The original ether extract, containing the neutral products of the decomposition reaction, was dried and the solvent removed. The 0.8 g. of residual oil was chromatographed on 100 g. of a mixture of anhydrous magnesium sulfate–Celite (5:1). Fractional sublimation of the first few fractions yielded as a first sublimate a semi-solid, purified by chromatography on alumina, 28 mg., m.p. and mixed m.p. with biphenyl, 69–70°. The second sublimate was an oil. Recrystallizations from hexane yielded 22 mg. of needles, m.p. 93–94°, identified as 3,4-benzcoumarin by the superimposability of the infrared spectra and by mixed m.p. 93–94°.

The other fractions from the chromatography of the neutral fraction were unsublimable oils that resisted crystallization.

Analysis for carbon dioxide in the products of decomposition of the peroxide was carried out in a separate run. A solution of 0.4034 g. (2.46 mmoles) of phthaloyl peroxide in 30 ml. of freshly distilled benzene was placed in a flask having an inlet and an outlet tube provided with break-off joints. The solution was degassed by the standard procedure and sealed under vacuum. The flask was placed in a bath at 80° for 48 hours, then cooled, and the carbon dioxide content was measured by sweeping the flask with nitrogen and collecting the gas in an absorption tube containing Ascarite; weight of carbon dioxide, 0.0836 g. (1.90 mmoles). A duplicate determination with 0.3012 g. (1.83 mmoles) of peroxide gave 0.0635 g. (1.44 mmoles) of carbon dioxide.

**Decomposition of Phthaloyl Peroxide in Carbon Tetrachloride in the Presence of Trichloroacetic Acid.**—A solution of 3.0 g. of the peroxide and 15 g. of trichloroacetic acid in 200 ml. of carbon tetrachloride was degassed, sealed under vacuum and placed in a bath at 80° for 30 days. The flask was cooled and opened. A 10-ml. portion was evaporated to dryness. Petroleum ether was added to dissolve the trichloroacetic acid. The solid residue of phthalic anhydride melted at 126–127°. Recrystallization from benzene–petroleum ether yielded material of m.p. 128–129°; mixed m.p. with phthalic anhydride, 129–130°.

The bulk of the carbon tetrachloride solution was chromatographed on 200 g. of silica gel. Elution with carbon tetrachloride-ether (9:1) yielded a 14.50-g. fraction. Trituration with cold water effected the removal of trichloroacetic acid. The residue of 0.50 g. was crude phthalic anhydride, m.p. 120–125°. Recrystallization yielded material of m.p. 129–130°, mixed m.p. with phthalic anhydride 130–131°. Further elution of the column with 20–30% ether in carbon tetrachloride yielded 1.41 g. of phthalic anhydride, m.p. 124–126°. Sublimation of a 0.20-g. portion afforded 0.185 g. of material of m.p. 130–131°. Total yield of phthalic anhydride was 1.91 g., corresponding to a 71% yield from the peroxide. Elution of the column with 50% ether in carbon tetrachloride gave 0.42 g. of phthalic acid, m.p. 195–200° dec., a yield of 14%.

In a separate run, a solution of 0.3988 g. (2.43 mmoles) of peroxide and 2.0 g. of trichloroacetic acid in 30 ml. of carbon tetrachloride was degassed, sealed under vacuum and heated at 80° for 30 days. Carbon dioxide analysis was carried out as described above. A gain in weight of 0.0617 g. for the Ascarite tube was observed, corresponding to 1.40 mmoles of carbon dioxide. The possibility exists that part of this gain in weight is attributable to hydrogen chloride.

**Decomposition of Phthaloyl Peroxide in Styrene.**—Five-ml. portions of a solution of 0.415 g. of phthaloyl peroxide in 50 ml. of freshly distilled styrene were placed in test-tubes. The tubes were degassed, sealed under vacuum and stored at 0°. After 18 hours a 2-ml. portion of a tube contained 4.8 mg. of peroxide (71% destruction of the peroxide). (A 16-mg. sample of the peroxide dissolved in 2 ml. of styrene and poured directly into 10 ml. of acetic acid gave a titer corresponding to 15.8 mg. of peroxide.) A second tube (no. 2) was kept at room temperature for a day to ensure complete decomposition of the peroxide. A 2-ml. portion was poured into methanol, giving 10 mg. of a precipitate melting over a wide range, 110–160°. This material shows strong absorption in the infrared at 1710, 1275 and 1120 cm.$^{-1}$, suggestive of a phthalate group.[16] A 25-ml. portion of pure styrene, heated at 80° for 1 hr. and poured into methanol, gave 96 mg. of polystyrene, softening above 200° (0.42% polymerization). A 0.192-g. portion of phthaloyl peroxide in 25 ml. of styrene at 80° for 1.0 hour yielded 238 mg. of precipitate insoluble in methanol; estimated weight of products based on tube no. 2 above, 125 mg.; weight of polystyrene, 113 mg. (0.50% polymerization). A solution of 0.094 g. of 91% benzoyl peroxide in 25 ml. of styrene (0.014 $M$) was heated for 1.0 hour at 80° giving 2.70 g. of polystyrene (11.9% polymerization).

**$\psi$-Phthaloyl Chloride.**—A sample of this compound was prepared by the method of Ott.[27] The ultraviolet absorption spectrum was taken on a sample of m.p. 86–89°, dissolved in ether. The spectrum is reported in Fig. 1.

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[27] E. Ott, "Organic Syntheses," Coll. Vol. 2, John Wiley and Sons, Inc., New York, N. Y., p. 528.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

# Cyclic Diacyl Peroxides. II. Reaction of Phthaloyl Peroxide with *cis*- and *trans*-Stilbene

BY FREDERICK D. GREENE

RECEIVED NOVEMBER 21, 1955

Phthaloyl peroxide and *trans*-stilbene undergo a quantitative and stereospecific reaction in refluxing carbon tetrachloride to yield the cyclic phthalate of *dl*-1,2-diphenylethanediol (A) and the 3,3-disubstituted phthalide, *dl*-*trans*-7-keto-2,3-diphenyl-8:9-benz-1,4,6-trioxaspirononane (B). Reaction of the peroxide with *cis*-stilbene affords the cyclic phthalate of *meso*-1,2-diphenylethanediol (D) and the 3,3-disubstituted phthalide (C). The products are stable under the conditions of formation. The reactions are first order in peroxide and first order in olefin. Two mechanisms of product formation are considered.

In part I of this series[1] we reported that the cyclic diacyl peroxide, phthaloyl peroxide, reacted extremely rapidly with styrene without producing polystyrene and suggested that reaction of the peroxide with olefins was general. In this paper we wish to report on the unusual nature of the reaction of phthaloyl peroxide with *cis*- and *trans*-stilbene.

## Results

Reaction of phthaloyl peroxide with *trans*-stilbene in refluxing carbon tetrachloride yields two isomeric compounds, A, m.p. 206–207°, and B, m.p. 125–126°, which were isolated by fractional recrystallization. Both compounds gave analyses corresponding to the addition of one mole of phthaloyl peroxide to one mole of *trans*-stilbene. The molecular weights determined cryoscopically in benzene were the same and indicated a molecular formula of $C_{22}H_{16}O_4$.

Examination of the infrared absorption spectra of the compounds revealed the following informa-

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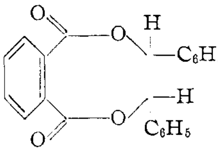
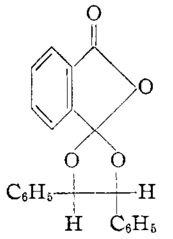
(1) F. D. Greene, THIS JOURNAL, **78**, 2246 (1956).

tion. Isomer A has strong bands at 1715, 1260 and 1100 cm.$^{-1}$. Bellamy[2] reports phthalate bands at 1730–1717, 1310–1250 and 1150–1100 cm.$^{-1}$ in very close accord with those of this isomer. Isomer B shows a single strong band in the carbonyl region at 1750 cm.$^{-1}$. Absorption at 1750 cm.$^{-1}$ is characteristic of $\gamma$-lactones possessing unsaturation in the ring (*cf.* phthalide, 1750 cm.$^{-1}$, 3-substituted phthalides, 1770–1750 cm.$^{-1}$).[3]

Alkaline hydrolysis of isomer A afforded *dl*-dihydrobenzoin (1,2-diphenylethanediol) in 80% yield and phthalic acid.[4] Alkaline hydrolysis of isomer B yielded *dl*-dihydrobenzoin in 81% yield and phthalic acid. In order to demonstrate that the alkaline hydrolysis of the phthalate A proceeded with acyl–oxygen fission, a sample was reduced with lithium aluminum hydride. The isolation of *dl*-dihydrobenzoin from this reduction and from the alkaline hydrolysis establishes the occurrence of acyl–oxygen fission in the alkaline hydrolysis. On the basis of the molecular formula, the spectral and hydrolytic data we assign isomer A the structure of the eight-membered ring cyclic phthalate[5] and isomer B the structure of a 3,3-disubstituted phthalide.



A



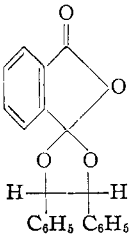
B

Isomers A and B account for over 95% of the starting materials. The infrared spectrum of the crude product mixture is a superposition of the spectra of pure A and B in a ratio of 1 to 3; the infrared spectrum of an authentic mixture of 25% of A and 75% of B was identical with that of the crude mixture. In control experiments it was shown that A and B are stable under the conditions of their formation and, indeed, are unaffected by heating at 200° for 6 hr.

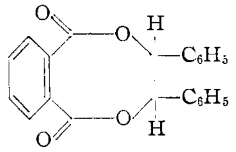
The type of isomerism exemplified by isomers A and B is not unique. Kirpal and Kunze have reported the isolation of the two analogous isomers of diethyl 3,4,5,6-tetrachlorophthalate.[6] This type of isomerism is also encountered with certain thiol esters of phthalic acid[7] and with phthaloyl chloride.

In order to evaluate the stereospecificity of this reaction, phthaloyl peroxide was allowed to react with *cis*-stilbene under the same conditions. A mixture was obtained from which were isolated by fractional recrystallization two different compounds, C, m.p. 198–199°, and D, m.p. 192–193°. Combustion analyses and molecular weights (Rast and cryoscopic in benzene) indicated the formula $C_{22}H_{16}O_4$, the same as for A and B. The infrared absorption spectrum of isomer C was very similar to that of isomer B, showing the single strong band in the carbonyl region at 1750 cm.$^{-1}$, but differing slightly between 1380 to 1340 and at 870 cm.$^{-1}$. The spectrum of isomer D showed strong absorption at 1715, 1260 and 1100 cm.$^{-1}$ and was very similar to that of isomer A.

Alkaline hydrolysis of isomer C afforded *meso*-dihydrobenzoin (86%) and phthalic acid. The *meso*-diol was identified by comparison of the infrared spectrum with an authentic sample and by mixed m.p. determination. Alkaline hydrolysis of D also afforded the *meso*-diol and phthalic acid, identified in the same way. These data allow the assignment of structures C and D to the isomers C and D, respectively.

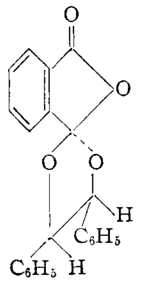


C

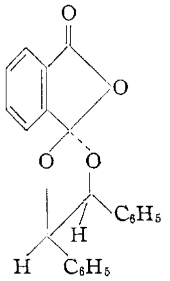


D

Two different forms of structure C are possible, one with the phenyls *syn* with respect to the benz-grouping, C-1, the other possessing the *anti*-relationship, C-2.



C-1



C-2

The infrared spectrum of the crude product mixture obtained from the reaction of phthaloyl peroxide with *cis*-stilbene was the superposition of the spectra of C and D in the ratio of 6 to 4. Examination of the spectrum in the region 900–840 cm.$^{-1}$ indicated that little or none of isomer B was present. However, the remarkable similarity between the spectra of isomers B and C suggests that C-1 and C-2 might also have very similar absorption spectra. Consequently, both C-1 and C-2 may be produced in this reaction, although we have succeeded in isolating only one lactone, isomer C of m.p. 198–199°, from the product mixture. We have no evidence for distinguishing between structures C-1 and C-2 for isomer C; steric considerations favor C-2. Control experiments demonstrated that C and D were stable under the conditions of their formation.

The ultraviolet absorption spectra of isomers A, B, C, D and dibenzyl phthalate (E) are shown in Fig. 1. Both the *cis*- and *trans*-cyclic phthalates

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(2) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 153.

(3) J. F. Grove and H. A. Willis, *J. Chem. Soc.*, 882 (1951).

(4) We wish to thank Professor Louis F. Fieser for furnishing us with samples of *meso*- and *dl*-dihydrobenzoin.

(5) E. W. Spanagel, French Patent 796,410 (April 7, 1936); *C. A.*, **30**, 6138 (1936), has reported the preparation of the cyclic phthalate derived from ethylene glycol.

(6) A. Kirpal and H. Kunze, *Chem. Ber.*, **62**, 2102 (1929).

(7) J. C. Sheehan and G. F. Holland, private communication.

show absorption at longer wave lengths and higher extinction coefficients than does dibenzyl phthalate. The slight difference between lactones B and C is similar to that observed in some cases recently examined by Cram, Allinger and Steinberg[8]; the isomer which more nearly possesses eclipsed phenyl groups, C, shows the lower extinction coefficient. Attention is called to the appreciable difference in spectra of the diastereomerically related cyclic phthalates, A and D.

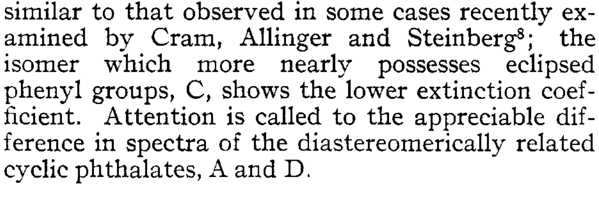


Fig. 1.—Ultraviolet absorption spectra of *trans*-cyclic phthalate (A, ———); *trans*-lactone (B, ......); *cis*-lactone (C, — —); *cis*-cyclic phthalate (D, ---------); and dibenzyl phthalate (E, — — —); all spectra were taken in ether solution on a Beckman model DU spectrophotometer.

**Kinetics of the Reaction.**—Phthaloyl peroxide reacts with *cis*- and *trans*-stilbene in carbon tetrachloride at 80° in a reaction that is cleanly first order in peroxide and first order in olefin. The reaction obeys second-order kinetics throughout the range studied, 0–90%, and is insensitive to oxygen. Fourfold variations in initial concentration produced negligible changes in the rate constants, $k_2$. The data are summarized in Table I.

TABLE I

RATE OF REACTION OF PHTHALOYL PEROXIDE WITH STILBENE IN CARBON TETRACHLORIDE AT 80°

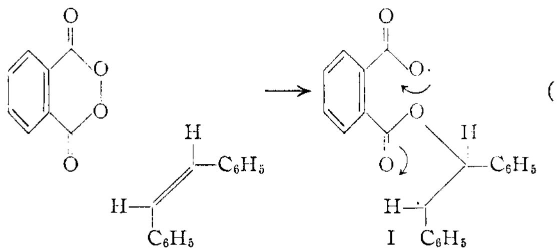
| Compound | $k_2 \times 10^3$, l. mole$^{-1}$ sec.$^{-1}$ | $k_P{}^a \times 10^3$, l. mole$^{-1}$ sec.$^{-1}$ | $k_L{}^b \times 10^3$, l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|---|
| *cis*-Stilbene | 7.18 ± 0.19 | 2.9 ± 0.15 | 4.3 ± 0.22 |
| *trans*-Stilbene | 13.7 ± .2 | 3.4 ± .17 | 10.3 ± .52 |

[a] Rate constant for formation of cyclic phthalate. [b] Rate constant for formation of lactone.

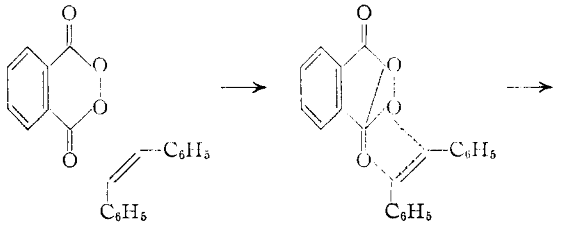
## Discussion

The reaction of phthaloyl peroxide with *cis*- and *trans*-stilbene raises several points of interest: the stereospecificity, the formation of the lactones and the speed of the reaction. Decomposition of phthaloyl peroxide in carbon tetrachloride (0.05 *M*) is only 50% complete after 12 days at 80°. Reaction of an equimolar solution of phthaloyl peroxide and *trans*-stilbene at 80° in the same solvent (0.05 *M* in each component) is 50% complete in 24 minutes. The close adherence of the reaction of peroxide with the stilbenes to second-order kinetics over at least 90% of the reaction indicates that both cyclic phthalate and lactone are being formed by bimolecular reactions. Two types of mechanisms are compatible with the observed kinetics: (a) bimolecular reaction of olefin and peroxide and (b) bimolecular reaction of olefin and a diradical.

With regard to the first alternative, the formation of cyclic phthalate by a head-on collision between the peroxy oxygen atom bridge and the double bond of the olefin is not unreasonable. The formation of lactone may occur by an off-center collision between the peroxy oxygen atoms and the double bond with the formation of diradical I. This diradical is favorably situated for the ring closure to form the lactone. The absence of *cis*-lactone (C) from the product mixture of the *trans*-stilbene reaction and the absence of the *trans*-lactone (B) from the product mixture of the *cis*-stilbene reaction imply that if lactone formation occurs by the two-step process, the second step must take place before rotation about the carbon– bond occurs. Lactone formation may occur directly from olefin and peroxide *via* a synchronous redistribution of charge, without proceeding through the intermediate diradical I.



(1)



lactone C (2)

The second alternative involves bimolecular reaction of the olefin and the diradical formed by oxygen–oxygen cleavage of phthaloyl peroxide.[9] (The insensitivity of rate to the presence of oxygen does not exclude this kind of diradical in view of the

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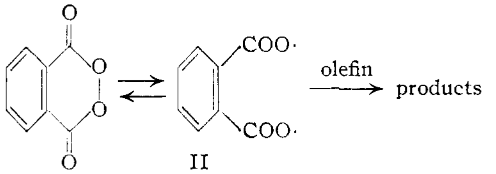
[8] D. J. Cram, N. L. Allinger and H. Steinberg, THIS JOURNAL, **76**, 6137 (1954).

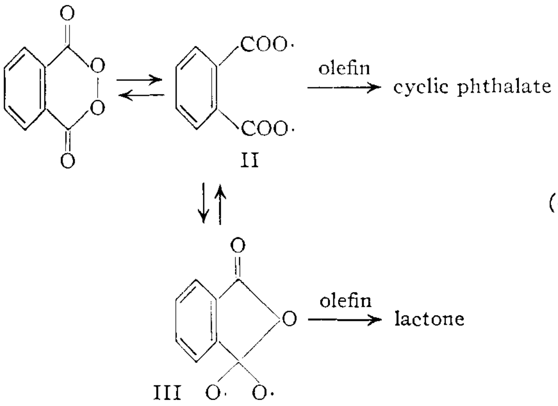
[9] Other cases which may involve oxygen diradical attack on olefins are the photochemical additions of *o*-quinones to olefins with the formation of the substituted 1,4-dioxa-2-cyclohexene system: G. O. Schenck and G. A. Schmidt-Thomée, *Ann.*, **584**, 199 (1953); A. Schönberg, W. I. Awad and G. A. Mousa, THIS JOURNAL, **77**, 3850 (1955); see also, A. Schönberg and A. Mustafa, *Chem. Revs.*, **40**, 190 (1947).



(3)

general insensitivity of oxygen and nitrogen radicals to molecular oxygen.) Reaction of diradical II with olefin could lead either to cyclic phthalate or lactone. If product formation occurs in this way, the great increase in the rate of disappearance of phthaloyl peroxide in carbon tetrachloride in the presence of olefins requires that the diradical II be formed by a reversible process.

In the first paper of the series,[1] evidence was presented in support of the six-membered ring structure for phthaloyl peroxide. The evidence was spectroscopic and applied to solutions of the compound in ether and in carbon tetrachloride at room temperature. If phthaloyl peroxide were in equilibrium with diradicals II and III, reaction of these diradicals with *trans*-stilbene could yield cyclic phthalate and lactone, respectively, of the observed stereospecificity and in a second-order reaction, provided that the equilibrium between II and III is rapid with respect to the rate of product formation.



(4)

Inspection of the data of Table I reveals that the difference in rate of reaction of *cis*- and *trans*-stilbene with phthaloyl peroxide is small ($k_{2trans}/k_{2cis}$: 1.9/1) and the difference is associated primarily with the difference in rate of lactone formation. It is of interest that a very similar order of reactivity has been observed in the attack on the stilbenes by the maleic anhydride radical ($k_{trans}/k_{cis}$: 1.5–2.0/1).[10] The magnitude of these differences is also comparable to that observed in the epoxidation of these same olefins by peracetic acid in acetic acid at 25.8°, although in this case the *cis*-isomer is slightly more reactive than the *trans* ($k_{2trans}/k_{2cis}$: 6.7/11.1).[11] The epoxidation reaction probably involves a direct formation of epoxide by a cyclic process rather than by a two-step process.[12] Consequently, it is difficult to distinguish between one-step and two-step mechanisms on the basis of the rate data. However, a clear distinction between diradical attack on olefin (eq. 3,4) and neutral peroxide attack on olefin (eq. 1,2) is possible for the situation in which reaction of diradical II with an olefin is much faster than reversal of diradical to peroxide, such a case approaching zero-order dependence in olefin concentration. This possibility and the scope of the reaction of phthaloyl peroxide with olefins are under investigation.

The cleanness and the speed of the reaction of phthaloyl peroxide with olefins, by whatever mechanism, is ultimately attributable to the diacyl peroxide ring. The distinction between reactivity associated with "electron strain" (repulsion of lone pair electrons of the adjacent peroxy oxygen atoms) and reactivity based on other features awaits the results of the study of other systems.

## Experimental[13]

**Phthaloyl peroxide** was prepared by the method described previously.[1] Material of 99.5% purity, prepared by recrystallization from methylene chloride, was used in the reactions with olefins.

***cis*-Stilbene.**—A sample was prepared by Mr. Reif according to the procedure of Buckles and Wheeler.[14] The ultraviolet absorption spectrum of this material was superimposable with that of the *cis*-isomer.[14]

**Reaction of Phthaloyl Peroxide with *trans*-Stilbene.**—A solution of 1.0 g. (0.0061 mole) of phthaloyl peroxide and 1.10 g. (0.0061 mole) of *trans*-stilbene (m.p. 123–124°) in 100 ml. of reagent carbon tetrachloride was refluxed overnight. The colorless solution was evaporated to a volume of 10 ml. and cooled, yielding 264 mg. of crystals, m.p. 187–200°. Recrystallization from carbon tetrachloride gave 210 mg. of cubic crystals, m.p. 206–207.5°, *trans*-cyclic phthalate, isomer A. The infrared absorption spectrum showed strong bands at 1715, 1260 and 1100 cm.$^{-1}$ (in chloroform).

*Anal.* Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68; mol. wt., 344. Found: C, 76.78; H, 4.74; mol. wt., 311 (Rast), 330 (cryoscopic in benzene).

Evaporation of the original carbon tetrachloride filtrate to dryness left an oil. Repeated fractional crystallizations from ether afforded an additional 163 mg. of pure A, m.p. 206–207° and 425 mg. of lactone, isomer B, m.p. 123–126°. Recrystallization of isomer B from ether–hexane yielded hexagonal rods, m.p. 125.5–126°; the infrared absorption spectrum of B showed a sharp band at 1750 cm.$^{-1}$ (in chloroform).

*Anal.* Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68; mol. wt., 344. Found: C, 76.73; H, 4.47; mol. wt., 355 (Rast), 335 (cryoscopic in benzene).

In a duplicate experiment, 0.50 g. of the peroxide and 0.55 g. of *trans*-stilbene in 50 ml. of carbon tetrachloride were heated at reflux for 16 hr. The cooled solution was extracted with sodium bicarbonate solution. The carbon tetrachloride layer was washed once with water and dried over anhydrous magnesium sulfate. Filtration and evaporation left 1.00 g. of semi-solid. The infrared absorption spectrum of a sample of this material which had been dried at 80° (0.1 mm.) for 1 hour was identical with that of a mixture of 75% of isomer B and 25% of isomer A.

**Reaction of Phthaloyl Peroxide with *cis*-Stilbene.**—Equimolecular amounts of the peroxide (1.0 g.) and the olefin (1.1 g.) in 100 ml. of carbon tetrachloride were refluxed overnight. The solution was evaporated to dryness and the resulting semi-solid was treated with ether and filtered. The insoluble residue amounted to 0.762 g., m.p. 167–195°. Two recrystallizations from benzene–hexane

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[10] F. M. Lewis and F. R. Mayo, THIS JOURNAL, **70**, 1535 (1948). It has also been reported that butadiene copolymerizes with *trans*-stilbene but not with *cis*-stilbene, C. S. Marvel and W. S. Anderson, *ibid.*, **76**, 5434 (1954).

[11] For a review of the epoxidation of a wide variety of olefins, see D. Swern, *ibid.*, **69**, 1692 (1947).

[12] P. D. Bartlett, *Rec. Chem. Prog.*, **11**, 51 (1950).

[13] Melting points are corrected. We are indebted to Dr. S. M. Nagy and his associates for analyses and infrared spectra, which were recorded with a Baird double beam infrared spectrophotometer equipped with a sodium chloride prism.

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

gave 380 mg. of colorless rosettes, m.p. 198–199°, the lactone isomer C. The infrared absorption spectrum showed a sharp band at 1750 cm.$^{-1}$.

*Anal.* Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68; mol. wt., 344. Found: C, 77.09; H, 4.86; mol. wt., 312 (Rast), 336 (cryoscopic in benzene).

Fractional recrystallization of the residual oil from ether–petroleum ether (b.p. 30–60°) yielded a second crop of 150 mg. of a solid and an oil. The solid was separated from the oil mechanically and recrystallized from benzene–petroleum ether, giving 80 mg. of small needles, m.p. 192–193°, isomer D, the *cis*-cyclic phthalate. The infrared absorption spectrum showed strong bands at 1715, 1260 and 1100 cm.$^{-1}$ (in chloroform).

*Anal.* Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68; mol. wt., 344. Found: C, 76.68; H, 4.87; mol. wt., 309 (Rast).

A 5-ml. portion of the original product-containing carbon tetrachloride solution was evaporated to dryness. The infrared absorption spectrum of the crude residue established that only isomers C and D were present, and in the ratio of 60% C to 40% D.

In a separate experiment, the crude reaction mixture was chromatographed on silica gel. Elution with methylene chloride yielded a mixture of phthalic anhydride and isomer D, from which a small amount of pure D was obtained through removal of the phthalic anhydride by sublimation and recrystallization of the residue. Elution with ether afforded a semi-solid. Three recrystallizations from chloroform–petroleum ether yielded small prisms, m.p. 159–160°, (evolution of bubbles at 200°). The infrared absorption spectrum (in potassium bromide pellet) showed a strong band at 3270 cm.$^{-1}$, absorption at 3000–2300 cm.$^{-1}$ and two sharp bands in the carbonyl region at 1714 and 1680 cm.$^{-1}$. The spectrum is suggestive of the hydroxy acid ester that might be formed by hydrolysis of either isomer C or D, but combustion analyses were consistently low in carbon.

*Anal.* Calcd. for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 72.06, 71.86, 72.00; H, 5.04, 4.89, 4.91.

**Rate of Reaction of Phthaloyl Peroxide with *cis*- and *trans*-Stilbene.**—Solutions of phthaloyl peroxide (99.5%) and olefin were prepared in reagent grade carbon tetrachloride and 5-ml. portions were transferred to Pyrex test-tubes. The tubes were sealed and placed in a thermostat at 80.0° for requisite time intervals. The rate of reaction was followed by iodometric titration of a 2-ml. aliquot for unreacted peroxide according to the procedure described in Part I.[1] An illustrative run is shown in Table II.

TABLE II

RATE OF REACTION OF *cis*-STILBENE[a] WITH PHTHALOYL PEROXIDE[a] IN CARBON TETRACHLORIDE AT 80°

| Time, sec. × $10^{-3}$ | Thiosulfate soln.,[b] ml. | $k_2 \times 10^3$, l. mole$^{-1}$ sec.$^{-1}$ |
|---|---|---|
| 0 | 12.00 | |
| 1.26 | 9.35 | 7.50 |
| 2.40 | 7.90 | 7.21[c] |
| 3.60 | 6.78 | 7.13[c] |
| 6.00 | 5.22 | 7.22 |
| 7.50 | 4.60 | 7.15[c] |
| 9.60 | 4.04 | 6.85 |
| 16.38 | 2.70 | 7.01 |
| 21.60 | 2.10 | 7.28 |
| | Av. $k_2$ | 7.17 ± 0.14 |

[a] Initial concentrations, 0.030 *M*. [b] 0.0099 *N*. [c] Tubes sealed under air, all others sealed under nitrogen.

**Alkaline Hydrolysis of Cyclic Phthalates and Lactones.**—The products of the reaction of phthaloyl peroxide with the olefins were hydrolyzed by the procedure described below for isomer C.

A mixture of 150 mg. of isomer C, m.p. 198–199°, 1 g. of sodium hydroxide, 1.5 ml. of water and 5 ml. of ethanol was refluxed overnight. The solution was diluted with 50 ml. of water and extracted with ether. Removal of the ether (after drying over magnesium sulfate) yielded 80 mg. of *meso*-dihydrobenzoin, m.p. 134–136°, in a yield of 86%. This material was identified as the *meso*-diol by mixed m.p., 135–136°, with an authentic sample,[4] and by infrared analysis. The infrared absorption spectra of the compound and the authentic sample were identical in every respect. The alkaline layer was acidified and extracted with ethyl acetate. Removal of the solvent after drying left a residue of 52 mg. of phthalic acid, dec. p. 200–201°, identified by sublimation to phthalic anhydride, m.p. 129–130°, mixed m.p. 130–131°.

By the same procedure, hydrolysis of isomer A, m.p. 206–207°, gave *dl*-dihydrobenzoin, m.p. 119–120°, in 80% yield, identified by comparison with an authentic sample[4]; infrared spectra superimposable, mixed m.p. 119–120°. Phthalic acid was isolated and characterized as described above.

Hydrolysis of isomer B, m.p. 125–126°, afforded *dl*-dihydrobenzoin, m.p. 118–120°, mixed m.p. 119–120°, in 81% yield, and phthalic acid. Positive identification of these compounds was effected as described above.

Hydrolysis of isomer D, m.p. 192–193°, afforded *meso*-dihydrobenzoin, m.p. 135–136°, mixed m.p. 135–136°, and phthalic acid. Both products were identified by the procedure previously described.

**Reaction of *trans*-Phthalate (Isomer A) with Lithium Aluminum Hydride.**—To a slurry of 200 mg. of lithium aluminum hydride and 10 ml. of ether was added 100 mg. of isomer A. After 10 minutes, the excess reductant was destroyed with water and the mixture was extracted with ether. The ethereal solution was dried over magnesium sulfate, filtered and evaporated to dryness. Three recrystallizations of the residual oil from ether–petroleum ether afforded 20 mg. of *dl*-dihydrobenzoin, m.p. 117–120°, mixed m.p. 118–120°, confirmed by the identity of the infrared spectra.

**Effect of Ethanol on the Lactones** (B and C).—The ultraviolet absorption spectra which were obtained from these products in ethanol solution were superimposable with that of dibenzyl phthalate (m.p. 43–45°) and markedly different from the spectra of the lactones in ether solution (see Fig. 1), indicating that the ethanol effected a rapid solvolysis of isomers B and C to the corresponding monoethyl phthalates.

**Thermal Stability of Products.**—A 20-mg. sample of isomer A, m.p. 206–207°, was heated at reflux in 10 ml. of carbon tetrachloride for 48 hr. After removal of the solvent, the residue was subjected to infrared analysis and shown to consist solely of the starting material, isomer A. In the same manner, isomers B, C and D were shown to be stable under the reaction conditions.

A sample of isomer B, m.p. 124–125°, was heated in a sealed tube at 215° for 6 hr. The infrared absorption spectrum was identical with the starting material.

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