

2,3-Bis-(trifluoromethyl)-*p*-dithiin (II).—A mixture of 45.2 g. (0.20 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene, 13 g. (0.50 mole) of acetylene and 50 ml. of benzene was heated under pressure at 50° for 45 hours, then at 70° for an additional 15 hours. Distillation of the reaction mixture gave 16.7 g. (37%) of recovered 3,4-bis-(trifluoromethyl)-1,2-dithietene and a residue of 10 g. (22%) of its crude dimer, along with 1.5 g. (3% yield) of 2,3-bis-(trifluoromethyl)-*p*-dithiin, b.p. 48° (10 mm.).

Anal. Calcd. for C₆H₂F₆S₂: C, 28.57; H, 0.80; F, 45.20; S, 25.42. Found: C, 28.29; H, 1.07; F, 45.25; S, 25.62.

The infrared spectrum contained bands for C=C at 6.28 μ and 6.47 μ . Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{isooctane}}$ 261 m μ (ϵ 3630), 269 m μ (ϵ 4490), 278 m μ (ϵ 3960); 330 m μ (ϵ 400), shoulder at 255 m μ . Nuclear magnetic resonance peaks were found for CF₃ at -1091 c.p.s. and unsaturated C-H at -78 c.p.s.

Adducts of 3-Hexyne with 3,4-Bis-(trifluoromethyl)-1,2-dithietene.—3,4-Bis-(trifluoromethyl)-1,2-dithietene (11.3 g., 0.05 mole) and 3-hexyne (4.5 g., 0.055 mole) were allowed to react at 25° for 17 days to give on distillation 2.3 g. (15% yield) of yellow 2,3-diethyl-5,6-bis-(trifluoromethyl)-*p*-dithiin, b.p. 77-79° (4 mm.).

Anal. Calcd. for C₁₀H₁₀F₆S₂: C, 38.96; H, 3.27; F, 36.98; S, 20.80; mol. wt., 308. Found: C, 39.48; H, 3.27; F, 36.93; S, 20.21; mol. wt., 291 (b.p. benzene).

A band in the infrared for C=C came at 6.34 μ . Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{isooctane}}$ 221 m μ (ϵ 4870), 260 m μ (ϵ 4810), 323 m μ (ϵ 460). Nuclear magnetic resonance showed a single peak for CF₃ at -1157 c.p.s.; and proton peaks for one kind of ethyl group; a quadruplet at +129, +137, +145 and +153 c.p.s. for CH₂; and a triplet at +209, +217 and +225 c.p.s. for CH₃.

Recrystallization of the distillation residue from methanol afforded 0.9 g. (7% yield) of 4a,8a-diethyl-2,3,6,7-tetrakis-(trifluoromethyl)-4a,8a-dihydro-*p*-dithiino[2,3-*b*]-*p*-dithiin, m.p. 132-133° (subl.).

Anal. Calcd. for C₁₄H₁₀F₁₂S₄: C, 31.46; H, 1.89; F, 42.66; S, 23.99. Found: C, 31.58; H, 2.02; F, 42.74; S, 23.96.

Infrared showed a band for C=C at 6.23 μ (KBr wafer). Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{isooctane}}$ 225 m μ (ϵ 8870), 297 m μ (ϵ 3310), 318 m μ (ϵ 2830). Nuclear magnetic resonance showed a single CF₃ peak and a single ethyl group to be present.

2,3-Dimethoxycarbonyl-4,5-bis-(trifluoromethyl)-thiophene.—3,4-Bis-(trifluoromethyl)-1,2-dithietene (11.3 g., 0.05 mole) and 7.8 g. (0.055 mole) of dimethyl acetylenedicarboxylate were allowed to react in 15 ml. of refluxing methanol for 8 hours. The dithiadene that was apparently formed lost sulfur during distillation to give a mixture of

sulfur and a thiophene, b.p. 76-78° (0.5 mm.). Recrystallization of the product from petroleum ether, with a filtration step included to remove free sulfur, gave 5.4 g. (32% yield) of 2,3-dimethoxycarbonyl-4,5-bis-(trifluoromethyl)-thiophene, m.p. 49°.

Anal. Calcd. for C₁₀H₆F₆O₄S: C, 35.72; H, 1.80; F, 33.91; S, 9.54. Found: C, 36.09; H, 2.06; F, 33.62; S, 9.71.

The infrared spectrum contained carbonyl bands at 5.70 and 5.75 μ , thiophene ring bands at 6.42 and 6.72 μ . Nuclear magnetic resonance revealed quadruplets for CF₃ groups at -1293, -1283, -1273 and -1263 c.p.s., and at -1160, -1150, -1140 and at -1130 c.p.s.; a methyl peak came at +62 c.p.s.

Mercuric Salt of 1,2-Dimercapto-1,2-bis-(trifluoromethyl)-ethylene (V).—A mixture of 56.5 g. (0.25 mole) of 3,4-bis-(trifluoromethyl)-1,2-dithietene and 80.2 g. (0.40 mole) of mercury was heated with agitation at 85° for 16 hours. The resulting solid was washed well with petroleum ether and with carbon disulfide. The residual solid was dissolved in methanol, and then the solution was filtered and diluted with water. The precipitate, 84.1 g. (79% yield) of pale yellow mercuric salt of 1,2-dimercapto-1,2-bis-(trifluoromethyl)-ethylene, m.p. >300°, was insoluble in most organic solvents, indicating a high molecular weight. An analytical sample was prepared by another precipitation from methanol.

Anal. Calcd. for C₄F₆HgS₂: F, 26.71; Hg, 47.01; S, 15.02. Found: F, 26.57; Hg, 46.55; S, 14.97.

The infrared spectrum contained a band for C=C at 6.15 μ (KBr wafer). Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{ethanol}}$ 325 m μ (ϵ 2310 based on a mol. wt. of 427), shoulders at 220, 285 m μ . The nuclear magnetic resonance spectrum had a single sharp peak in the CF₃ region (methanol solution).

Reaction of 12.5 g. (0.03 gram-mole) of the mercury salt and 9.9 g. (0.07 mole) of methyl iodide in 10 ml. of ethanol occurred at 25°. After 2 days the solution was decanted from mercuric iodide that had precipitated. Distillation gave 4.4 g. of oil, b.p. 67-74° (20 mm.), that was shaken with mercury and redistilled. There was thus obtained 3.2 g. (42% yield) of 1,2-bis-(methylthio)-1,2-bis-(trifluoromethyl)-ethylene (VI), b.p. 73° (20 mm.).

Anal. Calcd. for C₆H₆F₆S₂: C, 28.12; H, 2.36; F, 44.49; S, 25.02. Found: C, 28.44; H, 2.63; F, 44.56; S, 24.89.

A band in the infrared for C=C came at 6.48 μ . Absorption in the ultraviolet occurred at $\lambda_{\text{max}}^{\text{isooctane}}$ 294 m μ (ϵ 5,760). Nuclear magnetic resonance peaks were found for CF₃ at -1112 c.p.s. and for CH₃ at +143 c.p.s.

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Kinetics of the Epoxidation of Substituted α -Methylstilbenes

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The epoxidation of α -methylstilbene and ring-substituted α -methylstilbenes by peroxybenzoic acid in benzene solution has been studied kinetically. The rates are proportional to the product of the concentrations of stilbene and peroxyacid. The effect of substituents in the α -methylstilbenes and stilbenes⁴ have been discussed in terms of an asymmetric attack of peroxyacid on the double bond and the accessibility of the reagent or the magnitude of the resonance effect of the substituent. Also the effect of substituents on the peroxybenzoic acid has been estimated and these effects have been discussed in terms of the reactivity-selectivity relationships and the resonance contribution in the transition state.

Second-order kinetics have been observed for peroxyacid epoxidation of ethylenic compounds.¹ The reaction is subject to general acid catalysis

(1) (a) S. Medvedev and O. Blokh, *J. Phys. Chem. USSR*, **4**, 721 (1933); (b) D. Swern, *J. Am. Chem. Soc.*, **69**, 1692 (1947); (c) Ya. K. Syrkin and I. I. Moiseef, *Prog. Chem. USSR*, **29**, 425 (1960); (d) D. Swern, *Chem. Revs.*, **45**, 1 (1949); (e) S. L. Friess, *J. Am. Chem. Soc.*, **71**, 2571 (1949); see also D. Swern, "Organic Reactions," Vol. 7, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 378.

and a mechanism involving an attack of the peroxy acid molecule is preferable to that of OH⁺,^{2,3} because of the small salt effect and the dependence of product and/or rate on the nature of the peroxy acid. For peroxybenzoic acid (PBA), where no

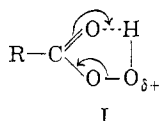
(2) A. Robertson and W. A. Waters, *J. Chem. Soc.*, 1574 (1948).

(3) F. L. Weisenborn and D. Taub, *J. Am. Chem. Soc.*, **74**, 1329 (1952).

TABLE I
 SUBSTITUTED α -METHYLSTILBENES

Substituent	Obsd.	M.p., °C.	Lit.	Carbon, %		Hydrogen, %		Chlorine, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found
<i>p</i> -Cl	76	78.77	78.71	5.73	5.64	15.50	15.53
<i>p</i> -CH ₃	70	92.26	92.05	7.74	7.76		
<i>p</i> -CH ₃ O	100.5	85.68	85.87	7.19	7.12		
<i>p'</i> -Cl	87	86.5 ¹¹		78.77	78.68	5.73	5.68	15.50	15.74
		~87.5							
<i>p'</i> -CH ₃	57	55 ~ 56 ¹¹		92.25	92.28	7.75	7.81		
<i>p'</i> -CH ₃ O		86 ~ 87 ¹¹							
H (<i>trans</i>)		81 ~ 82 ¹⁰							
H (<i>cis</i>)		47 ~ 48 ¹⁰							

catalysis of benzoic acid was observed, an intramolecular activation of the PBA (I) was proposed.^{2,4}



The proposal was supported by studies in the infrared which suggest that peracids form mainly intramolecular hydrogen bonds.^{5,6}

The fact that the rate of epoxidation of substituted ethylenes is increased by electron-releasing substituents suggests an electrophilic attack of peroxyacid on the double bond. For example, in epoxidations of substituted stilbenes with PBA, Hammett's ρ -value was *ca.* -1.2, while in those of stilbene with substituted PBA's, ρ was *ca.* +1.4, which means the rate increases with an increase of electron density in the double bond and decreases with an increase of electron density in the oxygen atom of the peroxyacids.⁴

To clarify the mechanism, *e.g.*, to determine whether peracid attacks the double bond symmetrically and to estimate the effect of substituents on the nature of the transition state, we chose to study the epoxidation of ring-substituted α -methylstilbenes with PBA and ring-substituted PBA in benzene. The mechanism was investigated kinetically.

Experimental

Materials.— α -Methylstilbenes were prepared by a procedure analogous to that of triphenylethylene,⁷ *i.e.*, via the condensation of substituted (or unsubstituted) benzylmagnesium chlorides with unsubstituted (or substituted) acetophenones or the condensation of α -phenylethylmagnesium bromide with substituted benzaldehydes, followed by hydrolysis and dehydration. The procedure was unsuccessful for the *p'*-methoxy derivative⁸ which was prepared by another process.⁹ Some of these substituted α -methylstilbenes prepared according to the above procedure are those reported to have *trans*-phenyl groups; hence the other new compounds should be the analogous geometrical isomers (see Table I).

Solvent benzene was purified by treatment with concd. sulfuric acid and then with sodium. Peroxybenzoic acid was prepared by methanolysis of benzoyl peroxide,¹² and

(4) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955). Catalysis by the stronger acid, CCl₃CO₂H, has been reported; see G. Berti and F. Bottari, *J. Org. Chem.*, **25**, 1286 (1960).

(5) H. T. Davison, *J. Chem. Soc.*, 2456 (1951).

(6) G. J. Minkoff, *Proc. Roy. Soc. (London)*, **A224**, 176 (1954).

(7) H. Adkins and W. Zartman, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 606.

(8) *p* and *p'* mean *para* position in 1- and 2-phenyl groups, respectively, in 1-methyl-1,2-diphenylethylene.

(9) J. Lévy, P. Gallais and D. Abragam, *Bull. soc. chim. France* [4] **43**, 880 (1928).

TABLE II

SECOND-ORDER RATE CONSTANTS (L. MOLE⁻¹ SEC.⁻¹) FOR EPOXIDATION OF SUBSTITUTED α -METHYLSTILBENES WITH PEROXYBENZOIC ACID IN BENZENE

Effect of initial concentrations of reactants and benzoic acid at 25°

α -Methylstilbene, 10 ⁻² M	PBA, 10 ⁻² M	Benzoic acid, 10 ⁻² M	$k_2 \times 10^2$
15.29	1.40	0	0.249
10.19	2.85	0	.256
10.19	1.44	0	.258
5.15	1.48	0	.262
5.10	2.22	8.19	.255
5.15	2.24	16.4	.255
			Av. 0.256

k_2 , 10⁻⁴ l. mole⁻¹ sec.⁻¹, for substituted α -methylstilbenes at different temperatures

Substituent	Temperature, °C.			E_a , kcal. mole ⁻¹	log A , sec. ⁻¹ l. mole ⁻¹
	10.0	25.0	40.0		
<i>p'</i> -Cl	5.65	17.8	49.7	12.8	6.68
<i>p</i> -Cl	5.16	17.3	46.4	13.0	6.72
H	7.91	25.6	68.8	12.8	6.78
<i>p</i> -CH ₃	17.2	50.8	138	12.3	6.74
<i>p'</i> -CH ₃	8.50	27.8	..	(13.2)	(7.10)
<i>p</i> -CH ₃ O	38.5	119	300	12.1	7.04
<i>p'</i> -CH ₃ O	21.0	59.5	..	(12.5)	(7.02)

used as its benzene solution, which was dried with sodium sulfate. *p*-Methoxy- and *p*-chloroperoxybenzoic acids were prepared by similar procedures.¹²

Reaction Products.— α -Methylstilbene was allowed to react overnight with a slight excess of PBA under the conditions of the rate measurements and, at the end of the reaction, the solution was washed with aqueous alkali. After distillation of solvent and a small amount of unreacted α -methylstilbene under vacuum, a white residue was obtained, which on recrystallization from dioxane gave the epoxide, m.p. 40°.

Anal. Calcd. for C₁₅H₁₄O: C, 85.60; H, 6.71. Found: C, 85.81; H, 6.57.

A Typical Procedure for Rate Measurements.—A benzene solution of α -methylstilbene of known concentration, thermostated in a brown flask, was treated with a thermostated solution of PBA of known concentration to start the reaction. Aliquots were taken out at appropriate intervals and the remaining PBA was estimated by iodometry. It was unnecessary to correct for the presence of α -methylstilbene and its epoxide. The reaction temperatures were 10.0, 25.0 and 40.0°.

Results and Discussion

The Substitution Effect in α -Methylstilbenes.

The rate was first-order with respect to α -methyl-

(10) D. J. Cram, F. D. Greene and C. H. Depuy, *J. Am. Chem. Soc.*, **78**, 790 (1956)

(11) P. L'Ecuyer and C. A. Olivier, *Can. J. Research*, **28B**, 648 (1950).

(12) G. Braun, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 431.

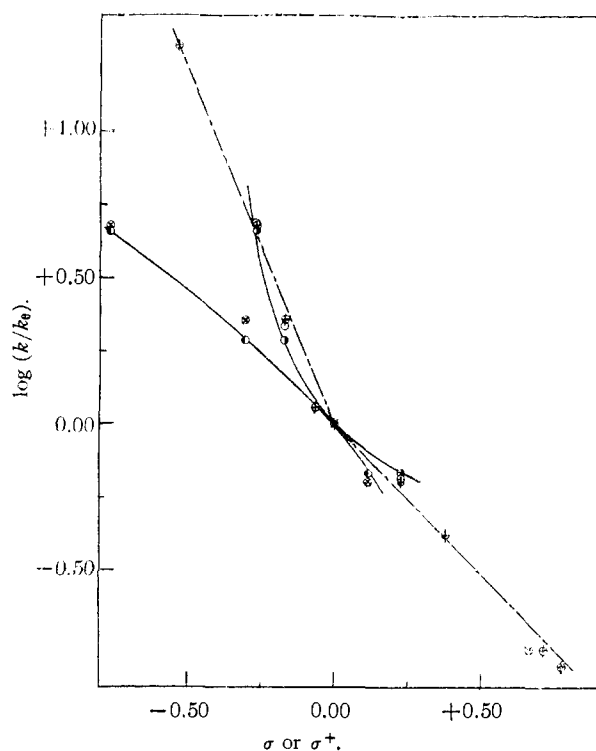
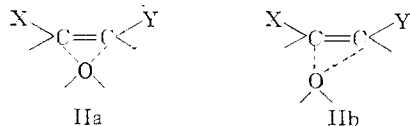


Fig. 1.—Plots of σ (Hammett and Jaffé) of σ^+ (Brown) vs. $\log(k/k_0)$ for the epoxidation of stilbenes^a and α -methylstilbenes at 25°: O, α -methylstilbenes with σ^b ; \ominus , α -methylstilbenes with σ ; \ominus , α -methylstilbenes with σ^+ ; \ominus , stilbenes with σ ; \otimes , stilbenes with σ^+ .

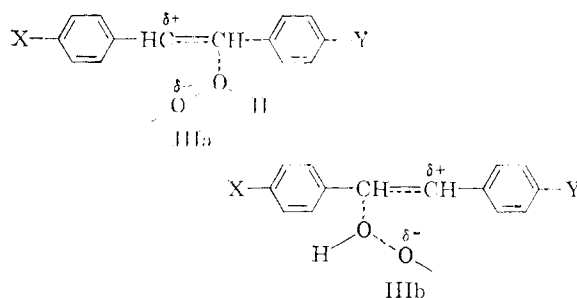
stilbene and PBA in various initial concentrations. There was no autocatalysis and also no acid catalysis was observed on addition of benzoic acid (Table II) as reported with simple ethylenic compounds.¹ As expected, the electron-releasing groups (CH_3 and CH_3O) in the *p*-position of α -methylstilbene increase the rate, while the electron-withdrawing group (Cl) decreases it, the former effect being considerably larger than the latter. The substituent effect in the epoxidation of substituted stilbenes with PBA⁴ showed a similar trend, *i.e.*, the slope of the line obtained from the plot of $\log(k/k_0)$ vs. σ for electron-withdrawing groups was found to be considerably smaller than that for electron-releasing groups (Fig. 1). No thorough discussion of this phenomenon has yet been given. The following two explanations may be advanced:

The Possibility of an Asymmetric Attack on Asymmetric Ethylenes.—Ethylene derivatives having different substituents on the doubly bound carbon atoms may be attacked asymmetrically (IIb) rather than symmetrically (IIa).



In the case of *p*-substituted stilbenes, stabilization of the partial positive charge on the doubly

^a Data from ref. 5. Plots of $\log(k/k_0)$ vs. σ^+ gave a concave curve, although Campbrell and co-workers have reported that the plots gave a straight line [D. R. Campbrell, J. O. Edwards, J. MacLachlan and K. Polgar, *J. Am. Chem. Soc.*, **80**, 5308 (1958)]. ^b At 10°.



bound atoms in the transition state III is an important factor, since there is little difference in steric effect.

If the transition state IIb is expressed by the combination of IIIa and IIIb, the contribution of IIIa is more (or less) important than that of IIIb, when X is more (or less) electron-releasing than Y. The effect of a substituent X on the stabilization of the positive charge is larger in IIIa than in IIIb, because of the conjugation between X and the positive carbon atom in IIIa. Hence substituent effects of electron-releasing groups are more favorable than those of electron-withdrawing groups.

In the case of stilbenes, the larger absolute value of ρ in *p*-methyl- and *p*-methoxy substituents compared with the electron-withdrawing groups (NO_2 , Cl and Br) may be explained in this way.

The Possibility of the Change in the Nature of Transition State.—The structure of a transition state may vary with the activity of the reactants. An electrophilic reagent may approach more closely to the double bond with an increase of the electron density in the substrate, increasing the interaction between reagent and substrate.

The larger effect of electron-releasing groups than electron-withdrawing group on the epoxidation rate is also explicable by this increased interaction between reagent and substrate in the transition state.

Although a continuous change of apparent ρ with varying σ is expected from this structural change in the transition state, two straight lines with different slopes (only two different ρ) was obtained with stilbenes; therefore, an effect of asymmetric attack seems to be more important in this case. In α -methylstilbenes, however, the observed ρ seems to vary continuously (Fig. 1) and, since both steric and electronic effects tend to direct the attack to the 2-carbon atom of 1-methyl-1,2-diphenylethylene, the variation of ρ may be attributed more to the difference in interaction of the reactive species in the transition state than to asymmetric attack. A relatively small difference in reactivities of *p*- and *p'*-chloromethylstilbenes shows that the effect of asymmetric attack is less important, in agreement with the above presumption.

Molecular models and ultraviolet absorption data¹³ suggest that the β -phenyl group is not located in the plane of the double bond. This leads to a smaller substituent effect from the *p'*- than from *p*-position because of the decreased

(13) (a) H. Ley and F. Rinke, *Ber.*, **56**, 773 (1923); (b) H. Suzuki, *Bull. Chem. Soc. Japan*, **25**, 145 (1952).

resonance ability of β -phenyl groups. The smaller value of k for p' -methyl- and p' -methoxy- α -methylstilbene compared with those for the p -position may be ascribed mainly to this effect.

Resonance Interaction and the Extent of Approach of Reagent to Substrate.—Some investigators proposed corrected σ -values for electrophilic reactions where p -electron-releasing groups show abnormally large effects, e.g., σ_e by Pearson, *et al.*, in the Beckmann rearrangement,^{14a} σ^+ by Deno, *et al.*, in the protonation of substituted triphenylcarbinols^{14b} and σ^+ by Brown, *et al.*, in solvolysis reactions.¹⁵ These corrected σ 's were correlated with each other by eq. 1^{16a} with parameter^{16b} r

$$\sigma^+ = \sigma + r \times \Delta\sigma_R \quad (1)$$

where r depends on the reaction and on the extent of resonance stabilization of the carbonium ion in the transition state.

The equilibrium and rate constants for anilines and phenols with strong electron-withdrawing groups in the p -position show abnormal effects. This fact together with eq. 1 suggests that abnormal substituent effects accompany strong resonance interactions which vary in magnitude with the change in the nature of the reactants. Hence, the extent of approach of the reagent discussed above corresponds to the magnitude of resonance, i.e., r in eq. 1.

As shown in Fig. 1, plots of $\log(k/k_0)$ vs. σ^+ (Brown) in the epoxidation of stilbenes gave a slightly concave curve, which seems to be due to an over-estimate of r ($r = 1.33$) in eq. 1. This is attributable to a smaller resonance contribution of the substituent¹⁷ in this transition state than that in the standard (solvolysis) reaction, because an attacking reagent, peroxyacid, is not a cation but a neutral molecule with a partial positive charge on oxygen atom.

Substituent Effect in PBA.—The second-order rate constants for p -substituted PBA decreased in the order $\text{Cl} > \text{H} > \text{MeO}$ for all α -methylstilbenes used (Table III). The rate increase with electron-withdrawing substituents in peroxyacid has been observed previously with stilbenes⁴ and sulfides,¹⁸ indicating the similar electrophilic attack of peroxy oxygen.

Brown, *et al.*,¹⁹ showed in aromatic electrophilic reactions a proportionality between the selectivity factor S_f and partial rate factor p_f which, accord-

(14) (a) D. E. Pearson, *et al.*, *J. Org. Chem.*, **17**, 1511 (1952); (b) N. C. Deno, J. J. Jaruzelski and A. Schriesheim, *J. Am. Chem. Soc.*, **77**, 3044, 3051 (1955).

(15) (a) H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957); (b) H. C. Brown and Y. Okamoto, *J. Org. Chem.*, **22**, 485 (1957).

(16) (a) Y. Yukawa and Y. Tsuno, *Bull. Chem. Soc. Japan*, **32**, 965, 971 (1959); see also ref. 15b. (b) If σ^+ by Deno is taken as standard ($r = 1.00$), then in σ^+ by Brown $r = 1.33$.

(17) A referee pointed out the possibility of a change in steric effect because tilting of the plane of the benzene and ethylene groups is not constant with p -substituents. This effect is reasonable only with p' -substituent in which the phenyl group is not located on the ethylene plane. However, with a p -substituent whose phenyl group is on the ethylene plane, the steric effect of the phenyl group seems to be negligible. The qualitative parallelism between p - and p' -substituent effects suggests that the above steric effect is not important, at least in the case of α -methylstilbenes.

(18) C. G. Overberger and R. W. Cummins, *J. Am. Chem. Soc.*, **75**, 4250 (1953).

(19) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953); H. C. Brown and W. H. Bonner, *ibid.*, **76**, 605 (1954); H. C. Brown and

TABLE III

THE RATES OF THE EPOXIDATION OF α -METHYLSTILBENES WITH SUBSTITUTED PBA IN BENZENE

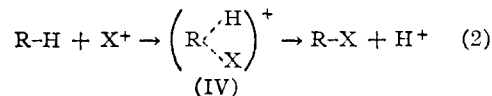
Second-order rate constant $k_2 \times 10^4$, l. mole⁻¹ sec.⁻¹

p -Substituents in α -methylstilbene	p -Substituents on PBA					
	At 10°			At 25°		
	MeO	H	Cl	MeO	H	Cl
MeO	22.0	38.4	88.4	65.6	124	258
Me	8.80	17.2	36.4	27.7	51.0	105
H ^a	4.67	7.91	18.3	14.3	25.7	56.2
Cl	2.86	3.10	10.7	9.50	16.7	34.8

^a Data from Table II.

ing to him, corresponded to the selectivity and the reactivity, respectively. However, as we have pointed out previously,²⁰ p_f corresponds to the intermolecular selectivity, so that Brown's correlation indicates that the intramolecular selectivity is proportional to the intermolecular selectivity. The reactivity should be expressed in terms of a rate constant k itself and is expected to correlate with selectivity.

For a test of the correlation between selectivity and reactivity, it is essential to confine the discussion to a series of closely related reactions. For instance, structural changes in substrates which cause a mechanistic change from $\text{S}_{\text{N}}1$ to $\text{S}_{\text{N}}2$ give rise to a change of ρ from negative to positive value.²¹ In common electrophilic reactions, this change of ρ value has not yet been observed, but in a typical electrophilic substitution (2), the transition state as well as the reactivity of X^+ may be



changed with the change of X^+ and/or R. When the electrophilicity of X^+ is increased with constant steric effect of X^+ and with constant R, a change of nature of IV, mainly due to the increased resonance interaction between R and X^+ , may occur and this change may lead to an increased electron shift from R to X^+ in IV.

It is expected that the absolute value of ρ (intermolecular selectivity) decreases with increasing electrophilicity of X^+ because of the correlation between reactivity and selectivity²⁰ on the one hand, and that it increases with increasing electrophilic activity of X^+ because of the increased resonance interaction on the other.

Table IV lists k/k_0 for the reaction of α -methylstilbenes with p -methoxy-, chloro- and unsubstituted PBA, where k and k_0 correspond to the rate constants for substituted and unsubstituted α -methylstilbenes with the same peroxyacid, respectively. Table IV indicates that (i) the change of k/k_0 with varying p -substituents in PBA is small and (ii) there is no clear correlation between k and ρ in equation $\rho = \log(k/k_0)/\sigma$; i.e., in p -methoxy- and p -methyl- α -methylstilbenes the

C. W. McGary, *ibid.*, **77**, 2300 (1955); H. C. Brown and C. R. Smoot, *ibid.*, **78**, 6255 (1956); H. C. Brown, *et al.*, *ibid.*, **80**, 4046 (1958); L. M. Stock and H. C. Brown, *ibid.*, **81**, 3323, 3315 (1959).

(20) Y. Ogata and I. Tabushi, *Bull. Chem. Soc. Japan*, **34**, 604 (1961).

(21) E.g., C. G. Swain and W. P. Langsdorf, Jr., *J. Am. Chem. Soc.*, **73**, 2813 (1951).

TABLE IV

THE EFFECTS OF SUBSTITUENTS IN α -METHYLSTILBENES k/k_0 and $\log(k/k_0)$ (in parentheses), in benzene at 10°; k/k_0 is the relative rate of substituted vs. unsubstituted α -methylstilbenes for the same PBA

<i>p</i> -Substit. in α -methylstilbene	<i>p</i> -Substituent in PBA		
	MeO	H	Cl
MeO	4.75 (0.677)	4.84 (0.686)	4.82 (0.683)
Me	1.88 (.276)	2.17 (.336)	1.98 (.297)
Cl	0.615 (-0.212)	0.653 (-0.185)	0.586 (-0.232)

values of k/k_0 increase from small values for *p*-methoxy-PBA (lowest reactivity) through the maximum for PBA, and then decrease again with *p*-chloro-PBA (highest reactivity). On the other hand, in the case of *p*-chloro- α -methylstilbene, k/k_0 decreases from *p*-methoxy-PBA to PBA and increases again from PBA to *p*-chloro-PBA.

Facts i and ii cited above may be ascribed to (a) a correlation between selectivity and reactivity, and (b) a change in the resonance contribution, which affects k/k_0 inversely to (a).²³

With *p*-methoxy- and *p*-methyl- α -methylstilbenes, the effect of the selectivity-reactivity relationship slightly exceeds the increase of resonance effect, and thus larger values of k/k_0 were observed for PBA than for *p*-chloro-PBA. However, the decrease of resonance effect in the transition state may be more important than the selectivity relationship with *p*-methoxy-PBA, so that k/k_0 decreases from PBA to *p*-methoxy-PBA. With *p*-chloro- α -methylstilbene, the decrease of resonance effect is less important and its increase is important; therefore the reverse is true.

Selectivity and the Nature of the Transition State.—The substituent constants in electrophilic

(22) The change of k/k_0 may be interpreted as follows: with *p*-methyl- and *p*-methoxy- α -methylstilbenes where the resonance interaction in the transition state seems to be larger than with α -methylstilbene, the effect of *p*-chloro substituent in PBA seems less important, since the increase of the resonance contribution approaches a limiting value determined by other less variable effects such as the steric effect.

reactions, σ^+ , are given by eq. 1. On the other hand, Brown and his co-workers showed the linear correlation 3 between the *para* partial rate factor and the selectivity factor, S_i , defined by

$$S_i = \log(p_i/m_i); \log p_i = \alpha \times S_i \quad (3)$$

Hence, the following equations are derived, where σ_I and σ_R are the inductive and resonance contribution in σ value, respectively.

$$\log p_i = \rho(\sigma_I + \sigma_R + r\Delta\sigma_R) \quad (4a)$$

$$\log m_i = \rho\sigma_I \quad (4b)$$

$$S_i = \rho(\sigma_R + r\Delta\sigma_R) \quad (4c)$$

On substitution of 4 into 3, α is given in 5.

$$\alpha = \frac{\sigma_I + \sigma_R + r\Delta\sigma_R}{\sigma_R + r\Delta\sigma_R} \quad (5)$$

The value of α in eq. 5 should vary with r . Hence, with electron-releasing substituents where $r\Delta\sigma_R$ is comparatively important, α decreases with an increase of r , since σ_I , σ_R and $\Delta\sigma_R$ are all negative and r is positive. In other words, in a series of electrophilic reactions, an intermolecular selectivity p_i becomes smaller compared with an intramolecular selectivity S_i with an increase of r , or the resonance contribution in the transition state.

Equation 5 may be transformed into 6. On substituting Brown's value of $\alpha = 1.36$ into eq. 6, the parameter r is calculated to be 0.92 which is

$$r = \frac{\sigma_I + (1 - \alpha)\sigma_R}{\Delta\sigma_R(\alpha - 1)} \quad (6)$$

smaller than r in Deno's¹⁴ σ^+ (evaluated by Yukawa¹⁶ 1.00) and than r in Brown's¹⁵ $\sigma^+(1.33)$.¹⁶ This change in r agrees with the above discussion.

For the epoxidation of α -methylstilbenes, r was estimated to be 0.5~0.6, and this smaller value may be due to smaller electron demand of the reaction where no carbonium ion is involved.

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Kinetics of the Peroxybenzoic Acid Epoxidation of Substituted Propenes and 2-Butenes in Benzene

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The rates of the epoxidation of 3-substituted 1-propenes and 1,4-disubstituted 2-butenes with peroxybenzoic acid in benzene have been measured. In general, electron-releasing groups accelerated the reaction, while no appreciable steric effect was observed with the substituents used. The substituent effect in propenes yields two straight lines in plots of $\log k$ vs. the σ^* of Taft, which is explained by a less efficient transmission of polar effect of electron-releasing groups and by an asymmetric attack of peroxyacid on the double-bonded carbon atoms. The substituent effect in 2-butenes is discussed in terms of additive hyperconjugation of hydrogen atoms at the 1- and 4- positions as well as by an inductive effect. The abnormally high reactivity of allyl alcohol is ascribed to activation by hydrogen bonding.

It is well known that the peroxyacid epoxidation of ethylene derivatives involves an electrophilic attack by the peroxyacid.¹ Our paper on the epoxi-

dation of α -methylstilbenes² reported that the effects of substituents showed deviations from

(1) For examples, see (a) D. Swern, *Chem. Revs.*, **45**, 1 (1949); (b) D. Swern, "Organic Reactions," Vol. 7, John Wiley and Sons, Inc.

New York, N. Y., 1953, p. 378; (c) Ya. K. Syrkin and I. I. Moiseef, *Prog. Chem. USSR*, **29**, 425 (1960).

(2) Y. Ogata and I. Tabushi, *J. Am. Chem. Soc.*, **83**, 3440 (1961).