

[CONTRIBUTION FROM THE INSTITUTE OF PHARMACEUTICAL CHEMISTRY, UNIVERSITY OF PISA]

Reaction of *cis*- and *trans*-Stilbene with Peroxybenzoic Acid in the Presence of Trichloroacetic Acid

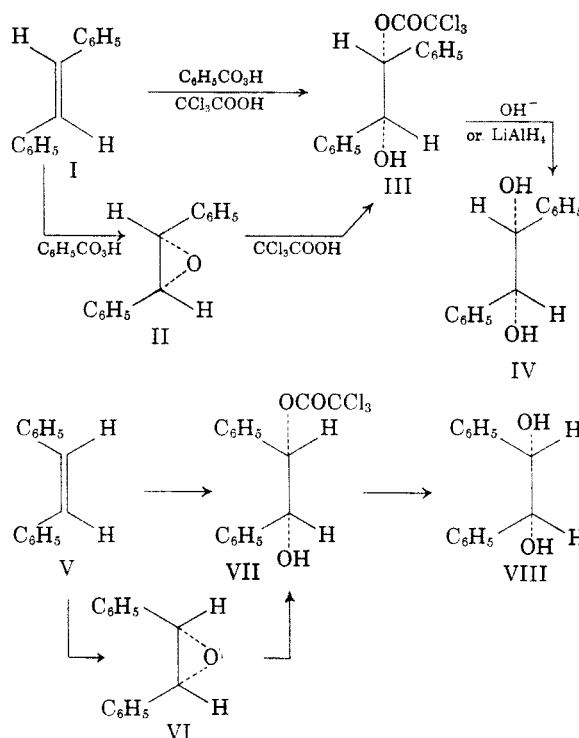
GIANCARLO BERTI AND FRANCESCO BOTTARI

Received December 31, 1959

It has been found that the rate of the reaction of peroxybenzoic acid with *cis*- and *trans*-stilbene is considerably increased by addition of trichloroacetic acid, in contrast to previous results with weaker acids. The monochloroacetates of the hydrobenzoin are formed by *cis*-addition, in a completely stereospecific way, as the main products of these reactions. The same products were obtained by treating *cis*- and *trans*-stilbene oxide with trichloroacetic acid. The kinetics of these reactions has been studied. The results are discussed, making some suggestions about a mechanism that could explain them. The absolute configurations of the optically active hydrobenzoin have been established.

Previous work¹ on the kinetics of the formation of hydroxy lactones from the stilbene-2-carboxylic acids with peroxybenzoic acid² had shown that these reactions are catalyzed by trichloroacetic acid. As these results are in contrast with the fact that the reactions of olefins with peroxyacids are not liable to acidic catalysis,³ it was thought interesting to investigate the influence of trichloroacetic acid on the reactions of the isomeric stilbenes with peroxybenzoic acid, whose kinetics have been studied extensively.^{3c,d} As expected, a very definite catalytic effect was observed in this case, too: reaction rates increased sharply with increasing acid concentrations. The epoxides (II and VI) were not isolated, the diastereomeric hydrobenzoin monochloroacetates (III and VII) being obtained instead, as the main products. They were formed in a stereospecific way and isolated in 72 and 44% yields, respectively, starting from *trans*- or *cis*-stilbene. The transformation of these esters into the corresponding hydrobenzoin, both by alkaline hydrolysis and by reduction with lithium aluminum hydride (to avoid inversions), proved their configurations. The fact that the esters obtained from *trans*- and from *cis*-stilbene respectively gave the (±)- and the *meso*-glycol (IV and VIII) showed that the reactions involve *cis*-addition of the OH and CCl₃CO₂ groups to the ethylenic double bonds of the stilbenes.

The same trichloroacetates (III and VII) were obtained in better yields from the stilbene oxides (II and VI) with trichloroacetic acid in benzene. Oily by-products were also formed which contained 15–20% of carbonyl compounds, as shown by precipitation with 2,4-dinitrophenylhydrazine. Fractional crystallization of the 2,4-dinitrophenylhydrazones yielded mainly diphenylacetaldehyde-



2,4-dinitrophenylhydrazone and a small amount of benzophenone-2,4-dinitrophenylhydrazone. No reasonable explanation can be given for the presence of the latter compound. No evidence was found for the formation of desoxybenzoin. 2,4-Dinitrophenylhydrazones were not obtained from the by-products of the reactions of the stilbenes with peroxybenzoic and trichloroacetic acid. This cannot be considered as a proof that the formation of the esters (III and VII) follows different routes in the two cases, because the carbonyl compounds could be formed and further transformed by the peroxy acid through a Baeyer-Villiger oxidation.

More stereochemical information was sought through the use of the optically active *trans*-stilbene oxides, which can be obtained easily from (+)- and (-)-*erythro*- α,β -diphenyl- β -hydroxyethyl-

(1) G. Berti and F. Bottari, *Gazz. chim. ital.*, **89**, 2380 (1959).

(2) G. Berti, *J. Org. Chem.*, **24**, 934 (1959).

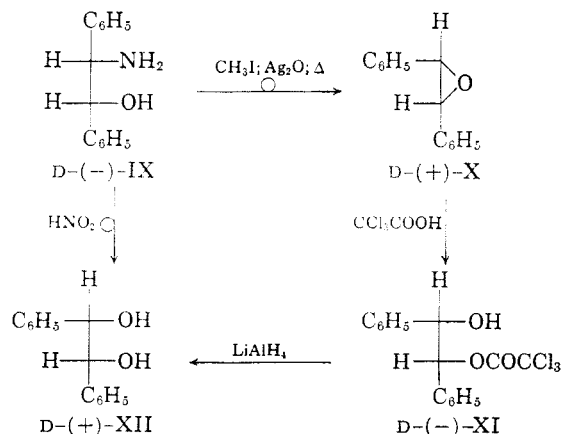
(3) (a) J. Boeseken and J. Stuurmann, *Rec. trav. chim.*, **56**, 1034 (1937); (b) S. Medvedev and O. Bloch, *J. Phys. Chem. U.S.S.R.*, **4**, 721 (1933); (c) B. M. Lynch and K. H. Pausacker, *J. Chem. Soc.*, 1525 (1955); (d) D. R. Campbell, J. O. Edwards, J. Maclachlan, and K. Polgar, *J. Am. Chem. Soc.*, **80**, 5308 (1958).

TABLE I
 RESULTS OF KINETIC RUNS AT 25°

Run No.	[CCl ₃ COOH], Mole/L.	[Stilbene], Mole/L.	[C ₆ H ₅ CO ₂ H], Mole/L.	Equation ^a	Range of $k_{2,5}$, Mole ⁻¹ L. Sec ⁻¹ × 10 ²	Trend of $k_{2,5}$	Equation ^a	Range of k_3 , Mole ⁻¹ L. Sec ⁻¹ × 10 ²	Trend of k_3
<i>trans</i> -Stilbene									
1	0.0333	0.0333	0.0333	Ia	1.18 -1.03	Decr.	Ib	4.67-4.81	Incr.
2	0.0412	0.0412	0.0412	Ia	0.940-0.954	None	Ib	3.17-4.51	Incr.
3	0.0666	0.0333	0.0333	IIa	1.31 -1.21	Decr.	IIb	3.76-3.63	None
4	0.0666	0.3330	0.0333	IVa	1.40 -1.18	Decr.	IVb	3.60-3.27	Decr.
5	0.0665	0.0665	0.0665	Ia	0.915-0.925	None	Ib	2.61-3.19	Incr.
6	0.0746	0.0746	0.0746	Ia	0.980-1.00	None	Ib	2.88-3.47	Incr.
7	0.0814	0.0407	0.0814	IIIa	1.02 -1.09	Incr.	IIIb	2.44-2.95	Incr.
8	0.1110	0.0555	0.0555	IIa	1.29 -1.23	Decr.	IIb	2.82-2.96	Incr.
9	0.1110	0.0555	0.0555	IIa	1.40 -1.31	Decr.	IIb	3.08-3.14	None
10	0.2055	0.1028	0.1028	IIa	1.57 -1.44	Decr.	IIb	2.55-2.45	None
11	0.4590	0.0459	0.0459	Va	2.13 -2.35	Incr.	Vb	2.22-2.46	Incr.
12	0.6070	0.0300	0.0300	Va	2.16 -2.23	None	Vb	1.96-2.02	None
13	0.7938	0.0460	0.0460	Va	2.19 -2.32	None	Vb	1.71-1.84	None
<i>cis</i> -Stilbene									
14	0.0563	0.0563	0.0563	Ia	1.09 -1.16	Incr.	Ib	3.38-4.04	Incr.
15	0.0814	0.0814	0.0814	Ia	1.05 -1.08	None	Ib	2.81-3.50	Incr.
16	0.4592	0.0563	0.0563	Va	1.74 -2.00	Incr.	Vb	1.82-2.10	Incr.

^a See Table II.

amine (IX).⁴ The (-)-epoxide, derived from (+)-IX, yielded the (+)-trichloroacetate, which was transformed by lithium aluminum hydride into a (-)-hydrobenzoin having the expected specific rotation; this offered a further proof of the stereospecificity of the reaction. The absolute configurations of the α,β -diphenyl- β -hydroxyethylamines are known.⁵ Their transformation into the epoxides through the quaternary hydroxides should involve an inversion only on the carbon atom carrying the amino group. Therefore, the (+)-epoxide should have the D-configuration (X), and the (-)-trichloroacetate (XI), as well as the (+)-hydrobenzoin (XII), should belong to the D-series too, unless an extremely unlikely double inversion is involved. The absolute configurations of the hydrobenzoin were not known before, but our find-



(4) J. Read and I. G. M. Campbell, *J. Chem. Soc.*, 2377 (1930).

(5) J. Weijlard, K. Pfister, E. F. Swanezy, C. A. Robinson, and M. Tishler, *J. Am. Chem. Soc.*, **73**, 1216 (1951).

ings agree with some results of Read and Steele,⁶ who obtained (+)-hydrobenzoin in low yield from the product of the reaction of (-)-*erythro*-IX with nitrous acid. This reaction should proceed without inversion on the β -carbon atom. Therefore, configuration XII must follow for the (+)-glycol.⁷

The opening of an epoxide ring in a *cis* way, although it is contrary to the normal rule, is no longer to be considered as an exception for stilbene derivatives, in the light of several examples in the recent literature of partial or total retention of configuration in the acid-catalyzed cleavage of oxiranes carrying at least one phenyl group on the ring.⁸ Ours seems, however, to be the first case of a complete *cis*-stereospecificity in an addition of this type to the two unsubstituted stilbenes and to their oxides. The present reactions have the advantage over similar ones,^{3d,9,10} of being faster (a few hours, instead of days), or giving, especially in the *trans* series, pure glycol esters with only one crystallization and in reasonably good yields. They can be interesting as preparative methods, partic-

(6) J. Read and C. C. Steele, *J. Chem. Soc.*, 910 (1927).

(7) This matter, however, is not at all clear and is being investigated further, because there is no agreement between the results of Read and Steele, who found that with nitrous acid both the (-)-*erythro* and the (+)-*threo*-diphenylhydroxyethylamines give the same (+)-glycol (XII), and those of Weijlard and co-workers (ref. 5), who showed that the two aminoalcohols have the opposite configurations on the β -carbon; either the latter assumption is wrong, or one of the reactions with nitrous acid gives an inversion on the β -carbon.

(8) For a recent review of this topic, see ref. 17.

(9) B. Witkop and C. M. Foltz, *J. Am. Chem. Soc.*, **79**, 197 (1957).

(10) D. Y. Curtin, A. Bradley, and Y. G. Hendrickson, *J. Am. Chem. Soc.*, **78**, 4064 (1956).

TABLE II
EQUATIONS

No.	Ratio of Concn. ^a	Order	Differential Equations	Integrated Equations
Ia	1:1:0.5	2.5	$\frac{dx}{dt} = k_{2.5}(a-x)^2 \left(\frac{a-x}{2}\right)^{0.5}$	$k_{2.5} = \frac{0.9428}{t} \left[\frac{1}{(a-x)^{1.5}} - \frac{1}{a^{1.5}} \right]$
Ib	1:1:1	3	$\frac{dx}{dt} = k_3(a-x)^3$	$k_3 = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$
IIa	1:1:1	2.5	$\frac{dx}{dt} = k_{2.5}(a-x)^2 \left(a - \frac{x}{2}\right)^{0.5}$	$k_{2.5} = \frac{2}{ta} \left[\frac{\sqrt{\frac{a-x}{2}}}{a-x} + \frac{0.5756}{\sqrt{2}} \log \frac{\sqrt{\frac{a-x}{2}} + \frac{x}{2} + \sqrt{\frac{a}{2}}}{\sqrt{\frac{a-x}{2}} - \frac{x}{2} - \sqrt{\frac{a}{2}}} - \frac{0.2664}{\sqrt{2}} \right]$
IIb	1:1:2	3	$\frac{dx}{dt} = k_3(a-x)^2(2a-x)$	$k_3 = \frac{1}{ta^2} \left[\frac{x}{a-x} + 2.303 \log \frac{a-x}{a-2x} \right]$
IIIa	1:2:1	2.5	$\frac{dx}{dt} = k_{2.5}(a-x)(2a-x) \left(a - \frac{x}{2}\right)^{0.5}$	$k_{2.5} = \frac{2.828}{ta} \left[-\frac{1}{\sqrt{2a-x}} + \frac{1.1513}{\sqrt{a}} \log \frac{\sqrt{2a-x} + \sqrt{a}}{\sqrt{2a-x} - \sqrt{a}} - \frac{0.1742}{\sqrt{a}} \right]$
IIIb	1:2:2	3	$\frac{dx}{dt} = k_3(a-x)(2a-x)^2$	$k_3 = \frac{1}{ta^2} \left[2.303 \log \frac{2a-x}{a-x} - \frac{a}{2a-x} - 0.193 \right]$
IVa	high:1:1 ^b	2.5	$\frac{dx}{dt} = k_{2.5}[\text{stilbene}](a-x) \left(a - \frac{x}{2}\right)^{0.5}$	$k_{2.5} = \frac{3.256}{t\sqrt{a}[\text{stilbene}]} \left[\log \frac{\sqrt{\frac{a-x}{2}} + \sqrt{\frac{a}{2}}}{\sqrt{\frac{a-x}{2}} - \sqrt{\frac{a}{2}}} - 0.7655 \right]$
IVb	high:1:2 ^b	3	$\frac{dx}{dt} = k_3[\text{stilbene}](a-x)(2a-x)$	$k_3 = \frac{2.303}{ta[\text{stilbene}]} \log \frac{a-x}{a-2x}$
Va	1:1:high ^b	2.5	$\frac{dx}{dt} = k_{2.5}(a-x)^2[(\text{CCl}_3\text{COOH})_2]^{0.5}$	$k_{2.5} = \frac{1}{t[(\text{CCl}_3\text{COOH})_2]^{0.5}} \left[\frac{1}{a-x} - \frac{1}{a} \right]$
Vb	1:1:high ^b	3	$\frac{dx}{dt} = k_3(a-x)^2[\text{CCl}_3\text{COOH}]$	$k_3 = \frac{1}{t[\text{CCl}_3\text{COOH}]} \left[\frac{1}{a-x} - \frac{1}{a} \right]$

^a [Stilbene]: [C₆H₅CO₂H]: [(CCl₃COOH)₂]^{0.5} for the equations of order 2.5; [stilbene]: [C₆H₅CO₂H]: [CCl₃COOH] for those of order 3. ^b The concentration of one of the reactants is considered constant, being much higher than those of the other two.

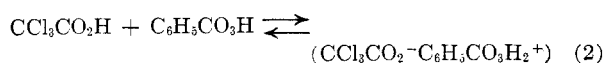
ularly for the optically active hydrobenzoins, which are quite difficult to prepare otherwise.

Kinetic measurements were carried out by following the disappearance of peroxybenzoic acid iodometrically, and in some cases that of stilbene spectrophotometrically. *trans*-Stilbene, which is more easily purified, was used for most determinations, but a few comparative runs were also made with *cis*-stilbene. The results obtained in a series of determinations, with trichloroacetic acid concentrations ranging from 0.033 to 0.79*M* did not fit well into a third order rate expression because, although some single runs gave rather constant values for k_3 up to more than half-life, other ones were much worse; the calculated constants showed a very sharp decrease with increasing acid concentrations (see Table I). In our previous work on the kinetics of the reactions of the stilbene-2-carboxylic acids with peroxybenzoic acid,¹ in which the trichloroacetic acid concentrations remained constant throughout the runs, we had found that the pseudo-second order rate constants were roughly proportional to the square roots of these concentrations. Therefore, the present results were calculated also on the basis of a rate equation of order 2.5:

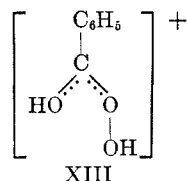
$$-\frac{d[\text{C}_6\text{H}_5\text{CO}_3\text{H}]}{dt} = k_{2.5} [\text{stilbene}] [\text{C}_6\text{H}_5\text{CO}_3\text{H}] [(\text{CCl}_3\text{CO}_2\text{H})_2]^{0.5} \quad (1)$$

As the integration of this differential equation is rather complicated, the ratios of initial concentrations of the reactants were chosen in such a way as to give somewhat simpler expressions. Table I shows the values of $k_{2.5}$, as calculated by means of the integrated equations given in Table II. These figures, although they are better for most of the runs than those obtained by third order kinetics, show a tendency to increase with increasing acid concentrations. A comparison of the two series of values ($k_{2.5}$ and k_3), the one increasing while the other decreases, seems to indicate that the order in trichloroacetic acid is not constant, changing between 0.5 and 1. This is confirmed by the fact that for single runs the values of $k_{2.5}$ show mostly a trend to decrease, those for k_3 to increase with time (see Table I, columns 7 and 10), according to what would be expected for rate constants calculated by a rate expression of too low or too high order, respectively.

The kinetic results can be explained, as assumed before,¹ by the hypothesis that trichloroacetic acid, present in part as a dimer, is involved in the rate-determining step. This acid, which is a very strong proton donor in nonpolar solvents, could act as a catalyst for the reaction by protonating the peroxy acid in an equilibrium reaction (2). The reactive



intermediate would therefore be an ion-pair,¹¹ in which the cation, possibly of the form XIII,



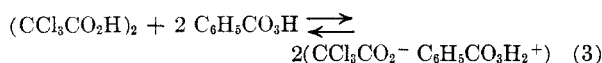
would be a stronger donor of OH^+ than the peroxybenzoic acid molecule. A rate-determining bimolecular reaction would thus take place between this intermediate and the olefin, which would however be dependent on the trichloroacetic acid concentration, if, as likely, the equilibrium in (2) is reached rapidly and its constant K is small. The over-all kinetics should be third order, with an observed constant $k_3 = Kk_2$, because the concentration of the reactive ion-pair would be given by

$$[(\text{CCl}_3\text{CO}_2\text{-C}_6\text{H}_5\text{CO}_3\text{H}_2^+)] = K[\text{CCl}_3\text{CO}_2\text{H}][\text{C}_6\text{H}_5\text{CO}_3\text{H}]$$

and the rate expression by

$$-\frac{d[\text{C}_6\text{H}_5\text{CO}_3\text{H}]}{dt} = Kk_2[\text{stilbene}][\text{C}_6\text{H}_5\text{CO}_3\text{H}][\text{CCl}_3\text{CO}_2\text{H}]$$

It is known,¹² however, that trichloroacetic acid is present as a dimer in benzene solutions. Equation (2) should therefore be replaced by the following:¹³



which would give the rate expression (1), where $k_{2.5} = k_2K^{0.5}$.

The fact that different runs gave results which indicated reaction orders varying between 2.5 and 3 could be explained by assuming that trichloroacetic acid was present only partially, and in different amounts, as a dimer. This could be caused by the presence of small quantities of water, which were hard to avoid, because of the hygroscopicity of the acid and the difficulty in drying completely the peroxy acid solutions without decomposing them. Bell and Arnold¹² found that trichloroacetic acid combines with water to give a 1:1 addition product which is monomeric in dilute benzene solutions, while at higher concentrations (around 0.7*M*), even in the presence of water, all of the acid is present as a dimer. This was confirmed by runs 11 to 13, in which the trichloro-

(11) A similar hypothesis of a complex formation between peroxyacids and other acids was made by Swern in *Organic Reactions*, **7**, 378 (1953). He based his data, however, on acidic catalysis in epoxidation reactions only on cases of different types of oxidations, as pointed out by Lynch and Pausacker (ref. 3c).

(12) R. P. Bell and M. H. M. Arnold, *J. Chem. Soc.*, 1432 (1935).

(13) This trimolecular equation is assumed for the sake of simplicity, but it probably is the resultant of two rapid subsequent bimolecular steps, which should give the same kinetic results.

acetic acid concentrations were much higher than those of the other reactants and were therefore practically constant throughout the reaction; the rate constants were calculated by the second order kinetic equation and divided by the square roots of the dimer concentrations, or by the monomer concentrations, to obtain $k_{2.5}$ or k_3 . Constancy was better for $k_{2.5}$.

The discrepancies in some of our results could also be explained by the following sources of errors. 1) Our calculations do not take into account the normal uncatalyzed reaction between the stilbenes and peroxybenzoic acid, which is much slower, but could have some importance in the runs with low catalyst concentration. 2) Decomposition of the peroxyacid by side-reactions (some runs, which were followed both iodometrically and spectrophotometrically, showed that there is a little difference between the rates of disappearance of the peroxy acid and of stilbene, the former being usually somewhat higher). 3) The yields of the esters III and VII are not quantitative; as the side-products do not contain chlorine, the disappearance of trichloroacetic acid is slower than expected. 4) Different lots of trichloroacetic acid were used. 5) The presence of trichloroacetic acid changes the dielectric constant of the solvent; this could affect the rate, particularly at the higher concentrations. Apparently, however, all these possible sources of error are not too important.

The fact that *cis*-stilbene, which in the uncatalyzed reaction with peroxybenzoic acid reacts almost twice as fast as *trans*-stilbene,^{3c} seems to be oxidized at about the same rate as the *trans*-isomer in the presence of trichloroacetic acid (see Table I) is not easy to explain in the light of the mechanism discussed above. However, solutions of *cis*-stilbene in benzene slowly developed a pink color, later turning to blue, in the presence of an excess of trichloroacetic acid. This could be due to a protonation of the ethylenic double bond, a reaction that would interfere with the electrophilic attack by the peroxyacid. Washing with alkali after twenty-four hours led to the recovery of a product that still had the ultraviolet absorption spectrum of *cis*-stilbene but only about 80% of its extinction coefficients. Probably a slow transformation into a dimer or polymer takes place, as in the case of the reaction of 1,1-diphenylethylene with trichloroacetic acid.¹⁴ *trans*-Stilbene does not give any color and is recovered unchanged under similar conditions.

The question could be raised as to why acidic catalysis of the reactions of olefins with peroxyacids apparently has not been observed before. The results in the literature are based, however, on tests with relatively weak acids: acetic,^{3a} benzoic,^{3c,d} and substituted benzoic.^{3b} Probably

only strong acids can produce ions of type XIII in significant amounts.

An alternative explanation of the catalytic action could be found in an exchange between trichloroacetic and peroxybenzoic acid, with formation of peroxytrichloroacetic acid, certainly a very strong epoxidizing agent. This hypothesis, that could possibly agree with our kinetic results, is, however, very unlikely if one has in mind the results of Hawthorne and co-workers,¹⁵ who found that no such exchange takes place between a strong acid and a weak peroxyacid, and those of Campbell and co-workers,^{3d} who did not observe any exchange of C¹⁴ between benzoic and peroxybenzoic acid.

The present kinetic data do not allow one to distinguish between a reaction path involving slow formation of an epoxide, followed by a rapid reaction with trichloroacetic acid, or direct interaction between a cationic intermediate of the peroxidation and the anion. No precise measurements of the rate of addition of trichloroacetic acid to the epoxides II and VII were made, but it was found, using the optically active *trans*-epoxides, that the half-life at 20° is smaller than one minute and that, therefore, this step could not influence the over-all reaction rate. It appears likely, anyway, that the epoxide does not form at all in the presence of trichloroacetic acid; a cationic intermediate, corresponding to the forms XIVa or XIVb, should react rapidly inside a cage of solvent with the trichloroacetic anion to give the esters III and VII, rather than lose a proton and yield the epoxides. The same intermediates would of course be obtained also from the epoxides and trichloroacetic acid. The differences in the yields of the trichloroacetates obtained from the stilbenes and from the epoxides could well be justified by some side-reactions produced by the peroxybenzoic acid, without assuming different mechanisms in the main reactions. The *cis*-stereospecificity could be explained, as postulated by Brewster¹⁶ for the reactions of *trans*- α -methylstilbene oxide with acetic acid, by a steric course determined by the reciprocal position of anion and cation in the ion-pairs XIV. It is therefore not necessary to assume the formation of a phenonium ion and a double inversion, as suggested by Parker and Isaacs¹⁷ to account for the *cis*-addition of peroxybenzoic acid to the *p*-methoxystilbenes, even if the rearrangement, which in our case produces diphenylacetaldehyde as a side-product, could involve such an intermediate. The same aldehyde, which is not a transformation product of the esters III and VII, was also obtained

(15) M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Am. Chem. Soc.*, **80**, 6393 (1958).

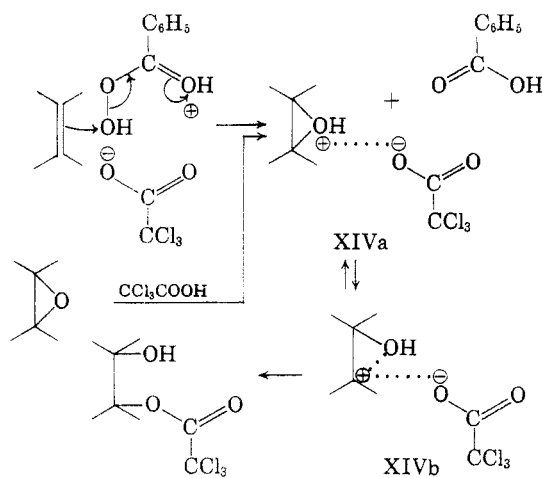
(16) J. H. Brewster, *J. Am. Chem. Soc.*, **78**, 4061 (1956).

(17) R. E. Parker and N. S. Isaacs, *Chem. Revs.*, **59**, 757 (1959).

(14) A. G. Evans, N. Jones, and J. H. Thomas, *J. Chem. Soc.*, 1824 (1955).

by House¹⁸ from the stilbene oxides with boron trifluoride and with magnesium bromide.

The present results must be integrated with many more tests, using different solvents, acids, and olefins, before a complete picture of the stereochemistry and mechanism of these reactions is available. We are continuing our work on this line.¹⁹



EXPERIMENTAL

Melting points were determined on a Kofler hot stage and are not corrected.

Materials. Thiophene-free benzene was distilled over sodium. Commercial *trans*-stilbene, crystallized twice from ethanol, melted at 123.5–124.5°. *cis*-Stilbene was prepared by the method of Buckles and Wheeler²⁰ and was distilled twice: b.p. 96–98/1 mm., n_D^{20} 1.6230. Solutions of peroxybenzoic acid in benzene were prepared by the method of Braun,²¹ as modified by Kolthoff and co-workers,²² dried over magnesium sulfate, then over calcium sulfate, and stored in a refrigerator; kinetic determinations were carried out with solutions not older than 2–3 days. *cis*- and *trans*-Stilbene oxides, prepared from the stilbenes with peroxybenzoic acid and recrystallized once from 70% ethanol, once from petroleum ether, melted at 40–42° and 70–71°, respectively. The optically active forms of *trans*-stilbene oxide were prepared by the method of Read and Campbell,⁴ based on the steam-distillation of the quaternary hydroxides obtained from (+)- and (-)-*erythro*- α,β -diphenyl- β -hydroxyethylamine. The (-)-hydroxy amine yielded the (+)-epoxide, m.p. 69–70°, $[\alpha]_D^{21} +365^\circ$ (*c* 0.500, benzene), the (+)-hydroxyamine gave the (-)-epoxide, m.p. 69–70°, $[\alpha]_D^{20} -370^\circ$ (lit.,⁴ m.p. 69–70°, $[\alpha]_D -374^\circ$) Chemically pure trichloroacetic acid was distilled under a pressure of 1 mm.; only center cuts were used.

(18) H. O. House, *J. Am. Chem. Soc.*, **77**, 3070 (1955).

(19) A referee has pointed out that our hypothesis about the effect of water on the kinetic order of the reactions should be tested by adding small amounts of water to some of the solutions. Work along these lines is being done at present, too, and preliminary results, although quite incomplete from a quantitative point of view, because of the difficulty in obtaining rigorously anhydrous solutions, seem to be in line with our assumptions. The complete results will be published at a later date.

(20) R. E. Buckles and N. G. Wheeler, *Org. Syntheses*, **33**, 88 (1953).

(21) G. Braun, *Org. Syntheses, Coll. Vol. I*, 431 (1951).

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

(\pm)-*threo*- α -Hydroxy- α' -trichloroacetoxybiphenyl (III). a) A solution of 0.90 g. (0.005 mole) of *trans*-stilbene, 0.006 mole of peroxybenzoic acid, and 0.006 mole of trichloroacetic acid in 60 ml. of benzene stored at room temperature for 2 days, was extracted with 20 ml. of sodium carbonate solution, and was washed with 10 ml. of water. The solvent was distilled and the residue, treated with 20 ml. of boiling petroleum ether (b.p. 40–70°), yielded 1.30 g. (72%) of needles, m.p. 115.5–116.5°.

Anal. Calcd. for $C_{16}H_{13}O_3Cl_3$: C, 53.43; H, 3.64; Cl, 29.58. Found: C, 53.63; H, 3.64; Cl, 28.93.

After elimination of the solvent from the mother liquor, an oil remained which gave only a trace of a precipitate with 2,4-dinitrophenylhydrazine reagent.

b) A solution of 0.98 g. (0.005 mole) of *trans*-stilbene oxide and 0.006 mole of trichloroacetic acid in 60 ml. of benzene, stored overnight at room temperature and treated as described in a), gave 1.40 g. (78%) of needles, m.p. 115.5–116.5°, which were found to be identical with the product from the reaction a). The oil which remained after evaporation of the solvent was dissolved in 20 ml. of ethanol and treated with a reagent prepared from 0.4 g. of 2,4-dinitrophenylhydrazine²³: a precipitate of mixed 2,4-dinitrophenylhydrazones (0.3 g.), melting between 135 and 165°, was formed. After two crystallizations from ethyl acetate it yielded 0.07 g. of an orange product, m.p. 240–241°. Concentration of the ethyl acetate solutions and dilution with ethanol gave a yellow compound, melting, after recrystallization from ethanol, at 149–151°. The identities of the two products as benzophenone 2,4-dinitrophenylhydrazone and diphenylacetaldehyde 2,4-dinitrophenylhydrazone¹⁸ were established by mixed melting points and comparison of the infrared spectra with those of authentic samples. The above reaction has been carried out several times, with different amounts of trichloroacetic acid and reaction times ranging from 10 min. to several days: the yields of III were quite constant (71–78%).

L-(+)- and D-(-)-*threo*- α -Hydroxy- α' -trichloroacetoxybiphenyl (XI). The reaction was repeated by method b), using optically active *trans*-stilbene oxide. A solution of 0.359 g. (0.0018 mole) of the (-)-epoxide, $[\alpha]_D^{20} -370^\circ$ and 0.0036 mole of trichloroacetic acid in 25 ml. of benzene was immediately transferred into a 10 cm. polarimeter tube. After 1 min. the observed rotation was -0.50° (calcd. initial value, -5°). After 45 min. it had changed to $+0.21^\circ$ and it remained stable at this value. The solution was washed with sodium carbonate, dried, and evaporated. The residue crystallized from petroleum ether (b.p. 40–70°) as prisms (0.470 g., 71.5%), m.p. 119–120.5°, $[\alpha]_D^{16} +10.9^\circ$ (*c* 2.878, benzene). The mother liquor gave, after evaporation, an oily residue of 0.157 g., $[\alpha]_D^{18} +5.5^\circ$. Similarly, starting from 0.332 g. of the (+)-epoxide ($[\alpha]_D^{21} +365^\circ$), 0.441 g. (71%) of product, m.p. 119–121°, $[\alpha]_D^{16} -11.1^\circ$ (*c* 2.750, benzene) was obtained, together with 0.09 g. of an oil, $[\alpha]_D^{17} -5.0^\circ$. When equal weights of the two enantiomeric products were crystallized from petroleum ether, optically inactive needles, m.p. 115.5–116.5°, were obtained, which did not depress the melting point of the racemic III.

(\pm)-*erythro*- α -Hydroxy- α' -trichloroacetoxybiphenyl (VII). *cis*-Stilbene (1.5 g., 0.0083 mole), treated, as described in a) for the *threo*-isomer, with 0.0091 mole of peroxybenzoic acid and with 0.011 mole of trichloroacetic acid, gave, after crystallization from petroleum ether, 1.3 g. (44%) of VII, m.p. 114–115.5° (mixed melting point with the *threo*-isomer, 99–103°).

Anal. Calcd. for $C_{16}H_{13}O_3Cl_3$: C, 53.43; H, 3.64; Cl, 29.58. Found: C, 53.80; H, 3.91; Cl, 29.75.

By method b) 0.005 mole of *cis*-stilbene oxide gave 1.16 g. (64%) of the same *erythro*-ester and an oily residue, which formed 0.37 g. of a mixture of 2,4-dinitrophenylhydrazones.

(23) R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, John Wiley and Sons, New York, 2nd. ed., 1956, p. 219.

TABLE III
 RUN No. 1

Titrimetric Determination			Spectrophotometric Determination		
Time (sec.)	Na ₂ S ₂ O ₃ (ml. 0.02N)	$k_{2.5}$ (mole ⁻¹ l. sec ⁻¹ × 10 ²)	Time (sec.)	Optical density at 320, m μ	$k_{2.5}$ (mole ⁻¹ l. sec ⁻¹ × 10 ²)
0	16.65	—	0	1.050	—
2050	15.12	1.18	2090	0.960	1.07
4710	13.68	1.13	4740	.850	1.22
9275	11.82	1.12	9295	.750	1.10
16290	10.12	1.06	16340	.650	1.00
24005	8.80	1.03	24055	.562	1.01

Fractional crystallization of the latter showed that it had about the same composition as that obtained in the reaction of the *trans*-epoxide with trichloroacetic acid. Modifications in the quantities of trichloroacetic acid and in reaction times gave slightly different yields (56–64%) of the *erythro*-ester.

Transformation of the trichloroacetates into hydrobenzoin.
 a) *By hydrolysis.* A solution of 0.26 g. of (–)-XI in 4 ml. of ethanol was treated with 2 ml. of a 0.2M solution of potassium hydroxide in ethanol and refluxed for 30 min. Water was added and the solution was extracted with ether. The ether extract was dried over magnesium sulfate and evaporated to dryness. The residue (0.14 g., 82%) melted at 145–147°, $[\alpha]_D^{25} +91.0^\circ$ (c 1.100, ethanol) [lit.,²⁴ (+)-hydrobenzoin, m.p. 148–149°, $[\alpha]_D^{20} +94.0^\circ$]. The same reaction when applied to (±)-III, gave a product, which, after crystallization from water, melted at 92°, from benzene, at 116–118° [lit.,²⁵ (±)-hydrobenzoin hydrate, m.p. 95–96°, anhydrous, m.p. 119–120°]. The *erythro*-ester (VII), treated in the same way, gave *meso*-hydrobenzoin, m.p. 128–130° [lit.,²⁵ m.p. 134°].

b) *By reduction with lithium aluminum hydride.* A solution of 0.463 g. of (+)-XI in 10 ml. of ether was slowly added, with stirring, to a slurry of 0.15 g. of lithium aluminum hydride in 20 ml. of ether. The mixture was refluxed for 30 min., then treated with a few drops of ethanol, with water, and with dilute sulfuric acid. The ether layer was dried over magnesium sulfate and evaporated. The residue weighed 0.232 g. (84%), and melted at 148–149°, $[\alpha]_D^{25} -94.5^\circ$ (c 0.998, ethanol) [lit.,²⁴ (–)-hydrobenzoin, m.p. 148–149°, $[\alpha]_D^{20} -93.5^\circ$]. Under similar conditions (±)-III and (±)-VII gave respectively (±)-hydrobenzoin, m.p. 121°, and *meso*-hydrobenzoin, m.p. 134–135°.

Miscellaneous tests. A solution of 0.92 g. of (±)-III and 0.6 g. of trichloroacetic acid in 20 ml. of benzene was refluxed for 30 min. After washing with sodium carbonate and evaporation, 0.81 g. of unchanged starting material was recovered. A test with 2,4-dinitrophenylhydrazine gave a negative result.

A solution of 0.10 g. of (±)-hydrobenzoin and 0.10 g. of trichloroacetic acid was stored for 2 days at room temperature, then refluxed for 30 min. The rotatory power of the solution remained unchanged and 0.094 g. of the starting material was recovered.

(24) F. Eisenlohr and L. Hill, *Ber.*, **70**, 942 (1937).

(25) C. Forst and T. Zincke, *Ann.*, **182**, 262 (1876).

A solution of 0.2 g. of *cis*-stilbene and 1.8 g. of trichloroacetic acid in 10 ml. of benzene was stored at room temperature. After about 1 hr. a pink color had developed, which changed to blue after 4 hr. After 24 hr. a sodium carbonate solution was added. The color disappeared after about 1 min. of shaking. The product which was recovered from the benzene solution had the same ultraviolet spectrum as *cis*-stilbene (maxima at 224 and 278 m μ); extinction coefficients were, however, about 20% too low on the whole curve, showing that the material contained only 80% of the stilbene. Under the same conditions *trans*-stilbene did not develop any color and was recovered unchanged.

Kinetics. The kinetic measurements were carried out with benzene solutions at 25.1 ± 0.1°. The reactions, whose results are summarized in Table I, were followed by iodometric titration of the peroxybenzoic acid. A benzene solution of an exactly weighed amount of stilbene in a 50-ml. flask was treated with the calculated volume of a titrated solution of trichloroacetic acid in benzene. The flask was brought to the bath temperature, a preheated titrated solution of peroxybenzoic acid was added, and the volume was made up with preheated benzene. Fractions of 5 ml. were drawn off and the reaction was quenched by stirring with an aqueous solution of 0.5 g. of potassium iodide and 3 ml. of acetic acid. The iodine was titrated with 0.02N sodium thiosulfate. The reactions were followed to at least 40% transformation, the faster ones to 60–70%. Parallel runs without trichloroacetic acid were carried out as a control for the method. The second order rate constants for *trans*-stilbene thus found ($k_2 = 4.25$ – 4.35) were in fairly good agreement with those of the literature (4.25–4.29^{3c}; 4.16–4.21^{3d}). The rate constants were calculated using the equations shown in Table II.

In some cases the reactions were also followed by determining the disappearance of the stilbenes spectrophotometrically. Together with the samples for the titrations, others of 2 ml. were drawn off, transferred to test tubes with ground stoppers, containing 2 ml. of 10% sodium carbonate, and shaken. About 1 ml. of the benzene layer was then transferred into another test tube containing some dry magnesium sulfate; 0.09 ml. of this solution was measured exactly with a micro-pipette and brought to 50 ml. with methanol. Optical densities of these solutions were read with a spectrophotometer, at 320 and 330 m μ for *trans*-stilbene and at 315 and 325 m μ for *cis*-stilbene, using as a blank a solution prepared in the same way, but without the stilbene. Preliminary tests had shown that at these wave-lengths and concentrations the compounds II, III, VI, and VII and the reaction products of II and VI with trichloroacetic acid were practically transparent. The results obtained by this second method were usually almost parallel to those obtained by the titrimetric method although there was some tendency, in most cases, to a slightly slower rate of disappearance of the stilbene, than of the peroxybenzoic acid. This effect could, however, be due to the formation of a side-product, which absorbs at the wave lengths used for the determination. Table III shows an example of the values of $k_{2.5}$ obtained by both methods.

Acknowledgment. The authors wish to express their gratitude to Dr. Bruno Macchia for help in the experimental work.