Young and Trahanovsky.[17] Comparison samples of products **1**, **3**, and **4** and 2,5-dihydrofuran were obtained commercially.

Reaction Procedures. The apparatus and techniques used for the reactions of hydrocarbons with O(^{3}P) have been described previously.[3] Reactions were run to less than 25% completion to avoid secondary oxidation of products. A high ratio of nitrous oxide to diene reactant (>25) was used in all reactions. Under these reaction conditions, no products of the direct[18] or mercury-sensitized[19] photorearrangement of the diene were observed (0.3% conversion could have been detected). The product composition from the reaction of 1,3-butadiene with O(^{3}P) is not affected by the duration of photolysis.[4]

During photolysis, a thin, pale-yellow polymer formed on the surface of the immersion lamp. Irradiation of a mixture of nitrogen (586 Torr), 1,3-butadiene (24 Torr), and mercury vapors resulted in the loss of 2% of the butadiene by polymerization on the lamp.

Vpc analysis of the product mixture from the reaction of 1,3-butadiene was performed by injection of gas-phase aliquots onto either a 5-ft column of 10% dinonyl phthalate or an 11-ft column of 20% tricresyl phosphate in polyethylene tubing at 25°. Double vpc purification of individual products gave samples of >98% purity.

Spectra of products **1**, **3**, and **4** closely corresponded to spectra of authentic commercial samples of these compounds. Spectrometric data on 3-butenal (**2**) include ir (vapor phase) 3110, 3020, 2910, 2830, 2740, 1740, 1645, 1405, 1300, 1125, 990, and 915 cm^{-1}; uv (vapor phase) λ_{max} 300 mμ (ϵ 22); nmr ($CDCl_3$ solvent) 0.21 (1 H, triplet, J = 1.8 Hz), 3.9–5.0 (3 H, multiplet), 6.8 (2 H, multiplet); mass spectrum (70 eV) m/e (rel intensity) 70 (54), 69 (9), 42 (88), 41 (100), 40 (53), 39 (96), 38 (34), 29 (60), 27 (60), 26 (19); high-resolution mass spectrum of parent peak, observed mass 70.0421 (calcd for C_4H_6O, 70.0418).

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Registry No.—**1**, 930-22-3; **2**, 7319-38-2; 1,3-butadiene, 106-99-0.

References and Notes

(1) Part II: J. J. Havel, W. T. Chamberlain, and P. M. Krautter, *J. Amer. Chem. Soc.*, **96**, 632 (1974).
(2) R. J. Cvetanovic, *J. Chem. Phys.*, **23**, 1203 (1955).
(3) J. J. Havel, *J. Amer. Chem. Soc.*, **96**, 530 (1974).
(4) R. J. Cvetanovic and L. C. Doyle, *Can. J. Chem.*, **38**, 2187 (1970).
(5) K. S. Sidhu, E. M. Lown, O. P. Strausz, and H. E. Gunning, *J. Amer. Chem. Soc.*, **88**, 254 (1966).
(6) A. Tsukamota and N. N. Lichtin, *J. Amer. Chem. Soc.*, **84**, 1601 (1962).
(7) R. J. Cvetanovic, *Advan. Photochem.*, **1**, 115 (1963).
(8) S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73**, 531 (1973).
(9) An authentic sample of **9** was available for comparison of vpc retention times.
(10) L. D. Hess and J. N. Pitts, Jr., *J. Amer. Chem. Soc.*, **89**, 1973 (1967).
(11) Corrected for the natural abundance of isotopes, for monodeuterated and undeuterated butadiene in the starting material, and for H_2CO^+. In the relevant mass region, the relative intensities of the ions of 3-butenal obtained from unlabeled 1,3-butadiene follow: m/e (rel intensity) (12), 29 (100), 30 (2.8), and 31 (7.2). The relative intensities of the ions of 3-butenal from the reaction of **10** follow: m/e (rel intensity) 28 (12), 29 (100), 30 (7.0), and 31 (7.1). These intensities include only ions containing one oxygen and one carbon atom plus hydrogen(s) or deuterium. Ions of corresponding mass containing two carbon atoms plus hydrogen(s) or deuterium(s) were resolved from the carbon–oxygen ions (the mass difference is $\geq$0.034 amu).
(12) H. C. Volger and W. Brackman, *Recl. Trav. Chim. Pays-Bas*, **84**, 1017 (1965).
(13) C. A. McDowell and S. Sifniades, *J. Amer. Chem. Soc.*, **84**, 4604 (1962).
(14) F. G. Ponomarev and E. A. Vodopyranova, *Nauch. Dokl. Vyssh. Shk., Khim. Khim. Tekhnol.*, 316 (1959).
(15) D. Craig and R. B. Fowler, *J. Org. Chem.*, **26**, 713 (1961).
(16) R. T. Hobgood and J. H. Goldstein, *J. Mol. Spectrosc.*, **12**, 76 (1964).
(17) L. B. Young and W. T. Trahanovsky, *J. Mol. Spectrosc.*, **32**, 2349 (1967).
(18) R. Srinivasan, *J. Amer. Chem. Soc.*, **85**, 4045 (1962).
(19) R. Srinivasan and S. Bone, *Tetrahedron Lett.*, 203 (1970).

Multipathway Bromination of Stilbenes. Competition between Carbonium and Bromonium Ion Intermediates

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A recent thermodynamic–kinetic approach to the transition state structure of the electrophilic bromination of olefins[1] leads to the conclusion that tensions in the ground state are preserved or even enhanced in the activated complex whatever the structure, bromonium or carbonium, of the intermediate. Therefore, it was proposed that bridged transition states are involved in all cases and that they lead to either bridged or open cationic intermediates. These results prompt us to report an extension of our study on the bromination of substituted stilbenes[2] which confirms that carbonium ion like and bromonium ion like transition states differ in their charge distribution.

We have shown elsewhere[2] that the bromination of stilbenes, $XC_6H_4C_xH{=}C_yHC_6H_4Y$, in methanol is a dual-path addition leading competitively to carbonium ions C_x^+ and C_y^+ through transition states where the charge is on one of the olefinic carbon atoms, without significant participation of the bromine atom. In this note, we investigate a new series of substituted stilbenes to determine how bromine participation modifies the carbonium pathway mechanism and to measure the differences between carbonium and bromonium ion like transition states. To establish the carbonium ion mechanism, we had selected stilbenes where one substituent at least was electron donating, favoring thus charge development on the benzylic carbon atom, α to the donor ring. Here, we attempt to determine whether bromonium ions occur in the bromination of stilbenes where both rings contain deactivating groups which disfavor formation of benzyl cations.

Bromination rate constants for X,Y-disubstituted stilbenes where X and Y are both electron attracting are given in Table I. The elementary rate constants for molecular bromine addition, k_{Br_2}, were measured in methanol at 25° either by the conventional method[3] (kinetic effects of the bromide ion concentration) or by an empirical equation established previously.[2a]

The reactivities of the deactivated stilbenes are first calculated as if the addition proceeds *via* the dual-path mechanism: the overall rate constant is the sum of the two partial rate constants k_x and k_y. Each partial rate constant follows the two-parameter equation $\log (k_x/k_0) = \rho_\alpha\sigma_X^+ + \rho_\beta\sigma_Y$ (eq 1) and $\log (k_y/k_0) = \rho_\alpha\sigma_Y^+ + \rho_\beta\sigma_X$ (eq 2), where ρ_α and ρ_β are −5.07 and −1.41, respectively. Comparison of the calculated and experimental values (Table II) reveals that the two carbonium ion scheme is inadequate for strongly deactivated stilbenes and that these latter react more rapidly than expected by the dual-carbonium path mechanism.

Bromonium Ion Intermediates. The attenuation of the effects of strongly electron-attracting substituents can most reasonably be interpreted in terms of an increase in the substituent–charge distance, so that the charge is on the bromine atom, *i.e.*, the transition states resemble bromonium ions **3**. In this case, the two substituents X and Y should have identical kinetic effects and there should be a linear free energy relationship between the reactivities, log k, and the sum of the Hammett constants: $\log k = \rho_{Br^+}(\sigma_X + \sigma_Y) + \log k_0'$. For the four stilbenes which deviate most

Table I
Bromination Rate Constants of Stilbenes Substituted by Strongly Electron-Attracting Groups

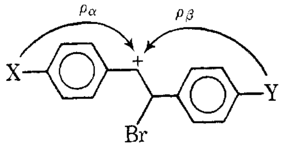
No.	X	Y	k_{exptl},[a] l. mol^{-1} min^{-1} 0.2 *M*	0.1 *M*	0.05 *M*	0.025 *M*	k_{Br_2}[c]	$k_{Br_3^-}$	Log k_{Br_2}[d]
1	*p*-NO_2	*m*-CF_3	0.18	0.22	0.32		1.8	0.13	0.25
2	*p*-NO_2	*m*-Cl	0.15	0.20	0.25		1.6	0.11	0.21
3	*p*-NO_2	*p*-Cl	0.34						0.60[e]
4	*p*-NO_2	H[b]	1.05	1.30	1.90		11.9	0.64	1.07
5	*m*-CF_3	*m*-CF_3		0.30	0.40	0.65	3.0	0.16	0.48
6	*m*-CF_3	H[b]	3.4						1.70[e]
7	*m*-Cl	*m*-Cl	0.40						0.70[e]
8	*m*-Cl	*p*-Cl[b]	1.80						1.40[e]
9	*m*-Cl	H[b]	5.2						1.90[e]

[a] Experimental rate constants measured in methanol at various sodium bromide concentrations at 25°. [b] Rate constants previously obtained (ref 2). [c] Elementary rate constants obtained by extrapolation to zero bromide ion concentration using the equation $k_g[1 + K(Br^-)] = k_{Br_2} + Kk_{Br_3^-}(Br^-)$.[3] [d] The precision of the experimental rate constants smaller than 1 is only 8–10%. The error on the extrapolated value can be in the range of 20%. However, the structural effects are discussed on the reactivities log k_{Br_2} and not on the rate constants. A maximum error of 30% on k_{Br_2} would lead to an error of 0.3 l.u. on log k_{Br_2}. Thus, variations of log k_{Br_2} smaller than 0.3 l.u. are not significant. [e] These values are obtained by extrapolation from empirical relationships between $(\log k_{exptl})_{0.2\,M\,NaBr}$ and log k_{Br_2}. For experimental rate constants higher than 1, there exists a linear relationship established in ref 2a. For smaller constants, the extrapolation has been made in each subpopulation with X constant and Y variable: for the *p*-nitro Y-substituted stilbenes, $(\log k_{exptl})_{0.2\,M\,NaBr} = 0.97 \log k_{Br_2} - 1.02$ ($r = 0.999$, $s = 0.007$); for *m*-chloro Y-substituted stilbenes, $(\log k_{exptl})_{0.2\,M\,NaBr} = 0.90 \log k_{Br_2} - 1.01$ ($r = 0.999$, $s = 0.0003$). This method leads to extrapolated elementary rate constants whose precision is of the same order as that of the experimental values.

markedly from the dual-path mechanism predictions (Table II, compounds 1, 2, 5, and 7), eq 3 is valid.

$$\log k = -1.0(\sigma_X + \sigma_Y) + 1.3 \qquad (3)$$

Although the correlation coefficient is only fair ($r = 0.96$, $s = 0.038$), deviations of the defining compounds from eq 3 are small, less than 0.1 l.u. (Compare Tables I and III). However, the errors on ρ_{Br^+} and log k_0' of eq 3 are about 0.5. Therefore, we can consider that the value of ρ_{Br^+} is rather similar to ρ_β (−1.4), which is the reaction constant for the substituent Y on the ring β to the carbonium ion **1**.



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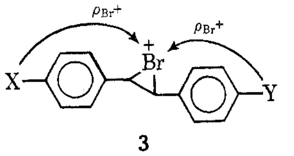


3

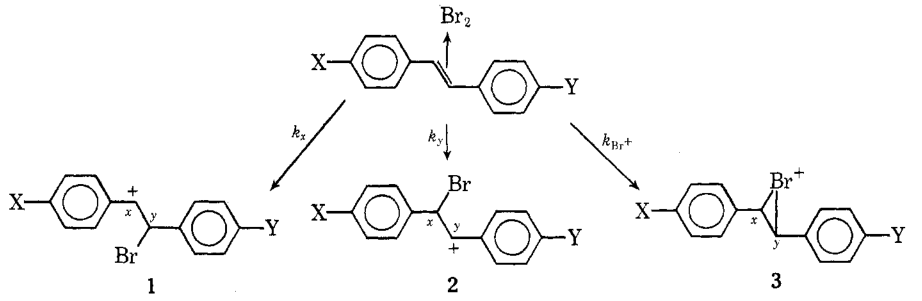
This is expected, since the substituents X and Y are in the same position with respect to the charge in the ion **3** as the substituent Y is in the ion **1**. In contrast, the values of log k_0 in eq 1 and 3, corresponding to the bromination of the unsubstituted stilbene *via* carbonium or bromonium ion intermediates **1** and **3**, are significantly different, +2.2 and +1.3, respectively.

Table II
Failure of the Carbonium Ion Mechanism for Strongly Electron-Attracting Stilbenes

No.	Log k_x[a]	Log k_y[a]	Log k_{calcd}	Δ log k[b]
1	−2.39	−1.54	−1.54	−1.80
2	−2.32	−0.90	−0.90	−1.10
3	−2.12	0.57	0.57	−0.07
4	−1.80	1.10	1.10	0.03
5	−1.06	−1.06	−0.76	−1.20
6	−1.60	1.61	1.61	−0.10
7	−0.36	−0.36	−0.06	−0.75
8	0.15	1.10	1.10	−0.30
9	−0.17	1.68	1.68	−0.20

[a] These values are calculated from eq 1 and 2 with $k_{calcd} = k_x + k_y$ (see ref 2a). [b] $\Delta \log k = \log k_{calcd} - \log k_{exptl}$.

General Scheme for the Bromine Addition to Aromatic Conjugated Olefins. The structure–reactivity relationships for bromination *via* bromonium ions and carbonium ions correspond to a scheme in which each type of intermediate is generated in a discrete pathway and imply thus three distinct transition states where the charge is either developed on the carbon atom C_x, on the atom C_y, or on the bromine atom. This description is rather different from the generally accepted mechanism[4] which features a single intermediate[5] with the charge distributed more or less equally between the three atoms. The multipathway scheme is, however, a good mathematical description of the results, whereas kinetic treatment of the usual model is im-



$\log k_x/k_0 = \rho_\alpha\sigma_X^+ + \rho_\beta\sigma_Y$ $\log k_y/k_0 = \rho_\alpha\sigma_Y^+ + \rho_\beta\sigma_X$ $\log (k_{Br^+}/k_0') = \rho_{Br^+}(\sigma_X + \sigma_Y)$

$\underbrace{\hspace{6cm}}$ carbonium ion mechanism

$\underbrace{\hspace{3cm}}$ bromonium ion mechanism

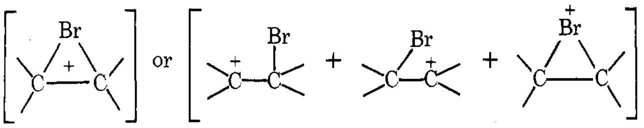
$$k = k_x + k_y + k_{Br^+}$$

Table III
Competition between Bromonium and Carbonium Ion Pathways in Stilbene Bromination

				Elementary calculated reactivities			Predominant intermediate[e]			Overall calculated and experimental reactivities	
Registry no.	No.	X	Y	Log k_x[a]	Log k_y[a]	Log k_{Br^+}[b]	C_x^+	C_y^+	Br^+[f]	Log k_{calcd}[c]	Δ[d]
51751-38-3	1	p-NO$_2$	m-CF$_3$	−2.90	−2.05	+0.15			+	0.15	+0.10
51751-39-4	2	p-NO$_2$	m-Cl	−2.86	−1.31	+0.20			+	0.20	+0.01
3757-16-2	3	p-NO$_2$	p-Cl	−2.64	+0.14	+0.34		+	+	0.55	+0.05
4003-94-5	4	p-NO$_2$	H	−2.27	+0.75	+0.57		+	+	0.96	+0.25
27892-96-2	10	p-NO$_2$	m-Me	−2.15	+1.13	+0.64		+	+	1.25	+0.20
7560-35-2	11	p-NO$_2$	p-Me	−1.99	+2.42	+0.74		+		2.42	−0.14
1472-68-0	12	p-NO$_2$	p-OMe	−1.83	+4.96	+0.84		+		4.96	−0.01
51751-40-7	5	m-CF$_3$	m-CF$_3$	−1.47	−1.47	+0.51			+	0.51	−0.03
28495-61-6	6	m-CF$_3$	H	−0.80	+1.33	+0.93		+	+	1.47	+0.24
3240-26-4	7	m-Cl	m-Cl	−0.75	−0.75	+0.61			+	0.61	−0.10
51751-41-8	8	m-Cl	p-Cl	−0.53	+0.80	+0.75		+	+	1.08	+0.32
24942-77-6	9	m-Cl	H	−0.16	+1.41	+1.00		+	+	1.55	+0.24
51751-42-9	13	m-Cl	p-Me	+0.11	+3.08	+1.15		+		3.08	−0.07
5415-08-7	14	m-Cl	p-MeO	+0.27	+5.62	+1.25		+		5.62	+0.13
5121-74-4	15	p-Cl	p-Cl	+1.02	+1.02	+0.89	+	+	+	1.46	+0.28
4714-23-2	16	p-Cl	H	+1.39	+1.63	+1.12	+	+	+	1.89	+0.18
22692-73-5	17	p-Cl	p-Me	+1.66	+3.30	+1.30		+		3.30	−0.13
5043-91-4	18	p-Cl	p-MeO	+1.82	+5.84	+1.40		+		5.84	+0.03
588-59-0	19	H	H	+2.00	+2.00	+1.30	+	+	+	2.34	+0.33
28495-59-2	20	m-Me	H	+2.38	+2.11	+1.42	+	+		2.60	+0.30
4714-21-0	21	p-Me	H	+3.67	+2.27	+1.52	+	+		3.69	−0.03

[a] Calculated by eq 1′ and 2′. [b] Calculated by eq 3. [c] $k_{calcd} = k_x + k_y + k_{Br^+}$. [d] $\Delta = \log k_{exptl} - \log k_{calcd}$. [e] Owing to imprecision of the bromonium equation (eq 3), we give only the nature of the intermediate, although the relative importance of each intermediate could be calculated by $(k_x \times 100)/(k_x + k_y + k_{Br^+})$ for C_x^+ and similarly for C_y^+ and Br^+. [f] Br^+ is the bromonium ion.

possible in the absence of a quantitative relationship between charge magnitude and the ρ value.[9]



However, the equivalence of the two descriptions is questionable only in borderline cases where several pathways compete. This does not discredit our conclusion regarding the differences between carbonium and bromonium ion-like transition states, since there are compounds (1, 2, 11, 12, 13, 14, or 17 of Table III) whose bromination passes through only one transition state which can be either **1**, **2**, or **3**.

Competition between Bromonium and Carbonium Ion Pathways. Since we have now identified a discrete pathway for bromonium ion formation, we shall examine the competition between bromonium and carbonium ion pathways. From data for stilbenes with at least one electron-donating substituent, we had concluded that bromine participation was unimportant. However, substituent effects on the bromonium ion pathway are weaker than on the carbonium ion one, since ρ_α (−5.0) is considerably higher than ρ_{Br^+} and the existence of pathway 3 could have been neglected in the carbonium treatment. We have, therefore, reexamined the previous data[2b] and recalculated the parameters of the carbonium ion mechanism from the elementary rate constants k_{Br_2} of only those stilbenes with at least one strongly electron-donating substituent, namely, p-hydroxy, p-methoxy, or p-methyl. In this way, we obtain the following equations ($r = 0.981$, $s = 0.005$).

$$(\log k_x)_{Br_2} = -5.4\sigma_X^+ - 1.6\sigma_Y + 2.00 \quad (1')$$

$$(\log k_y)_{Br_2} = -5.4\sigma_Y^+ - 1.6\sigma_X + 2.00 \quad (2')$$

The parameters ρ_α and ρ_β, −5.4 and −1.6, are approximately identical with those obtained previously, −5.1 and −1.4, respectively. From eq 1′, 2′, and 3, we have calculated the relative importance of each pathway for a number of stilbenes (Table III). Differences between experimental and calculated overall rates are also given only for guidance, since the bromonium equation (eq 3) is too rough to allow any quantitative conclusion. For the same reasons, we give only the structure of the existent intermediate and not the exact value of its contribution. The results confirm the predominance of the carbonium and bromonium mechanism for stilbenes with strongly electron-donating (11, 12, 13, 14, 17, and 18) or electron-attracting groups (1, 2, 5, and 7), respectively. For some electron-attracting substituents (3, 4, 8, 9, 15, and 16), the bromonium ion pathway competes with the carbonium one. This intervention does not lead to significant accelerations with respect to the carbonium ion predictions. Typical examples are given by the p-nitro- or p-nitro-m'-methylstilbenes,for which the neglect of the third pathway induces an error on the reactivity of about 0.2 l.u. In the same way, it must be noted that for stilbene itself, the results of Table III indicate a slight preference for the carbonium ion pathway. However, the difference between calculated and experimental reactivities is particularly high. Therefore, we can only assume that this compound is a borderline case for which carbonium and bromonium intermediates are of comparable stability.

In short, once parameters for the linear free energy relationship describing reactivity in the absence of assistance have been determined with precision, it is possible to discern cases where there are significant deviations and to determine the parameters of the assisted reaction. Thereafter, the small contribution of the assisted pathway can be calculated for compounds previously considered to be unassisted. It turns out that these small contributions for an assisted pathway do not affect the linearity of the original equation. The long controversy[12] on the assistance or absence of assistance by the phenyl ring in solvolysis of secondary tosylate, PhCH$_2$CH(OTs)CH$_3$, has been largely settled by an extensive investigation of substituent effects,[10] which has revealed that there is, in fact, competition between the two mechanisms and that the importance of assistance depends on the ring substituent.

Our results concerning substituent effects on the forma-

Table IV

Stilbene X	Y	Mp, °C
p-NO$_2$	m-CF$_3$[a]	123
p-NO$_2$	m-Cl[b]	118
p-NO$_2$	p-Cl[b]	185
m-CF$_3$	m-CF$_3$[c]	112
m-Cl	m-Cl[d]	95

[a] *Anal.* Calcd: C, 61.43; H, 3.41; N, 4.77. Found: C, 61.08; H, 4.09; N, 5.40. [b] Reference 15. [c] *Anal.* Calcd: C, 60.76; H, 3.18. Found: C, 61.25; H, 3.52. [d] D. E. Bissings and A. J. Speziale, *J. Amer. Chem. Soc.*, **87**, 2683 (1965).

tion of carbonium and bromonium ion intermediates in stilbene bromination show that the transition states which lead to these intermediates are significantly different in their charge distributions. This confirmation of our previous work is apparently contradictory with the arguments of Yates, *et al.*,[1] who proposed a single transition state structure regardless of the intermediate. In reality, the thermokinetic data signify only that the magnitude of the interactions is retained or slightly increased in passing from the initial to the transition states, *i.e.*, no rotation occurs at this stage.[13] In our opinion, bromine bridging is not the only explanation consistent with strain conservation; counterion effects, interactions between the C–Br bond and the p orbital,[14] or some compensation of substituent–substituent interactions of the ground state by the bromine–substituent interactions of the transition state cannot as yet be excluded.

Experimental Section

Synthesis of Stilbenes. The p-nitro, Y-substituted stilbenes (Table IV) were prepared by condensation of Y-substituted benzaldehydes with p-nitrophenylacetic acid in the presence of piperidine.[15]

The di-m,m'-trifluoromethyl-and di-m,m'-chlorostilbenes were synthesized by pyrolysis of azines obtained from benzaldehydes and hydrazine.[16]

Kinetic Measurements. The bromination rate constants were measured in methanol at 25° for various bromide ion concentration by amperometric titration, as described previously.[17]

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References and Notes

(1) K. Yates and R. S. McDonald, *J. Org. Chem.*, **38**, 2465 (1973).

(2) (a) M. F. Ruasse and J. E. Dubois, *J. Org. Chem.*, **37**, 1770 (1972); (b) J. E. Dubois and M. F. Ruasse, *ibid.*, **38**, 493 (1973).

(3) J. E. Dubois and F. Garnier, *Bull. Soc. Chim. Fr.*, 4512 (1967); J. E. Dubois and X. Q. Huyñh, *Tetrahedron Lett.*, 3369 (1971).

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

(5) The term "bromonium" is generally used to name this delocalized intermediate[6] so that bromonium ions are usually classified as nonclassical ions.[7] In fact, the "onium" suffix refers to species in which cationic charge is developed on a defined atom: carbonium, oxonium ions, for example.[8]

(6) R. D. Bach and H. F. Henneike, *J. Amer. Chem. Soc.*, **92**, 5589, (1970); G. A. Olah and P. J. Szilagyi, *J. Org. Chem.*, **36**, 1121 (1971).

(7) J. G. Traynham, *J. Chem. Educ.*, **40**, 392 (1963); S. Winstein, E. Grunwald, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **70**, 821 (1948).

(8) H. Perst, "Oxonium Ions," Academic Press, New York, N. Y., 1971, p 8.

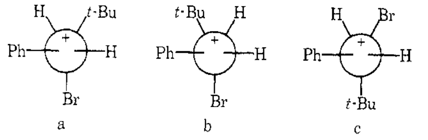
(9) An identical problem exists for the solvolysis of secondary systems where the assistance by a neighboring aryl group is possible: the widely accepted[10] scheme of Winstein[11] implies two discrete transition states for the assisted and unassisted pathways.

(10) C. J. Lancelot and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4291, 4296 (1969); C. J. Kim and H. C. Brown, *ibid.*, **91**, 4286, 4287, 4289 (1969).

(11) E. F. Jenny and S. Winstein, *Helv. Chim. Acta*, **41**, 807 (1958); A. Diaz, I. Lazdins, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 6546 (1968).

(12) H. C. Brown, K. J. Morgan, and F. J. Chloupek, *J. Amer. Chem. Soc.*, **87**, 2137 (1965); D. J. Cram, *ibid.*, **86**, 3767 (1964).

(13) The discussion of Yates, *et al.*, is based on comparison of thermodynamic parameters of ground and transition states, for cis and trans pairs of olefins selected as models for carbonium or bromonium ion intermediates. The conclusions for the carbonium ion brominations are inferred from stilbenes and β-*tert*-butylstyrenes. Our results for stilbene itself strenghten doubts expressed by Yates as to the free carbonium structure of the intermediate. The β-*tert*-butylstyrenes are sterically congested both in the initial state and in the intermediate. Conformational analysis of the intermediate reveals that the bromine–phenyl and *tert*-butyl–phenyl interactions are high for all conformations. In particular, rotation in b, which is directly generated from the cis olefin, requires eclipsing of the phenyl ring with bromine or *tert*-butyl, involving thus a nonnegligible energy barrier.



(14) A. R. Lyons and M. C. R. Symmons, *J. Amer. Chem. Soc.*, **93**, 7330 (1971).

(15) H. Veschambre and A. Kergomard, *Bull. Soc. Chim. Fr.*, 336 (1966).

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

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

On the Absolute Configuration of Two *trans*-p-Menthane-2,3-diols

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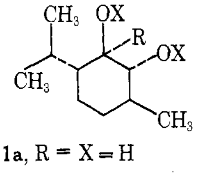
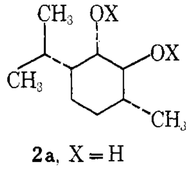
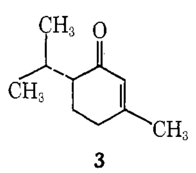
In order to determine the absolute configuration of substituted benzene dihydrodiols obtained in small quantities from enzymatic reactions,[1] it is necessary to employ spectroscopic methods rather than chemical correlations. We have recently applied the dibenzoate chirality rule of Nakanishi[2] (DCR) to ascertain the absolute configuration of a substituted *cis*-cyclohexane-1,2-diol and have verified this assignment by X-ray analysis.[3] Although the dibenzoate chirality rule has been applied to a wide variety of compounds,[2] its extension to the monocyclic *trans*-cyclohexane-1,2-diol system has not previously been reported. The diols **1a** and **2a** were selected for this study, since they can be prepared by hydroboration[4] of piperitone (**3**) whose absolute stereochemistry is known and therefore provides a check of the dibenzoate chirality rule.



1a, R = X = H
b, R = D; X = H
c, R = H; X = COPh



2a, X = H
b, X = COPh



3

Although Klein and Dunkelblum[4] had assigned the relative stereochemistry of **1a** and **2a** from 60-MHz nmr spectra and mechanistic consideration, their published data for **2a** were inconclusive.[5] In our hands, the absorption for carbinol hydrogens in **2a** at 60 MHz overlapped and could not be analyzed. However, these absorptions were separated in the 220-MHz nmr spectrum and the coupling constants so determined (Table I) confirmed the assigned configurations

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