Reduction with Lithium Aluminum Hydride.—Dropwise addition of 160 ml. of a benzene solution containing 0.29 equivalent of peroxidized butadiene to 25 g. (0.66 moles) of lithium aluminum hydride in 600 ml. of ether produced a mildly exothermic reaction. After four hours at reflux, the excess hydride was destroyed by the slow addition of 98 ml. of ethyl acetate followed by 10 ml. of water. The aluminum complex was destroyed by addition of 200 ml. of 30% sodium hydroxide and the resulting emulsion was extracted thoroughly with ether. Distillation of the ether extracts separated 9.9 g. (43%) boiling in the range 91–132° (14 mm.). This comprised two products: **3-Butene-1,2-diol**, b.p. 94.5–96° (14 mm.), n^{25}_{D} 1.4598. *Anal.* Calcd. for $C_4H_8O_2$: C, 55.80; H, 9.31. Found: C, 56.00; H, 9.37.

trans-**2-Butene-1,4-diol**, b.p. 132° (14 mm.), n^{25}_{D} 1.4750. *Anal.* Found: C, 55.32; H, 9.38.

The bis-(α-naphthylurethan) of the *trans*-2-butene-1,4-diol, recrystallized from 1-butanol, melted at 220°. *Anal.* Calcd. for $C_{26}H_{22}N_2O_2$: N, 6.57. Found: N, 6.37. Infrared spectra were consistent with the above assignments.

An alternate procedure giving higher yields involved treatment of the reduction mixture with acetic anhydride according to the method of Lardon and Reichstein.[12] A solution of 8.2 g. (0.095 equivalent) of butadiene peroxide in 30 ml. of dioxane was added dropwise to a stirred solution of 12.5 g. (0.33 mole) of lithium aluminum hydride in 300 ml. of dry ether. Reflux was maintained for 3 hours after addition was complete, and the resulting solution allowed to stand overnight; 70 ml. of acetic anhydride was added cautiously, followed by a more rapid addition of a mixture of 50 ml. of acetic anhydride and 30 ml. of pyridine. The solvent was removed by warming until the solution temperature reached 70°. The residue was saturated with sodium potassium tartrate and extracted with chloroform. The extracts were concentrated and distilled. Two fractions were separated: (a) b.p. 100–124° (20 mm.), 2.93 g., and (b) b.p. 124–134° (20 mm.), 5.47 g. Upon redistillation, fraction a gave b.p. 111° (20 mm.), n^{25}_{D} 1.4295, and fraction b gave b.p. 133° (20 mm.), n^{25}_{D} 1.4406, sapon. equiv. 86.0 (calcd. for $C_8H_{12}O_4$, 86.0). No higher boiling esters were found. These products correspond to known diacetates of 3-butene-1,2-diol and *trans*-2-butene-1,4-diol, respectively.[13,14]

Reaction with Phenylhydrazine.—When a mixture of 1 g. of butadiene peroxide and 5 ml. of phenylhydrazine was warmed cautiously on a steam-bath, a vigorous reaction occurred, and water was evolved. After four hours, a mixture of 5 ml. of acetic acid and 15 ml. of ethyl alcohol was added. The hot solution was diluted with water until permanent turbidity resulted, treated with charcoal, filtered and cooled. The resulting brown crystals, 0.25 g., were recrystallized from alcohol and from benzene to produce brilliant yellow platelets melting with decomposition at 173–175°. This corresponds to the bis-(phenylhydrazone) obtained by Kharasch[8] from 1,4-bis-(*t*-butyldioxy)-2-butene and to the known bis-(phenylhydrazone) prepared from fumaraldehyde.[15]

---

[12] A. Lardon and T. Reichstein, *Helv. Chim. Acta*, **32**, 2003 (1949).

[13] A. N. Pudovic, *J. Gen. Chem.* (*USSR*), **19**, 1179 (1949); *C. A.*, **44**, 1005 (1950).

[14] C. Prévost, *Compt. rend.*, **183**, 1292 (1926).

[15] D. L. Hufford, D. S. Tarbell and T. R. Koszalka, This Journal, **74**, 3014 (1952).

Wilmington 98, Del.

[Contribution of the Metcalf Chemical Laboratories of Brown University]

Studies of the Peroxybenzoic Acid Oxidation of *p*-Methoxyl Substituted Stilbenes

By Donald R. Campbell,[1] John O. Edwards, Jane Maclachlan and Katalin Polgar

Received April 30, 1958

The mechanism of the anomalous oxidation of *p*-methoxyl substituted stilbenes by peroxybenzoic acid to give glycol monobenzoate esters has been investigated. The kinetics of the peroxybenzoic acid oxidation of *trans*-stilbene, *trans*-*p*-methylstilbene, *cis*-*p*-methoxystilbene and *trans*-*p,p'*-dimethoxystilbene have been studied by following both the disappearance of the peroxybenzoic acid and the formation of benzoic acid. The results of the kinetic studies support the proposed formation of an epoxide intermediate by a second-order reaction which is not acid catalyzed, followed by a slower opening of the epoxide by benzoic acid present in the system. Studies of the reaction of the epoxide of *trans*-*p*-methoxystilbene with benzoic acid have given results which agree with those obtained by the kinetic studies of the oxidation. The products obtained include glycol monobenzoate esters and ketones. The ketones obtained demonstrate an interesting tendency for epoxide rearrangement which suggests a correlation with the over-all retention of configuration of the esters.

It has been widely accepted that the formation of glycols or glycol esters from olefins by peroxyacid oxidation results in over-all inversion of configuration.[2] Recently,[3,4] however, it has been shown that peroxyacid oxidation of certain olefins yields glycols and glycol esters with over-all retention of configuration. Therefore, it has been suggested[3] that the use of peroxyacids for purposes of configuration assignment on olefins should be avoided until the reaction is better understood.

While it is commonly assumed[5] that the formation of glycols or glycol esters is through an epoxide intermediate, there has been no evidence to justify such an assumption in all cases of peroxyacid oxidation of olefins. The most convincing evidence presented has been the demonstration that epoxides often yield the corresponding glycols and glycol esters and that epoxides are formed from peroxyacid oxidation of olefins after shorter periods of oxidation and under milder conditions than those employed for obtaining glycols or esters. There has not been unanimous agreement on the role of the epoxide, however. Levy and Abragam[6] have postulated that esters are formed by the addition of the elements of peroxyacids to olefins and are intermediates in the formation of epoxides, while Muskat and Herrman[7] have shown the formation of epoxides from certain glycol esters.

Thus it was felt that in the case of the anomalous formation of glycol monobenzoate esters with re-

---

[1] National Science Foundation Predoctoral Fellow, 1956–1957, 1957–1958.

[2] S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol. I, R. C. Elderfield, editor, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 27.

[3] D. Y. Curtin, A. Bradley and Y. G. Hendrickson, This Journal, **78**, 4064 (1956).

[4] J. H. Brewster, *ibid.*, **78**, 4061 (1956).

[5] (a) D. Swern, *Chem. Revs.*, **45**, 30 (1949); (b) D. Swern, "Organic Reactions," Vol. VII, John Wiley and Sons, Inc., New York, N. Y., 1953, Chapter 7.

[6] J. Levy and D. Abragam, *Bull. soc. chim. France*, [4] **45**, 378 (1929).

[7] I. E. Muskat and M. Herrman, This Journal, **54**, 2001 (1932).

tention of configuration the role of the epoxide was in question. Experiments were therefore performed in order to ascertain whether the glycol monobenzoate esters obtained from *p*-methoxyl substituted stilbenes are formed from benzoic acid derived entirely from the peroxybenzoic acid involved in the olefin oxidation, or whether a contribution is made by any benzoic acid present in the solution due to the use of impure peroxybenzoic acid or to decomposition of peroxybenzoic acid by side reactions.

Results

Peroxybenzoic acid was added to a solution of *trans-p*-methoxystilbene and C^{14}-benzoic acid in benzene or chloroform and the solution was allowed to stand for 96 hours. The glycol monobenzoate ester was then isolated and its observed activity compared with the activity calculated for an ester formed entirely from the radioactive benzoic acid initially present in the solution. The results shown in Table I indicate that the ester is formed almost non-preferentially from both benzoic acid initially present and from benzoic acid derived from peroxybenzoic acid. These data support a mechanism of the type

$$\text{olefin} + \text{peroxyacid} \xrightarrow{k_1} \text{epoxide} + \text{acid}$$

$$\text{epoxide} + \text{acid} \xrightarrow{k_2} \text{ester}$$

where k_1 is much greater than k_2 and are in agreement with the magnitude of the rate constants reported below.

In order to validate the results shown in Table I, it was necessary to demonstrate that no exchange of C^{14} occurred between the benzoic acid and the peroxybenzoic acid under the conditions of these tests. Exchange studies were therefore carried out in a manner similar to that described previously,[8] and exchanges of less than 0.95% were observed. Studies of exchange between benzoic acid and the ester also were conducted, and no measurable exchange was observed under the test conditions.

TABLE I

FRACTION OF ESTER FORMED FROM RADIOACTIVE BENZOIC ACID ON OXIDATION OF *trans-p*-METHOXYSTILBENE BY PEROXYBENZOIC ACID AFTER 96 HOURS

	I	II	III	IV
Olefin (*M*)	0.126	0.191	0.119	0.0953
$C_6H_5CO_2OH$ (*M*)	.154	.198	.137	.0905
$C_6H_5CO_2H$ (*M*)	.178	.243	.107	.0965
$C_6H_5CO_2H$ (c.p.m.)[a]	3980	3570	4010	4305
Ester (c.p.m.) calcd.[b]	1397	1252	1405	1510
Ester (c.p.m.) obsd.	832	702	649	881
% label calcd.[c]	54	55	44	52
% label obsd.[d]	59	56	46	59

[a] C^{14}-Benzoic acid added plus benzoic acid present in the peroxybenzoic acid solution. [b] Calcd. activity for ester formed entirely from benzoic acid initially present. [c] Percentage = $(C_6H_5CO_2H)(C_6H_5CO_2H + C_6H_5CO_2OH)^{-1} \times 100$. [d] Percentage = (obsd. ester activity)(calcd. ester activity)$^{-1} \times 100$.

Infrared spectra of the esters were obtained; these were in agreement with that reported for the glycol monobenzoate ester of *p*-methoxystilbene,[3] as were the carbon and hydrogen analysis and the melting points.

If it is assumed that formation of glycol monobenzoate esters is by way of epoxide intermediates, then it is to be expected that plots of benzoic acid concentration with time would give curves characteristic of series reactions, *i.e.*, curves having maxima. Therefore, *trans-p*-methoxystilbene, *cis-p*-methoxystilbene and *trans-p,p'*-dimethoxystilbene were each oxidized by peroxybenzoic acid in benzene at 25° and the values of the second-order rate constant obtained both by iodometric titration of the peroxybenzoic acid and by determination of the benzoic acid by titrating with sodium hydroxide according to the method of Wolf.[9] The values of the rate constants obtained by following the disappearance of peroxybenzoic acid are shown in Table II, and are in agreement with those reported by Lynch and Pausacker.[10] The values of the rate constants obtained by following the benzoic acid concentration showed deviations after the first 40% of the reactions, indicating that some of the benzoic acid formed was consumed by subsequent reactions. A plot, typical of those obtained, is shown in Fig. 1 and is in agreement with the above mechanism.

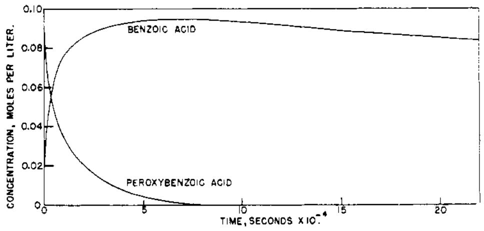


Fig. 1.—A graph showing the rate of loss of peroxybenzoic acid and the rate of change of benzoic acid concentration as a function of time in the oxidation of *p*-methoxyl-*trans*-stilbene in benzene at 25°.

The effect of added acid on the rate of oxidation was studied in the manner reported by Lynch and Pausacker[10] and, in agreement with their work, no acid catalysis was observed.

In tests using chloroform as solvent it was found that Wolf's method[9] could not be used to determine benzoic acid because of a drift in *p*H. However, by running the oxidations in chloroform containing C^{14}-benzoic acid and following the activity of the benzoic acid extracted in a manner similar to that employed before,[8] it was possible to compare benzoic acid formation with peroxybenzoic acid consumption. An increase in benzoic acid concentration was shown by a decrease in specific activity. Since an increase in benzoic acid concentration is shown in chloroform as well as in benzene and since radioactive esters are obtained from reactions run in either solvent when C^{14}-benzoic acid is present, it appears probable that the same intermediate is formed in chloroform and in benzene.

---

(8) G. Levey, D. R. Campbell, J. O. Edwards and J. Maclachlan, THIS JOURNAL, **79**, 1797 (1957).

(9) R. Wolf, *Bull. soc. chim. France*, 644 (1954).

(10) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955).

TABLE II

REACTION RATE CONSTANTS FOR THE OXIDATION OF SUBSTITUTED STILBENES BY PEROXYBENZOIC ACID IN BENZENE AT 25°

Olefin, stilbene	Olefin, mole/l.	$C_6H_5CO_2OH$, mole/l.	$C_6H_5CO_2H$, mole/l.	k_1 from $C_6H_5CO_2H$[d]	k_1 from $C_6H_5CO_2OH$[d]	k_1 from Lynch and Pausacker[d]
trans-Stilbene	0.1111	0.0922	0.0211	0.40[a]	0.416	0.425
trans-Stilbene	.1668	.0922	.0211	.40[a]	.421	.429
trans-p-Methyl-	.1545	.0673	.0255	.89[a]	.889	.972
trans-p-Methyl-	.1031	.0902	.0360	.83[a]	.827	.964
trans-p-Methoxy-	.0954	.0891	.0220	1.8[a]	1.90	2.02
trans-p-Methoxy-	.0635	.0997	.0719	2.0[a]	1.95	2.02
trans-p-Methoxy-	.0714	.1341	.000		2.05	
trans-p-Methoxy-	.0714	.1340	.0410		1.98	
trans-p-Methoxy-	.0714	.1332	.0820		2.05	
trans-p,p'-Dimethoxy-	.01321	.01471	.00384	7.3[b]	8.12	8.36
trans-p,p'-Dimethoxy-	.01321	.02942	.00768	7.6[b]	8.16	8.30
cis-p-Methoxy-[c]	.0511	.0464	.0121	2.0[b]	2.06	
cis-p-Methoxy-	.0511	.0700	.0102	2.0[b]	2.51	

[a] For first 40% of reaction. [b] For first 25% of reaction. [c] The values reported for *cis-p*-methoxystilbene are of less reliability due to questionable purity of the olefin. [d] All rate constants should be multiplied by 10^{-3}, units are liters-mole^{-1}-sec.$^{-1}$.

It was desirable to compare the results obtained using *p*-methoxyl substituted stilbenes with those obtained using a compound believed to give an epoxide product rather than an ester. Therefore tests similar to those conducted with the *p*-methoxyl substituted stilbenes were made using unsubstituted stilbene and using *trans-p*-methylstilbene. It was found that the benzoic acid concentration was at all times equal, within experimental error, to the peroxybenzoic acid consumed, confirming the observation that neither olefin gives esters under these conditions.

In order to determine the kinetics of the *cis* opening of the epoxide of *p*-methoxystilbene by benzoic acid,[3] the benzoic acid concentration of a mixture of benzoic acid and this epoxide in benzene was determined at various times. The method of initial slopes was used to obtain values of the rate of change of concentration with time. The data are shown in Table III; as expected, they indicate that the reaction is much slower than the oxidation of the related stilbene by peroxybenzoic acid. From the initial slope data, it appears that the reaction is first order in epoxide and first order in benzoic acid.

TABLE III

RATE OF REACTION OF *trans-p*-METHOXYSTILBENE OXIDE AND BENZOIC ACID IN BENZENE AT 25.0°

Epoxide, mole/l.	$C_6H_5CO_2H$, mole* l.	Initial slopes mole/l. $\times 10^8$	k_2, liter/mole-sec. $\times 10^5$
0.0872	0.0534	7.1	1.5
.0425	.0534	3.5	1.5
.0425	.1008	6.5	1.5
.0831	.0527	6.6	1.5
.0442	.0527	3.3	1.4
.0442	.0973	6.9	1.6

Attempts at product determination were made after oxidation of *p*-methoxystilbene by peroxybenzoic acid in dry benzene at 25°. After two weeks reaction time, analysis by isotope dilution methods showed a yield of 65.2% of the *threo*-glycol monobenzoate ester and a yield of 5.9% of a ketone, which was shown to be *p*-methoxybenzyl phenyl ketone by its melting point, infrared spectrum and oxime derivative. Analysis by treatment with sodium bisulfite and then titration with sodium hydroxide did not show the presence of any aldehyde. When this experiment was repeated under the same conditions, similar results were obtained. When the experiment was carried out using benzene saturated with water as the solvent, yields of 56.8 and 18.5% were obtained for the ester and ketone, respectively; repetition of this experiment gave similar results.

Attempts were made to isolate the epoxide of *trans-p*-methoxystilbene by working up the reaction mixture after periods of 10, 24 and 48 hours, *i.e.*, before completion of the esterification reaction. When chromatography was not used, an oil was obtained which gave the *threo*-glycol monobenzoate ester and a few crystals of the *p*-methoxybenzyl phenyl ketone on standing. However, when chromatography over activated alumina was conducted only the ester and ketone could be isolated.

The ketone obtained suggests that the epoxide has rearranged with migration of hydrogen. Therefore, further experiments were conducted to verify this interesting rearrangement. *trans-p*-Methoxystilbene showed no change in its infrared spectrum when dissolved in dry benzene for 48 hours. However when *trans-p*-methoxy stilbene oxide in dry benzene was adsorbed on alumina and eluted after 48 hours, an oil was obtained which had strong absorption in the carbonyl region of the infrared spectrum, and which was shown by isotope dilution analysis to consist of 14.6% *p*-methoxybenzyl phenyl ketone. *trans*-Stilbene oxide and *trans-p*-methylstilbene oxide showed no change.

On treating *trans-p,p'*-dimethoxystilbene with peroxybenzoic acid in dry benzene for reaction times of 48 hours and of 7 days, a material believed to be a glycol monobenzoate ester was obtained, as was an oil which on standing or chromatography gave desoxyanisoin (*p*-methoxybenzyl anisyl ketone). After only 10 hours reaction time a material which melted in the range to be expected of the epoxide and an oil which gave desoxyanisoin on standing were obtained. *trans-p*-Methylstilbene and *trans*-stilbene gave only the corresponding epoxides in nearly quantitative yields after 48 hours.

Experimental

Materials.—Peroxybenzoic acid was prepared by the method of Braun[11] using the modifications of Kolthoff,[12] and using dry, thiophene-free benzene or dry phosgene-free chloroform as the solvent. C^{14}-Benzoic acid (0.25 mc.), obtained from New England Nuclear Corp., was diluted with 25 g. of reagent grade benzoic acid. An infinitely thick sample of the resulting tagged benzoic acid gave an average counting rate of 8441 c.p.m. *trans-p*-Methoxystilbene was prepared by the method of Meerwein[13] from *p*-anisidine and cinnamic acid and gave a m.p. of 135–136°.

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.55; H, 6.78.

trans-p,p'-Dimethoxystilbene was prepared by the method of Tadros, Ekladius and Sakla[14] from anisaldehyde and ethylene glycol and gave a m.p. of 213–214°.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71. Found: C, 80.03; H, 6.74.

Other standard chemicals were reagent grade or were purified before use.

Determination of Radioactivity of Esters from Peroxybenzoic Acid Oxidation of *p*-Methyl Substituted Stilbenes.—The substituted stilbene and C^{14}-benzoic acid were dissolved in benzene or chloroform and brought to constant temperature. The appropriate volume of peroxybenzoic acid solution was brought to the same temperature and the reagents mixed. After a suitable time interval the solution was washed with 2% sodium carbonate solution and with water, dried over sodium carbonate, and the solvent removed in a stream of dry air. The resulting crystals of glycol monobenzoate ester were recrystallized from benzene–ligroin and counted as infinitely thick samples. Coincidence corrections were not applied. When it was desired to count the benzoic acid present in the reaction mixture, the acid was separated as described previously,[8] recrystallized and counted as an infinitely thick sample.

Kinetic Studies of Peroxybenzoic Acid Oxidation of Certain Stilbenes.—Reaction mixtures were prepared as described above, excluding the use of C^{14}-benzoic acid, and sampled at appropriate times. The peroxybenzoic acid was determined by titrating with sodium hydroxide in the manner of Wolf.[9]

Kinetic Studies of the Opening of *trans-p*-Methoxystilbene Oxide by Benzoic Acid.—*trans-p*-Methoxystilbene oxide, m.p. 81–82°, prepared by the method of Orekhoff and Tiffeneau[15] from *p*-methoxystilbene, was dissolved in benzene, brought to constant temperature, and a solution of benzoic acid in benzene of the same temperature added. The benzoic acid was determined after various times by the method of Wolf.[9]

Reaction of *trans-p*-Methoxystilbene with Peroxybenzoic Acid.—*trans-p*-Methoxystilbene (5.000 g., 2.38×10^{-2} mole, m.p. 135–136°) was treated with 100 ml. of 0.256 *m* peroxybenzoic acid in dry benzene for two weeks at 25°. The benzene solution was washed with sodium carbonate and with water, and dried over sodium carbonate. On evaporation of the solvent a yellow oil was obtained which on radioisotope dilution analysis showed yields of 65.2% of the *threo*-glycol monobenzoate ester and 5.94% of *p*-methoxybenzyl phenyl ketone; in a similar experiment yields of 54.0 and 7.11% of the ester and ketone, respectively, were obtained. In another experiment, which was similar except that the yellow oil was recrystallized from benzene–ligroin, a 26% yield of the *threo*-glycol monobenzoate ester,[16] m.p. 119–120°, was isolated. The remaining oil was chromatographed over activated alumina (Merck, reagent grade, heated to 100° for 12 hours) and eluted with benzene. The fractions obtained, in order of elution, were an oil which failed to crystallize, but which gave an infrared spectrum similar to that of the corresponding epoxide, and 0.482 g. of *p*-methoxybenzyl phenyl ketone,[16] m.p. 95–96°; the oxime derivative[17] melted at 130–131°. Another experiment which was similar, except that chromatography was not employed, gave 28% of the *threo*-glycol monobenzoate ester and an oil which gave a small amount of *p*-methoxybenzyl phenyl ketone on standing. When the experiment was repeated for a reaction period of 10 hours, only a pale yellow oil was obtained which after two weeks gave a few crystals of *p*-methoxybenzyl phenyl ketone.

When *trans-p*-methoxystilbene was oxidized by peroxybenzoic acid in benzene saturated with water for 115 hours, the yields of *threo*-glycol monobenzoate ester and ketone were 56.8 and 18.50%, respectively; a repetition of this experiment gave similar results.

Reaction of *trans-p,p'*-Dimethoxystilbene with Peroxybenzoic Acid.—*trans-p,p'*-Dimethoxystilbene (2.024 g., 8.42×10^{-3} mole, m.p. 213–214°) was treated with 200 ml. of 0.0773 *M* peroxybenzoic acid in benzene and 1.000 g. (8.20×10^{-2} mole) of C^{14}-benzoic acid for 48 hours at 25° and washed as described above. Recrystallization gave 0.734 g. of a material melting at 117–122°; attempts at further recrystallization of this material failed. The crude material was radioactive (320 c.p.m.) and appeared to be the glycol monobenzoate ester from its infrared spectrum, which was similar to, but not identical to, that obtained from the glycol monobenzoate ester of *p*-methoxystilbene.

The oil remaining from the first crystallization was treated with benzene–ligroin and after 3 days 0.604 g. (28%) of fine white needles of desoxyanisoin (*p*-methoxybenzyl anisyl ketone)[16] were obtained, m.p. 106–108°. The oxime derivative[18] showed a melting point of 123–124°.

In another experiment 1.000 g. of *trans-p,p'*-dimethoxystilbene was treated for 7 days at 25° with 325 ml. of 0.0238 *M* peroxybenzoic acid in benzene and 1.000 g. of C^{14}-benzoic acid. Recrystallization gave 0.273 g. (26%) of desoxyanisoin and 0.537 g. of a pale yellow oil which was radioactive (617 c.p.m.) and gave an infrared spectrum similar to that expected of the glycol monobenzoate ester. A similar experiment of 16 hours reaction time gave an oil which on standing yielded desoxyanisoin as the only isolable material. Another experiment of 10 hours reaction time was conducted in a similar manner and on chromatography gave 0.031 g. of an unidentified oil with an aldehyde-like odor, 0.307 g. of desoxyanisoin and 0.280 g. of crystals melting at 75–76° and giving an infrared spectrum similar to, but not identical to, that of the epoxide of *trans-p*-methoxystilbene.

Reactions of *trans*-Stilbene and *trans-p*-Methylstilbene with Peroxybenzoic Acid.—*trans*-Stilbene (1.023 g., 5.70×10^{-3} mole, m.p. 124°) was treated with 100 ml. of 0.112 *M* peroxybenzoic acid and 0.6307 g. (5.17×10^{-3} mole) of C^{14}-benzoic acid in benzene for 48 hours at 25°. The benzene solution was washed with 2% sodium carbonate and with water, dried, and the solvent evaporated. Recrystallization of the residue gave 94% yield of *trans*-stilbene oxide,[16] m.p. 68–69°. Another experiment gave 96% of this epoxide.

Similar experiments using *trans-p*-methylstilbene, m.p. 120°, prepared by the method of Meerwein,[13] gave 95% of the corresponding epoxide.[16]

Reaction of *trans-p*-Methoxystilbene Oxide with Benzoic Acid.—*trans-p*-Methoxystilbene oxide (0.2517 g., 1.12×10^{-3} mole, m.p. 80–81°) was treated with 0.3033 g. (2.48×10^{-3} mole) of benzoic acid in 100 ml. of benzene for 13 days. A portion of the benzene solution (80 ml.) was washed with sodium carbonate solution and with water, dried and the solvent evaporated. The residue was recrystallized from benzene–ligroin and gave 0.077 g. of the *threo*-glycol monobenzoate ester, m.p. 117–119°, mixed melting point 118°. The yellow oil remaining was dissolved in benzene–ligroin and allowed to stand at 0° for 36 hours. Crude crystals separated and on recrystallization gave an additional 0.081 g. of *threo*-glycol monobenzoate

---

(11) G. Braun, "Organic Syntheses," Coll. Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 431.

(12) I. M. Kolthoff, T. S. Lee and M. A. Mairs, *J. Polymer Sci.*, **2**, 199 (1947).

(13) H. Meerwein, E. Büchner and K. Van Emster, *J. prakt. Chem.*, **152**, 237 (1939).

(14) W. Tadros, L. Ekladius and B. Sakla, *J. Chem. Soc.*, 2351 (1954).

(15) A. Orekhoff and M. Tiffeneau, *Bull. soc. chim. France*, **37**, 1410 (1925).

(16) As shown by melting point (cor.), infrared spectrum and analysis.

(17) M. Tiffeneau and A. Orekhoff, *Bull. soc. chim. France*, **37**, 433 (1925).

(18) J. C. Irvine and A. M. Moodie, *J. Chem. Soc.*, **91**, 542 (1907).

ester, and 0.023 g. of *p*-methoxybenzyl phenyl ketone. A subsequent experiment failed to yield any workable fractions.

Rearrangement of *trans-p*-Methoxystilbene Oxide over Alumina.—*trans-p*-Methoxystilbene oxide (0.100 g., 3.02 × 10^{-4} mole, m.p. 81–82°) in 10 ml. of benzene was adsorbed on activated alumina (Merck, reagent grade, heated to 100° for 12 hours) for 48 hours. Elution with benzene gave a yellow oil which was recrystallized from benzene–ligroin. On standing for 48 hours, 0.056 g. of crude crystals was obtained which on recrystallization from benzene–ligroin gave 0.015 g. of *p*-methoxybenzyl phenyl ketone.[16] In another experiment, using 0.8157 g. of *trans-p*-methoxystilbene oxide, radioisotope dilution analysis of the reaction mixture after elution from the aluminum showed the presence of 14.6% *p*-methoxybenzyl phenyl ketone.

Radioisotope Dilution Analysis.—The C^{14}-tagged *threo*-glycol monobenzoate ester of *p*-methoxystilbene oxide was prepared by the reaction of *p*-methoxystilbene with peroxybenzoic acid in the presence of C^{14}-benzoic acid. The C^{14}-tagged *p*-methoxybenzyl phenyl ketone was prepared from C^{14}-*p*-methoxybenzophenone by the method of Tiffeneau and Orekhoff.[17] The C^{14}-*p*-methoxybenzophenone was prepared from C^{14}-benzoic acid by converting to C^{14}-benzoyl chloride with PCl_5 and treatment with anisole in the presence of $AlCl_3$.

A known weight of approximately 0.8 g. of tagged compound of known activity was added to a known weight of 1 to 2 g. of sample and the mixture recrystallized from benzene–ligroin. The recrystallized mixture of tagged and untagged compound was then counted as an infinitely thick sample.

Discussion

The oxidation of *p*-methoxyl substituted stilbenes by peroxybenzoic acid yields an intermediate by a second-order reaction which is not acid catalyzed. The intermediate is then consumed by a slower reaction to form a *cis* addition glycol monobenzoate ester. It seems certain that the intermediate is the stilbene oxide for the following reasons: (a) the rate of loss of peroxybenzoic acid is the same as the rate of formation of benzoic acid in the first and faster reaction, thus the stoichiometry is that expected for transfer of one oxygen atom to the stilbene; (b) the reaction of the intermediate with benzoic acid is slow as is the reaction of *p*-methoxystilbene oxide with benzoic acid; (c) a partial yield of *p*-methoxystilbene oxide can be identified by infrared in the reaction mixture along with other products (ketone and monoester) the same as those isolated from the direct reaction of epoxide with benzoic acid; and (d) the rate constants for the oxidations of various stilbenes form a self-consistent set of values (see next paragraph).

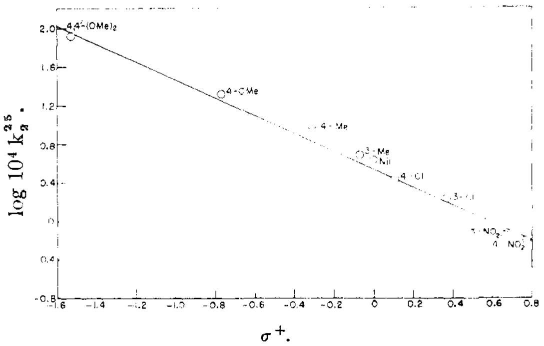
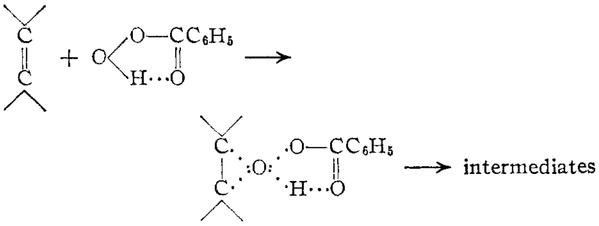


Fig. 2.—Correlation of the rate constants for oxidation of substituted stilbenes by peroxybenzoic acid in benzene at 25°.

Although the rate constants reported by Lynch and Pausacker[10] and here for the oxidations of substituted stilbenes do not correlate well when the σ-values of Hammett are used, they form an excellent plot when the newer σ-values of Brown and Okamoto[19] are employed; the data are shown in Fig. 2. These results indicate that certain substituents on the phenyl rings of the stilbenes can interact with the double bond through resonance to make the double bond carbons more nucleophilic. This is, of course, the direction expected since peroxybenzoic acid is an electrophilic reagent.

Isotope tracer studies[8] have shown that there is little or no exchange between peroxyacids and the corresponding acid anions; thus a mechanism involving a free OH^+ seems unlikely. However, since the infrared spectrum[20] shows that peroxybenzoic acid is highly hydrogen bonded internally, an oxidation step of the type suggested by Bartlett[21] is not unreasonable.



The epoxide intermediate so formed apparently rearranges easily. The *p*-methoxybenzyl phenyl ketone[22] obtained from *trans-p*-methoxystilbene is probably formed by an acid-catalyzed rearrangement involving the initial formation of the most stable carbonium ion and subsequent shift of hydrogen. The product obtained is in agreement with a carbonium ion stabilized by resonance contributions from the anisyl group. The desoxyanisoin obtained from *trans-p,p'*-dimethoxystilbene may be accounted for by a similar rearrangement.

The anomalous *cis* opening of the epoxide to yield glycol esters also may be explained by the formation of an open carbonium ion under the influence of the *p*-methoxyl group, if attack of the benzoate occurs before a 90° rotation of the central bond can take place as models suggest. The fact that only the *p*-methoxysubstituted stilbene oxides were observed both to rearrange and to form *cis*-glycol esters lends support to the postulation of a single intermediate, possibly the carbonium ion, for both the ketone and ester formation.[23]

Acknowledgment.—We gratefully acknowledge financial support by the U. S. Atomic Energy Commission and by the BECCO Chemical Division of Food Machinery and Chemical Corp.

PROVIDENCE 12, R. I.

---

(19) H. C. Brown and Y. Okamoto, THIS JOURNAL, **79**, 1913 (1957).

(20) (a) W. H. T. Davison, *J. Chem. Soc.*, 2456 (1951); (b) P. A. Giguère and A. W. Olmos, *Canad. J. Chem.*, **30**, 821 (1952); (c) G. J. Minkoff, *Proc. Roy. Soc.* (*London*), **224A**, 176 (1954).

(21) P. D. Bartlett, *Record Chem. Progr.*, **11**, 47 (1950).

(22) A. Bradley, Ph.D. Dissertation, Faculty of Pure Science, Columbia University, 1952, has reported the rearrangement of *trans-p*-methoxystilbene oxide to *p*-methoxybenzyl phenyl ketone when treated with hot glacial acetic acid.

(23) The authors are grateful to a referee for an enlightening discussion of this reaction and its mechanism.