benzofurazan prepared by the method of Gaughran *et al.* (1). In all cases, the remainder of the flask contents was unidentified.

Acknowledgment

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1. R. J. Gaughran, J. P. Picard, and I. V. R. Kaufman. J. Am. Chem. Soc. **76**, 2233 (1954).
2. K. H. Pausacker and J. G. Scroggie. J. Chem. Soc. 4499 (1954).
3. P. A. F. Smith and J. H. Boyer. Org. Syn. **31**, 14 (1951).
4. M. E. Synerholm, N. W. Gilman, J. W. Morgan, and R. K. Hill. J. Org. Chem. **33**, 1111 (1968).
5. J. A. Attaway, R. W. Wolford, and G. E. Alberding. Anal. Chem. **34**, 671 (1962).
6. T. Mukaiyama and M. Iwanami. J. Am. Chem. Soc. **79**, 73 (1957).
7. M. Metayer. Bull. Soc. Chim. France, 802 (1951).
8. W. Siefken. Ann. **562**, 75 (1949).

Anodic addition of hydroxy and benzoyloxy groups to stilbenes[1]

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The anodic reaction of benzoic acid in acetonitrile has been carried out in the presence of *trans*- and *cis*-stilbenes using platinum electrodes. The reaction with added *trans*-stilbene gave meso-hydrobenzoin dibenzoate together with *threo*-2-benzoyloxy-1,2-diphenylethanol. Under similar conditions, *cis*-stilbene also gave these products. No evidence for the isomerization of *cis*-stilbene to the *trans*-isomer during the electrolysis was found. Stereoisomeric *dl*-hydrobenzoin dibenzoate and erythro-2-benzoyloxy-1,2-diphenylethanol were not obtained from either stilbene. For comparison, the "wet" Prévost reaction of *cis*-stilbene with silver acetate and iodine was studied. These results are discussed on the basis of a stepwise oxidation mechanism which involves a cyclic 1,2-benzoxonium ion intermediate.

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Over the last decade, considerable attention has been devoted to electrochemical addition reactions. An example of such reactions is the polymerization of vinyl monomers during the Kolbe electrolysis (1, 2). The free radicals produced by the Kolbe electrolysis are capable of attacking 1,3-dienes present, giving rise to the additive dimers (3–5). Smith *et al.* (6) have investigated the stereochemistry of the addition of free radicals to dienes in the anodic oxidation of carboxylic anions.

A previous communication (7) from this laboratory indicated that the electrolysis of sodium methoxide in methanol in the presence of *trans*- and *cis*-stilbenes afforded a mixture of meso- and *dl*-hydrobenzoin dimethyl ethers. More *cis*-adduct than *trans*-adduct was formed in each case. These results seem to be consistent with simultaneous addition of two methoxy radicals to a carbon–carbon double bond of an adsorbed stilbene from one side of the double bond, analogous to the catalytic hydrogenation of unsaturated compounds. An alternative mechanism involves a benzylic cation intermediate formed from stilbene during a stepwise two-electron transfer to the anode (8).

Recently, Mango and Bonner (9) found that electrolysis of sodium acetate in acetic acid in the presence of *trans*-stilbene yielded mainly meso-hydrobenzoin diacetate under anhydrous conditions, and *threo*-2-acetoxy-1,2-diphenylethanol together with a mixture of epimers of 1,2-diphenyl-1-propyl acetate under moist conditions. The stereoisomeric *erythro*-hydroxyacetate was not obtained from either experiment with added *trans*-stilbene. They concluded that the mechanism involved a cyclic acetoxonium ion intermediate **1** which was formed stereoselectively on the surface of an anode. Although the details of the formation of the cyclic intermediate ion, **1**, in this mechanism were not completely clear from their work, they suggested two possibilities; one-step and two-step oxidation mechanisms, as illustrated in Schemes 1 and 2, respectively.

The present study deals with the mechanism of

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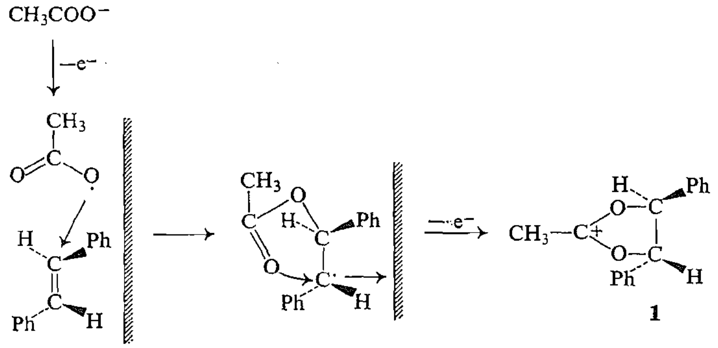
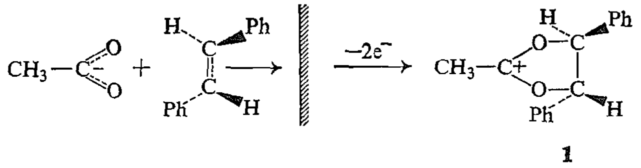


Scheme 1



Scheme 2

anodic addition of hydroxy and benzoyloxy groups to the stilbenes.

Results and Discussion

The electrolysis of benzoic acid in acetonitrile containing a small amount of triethylamine was conducted in the presence of *trans*-stilbene. After the usual work-up, the products which could be isolated were characterized by comparison with authentic samples, and found to consist of meso-hydrobenzoin dibenzoate **2** and *threo*-2-benzoyloxy-1,2-diphenylethanol, **3**. When benzoic acid was electrolyzed in the presence of *cis*-stilbene, it was also converted into a mixture of **2** and **3** in a fairly good yield. Each electrolysis was repeated several times, but no other compounds could be identified. In some cases, however, a small amount of a thick yellow oil, which gave an infrared (i.r.) spectrum displaying major absorption bands at 710, 760, 1110, 1270, 1670, and 1710 cm^{-1}, was produced. None of the stereoisomeric *erythro*-monobenzoate and *dl*-dibenzoate was obtained in either case. The relative yield of the diester, **2**, to the monoester, **3**, appeared to be affected by water present in the solvent; the ratio increased markedly when the solvent freshly distilled from phosphorus pentoxide, while it decreased when the solvent had been stored without any protection from moisture.

There was no evidence of isomerization of *cis*- to *trans*-stilbene under the electrolytic conditions employed; ultraviolet (u.v.) spectra of crude *cis*-stilbene recovered from the electrolyzed mixture showed no absorbance at 295 and 310 mμ characteristic for the *trans*-isomer.

As has been established in the stereochemistry of the "dry" and "wet" Prévost reactions, the stereoselective addition of hydroxy and benzoyloxy groups to the stilbenes, i.e., *cis*-hydroxylation and *trans*-benzoyloxylation, strongly suggests the formation of a common cyclic benzoxonium ion intermediate, **4**, from both stilbenes.

The inversion of configuration during anodic addition to *cis*-stilbene also suggests that the formation of **4** proceeds through a stepwise transfer of two electrons to the anode. If a cyclic ion intermediate were formed from an adsorbed *cis*-stilbene on the anode surface in one step as illustrated in Scheme 2, the *cis*-stilbene would be converted with retention of configuration into *dl*-hydrobenzoin dibenzoate and *erythro*-monobenzoate.

The u.v. analyses rule out the possibility of *cis–trans* inversion before the attack of a benzoate anion or radical on an anodically adsorbed stilbene.

The Prévost reaction on *cis*-stilbene, which so far as we know has not been reported, was examined using silver acetate in wet acetic acid. It also afforded *threo*-2-acetoxy-1,2-diphenylethanol as the sole product, but the epimeric *erythro*-monoacetate was not produced.

Winstein and Seymour (10) have suggested that the diastereomeric stilbene dichlorides are first converted mainly into *erythro*-acetoxychloride when the dichlorides are treated with silver acetate in dry or moist acetic acid. The present investigation, however, affords evidence for the possible inversion of configuration during the formation of the cyclic ion intermediate **4**.

Our conclusion, based on the evidence above, is that the anodic addition of hydroxy and benzoyloxy groups to stilbenes proceeds via the formation of the cyclic benzoxonium ion intermediate **4** with the more stereochemically favorable configuration. It seems probable that two electrons are transferred stepwise from stilbene or from benzoate anion and stilbene to the anode.

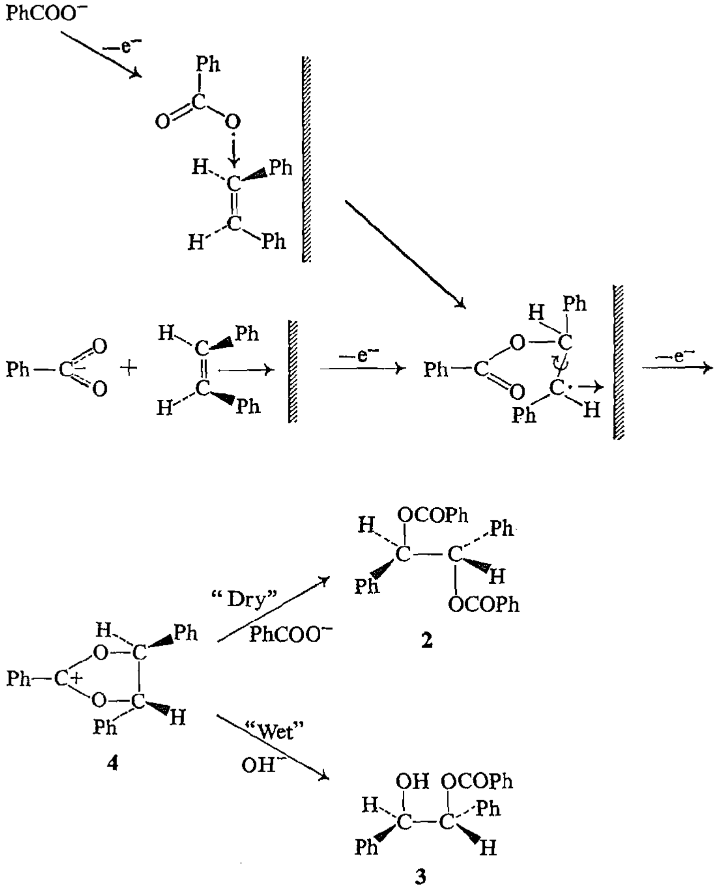
Experimental

All melting points and boiling points are uncorrected. The i.r. spectra were obtained with a Shimadzu IR spectrophotometer IR-27C. The electrolyses were carried out in a cylindrical glass cell equipped with a reflux condenser, thermometer, and electrode unit. The electrode unit consisted of two platinum foil electrodes having an area of ca. 3 cm^2 each, spaced 1 cm apart. The cell was immersed in a water-bath, and the contents were stirred magnetically.

Electrolysis of Benzoic Acid in the Presence of trans-Stilbene

A solution of benzoic acid (6.1 g, 0.05 mole) and *trans*-stilbene (4.5 g, 0.025 mole) in acetonitrile (90 ml) containing triethylamine (2 g) was electrolyzed at 20–25 °C for 14 h (electric current; 0.1 A, applied potential; 31–35 V).

The bulk of the solvent was removed by evaporation at reduced pressure, and the residue was dissolved in chloroform. The chloroform solution was extracted twice with 5% aqueous sodium bicarbonate solution, then washed with water, dried over anhydrous magnesium sulfate, filtered, and evaporated to give a thick brown oil (7 g). A portion (3 g) of the crude product was chromatographed on silica gel (50 g), and eluted with chloroform–methanol mixtures. After removal of the solvent, the



collected fractions were combined on the basis of the i.r. and thin-layer chromatography (t.l.c.) analyses.

The first combined residue (0.8 g) was shown by its i.r. spectrum to be unchanged stilbene. Recrystallization from *n*-hexane – benzene yielded white crystals, m.p. 122–124 °C, which showed no melting point depression when mixed with authentic *trans*-stilbene.

The second combined fraction (1.2 g) was recrystallized from *n*-hexane – benzene yielding 0.8 g of white crystals, m.p. 243–245 °C, which was identified as meso-hydrobenzoin dibenzoate, **2**, (m.p. 244–245 °C (11)). The product and an authentic sample of **2** had identical i.r. spectra and, on admixture, showed no melting point depression.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25. Found: C, 79.83; H, 5.61.

The third fraction, a yellow oil, gave an i.r. spectrum with major absorption bands at 710, 760, 1110, 1270, 1670, and 1710 cm^{-1}, and was examined by t.l.c. It consisted of several compounds, which were not further investigated.

The electrolysis was repeated in slightly wetted solvent. After working up the electrolyzed mixture in a manner similar to the experiment described above, the crude product (11.6 g) was subjected to chromatographic separation, and gave 4 combined fractions. The first combined fraction (0.2 g) consisted mainly of unchanged *trans*-stilbene, m.p. and mixed m.p. 121–123 °C. The second combined fraction (1.5 g) was filtered to separate a thick solid (0.03 g), m.p. 183–228 °C. The solid was washed with a *n*-hexane – benzene mixture, and recrystallized from boiling toluene to yield white crystals, m.p. 237–240 °C, which were identified as **2** (mixed m.p. 240–242 °C).

The third combined residue (3.9 g) was dissolved in benzene and, after addition of *n*-hexane to the solution, yielded a white solid (3.1 g), m.p. 149–152 °C. It was identified after recrystallization from benzene – *n*-hexane mixture as *threo*-2-benzoyloxy-1,2-diphenylethanol, **3**, m.p. 152.5–154.5 °C, undepressed on admixture with an authentic sample. The i.r. spectra of the product and authentic **3** were identical.

Anal. Calcd. for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.12; H, 5.74.

A dark-brownish residue (0.5 g) was not investigated.

Electrolysis of Benzoic Acid in the Presence of cis-Stilbene

A solution of benzoic acid (6.1 g, 0.05 mole) and *cis*-stilbene (4.5 g, 0.025 mole) in acetonitrile (90 ml) containing triethylamine (2 g) was electrolyzed in the manner described above for experiments with *trans*-stilbene. After the electrolysis, a portion (3.2 g) of the crude product (9.6 g) was subjected to chromatographic separation.

The first combined residue (0.61 g) was shown to be unchanged *cis*-stilbene by its i.r. spectra. The u.v. spectrum of this residue in ethanol solution showed the absorption band at 280 mμ, but no absorptions at 295 and 310 mμ which are characteristic for *trans*-stilbene.

The second combined residue (0.2 g), a white solid, was identified after recrystallization from toluene as **2**, m.p. 244–245 °C, not depressed by mixture with an authentic sample. The i.r. spectra of these two samples were identical.

Anal. Calcd. for $C_{28}H_{22}O_4$: C, 79.60; H, 5.25. Found: C, 80.56; H, 5.37.

The third combined residue (0.6 g) gave, after recrystallization from *n*-hexane – benzene, white crystals, m.p. 150–152 °C, not depressed by mixture with an authentic **3**.

Anal. Calcd. for $C_{21}H_{18}O_3$: C, 79.22; H, 5.70. Found: C, 79.83; H, 5.94.

A portion (0.1 g) of the third fraction was heated under reflux with 20% potassium hydroxide in aqueous ethanol for 2.5 h, and the solvent was then removed under reduced pressure. The residue was extracted three times with ether, and the combined ethereal solutions were washed twice with sodium bicarbonate solution, then with water, and were then dried over anhydrous magnesium sulfate. The evaporation of ether left a small amount of a white solid, which was characterized after two recrystallizations from *n*-hexane – benzene mixtures as *dl*-hydrobenzoin, m.p. 119–120 °C, undepressed on admixture with an authentic sample.

The last combined residue (0.34 g) was a dark-brownish semisolid, which was not characterized.

Authentic **2** (m.p. 244–245 °C, 78% yield) was prepared from meso-hydrobenzoin. Authentic **3** (m.p. 154.5 °C, 76.5% yield) was prepared from *erythro*-1-benzoyloxy-2-bromo-1,2-diphenylethane by a method similar to that described by Wiberg and Saegebarth (11), and was hydrolyzed to give authentic *dl*-hydrobenzoin, m.p. 118 °C.

The "Wet" Prévost Reaction on cis-Stilbene

The method used here was virtually identical with that of Mango and Bonner (9). To a solution of *cis*-stilbene (4.5 g, 0.025 mole) and silver acetate (10.5 g, 0.06 mole) in glacial acetic acid (75 ml) containing water (1 ml) was added powdered iodine (6.4 g, 0.05 mole) in small portions with vigorous stirring over a period of 1 h at room temperature. After all of the iodine was added to the solution, the mixture was heated at 90–95 °C for 3 h with vigorous stirring. The usual work-up of the reaction mixture gave a thick oil (5.3 g), which crystallized on standing. Recrystallization from a benzene – *n*-hexane mixture gave white crystals, m.p. 87–89 °C, undepressed on admixture with authentic *threo*-2-acetoxy-1,2-diphenylethanol.

1. S. GOLDSCHMIDT and E. STOCKEL. Chem. Ber. **85**, 630 (1952).
2. W. B. SMITH and H.-G. GILDE. J. Am. Chem. Soc. **82**, 659 (1960).
3. R. V. LINDSEY, JR. and M. L. PETERSON. J. Am. Chem. Soc. **78**, 2073 (1956).
4. W. B. SMITH and H.-G. GILDE. J. Am. Chem. Soc. **81**, 5325 (1959).
5. M. YA. FIOSHIN, A. I. KAMNEVA, L. A. MIRKIND, and L. A. SALIMIA. Chem. Abstr. **55**, 18586 (1961).
6. W. B. SMITH and H.-G. GILDE. J. Am. Chem. Soc. **83**, 1355 (1961).
7. T. INOUE, K. KOYAMA, T. MATSUOKA, K. MATSUOKA, and S. TSUTSUMI. Tetrahedron Letters, 1409 (1963).
8. T. INOUE, K. KOYAMA, T. MATSUOKA, and S. TSUTSUMI. Bull. Chem. Soc. Japan, **40**, 162 (1967).
9. F. D. MANGO and W. A. BONNER. J. Org. Chem. **29**, 1367 (1964).
10. S. WINSTEIN and D. SEYMOUR. J. Am. Chem. Soc. **68**, 119 (1946).
11. K. B. WIBERG and K. A. SAEGEBARTH. J. Am. Chem. Soc. **79**, 6256 (1957).