or chloroform solution, even of the most reactive substrates studied, *viz.*, 1-(*p*-methoxyphenyl)-1-phenylethylene, gives substitution products, *e.g.*, 1,1-diphenyl-2-bromoethylene from 1,1-diphenylethylene, in high yield.[36] In the methanolic solvent used in the present study, some solvent attack (giving methoxy bromo products) is conceivable, but would not alter the observed kinetics or conclusions. Dibromination, either at the 1 position or in the aromatic ring, was not apparent in any case (all the reactants followed clean second-order kinetics); moreover, the 2-bromo substituent (in the product) deactivated the olefin greatly to electrophilic attack; 2-bromo-1,1-diphenylethylene was brominated under the conditions used to study the kinetics approximately 10^5 times less rapidly than the parent 1,1-diphenylethylene.

Registry No.—1,1-Di-*p*-fluorophenylethylene, 6175-14-0.

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[36] P. Peiffer and R. Wiziner, *Justus Liebigs Ann. Chem.*, **461**, 132 (1928).

Bromination of 1,1-Diphenylethylenes. II. Resonance Saturation and Geometrical Effects on the Reactivity of Multiply Substituted Derivatives[1,2]

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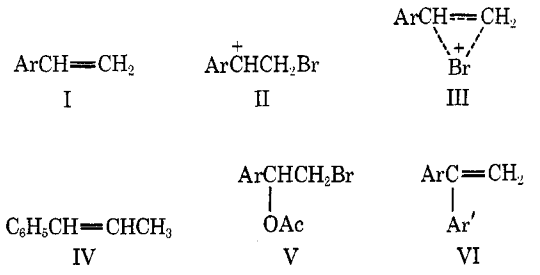
The substituent effects for multiple substitution on the kinetics of bromination of 1,1-diarylethylenes are not additive and exhibit apparent saturation of π-electron resonance stabilization. The majority of the rate constants can, however, be correlated, using a single reaction constant, by the linear parametric equation $\log k/k_0 = \rho(\sigma^+ + \sigma)$, with $\rho = -3.26$ and $\log k_0 = 3.169$. This is tantamount to postulating an unsymmetrical transition state in which one of the aryl rings remains planar and conjugated with the developing carbonium ion, the other ring (of necessity due to steric restriction) lying out of this plane. This equation is rigorously tested with 32 meta- and para-substituted diarylethylenes varying in reactivity by 7 powers of 10 (in MeOH at 25°). An alternative transition state in which both aryl rings are equally inclined to the plane of the carbonium ion proves less exact. A more detailed treatment, to include data for compounds which deviate from the above modified Hammett equation, requires that the presence of a substituent in one of the aryl rings also changes the ρ value for substituent variation in the second ring. The varying ρ's thus obtained for the bromination of 1-(substituted phenyl)-1-arylethylenes are -2.27 (substituent = *p*-MeO); -3.03 (*p*-Me); -3.57 (H); -3.67 (*p*-Br); -3.42 (*m*-Me); -3.69 (*m*-MeO); -4.08 (*m*-Cl); -4.65 (*m*-NO_2). The ρ values are proportional to the σ^+ of the substituent which is held constant. A similar multiple ρ treatment is found also to be applicable to data for the solvolysis of benzhydryl chlorides.

Recent studies by Yates and Rolston[4,5] and by Fahey and Schneider[6] have conclusively demonstrated that the electrophilic bromination of styrene derivatives I involves open benzylic-type carbonium ions II rather than cyclic bromonium ion intermediates III, as had previously been supposed. Thus bromination of *cis*- and *trans*-1-phenylpropene (IV) is nonstereoselective, both in carbon tetrachloride[6] and acetic acid solvents,[4] although the trans adduct is favored under most conditions. In acetic acid, solvent attack gives exclusively 1-acetoxy-2-bromo (V), rather than 1-bromo-2-acetoxy, products.[4] Kinetic evidence also supports this conclusion, since the ρ values for the bromination of styrenes (-4.21 in acetic acid[5] and -4.30 in methanol)[7] are comparable to those commonly reported for α-phenylcarbonium ion formation (as in the solvolysis of carbinyl chlorides, where $\rho = -4.54$.)[8] Similar evidence has been presented[9] to support the existence of open-chain vinyl cationic species in the bromination of phenyl acetylenes.



$ArCH{=}CH_2$ I; $Ar\overset{+}{C}HCH_2Br$ II; III; $C_6H_5CH{=}CHCH_3$ IV; V; VI

This polarization of charge in the transition state would be expected to be far greater in the bromination of 1,1-diarylethylenes (VI). However, the rate enhancement reported on the introduction of one phenyl ring at the double bond (*i.e.*, styrene *vs.* ethylene) is greater (130-fold) than that for the introduction of the second aryl ring: 1,1-diphenylethylene is brominated only *ca.* 25 times more rapidly than styrene.[10] Clearly, part of this difference is due to the inability of the two aryl rings to be simultaneously coplanar with the double bond in VI (or in the carbonium ion formed from VI, which would have a similar sp^2 hybridized carbon center). However, the overall effect is an apparent "saturation" of resonance stabilization by the phenyl ring. Most reported cases of such saturation also involve substituents placed in such di- or triarylcarbonium ions[11-13] or carbanions.[14] It is of interest therefore to examine diphenylethylenes in which both aryl rings are substituted to discover whether simple geometric effects

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[1] Part I: J. E. Dubois, A. F. Hegarty, and E. D. Bergmann, *J. Org. Chem.*, **37**, 2218 (1972).

[2] Some of the results presented here have been reported in communication form: E. D. Bergmann, J. E. Dubois, and A. F. Hegarty, *Chem. Commun.*, 1616 (1968); J. E. Dubois and W. V. Wright, *Tetrahedron Lett.*, 3101 (1967).

[3] (a) Chemistry Department, University College, Cork, Ireland; (b) 1851 Postdoctoral Fellow, 1967–1968; (c) NATO Postdoctoral Fellow, 1965–1966; (d) The Hebrew University of Jerusalem, Israel.

[4] J. H. Rolston and K. Yates, *J. Amer. Chem. Soc.*, **91**, 1469, 1477 (1969).

[5] J. H. Rolston and K. Yates, *ibid.*, **91**, 1483 (1969).

[6] R. C. Fahey and H. J. Schneider, *ibid.*, **90**, 4429 (1968).

[7] J. E. Dubois and A. Schwarz, *Tetrahedron Lett.*, 2167 (1964).

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

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

[10] J. E. Dubois and A. Schwarz, *C. R. Acad. Sci.*, **259**, 2227 (1964).

[11] J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1962, p 100.

[12] S. Nishida, *J. Org. Chem.*, **32**, 2697 (1967).

[13] E. Berliner and M. Q. Malter, *ibid.*, **33**, 2595 (1968).

[14] L. D. McKeever and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 4544 (1966).

alone can account for the nonadditivity, using as a basis for normal behavior the ρ value previously obtained unequivocally for the monosubstituted compounds[1] under the same conditions.

Results and Discussion

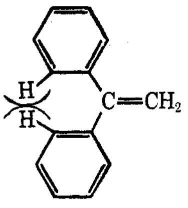
The rate constants for the bromination of disubstituted 1,1-diarylethylenes are summarized in Table I.

TABLE I
RATE CONSTANTS FOR THE BROMINATION OF SUBSTITUTED 1,1-DIARYLETHYLENES, $XC_6H_4C(=CH_2)C_6H_4Y$, IN METHANOL AT 25°

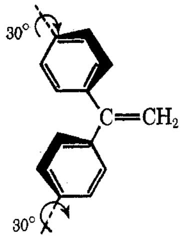
	Substituents		k_{obsd},
Compd	X	Y	l. mol^{-1} sec^{-1}
1	*p*-MeO	*p*-MeO	3.47×10^6
2	*p*-MeO	*p*-Me	9.73×10^5
3	*p*-MeO	*m*-Me	5.57×10^5
4	*p*-MeO	*p*-Br	1.07×10^5
5	*p*-Me	*p*-Me	9.83×10^4
6	*p*-MeO	*m*-Cl	5.03×10^4
7	*p*-MeO	*m*-Br	5.02×10^4
8	*p*-Me	*m*-Me	2.70×10^4
9	*p*-Me	*p*-F	9.93×10^3
10	*p*-MeO	*m*-NO_2	8.13×10^3
11	*p*-MeO	*p*-NO_2	7.31×10^3
12	*m*-Me	*m*-Me	6.45×10^3
13	*p*-Me	*p*-Br	4.12×10^3
14	*m*-MeO	*m*-MeO	1.31×10^3
15	*p*-F	*p*-F	1.23×10^3
16	*p*-Me	*m*-Br	8.80×10^2
17	*p*-Me	*m*-Cl	7.20×10^2
18	*m*-Me	*m*-F	1.83×10^2
19	*p*-Me	*m*-NO_2	1.28×10^2
20	*p*-Cl	*p*-Cl	1.27×10^2
21	*p*-Br	*p*-Br	1.03×10^2
22	*m*-MeO	*m*-Br	6.35×10
23	*m*-Cl	*m*-Cl	2.87

These constants, together with those previously reported for the monosubstituted 1-phenyl-1-arylethylenes,[1] cannot be correlated by plotting log k against any one one of the available sets of σ constants, *e.g.*, the σ^+ values proposed for electrophilic side chain reactions,[8] or ordinary Hammett σ values.[15] When either of these σ scales are used, curved plots with wide scatter of the points are obtained. Moreover, it is clear that the rate enhancements resulting from the combined effects of two substituents is not equal to the sum of the effects of the two substituents acting independently. This is most clearly seen by comparing the rate enhancements brought about by mono- and symmetrical disubstitution by the same substituent group (*e.g.*, *p*-MeO). This observed nonadditivity may be attributed to a combination of two major factors: (a) the geometry of the system and (b) the saturation of electronic effects in multiply substituted compounds.

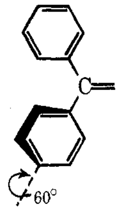
A. Stereochemical Factors.—In 1,1-diphenylethylene (VII) it is not possible, because of interactions between the ortho hydrogens, for the two rings to lie in the plane of the double bond. From studies of the dipole moments of this system, Coates and Sutton[16] concluded that a conformation VIII in which the two rings were rotated out of the plane of the double bond by equal angle of *ca.* 30° (a propeller-like conformation) was the most stable; the repulsions between the ortho hydrogens in VII were then balanced by the decrease in resonance energy resulting from further rotation. More recently Casalone and Simonetta[17] have calculated an angle of rotation of *ca.* 35° for each ring from crystal studies on 1,1-di-(*p*-nitrophenyl)ethylene. These general concepts have since been confirmed by other studies using a variety of techniques on this[18,19] and other similar systems,[20] *e.g.*, benzophenones,[21] thiobenzophenones,[22] and tetraphenylcumulenes.[23] However, this structure VIII is not unequivocally established, since most of the data would also agree with a conformation (or a rapidly equilibrating mixture of conformations) in which one of the rings remains conjugated with the double bond, the other ring being twisted out of this plane by an angle greater than 60° (IX). Because of the similarity of the two ultraviolet absorptions of 1,1-diphenylethylene (at 251 and 224 mμ in 95% ethanol) with those of styrene and simple unconjugated phenyl, Jones[24] proposed that 1,1-diphenylethylene had this perpendicular-planar structure IX. Further investigations using 2-methyl-substituted 1,1-diphenylethylenes, however, led Suzuki[25] to conclude that the rings were equally twisted, since the 2-methyl groups could be accommodated (and this is true only for VIII) without a large difference in the position of absorption. This conclusion in favor of VIII is also supported by the observation of a single nmr signal (even at −90°) for the two olefinic protons of 1,1-diphenylethylene;[19] on this basis, if we assume that the two rings are not equivalent, then interconversion between them must be rapid.



VII



VIII



IX

The energy difference between the two conformations (estimated assuming that the fractional reduction in resonance interaction due to the rotation of a phenyl ring out of coplanarity by an angle ϕ is, to a first approximation, related to $\cos^2 \phi$)[26] is not very great in the initial diphenylethylene. However, it may be critical in the transition state of the bromination reaction where the greater requirements of the stabiliza-

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[15] D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

[16] G. E. Coates and L. E. Sutton, *J. Chem. Soc.*, 567 (1942).

[17] G. Casalone and M. Simonetta, *J. Chem. Soc. B*, 1181 (1971).

[18] M. Simonetta and S. Carra, *Tetrahedron, Suppl.* **2**, **19**, 467 (1963).

[19] R. van der Linde, O. Korver, P. K. Korver, P. J. van der Haak, J. U. Veenland, and T. J. de Boer, *Spectrochim. Acta*, **21**, 1893 (1965); M. Rabinovitz, I. Agranat, and E. Bergmann, *Israel J. Chem.*, **7**, 795 (1969).

[20] I. I. Schuster, A. K. Colter, and R. J. Kurland, *J. Amer. Chem. Soc.*, **90**, 4679 (1968).

[21] J. Barassin, G. Queguiner, and H. Lumbroso, *Bull. Soc. Chim. Fr.*, 4707 (1967).

[22] O. Korver, J. U. Veenland, and T. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, **81**, 103 (1962).

[23] H. Fischer and W. D. Hell, *Angew. Chem., Int. Ed. Engl.*, **6**, 954 (1967).

[24] R. N. Jones, *J. Amer. Chem. Soc.*, **65**, 1818 (1943); O. Korver, J. U. Veenland, and T. H. de Boer, *Recl. Trav. Chim. Pays-Bas*, **84**, 806 (1965).

[25] H. Suzuki, *Bull. Chem. Soc. Jap.*, **33**, 619 (1960).

[26] B. M. Wepster in W. Klyne and P. B. D. de la Mare, "Progress in Stereochemistry," Vol. 2, Butterworths, London, 1958, pp 102, 122.

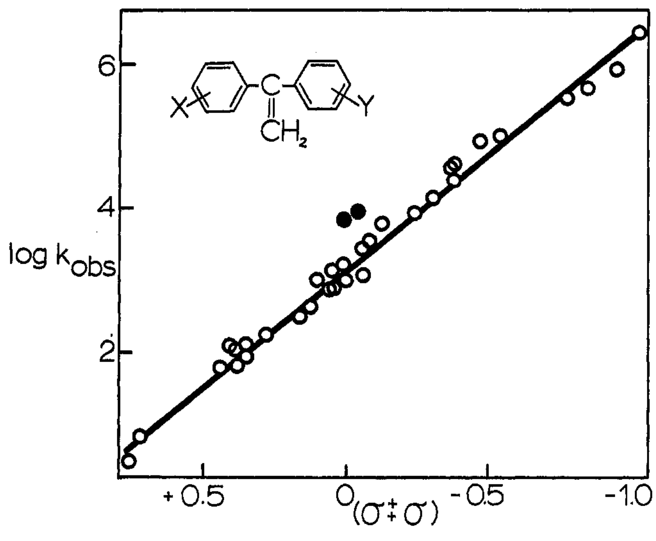

Figure 1.—Plot of log k for the bromination of 1,1-diarylethylenes in MeOH at 25° *vs.* $(\sigma^+ + \sigma)$, assuming a perpendicular–planar structure (IX) for the transition state. The σ^+ value is applied to all monosubstituted compounds (data from ref 1), and in disubstituted compound to the substituent with the largest $\Delta\sigma^+$ value. The two points (●) refer to data for 1-(p-methoxyphenyl)-1-(m- and p-nitrophenyl)ethylene (see text).

tion of a carbonium ion are involved, since it has been demonstrated[27] that, while inductive effects of substituents are transmitted with about equal effect regardless of the angle of twist ϕ, resonance effects are critically dependent on this angle, reaching a maximal value when the π orbitals of the phenyl ring and the vacant p orbital of the carbonium ion can best overlap.

Two simple approaches, 1 and 2, have been used to examine how closely the transition states of the bromination reactions can be related to the prependicular–planar (IX) and equally rotated (VIII) structures.

(1) The ratios log $k_{\mathrm{MeO}}/k_{\mathrm{H}}$ and log $k_{(\mathrm{MeO})_2}/$log k_{MeO} are 2.35 and 0.97, respectively, and are approximately proportional to the σ^+ and σ values of the MeO group. This suggested an approach in which the kinetic data were correlated by assigning a σ^+ value to the substituent in all monosubstituted compounds and a σ value to the second substituent in a disubstituted compound. This assumes that the substituted ring in the transition state has a sufficiently important resonance interaction with the charged center that it aligns to permit optimal orbital overlap. The other ring, therefore, because of steric interactions, remains out of the plane sufficiently (at an angle >60°) so that there is essentially no resonance interaction between substituents in this ring and the reaction center. Application of this simple treatment, *viz.*, $\log k = \rho\,(\sigma^+ + \sigma) + \log k_0$, gives an excellent relationship with $\rho = -3.26$, $r = 0.995$, $s = 0.596$, and $\log k_0 = 3.169$.[28] Kinetic data for 32 ethylenes was used in this correlation (see Table I and Table I of ref 1); two disubstituted compounds in which both strong electron-donating and attracting groups were present, *viz.*, 1-(p-methoxyphenyl)-1-(m- and p-nitrophenyl)ethylenes, were omitted, but there were no other serious deviations from this equation (see Figure 1).

Significantly, when there was a choice in unsymmetrically disubstituted compounds as to which ring is to remain planar, a better fit is invariably obtained by applying the σ^+ value (and by implication the planar ring) to the strongest resonance-donating substituent (as measured by the magnitude of the difference $\sigma^+ - \sigma$). This is clearly seen by comparing the calculated and observed rate constants for the two arrangements which are listed in Table II. However, it is not possible to bring the methoxy nitro compounds onto this correlation by using any combination of σ and σ^+ values.

TABLE II

OBSERVED AND CALCULATED RATE CONSTANTS IN THE BROMINATION OF $XC_6H_4C(=CH_2)C_6H_4Y$, USING THE EXPRESSION LOG $k/k_0 = \sigma^+ + \sigma$

Compd	X	Y	σ^+_{X}	σ_{Y}	Log k^a_{calcd}	Log k_{obsd}
2	p-MeO	p-Me	−0.778	−0.170	6.259	5.989
	p-Me	p-MeO	−0.311	−0.268	5.056	
b	p-MeO	H	−0.778	0.000	5.705	5.578
	H	p-MeO	0.000	−0.268	4.052	
4	p-MeO	p-Br	−0.778	+0.232	4.949	5.028
	p-Br	p-MeO	+0.150	−0.268	3.553	
9	p-Me	p-F	−0.311	+0.062	3.980	3.997
	p-F	p-Me	−0.073	−0.170	3.961	
13	p-Me	p-Br	−0.311	+0.232	3.426	3.614
	p-Br	p-Me	+0.150	−0.170	3.234	

[a] Log $k_{\mathrm{calcd}} = -3.26(\sigma^+_{\mathrm{X}} + \sigma_{\mathrm{Y}}) + 3.169$; k in l. mol^{-1} sec^{-1}. [b] Data from Table I of ref 1.

A more exact test of this model would assume that the substituent X with the largest electron-donating power by resonance still acts in a disubstituted compound with the same σ value used when it alone was present. The monosubstituted compounds have been shown to fit the equation $\log k/k_0 = -3.57\ (\sigma_0 + 0.84\ \Delta\sigma^+)$ to a high degree of accuracy.[1] The σ_{Y} value (which refers to the second substituent Y), required to duplicate the observed kinetic results for the disubstituted compounds, may then be calculated (Table III). If the assumptions that ρ is constant throughout the series and that IX is a good model for the transition state are correct, one would expect that (1) σ_{Y} for a given substituent would be constant and independent of the nature of X, and (2) that the σ_{Y} values calculated would be close to the ordinary Hammett σ

TABLE III

CALCULATED σ AND R VALUES FOR DISUBSTITUTED 1,1-DIPHENYLETHYLENES, $XC_6H_4C(=CH_2)C_6H_4Y$

Compd	X	Y	$\sigma_{\mathrm{Y}}{}^a$	$\sigma_{\mathrm{total}} - \Sigma\sigma^0$ ^{b}	R^c
1	p-MeO	p-MeO	−0.20	−0.72	0.54
2	p-MeO	p-Me	−0.10	−0.45	0.53
4	p-MeO	p-Br	+0.17	−0.70	0.85
5	p-Me	p-Me	−0.21	−0.24	0.65
9	p-Me	p-F	+0.06	−0.30	0.65
10	p-MeO	m-NO_2	+0.50	−0.79	1.15
11	p-MeO	p-NO_2	+0.51	−0.87	1.28
13	p-Me	p-Br	+0.18	−0.28	0.83
15	p-F	p-F	+0.07	−0.38	0.66
20	p-Cl	p-Cl	+0.18	−0.24	0.73
21	p-Br	p-Br	+0.18	−0.25	0.85

[a] $\sigma_{\mathrm{Y}} = \sigma_{\mathrm{total}} - (0.84\ \Delta\sigma_{\mathrm{X}}{}^+ + \sigma_{\mathrm{X}}{}^0)$. [b] $\sigma_{\mathrm{total}} = -(\log k - 3.25)/3.57$. [c] $R = (\sigma_{\mathrm{total}} - \Sigma\sigma^0)/\Sigma\Delta\sigma^+$.

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(27) A. F. Hegarty and J. E. Dubois, *Tetrahedron Lett.*, 4839 (1968).

(28) The symbols used throughout the r, correlation coefficient; s, standard deviation; and k_0, calculated rate constant when $\sigma = 0$ (see, *e.g.*, C. A. Bennett and N. L. Franklin, "Statistical Analysis in Chemistry and Chemical Industry," Wiley, New York, N. Y., 1954, p 245).

values. It is clear from the data listed in Table III that neither of these conditions is observed exactly. Thus, taking *p*-bromo ($\sigma = +0.232$) as an example, σ_Y is (+0.17, +0.18, +0.18) with X (*p*-MeO, *p*-Me, *p*-Br). However, if a limited set of data is chosen (ignoring again the methoxy nitro compounds), there is approximate agreement with 1 and 2; this accounts for the success of the simple $\log k/k_0 = \rho\ (\sigma^+ + \sigma)$ treatment used previously. A more detailed treatment of the data cannot be carried out without assuming that ρ varies.

(2) The alternative approach, using structure VIII as a model, would assume that the system has a relatively rigid configuration in which the two rings were twisted equally out of the plane in the olefin and retained this structure in the transition state of the bromination reaction, independent of the substituents present in the aromatic rings.[29] In this case the substituents in both mono- and disubstituted compounds would each transmit by resonance the same fraction for the stabilization of the carbonium ion. Yukawa and Tsuno[30] have developed a modified form of the Hammett equation applicable to electrophilic reactions for which the Brown–Okamoto σ^+ values either over- or undercorrect for the resonance contributions of the substituents. In the equation

$$\log k/k_0 = \rho(\sigma^0 + R\Delta\sigma^+)$$

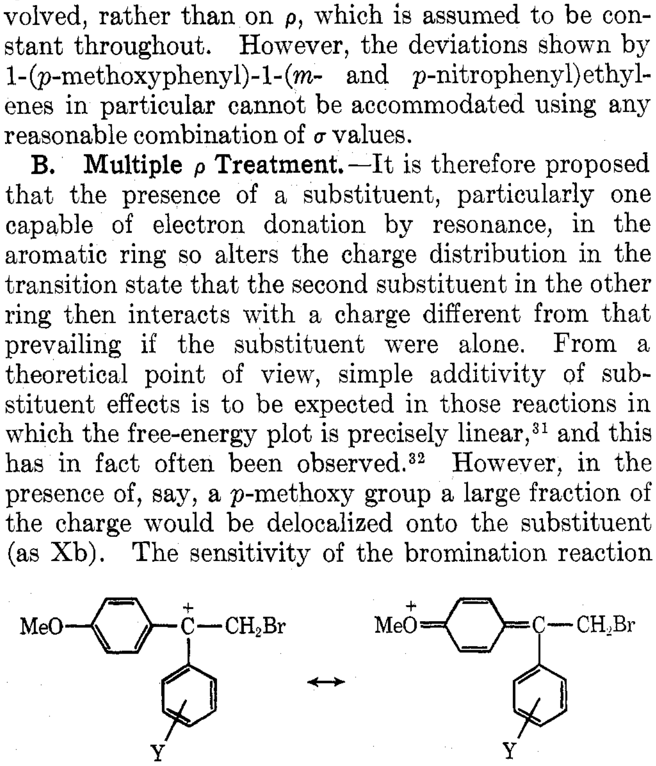
the extra parameter *R* is a reaction constant indicative of the degree of resonance in the transition state, and $\Delta\sigma^+$ ($\sigma^+ - \sigma^0$) is the measure of the resonance contribution of a given substituent. Applying this equation to the results obtained for the bromination of 32 1,1-diarylethylenes (using $\Sigma\sigma^0$ and $\Sigma\Delta\sigma^+$ in place of σ^0 and $\Delta\sigma^+$) gave $\rho = -3.54$, $R = 0.59$ with $r = 0.991$ and $s = 0.714$. The nitro methoxy compounds again deviated significantly and were omitted from this correlation.

Although this ρ value corresponds almost exactly to that obtained using the meta-substituted compounds alone,[1] the *R* value is decidedly different from that reported for the monosubstituted compounds (0.84 *vs.* 0.59); it is difficult to rationalize how this might be so. This low *R* implies that a relatively small fraction of resonance is transmitted from the substituent in the transition state. If this is related to the angle of twist using the $\cos^2 \phi$ relationship, it is found that ϕ is *ca.* 40° for each ring. This is a significantly larger angle than any of the estimates on 1,1-diphenylethylenes. Moreover, the correlation coefficient shows that this is a less precise treatment of the data and thus does not justify the introduction of the extra parameter *R*. More seriously, the mono- and disubstituted compounds deviate from the relationship in opposite directions: it is clear that the closeness of the fit observed, such as it is, is due rather to the large body of data used in the computation than to the fact that the Yukawa–Tsuno equation is able to deal with the data for the mono- and disubstituted compounds simultaneously.

Simple inductive effects appear to be additive for substituents in both rings. Thus the five di-meta-substituted 1,1-diphenylethylenes (including both symmetrically and unsymmetrically substituted compounds) are excellently correlated with σ_m to give much the same ρ (-3.65, with $r = 0.997$, $s = 0.377$) as obtained for mono-meta substitution. This fact was used to rigorously test the approach 2 as follows. Using the Yukawa–Tsuno equation in the form $\log k/k_0 = -3.57\ [\Sigma\sigma^0 + R\Sigma\Delta\sigma^+]$, the fractional resonance contribution, *R*, for each disubstituted compound was calculated (Table III). If there is no interaction between the substituents, then *R* should be constant throughout the series. Although this is true to a very limited extent, particularly when $\sigma_{\text{total}} - \Sigma\sigma^0$ is not large, it is clear that *R* seems to vary in a general way with both substituents. Thus, when X = MeO, *R* is successively equal to 0.54, 0.53, 0.83, 0.85, and 1.28 when the second substituent Y is MeO, Me, H, Br, NO_2.

Thus we conclude, from a consideration of stereochemical factors alone, that in the transition state of the bromination of 1,1-diphenylethylenes, the favored configuration is unsymmetrical. One of the aryl rings is conjugated with the vacant p orbital of the forming carbonium ion, the other being rotated through a large enough angle so that substituents in this ring do not conjugatively stabilize the forming carbonium ion. This description places the onus of the observed nonadditivity of substituent effects on the geometry of the system and on the magnitude of the σ constants involved, rather than on ρ, which is assumed to be constant throughout. However, the deviations shown by 1-(*p*-methoxyphenyl)-1-(*m*- and *p*-nitrophenyl)ethylenes in particular cannot be accommodated using any reasonable combination of σ values.

B. Multiple ρ Treatment.—It is therefore 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 charge different from that prevailing if the substituent were alone. From a theoretical point of view, simple additivity of substituent effects is to be expected in those reactions in which the free-energy plot is precisely linear,[31] and this has in fact often been observed.[32] However, in the presence of, say, a *p*-methoxy group a large fraction of the charge would be delocalized onto the substituent (as Xb). The sensitivity of the bromination reaction to the variation of the second substituent Y, now more remote from the positive charge, is much reduced. The change in the response of the reaction to the variation of Y would be expected to be some function of



Xa Xb

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[29] The presence of a *p*-methoxy group in one of the rings in 1,1-diphenylethylene brings about a small separation of the nmr signals for the terminal olefinic protons (with *p*-bromo or *p*-methyl substituents, the protons remain equivalent). Van der Linde, *et al.*,[19] therefore concluded that the effect of substituents on the conformations of 1,1-diphenylethylenes is not very great.

[30] Y. Tsuno, I. Isabata, and Y. Yukawa, *Bull. Chem. Soc. Jap.*, **32**, 960 (1959); Y. Yukawa and Y. Tsuno, *ibid.*, **32**, 965, 971 (1959); *J. Chem. Soc. Jap.*, **86**, 875 (1965).

[31] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 192.

[32] H. H. Jaffe, *Chem. Rev.*, **53**, 191 (1953).

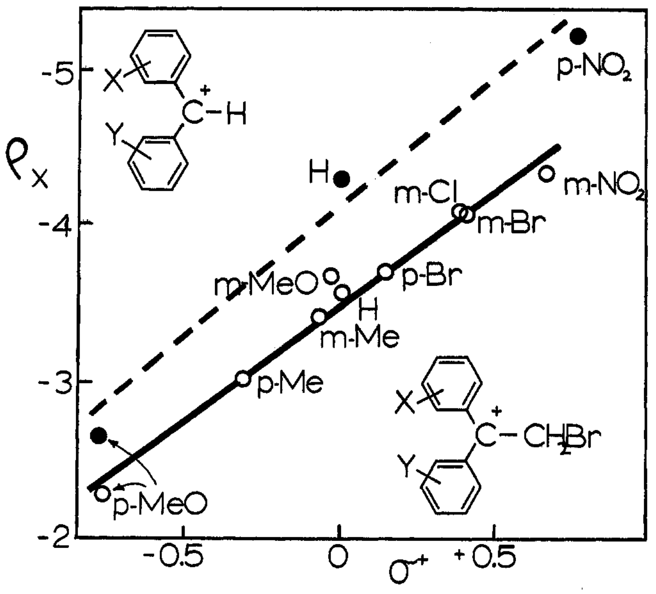

Figure 2.—Plots of (a) the ρ values (●) derived in Table V for the solvolysis of $XC_6H_4(Ar)CHCl$ in 90% acetone (X = constant for each of the points, while the substituent in Ar varies) and (b) ρ values (○) obtained similarly for the bromination of $XC_6H_4(Ar)C = CH_2$ in methanol *vs.* the σ^+ value of the substituent X (Table IV).

the electron-withdrawing or donating power (as measured by its σ^+ value) of the first substituent. As a subsidiary effect, for maximum delocalization (as in Xb) the ring containing the *p*-methoxy group would have to be in the plane of the carbonium ion;[27] in this situation Y cannot stabilize the transition state to the same degree as in the absence of the *p*-methoxy group, *i.e.*, the para positions of the two rings become nonequivalent.

We have therefore examined the reactivity of various groups of compounds in which one of the substituents (X) was held constant while the other (Y) was varied. Since the σ value appropriate to the second substituent Y is indefinite, two series of compounds (X = *p*-MeO and *p*-Me) which included extensive data for (Y =) meta substituents were employed. Since the meta substituents act largely inductively, their influence on the rate of bromination is independent of the angle of rotation of the second ring.[27] The calculated ρ values for the variation of Y when X = *p*-MeO and *p*-Me are −2.27 and −3.03, respectively (see Table IV).

For the other series of compounds in Table IV in which the substituent is held constant and Y varied, a sufficient number of meta-substituted compounds were not available. In these cases the assumption was made that the value of *R* is the same (0.84) as that obtained for the correlation of the monosubstituted derivatives (*i.e.*, where X = H).[1] This is not unreasonable in view of the fact that none of the substituents Y involved are capable of strong resonance stabilization of the carbonium ion center. The calculated ρ values thus obtained (which refer to the constant substituent X) are listed in Table IV; satisfactory correlations were obtained in all cases.

The well-defined value of ρ obtained when the constant substituent X = *p*-MeO (*viz.*, −2.27) permits the use of the Yukawa–Tsuno equation to calculate the *R* value applicable to substituents in the second ring Y which are able to further stabilize the developing carbonium ion by conjugation (*i.e.*, $\Delta\sigma^+ > 0$). Using data for compounds **1**, **2**, and **4** (Table I) an *R* value of 0.4 is obtained. This value is significantly lower than that obtained (0.84) for the monosubstituted ethylenes.[1] This must mean that the second less electron-donating substituent interacts conjugatively with the developing charge to a smaller extent (but not negligibly) than the first *p*-methoxy substituent. Assuming that *R* = 1.0 when the aryl ring is coplanar with the carbonium ion[33] and that a $\cos^2 \phi$ relationship holds for the effect of the angle of rotation ϕ upon the transmission of conjugative effects, then *R* = 0.84 and 0.4 represent angles of 23 and 49°, respectively. Thus it appears that (as tentatively suggested above), a substituent capable of strong conjugation with the reaction center distorts the equivalence of the two aryl rings in the transition state.

TABLE IV

CALCULATED ρ VALUES FOR THE VARIATION OF SUBSTITUENT Y WITH SUBSTITUENT X HELD CONSTANT [DATA FROM BROMINATION OF ETHYLENES $XC_6H_4C(=CH_2)C_6H_4Y$][a]

Substituent X	ρ	r	σ^+ (X)	Substituents Y used
p-MeO	−2.27	0.999	−0.78	H, *p*-NO$_2$, *m*-NO$_2$, *m*-Br, *m*-Cl, *m*-Me
p-Me	−3.03	0.996	−0.311	H, *m*-NO$_2$, *m*-Br, *m*-Me
m-Me	−3.42	0.999	−0.066	*p*-MeO, *p*-Me, H, *m*-Me, *m*-F
m-MeO	−3.69	0.999	−0.048	*m*-MeO, *m*-Br, H
p-Br	−3.67	0.999	+0.150	*p*-MeO, *p*-Me, H
m-Cl	−4.08	0.999	+0.399	*p*-Me, *m*-Cl, H
m-Br	−4.05	0.994	+0.405	*p*-MeO, *p*-Me, *m*-MeO
m-NO$_2$	−4.65	0.999	+0.674	*p*-MeO, *p*-Me, H
H	−3.57	0.999	0	See ref 1

[a] Kinetic data from Table I and Table I of ref 1.

Saturation of Resonance.—The ρ values obtained (Table IV) are related in a general way to the electron disturbance of the substituent X which is retained constant (as measured by its σ^+ value); see Figure 2. By extrapolation from these data, when $\sigma^+ \sim -2.2$ then $\rho = 0$, implying that, when one of the aryl groups contained a substituent with such (or greater) electron-donating power, the rate of bromination of the ethylene would be independent of the nature of further substitution; *i.e.*, the system would be "saturated."

We have applied a similar treatment to the data of Fox and Kohnstam[34] for the solvolysis of 1-aryl-1-(*p*-methoxy, *p*-nitro, and unsubstituted phenyl) carbinyl chlorides, using the Yukawa–Tsuno treatment (see Table V). The ρ values again differ as the first

TABLE V

CALCULATED REACTION CONSTANTS FOR THE SOLVOLYSIS OF 1-(*p*-X-PHENYL)-1-ARYLCARBINYL CHLORIDES[a]

Substituent X	ρ^b	R	r
MeO	−2.63	1.20	0.999
H	−4.31	1.44	0.996
NO$_2$	−5.26	1.50	0.996

[a] Calculated from data in J. R. Fox and G. Kohnstam, *Proc. Chem. Soc.*, 115 (1964).

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[33] This assumption may be in error, since values of *R* considerably in excess of unity have been reported; see, for example, J. E. Dubois and A. F. Hegarty, *J. Chem. Soc. B*, 638 (1969).

[34] J. R. Fox and G. Kohnstam, *Proc. Chem. Soc.*, 115 (1964).

substituent is changed and decrease with increased electron-donating power of the constant substituent (see Figure 2), *i.e.*, in the order p-NO_2 > H > p-MeO. Although no clear distinction is apparent in this case between the use of σ and σ^+ values for the second substituent, the resonance interaction constant, *R*, does decrease when X = OMe, showing that in this case less resonance stabilization by the substituents Y is involved than when X = H or p-NO_2.

The data of Nishida[12] for the solvolysis of benzhydryl chlorides in methanol differs from that of Fox and Kohnstam[34] in that plots of log *k* *vs.* σ^+ were obtained with little curvature (which implies that $R = 1.0$ throughout). However, the same decrease in sensitivity to substituent variation on the introduction of electron-donating groups is noted. The general features of a plot of ρ_X *vs.* $\sigma^+{}_X$ were the same[35] (as Figure 2) except that a folded line about $\sigma^+ = 0$ was obtained.

It is possible that this effect (whereby substantial delocalization of charge onto a side chain from the reaction center causes a decrease in the sensitivity of the reaction to the effect of a second substituent now placed further from the charged center) is quite general, but only observed[11] when compounds differing greatly in in reactivity are studied. It is operative not only when the two substituents concerned are on different rings (although, of necessity, it is exaggerated in this case), but also when both substituents are on the same ring. Thus in the bromination of substituted benzenes (PhX)) the sensitivities to further substituent variation decrease in the order X = H > Me > MeO > NMe_2; here again a similar general relationship can be obtained between the ρ values calculated for the substituent X and its σ^+ value.[36]

In conclusion, although clear nonadditivity of substituent effects is evident in the bromination of 1,1-diphenylethylenes, it is not possible to attribute this entirely to the stereochemistry of the system. Apparently no single ρ value is involved throughout the series, but various ρ values are obtained with good precision when one of the rings (say Ar in VI) is kept constant while substituents in the second ring (Ar′) are varied. The multiple ρ values thus obtained are close to the value for monosubstitution (VI, Ar = Ph) only when the substituent in the Ar ring does not differ greatly in electron disturbance from hydrogen (*e.g.*, Ar = p-BrC_6H_5 or m-MeC_6H_4), accounting for the apparently good correlations previously obtained with more limited data.[37] Use of the variable ρ value for the first ring accounts accurately for the data for the bromination of all multiply substituted 1,1-diphenylethylenes and the solvolysis of benzhydryl chlorides and clearly deserves to be applied in other similar cases.

Experimental Section

Substrates.—The diphenylethylenes were prepared by the general methods involving Grignard reagents which have previously been described.[1] In addition, a further method (an example of which follows) was found to be applicable to the synthesis of symmetrically disubstituted olefins. Those olefins with nitro substituents were prepared by a modification of the Wittig reaction. Data for the olefins are listed in Table VI.

TABLE VI

ANALYTICAL AND PHYSICAL DATA FOR 1,1-DIARYLETHYLENES $[XC_6H_4C(=CH_2)C_6H_4Y]$

X	Y	Bp, °C (mm), or mp, °C	Yield, %
p-MeO	p-Me	74–74.5[a]	63
p-Br	p-MeO	86–87[a,b]	55
p-F	p-Me	173–175 (24)[a]	40
p-MeO	m-NO_2	178 (0.5)[a,c]	25
p-MeO	p-NO_2	85.5[a,d]	30
m-Me	m-Me	183–185 (25)[a]	46
p-Br	p-Me	64.5–65[a]	63
m-MeO	m-MeO	228–230 (30)[a]	20
m-F	m-Me	98 (0.5)[a]	60
m-Br	m-MeO	150 (0.5)[a,e]	55
m-Cl	m-Cl	150 (0.5)[a]	55
p-MeO	m-Br	145–149 (0.3)[a,f]	56
p-MeO	m-Cl	132 (0.2)[a,g] (mp 27)	50
m-NO_2	p-Me	72[a]	11
p-Me	m-Br	43[a]	53
p-MeO	m-Me	152–155 (0.5)[a]	9
p-Me	m-Me	128 (1.5)[a]	77

[a] Satisfactory analytical data (±0.35%) were reported for these compounds: Ed. [b] Recrystallized once from petroleum ether (bp 40–60°) and then from absolute ethanol. [c] Distillation at this temperature caused decomposition; this olefin was purified on a silica gel column using benzene–hexane (1:1) as eluent. [d] The oily residue obtained on evaporation of the chloroform was purified by chromatography (silica gel, 1:2 benzene–hexane as eluent). [e] Calcd: MeO, 10.7. Found: MeO, 10.6. [f] Calcd: MeO, 10.7. Found: MeO, 10.9. [g] Calcd: MeO, 12.7. Found: MeO, 12.6.

1,1-Di(m-tolyl)ethylene.—The Grignard reagent, prepared from magnesium (5.0 g) and m-bromotoluene (34.2 g) in 150 ml of anhydrous ether, was treated at 0° with a solution of ethyl acetate (8.8 g) in 10 ml of ether. After standing for 12 hr at room temperature, the mixture was refluxed for 30 min and, on cooling, the adduct was decomposed with dilute sulfuric acid–ice. The ether layer was washed with water (2 × 20 ml) and then with a saturated sodium carbonate solution (20 ml). After drying ($MgSO_4$), the ether was evaporated and the oily residue was distilled, bp 175–180° (20 mm), with spontaneous dehydration. To remove the small amount of water that distilled, dry ether (10 ml) was added to the distillate, and the solution was dried over calcium chloride and redistilled, bp 185–187° (27 mm), yielding 9.0 g of the ethylene.

1-(m-Nitrophenyl)-1-(p-tolyl)ethylene.—To a suspension of NaH [prepared by washing 2.4 g of NaH (50%) in mineral oil with hexane] in 100 ml of dry DMF was added 10 g of triethyl phosphonoacetate. The temperature was kept at 20° during the addition. When the evolution of hydrogen gas had ceased, 10 g of 4-methyl-3′-nitrobenzophenone was added and the mixture was heated to 120° for 12 hr. The red mixture was decomposed with 1.5 l. of cold water and extracted with 3 × 300 ml of CH_2Cl_2. The organic layer was washed twice with water, dried over $MgSO_4$, and concentrated. The deep brown residue was taken in 100 ml of 10% methanolic KOH and refluxed for 2 hr, diluted with water, and extracted with 2 × 50 ml of CH_2Cl_2 to remove nonacidic material. The aqueous solution was acidified and extracted with 2 × 100 ml of CH_2Cl_2, washed with water, and dried. Removal of the solvent gave 3.5 g of a solid which was taken up in 20 ml of quinoline. Cu powder was added and the

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(35) Moreover, much the same substituents [m-Me, p-Br in the present study, m-Me, p-Cl in solvolysis, S. Nishida, *J. Org. Chem.*, **32**, 2695 (1967)] gave ρ values close to that observed for the monosubstituted compounds.

(36) Using $\rho = -12.1$ for the bromination of benzenes [L. M. Stock and H. C. Brown, *Advan. Phys. Org. Chem.*, **1**, 35 (1963)]; $\rho = -10.7$ for toluenes [J. E. Dubois, P. Alcais, and F. Rothenburg, *J. Org. Chem.*, **33**, 439 (1968)]; $\rho = -6.76$ for anisoles [J. E. Dubois and J. J. Aaron, *J. Chim. Phys.*, 1354 (1964)]; and $\rho = -2.2$ for dimethylanilines [J. E. Dubois and R. Uzan, *Bull. Soc. Chim. Fr.*, 598 (1971)]. A plot of ρ *vs.* σ^+ gives a reasonable correlation with a slope of -5.23 ($r = 0.983$, $s = 1.51$), in spite of the approximation involved in the determination of ρ.

(37) S. Altscher, R. Baltzly, and S. W. Blackman, *J. Amer. Chem. Soc.*, **74**, 3649 (1952); S. Nishida, *J. Org. Chem.*, **32**, 2692 (1967).

mixture was refluxed for 3 hr to effect decarboxylation, diluted with 10% HCl, and extracted with 2 × 50 ml of CH_2Cl_2. The organic layer was washed with water and dried over $MgSO_4$. Removal of the solvent and chromatography of the residue on Florisil (eluent hexane–ether) gave 1.1 g of the ethylene, mp 72° (from petroleum ether, bp 40–60°); see Table VI for analytical data.

Kinetic Measurements.—The kinetic measurements were carried out at 25° in methanol containing 0.20 *M* sodium bromide. The purification procedure used for the solvent has previously been described.[1] It has been shown previously that under these conditions Br_2 is the only electrophile of importance. Each experiment was repeated a minimum of five times and the rate values listed in Table I are accurate to better than ±2% (compounds **5–23**) or ±4% (compounds **1–4**).

The various electrometric methods used to follow the disappearance of bromine at low concentration have been described in detail elsewhere.[38] To ensure the accuracy of the rate constants listed, comparison was continually made with substrates whose bromination rates have been well established (see ref 1 for details).

Registry No.—**1,** 4356-69-8; **2,** 13392-76-2; **3,** 13392-77-3; **4,** 34564-83-5; **5,** 2919-20-2; **6,** 34564-84-6; **7,** 34564-85-7; **8,** 22057-87-0; **9,** 365-23-1; **10,** 34564-88-0; **11,** 28358-68-1; **12,** 10605-48-8; **13,** 34564-89-1; **14,** 1488-34-2; **15,** 6175-14-0; **16,** 34564-91-5; **17,** 34564-92-6; **18,** 28358-71-6; **19,** 34564-93-7; **20,** 2642-81-1; **21,** 10605-43-3; **22,** 28358-69-2; **23,** 29265-85-8.

[38] R. P. Bell and D. Dolman, *J. Chem. Soc. B*, 500 (1968); J. E. Dubois and G. Mouvier, *C. R. Acad. Sci.*, **255**, 1104 (1962); J. E. Dubois, P. Alcais, and G. Barbier, *J. Electroanal. Chem.*, **8**, 359 (1964); see also ref 1.

Comparisons of the Reactions of Butadiene with Chlorine, Bromine, Acetyl Hypochlorite, and Acetyl Hypobromite

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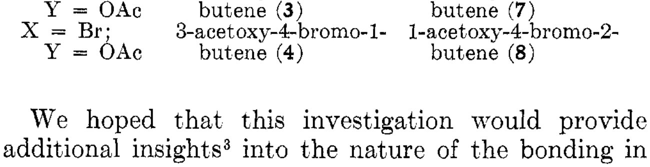
The addition reactions of butadiene with the indicated electrophiles were studied in various solvents with the object being to gain additional insights into the nature of the bonding in the halonium ion intermediates. The following observations were made. (a) All of the electrophiles reacted with butadiene to give both 1,2 and 1,4 addition. The hypohalites (ClOAc, but particularly BrOAc), however, gave considerably less 1,4 addition than the halogens. (b) The 1,2-addition product from the hypohalites (ClOAc and BrOAc) showed exclusively Markovnikov orientation. (c) A study of the bromination and chlorination of butadiene in acetic acid is reported. Solvent incorporation is much greater in chlorination than bromination. (d) There is considerably more attack by acetic acid at the terminal vinylic carbon atom during chlorination than during bromination. Also in nonpolar solvents acetyl hypochlorite gave more 1,4 addition than acetyl hypobromite. (e) The bromine systems (Br_2 and BrOAc) show a general trend toward greater 1,4 addition as the solvent polarity increases, whereas the chlorine systems are insensitive to solvent polarity. On the basis of some of the above observations, we suggest that the intermediate chloronium ion formed in the addition of chlorine or acetyl hypochlorite to butadiene has extensive delocalization of the charge into the neighboring vinylic system. This is in contrast to the bromonium ion which we have described previously (and also supported by this study) as having the charge shared between the secondary carbon and bromine atoms with little delocalization into the vinylic system.

The most probable reactions of the electrophiles and butadiene, and the products expected from the reactions, are outlined below, in which X refers to Cl and Br, and Y represents Cl, Br, and OAc.



$$CH_2{=}CHCH{=}CH_2 \xrightarrow{X\text{-}Y} \underset{X}{CH_2}\underset{Y}{CH}CH{=}CH_2 + XCH_2CH{=}CHCH_2Y$$

	1,2 addition	1,4 addition[2]
X = Y = Cl	3,4-dichloro-1-butene (**1**)	1,4-dichloro-2-butene (**5**)
X = Y = Br	3,4-dibromo-1-butene (**2**)	1,4-dibromo-2-butene (**6**)
X = Cl; Y = OAc	3-acetoxy-4-chloro-1-butene (**3**)	1-acetoxy-4-chloro-2-butene (**7**)
X = Br; Y = OAc	3-acetoxy-4-bromo-1-butene (**4**)	1-acetoxy-4-bromo-2-butene (**8**)

We hoped that this investigation would provide additional insights[3] into the nature of the bonding in the halonium ion intermediates involved in these reactions. In particular, we focused our attention on the following areas: (a) to determine if anti-Markovnikov products are formed when ClOAc and BrOAc are added to butadiene; (b) to study the variation in the 1,2- to 1,4-product ratios when the anion is changed but the cation remains the same (Cl_2, ClOAc and Br_2, BrOAc), and when only the cation is changed (BrOAc, ClOAc); (c) to examine the effect of solvent polarity on these reactions; and (d) to compare the amount and position of solvent attack when butadiene is brominated and chlorinated in acetic acid.

No investigations of the reactions of acetyl hypochlorite or hypobromite with butadiene have appeared in the literature. The chlorination[2] and bromination[4] of butadiene has recently been studied, but only in nonpolar solvents.

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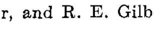
[2] The trans isomers would be expected, since previous studies on butadiene have shown that only trace amounts of the cis isomers are found during bromination,[4a] bromination in methanol (methoxy bromide formation),[3a] and chlorination [M. L. Poutsma, *J. Org. Chem.*, **31**, 4167 (1966)].

[3] On the basis of our previous studies [(a) V. L. Heasley and P. H. Chamberlain, *J. Org. Chem.*, **35**, 539 (1970); (b) V. L. Heasley, G. E. Heasley, S. K. Taylor, and C. L. Frye, *ibid.*, **35**, 2967 (1970)] we postulate that the halonium ion intermediate involved in the bromination of butadiene is best represented as follows.



[4] (a) V. L. Heasley and S. Taylor, *J. Org. Chem.*, **34**, 2779 (1969); (b) L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Amer. Chem. Soc.*, **81**, 5943 (1959).