivity of the attack on a bromonium ion is, therefore, very similar to that on a carbonium ion. Thus the stereochemical investigation of any dependence of



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

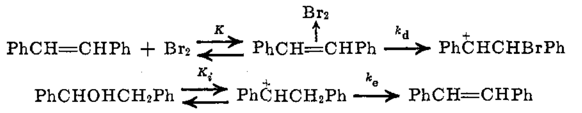
(38) R. W. Taft, "Steric Effects in Organic Chemistry," S. M. Newman, Ed., Wiley, New York, N. Y., 1956, p 556.

(39) C. J. Lancelot and P. Von Ragué Schleyer, *J. Amer. Chem. Soc.*, **91**, 4291 (1969).

(40) A. Landis and C. A. Van der Werf, *ibid.*, **80**, 5277 (1958).

(41) D. S. Noyce, D. R. Hartter, and F. B. Miles, *ibid.*, **90**, 3794 (1968).

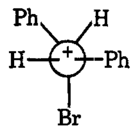
(42) The intervention of a preequilibrium step in the two reactions makes composite the experimental rate constants, $k_{\mathrm{exp}}^{\mathrm{bromat}} = Kk_{\mathrm{d}}$ and $k_{\mathrm{exp}}^{\mathrm{dehydr}} = K_ik_e$. In bromination it has been claimed[21] that the structural effects af-



$$\mathrm{PhCH{=}CHPh} + \mathrm{Br_2} \underset{}{\overset{K}{\rightleftharpoons}} \mathrm{PhCH}\overset{\overset{\mathrm{Br_2}}{\uparrow}}{=}\mathrm{CHPh} \xrightarrow{k_{\mathrm{d}}} \mathrm{Ph\overset{+}{C}HCHBrPh}$$

$$\mathrm{PhCHOHCH_2Ph} \overset{K_i}{\rightleftharpoons} \mathrm{Ph\overset{+}{C}HCH_2Ph} \xrightarrow{k_e} \mathrm{PhCH{=}CHPh}$$

fect essentially the preequilibrium step. In dehydration, substituent effects on the deprotonation of the carbonium ion would lead to a positive reaction constant; since the global ρ is negative, these effects would act essentially also on the preequilibrium step. Thus, if the structural effects are operative on the nonrate-determining first step rather than on the step involving the formation or the destruction of the carbonium ions, comparison of ρ values may be unsuitable to determine the structure of the C_y path intermediate. Moreover, the reaction media are very different, aqueous sulfuric acid in one case, methanol in the second. However, this latter difference can be minimized in comparing preferentially to the ρ values, the ratios $\rho_8^\beta/\rho_7^\alpha$ and $\rho\beta/\rho\alpha$, which represent the damping factors for the transmission of substituent effects by methylene or bromomethylene groups, respectively.



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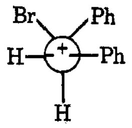

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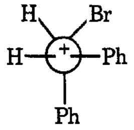

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the structure of the intermediate upon substituent character would necessitate the analysis of small variations of the syn/anti ratio and the measurement of conformational equilibria of the carbonium ions C_x^+ and C_y^+, from pairs of cis- and trans-substituted stilbenes.

To avoid this tedious stereochemical analysis for the determination of the structure of the C_y path intermediate, we have investigated another more direct method, extending the two competitive path scheme to the treatment of bromination kinetics of stilbenes with substituents in both rings. The results of this study will be presented in a forthcoming paper.

However, even if the structure of one of the two intermediates cannot be clearly defined, it appears from this analysis of the bromination of trans-monosubstituted stilbenes in methanol that a two competitive path mechanism leads to a rational approach of the addition reactions at two discrete centers.

Experimental Section

Synthesis of Stilbenes.—Trans-unsubstituted stilbene and the *p*-hydroxy stilbene are commercially available. The other stilbenes were prepared by methods F, G, H, and K (Table V), described below.

TABLE V

SYNTHESIS OF MONOSUBSTITUTED STILBENES

X	Synthesis method	Mp, °C	Ref
p-NMe$_2$	F	149–150	*b*
p-OH	*a*	192–193	*c*
p-OMe	G	137	*d*
p-Me	F	120	*d*
m-Me	F	47–48	*e*
H	*a*	125	*f*
p-Cl	F	130	*g*
p-Br	F	140	*d*
m-Cl	H	73–74	*h*
m-CF$_3$	H	66–67	*i*
p-CF$_3$	H	132–133	*i*
p-NO$_2$	J	155–156	*c*

[a] Commercially available. [b] M. Syz and H. Zollinger, *Helv. Chim. Acta*, **48**, 517 (1965). [c] H. Veschambre and A. Kergomard, *Bull. Soc. Chim. Fr.*, 336 (1966); 2846 (1967). [d] Reference 45. [e] J. I. G. Cadogan, E. G. Duell, and P. W. Inward, *J. Chem. Soc.*, 4165 (1962). [f] W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, **463**, 116 (1928). [g] Reference 43. [h] F. Bergmann, J. Weizman, and D. Shapiro, *J. Org. Chem.*, **9**, 408 (1944). [i] C. S. Wood and F. B. Mallory, *ibid.*, **29**, 3373 (1964).

Method F.—The aryl benzyl carbinols were prepared by condensation of benzylmagnesium chloride with the substituted benzaldehyde, as described by House.[43] The subsequent dehydrations were made with phosphoric anhydride in cold benzene.

$$C_6H_5CH_2MgCl + XC_6H_4CHO \longrightarrow C_6H_5CH_2CHOHC_6H_4X$$

$$C_6H_5CH_2CHOHC_6H_4X \xrightarrow{P_2O_5} C_6H_5CH{=}CHC_6H_4X$$

Method G.—*trans-p*-Methoxystilbene was obtained from *trans-p*-hydroxystilbene by methylation with dimethyl sulfate in aqueous alkali solution following the conventional procedure.[44]

Method H.—The aryl diazonium salts were condensed with styrene in the presence of cupric chloride as described by Tashckuk and Dombrovskii[45] and led to the aryl phenyl chloroethanes, which were dehydrohalogenated in pyridine to the corresponding stilbenes.

$$XC_6H_4N_2Cl + C_6H_5CH{=}CH_2 \longrightarrow XC_6H_4CH_2CHClC_6H_5$$

$$XC_6H_4CH_2CHClC_6H_5 \xrightarrow{\text{pyridine}} XC_6H_4CH{=}CHC_6H_5$$

Method J.—*trans-p*-Nitrostilbene was obtained by decarboxylation of the *p*-nitrophenylcinnamic acid.[46]

Kinetic Method.—The stilbenes were purified by column chromatography on alumina with petroleum ether (bp 40–65°) or mixtures of benzene and petroleum ether and by further recrystallizations in appropriate solvents. Purity was checked by thin layer chromatography.

Methanol and sodium bromide were treated as previously described.[22]

Five kinetic methods were used to measure the rate constants: couloamperometry[9] for constants greater than 10^6 l. mol^{-1} min^{-1}; coulometric concentrostat[10] for constants in the range 10^3–10^6 l. mol^{-1} min^{-1}; potentiometry[12] for constants in the range 30–10^3 l. mol^{-1} min^{-1}; spectrometry[11] for the parent stilbene; amperometric titrations[13] for the rate constants between 1 and 15 l. mol^{-1} min^{-1}.

Measurement of the Q Ratio.—The second-order rate constants were measured at various sodium bromide concentrations (Table VI). The values of $k_g[1 + K\,(\mathrm{Br}^-)]$, where K is the tribromide equilibrium constant (177 in methanol at 25°[23b]), were plotted against (Br$^-$), the bromide ion concentration. The slope of the linear regression equals $Kk_{\mathrm{Br}_3^-}$, and the intercept is k_{Br_2}.

TABLE VI

(NaBr), M	k_g, l. mol^{-1} min^{-1} 4-NMe$_2$	 4-NO$_2$	 H[a]
0.2	224 × 10^6	1.05	32.7
0.1	316 × 10^6	1.34	48.5
0.05	426 × 10^6	1.91	78.2
k_{Br_2}	312 × 10^7	11.9	655
Q	20	17	43

[a] Reference 23b.

Measurements of the Regioselectivity.—A slight excess (10%) of bromine was added to 200 ml of a solution of stilbene (10^{-3} M) in methanol, 0.2 M NaBr. This solution was kept over 1 hr or one night, depending on the rate of the bromination. After removal of the most of the solvent under reduced pressure at room temperature, the solution was diluted with water and extracted carefully with ether. The extracts were washed with a hyposulfite solution and then with water. After evaporation of ether, 100 ml of a 5% methanolic sodium hydroxide solution was added to the residue and the solution was refluxed for 3 hr and then cooled. The solution was concentrated under vacuum to about 50 ml, and acidified with 1 M sulfuric acid. The acidic solution was kept for 1 hr and extracted with three portions of 50 ml of ether. The organic layer was washed with water, dried, concentrated, and analyzed by vpc. The analysis was carried out on a Varian AE 1400 apparatus, on a 10 ft 10% SE-30 at 180–200° depending on the nature of the substituent. Ketones, tolan, and bromo olefins were identified by comparison of their retention time with those of authentic samples. Quantitative results were obtained from areas of the peaks after standardizing the response of the detector. The values of Table IV are the average values of three experiments. The error is about 2%.

The bromination experiments can be carried out in excess of stilbene and the dehydrohalogenations can be made by adding the alkali solution directly to the reduced solution of the bromination.

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[43] H. O. House, *J. Amer. Chem. Soc.*, **77**, 3070 (1955).

[44] G. S. Hiers and F. D. Hager, "Organic Syntheses," Collect. Vol. I, Wiley, New York, N. Y., 2nd ed, 1941, p 58.

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However, in this way stilbene is present in the product mixtures and the chromatographic analysis is consequently less accurate, because its retention time is similar to that of the corresponding ketones.

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Steric Crowding in Organic Chemistry. II. Spectral and Conformational Properties of Highly Substituted Phenylcarbinols[1]

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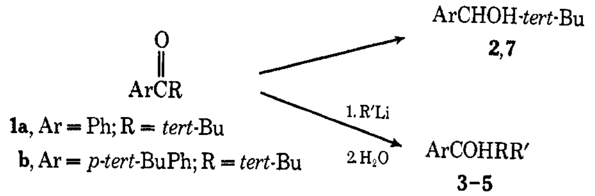
A series of highly substituted aryl carbinols ArCOHRR′ (**2–14**) has been prepared. The hydroxyl stretching frequencies of the alcohols in CCl_4 were measured and, although multiple bands were observed in some cases, the spectra were interpreted in terms of a predominant conformation with the oxygen in the plane defined by the carbinol carbon and the aromatic ring. The first overtone of the hydroxyl stretching frequency in the near-infrared showed the same multiple bands. The downfield chemical shift of the hydroxyl protons on addition of DMSO was examined. The magnitude of this shift was smaller in the more crowded compounds. The ρ values for the effect of para substituents on the chemical shifts are about 0.5 for all series examined and are insensitive to the size of attached groups. The effect of tris(dipivalomethanato)europium on the chemical shifts was examined, and the shifts of the aromatic protons were correlated with the distance and angle dependence of the pseudocontact shift equation. The geometries of the Eu complexed alcohols were interpreted in terms of a predominant conformation with a coplanar arrangement of the aryl-C-O-Eu atoms.

α-Phenylcarbinols display multiplicity in their hydroxyl stretching frequencies in the infrared which has been interpreted in terms of the conformations of the molecules.[3] The nmr chemical shift of the hydroxyl proton of phenylcarbinols in dimethyl sulfoxide (DMSO) solution has also been used as a probe for examining the structures of the carbinols,[4] and the nmr spectra of α-aryldi-*tert*-butylcarbinols have been related to their conformational properties.[5]

The present investigation was designed to examine the role of very bulky substituents on the spectroscopic properties of α-arylcarbinols. The accompanying paper[6] considers the spectral properties and reactivity of ferrocenylcarbinols. The reactivity of the aryl compounds will be presented elsewhere.[7]

Results

A series of highly substituted arylcarbinols (**2–5**, **7**) were prepared by reduction, or by addition of the appropriate alkyllithium to *tert*-butyl aryl ketones (**1a**, **b**) (Table I).



Phenyldi-*tert*-butylcarbinol (**6**) was prepared by the addition of phenyllithium to di-*tert*-butyl ketone to minimize 1,6-conjugate addition to the para position of **1a**, a reaction often observed in the reaction of **1a** with organometallic reagents.[3e,8] Similarly, phenyl-*tert*-butylneopentyl- and phenyldineopentylcarbinols (**8** and **9**) and their derivatives having a para substituent on the phenyl ring (**10–14**) were prepared by the addition of the corresponding aryllithium to *tert*-butyl neopentyl and dineopentyl ketones, respectively.

Hydroxyl stretching frequencies for the alcohols were measured for CCl_4 solutions and are summarized in Table I. The frequencies for compounds **2–7** were measured for 0.4 and 0.04 *M* solutions. At the higher concentration intramolecular hydrogen bonds around 3500 cm^{-1} could also be observed for **2–4**. The frequencies for compounds **8–15** were measured for 0.004 *M* solutions. The frequency reported for **6** is somewhat improved over that reported previously.[3e] Compound **6** also showed near-infrared absorption frequencies at 7117 and 7060 cm^{-1} with relative intensities 5 and 3, respectively, for either 0.13 *M* or 0.03 *M* solutions in CCl_4.

The nmr spectral parameters of the carbinols in various solvents are also given in Table I. The influence of the concentration of DMSO in CCl_4 on the hydroxyl chemical shift of **2** is given in Table II. Plots of the hydroxyl chemical shifts of the para-substituted aryldineopentylcarbinols and the aryl-*tert*-butylneopentylcarbinols in DMSO *vs.* the σ parameters of the substituents were linear, with ρ values of 0.50 and 0.47, re-

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