The Electrolytic Hydroxylation and Acetoxylation of Diaryl Alkenes

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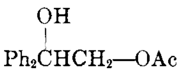
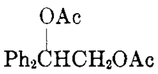
Received January 13, 1964

When sodium acetate in acetic acid was electrolyzed in the presence of 1,1-diphenylethylene, the latter was converted into a mixture of 2-*O*-acetyl-1,1-diphenylethylene glycol (I) and its corresponding diacetate (II). The mechanism of this novel electrolytic hydroxylation and acetoxylation reaction was investigated stereochemically by conducting similar electrolyses in the presence of *trans*-stilbene. Under anhydrous conditions, this diaryl alkene afforded mainly *meso*-1,2-di-*O*-acetyl-1,2-diphenylethylene glycol (IX). In moist acetic acid *trans*-stilbene yielded *threo*-1-*O*-acetyl-1,2-diphenylethylene glycol (VIII) and a mixture of the epimers of 1,2-diphenyl-1-propyl acetate (X). None of the epimeric *erythro*-1-*O*-acetyl-1,2-diphenylethylene glycol (VII) was obtained from *trans*-stilbene in either experiment. These results exclude an epoxide mechanism for the formation of such electrolytically produced hydroxylation and acetoxylation products, and are in accord with a mechanism involving an intermediate cyclic 1,2-acetoxonium ion which is formed stereoselectively at the electrode surface.

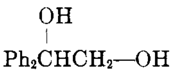
Recently we have reported the isolation of the skeletally unrearranged product, 2-*O*-acetyl-1,1-diphenylethylene glycol (I), from the Kolbe electrolysis of a mixture of sodium acetate and sodium 3,3-diphenylpropanoate.[1] It was suggested that the monoacetate I might have arisen as a result of the intermediate formation of 1,1-diphenylethylene during the electrolysis, since it is well known that olefins are formed, often in good yield, during Kolbe electrolyses of aliphatic monobasic acids.[2] The experimental testing of this hypothesis and its extention to include other aryl-substituted alkenes is the subject of the present paper.


$\mathrm{Ph_2C(OH)CH_2{-}OAc}$

I


$\mathrm{Ph_2C(OAc)CH_2OAc}$

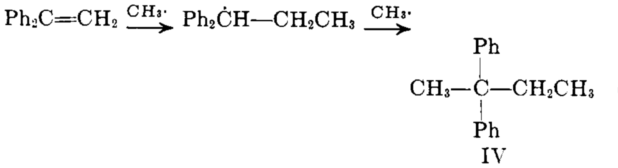
II


$\mathrm{Ph_2C(OH)CH_2{-}OH}$

III

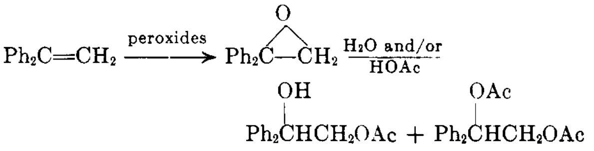
When 1,1-diphenylethylene was slowly added dropwise to an electrolyzing solution of sodium acetate in glacial acetic acid, two esters could be isolated on chromatographic separation of the crude electrolysis product. The first of these (16% of crude product) was 1,2-di-*O*-acetyl-1,1-diphenylethylene glycol (II), and the second (46%) was the previously encountered monoacetate I. The structures of these esters followed from microanalytical and n.m.r. data and from the facts that II could be readily hydrolyzed to the known 1,1-diphenylethylene glycol (III) and that the latter glycol could be monoacetylated to produce I. When the above experiment was repeated with the modification that the 1,1-diphenylethylene was added in a single batch to the electrolyzing medium, a complex mixture resulted. From this, a small amount (2.3%) of what appeared to be 2,2-diphenylbutane (IV) was the only homogeneous product isolated. The formation of IV may be rationalized as shown in eq. 1 and 2.

$$\mathrm{CH_3COO^-} \xrightarrow[\text{anode}]{-e^-} \mathrm{CH_3COO\cdot} \longrightarrow \mathrm{CH_3\cdot} + \mathrm{CO_2} \qquad (1)$$

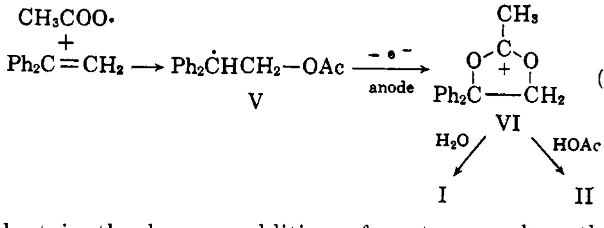

$$\mathrm{Ph_2C{=}CH_2} \xrightarrow{\mathrm{CH_3\cdot}} \mathrm{Ph_2\dot{C}H{-}CH_2CH_3} \xrightarrow{\mathrm{CH_3\cdot}} \mathrm{CH_3{-}C(Ph)_2{-}CH_2CH_3} \qquad (2)$$

IV

Attention was next turned to the mechanism of formation of the electrolytic hydroxylation and acetoxylation products, I and II. Two paths appeared as *a priori* possibilities. The first involved epoxidation of the 1,1-diphenylethylene by electrolytically produced peroxides or peracids, followed by acetolysis and acetylation of the intermediate epoxide (eq. 3). The presence of peroxides and peracids during Kolbe electrolyses has been documented,[3-4] particularly at low temperatures, and these intermediates have been postulated as being involved in the mechanism of the Kolbe reaction.[7] The second mechanism involved addition of an acetoxy radical to the 1,1-diphenylethylene to give the resonance-stabilized benzhydryl radical V, whose subsequent anodic oxidation might produce the cyclic acetoxonium ion VI. The latter would in turn be capable of solvolysis to the observed products I and II (eq. 4). The first step in this mechanism has precedent in the known addition of acetoxy and methyl radicals to conjugated dienes[8] and to aromatic nuclei[9,10] under electrolytic conditions, and in the initiation of vinyl polymerization by electrolyzing solutions of carboxylic acids.[11]


$$\mathrm{Ph_2C{=}CH_2} \xrightarrow{\text{peroxides}} \mathrm{Ph_2\overset{O}{C{-}C}H_2} \xrightarrow[\mathrm{HOAc}]{\mathrm{H_2O\ and/or}} \mathrm{Ph_2C(OH)CH_2OAc} + \mathrm{Ph_2C(OAc)CH_2OAc} \qquad (3)$$

I II



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[1] W. A. Bonner and F. D. Mango, *J. Org. Chem.*, **29**, 430 (1964).

[2] M. J. Allen, "Organic Electrode Processes," Reinhold Publishing Corp., New York, N. Y., 1958, p. 102.

[3] F. Fichter and R. Zumbrunn, *Helv. Chim. Acta*, **10**, 869 (1927).

[4] F. Fichter and H. Buess, *ibid.*, **18**, 445 (1935).

[5] G. Hallie, *Rec. trav. chim.*, **57**, 152 (1938).

[6] E. Denina, G. Ferrero, and F. S. de Paolini, *Gazz. chim. ital.*, **68**, 443 (1938).

[7] See ref. 1, p. 97 ff.

[8] W. B. Smith and H. G. Gilde, *J. Am. Chem. Soc.*, **81**, 5325 (1959); **83**, 1355 (1961).

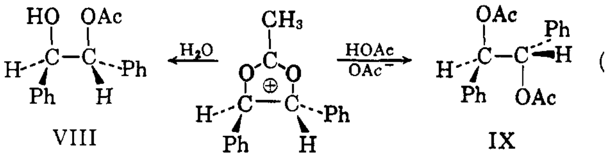
[9] T. Hayashi and C. L. Wilson, Abstracts of Papers, 126th National Meeting of the American Chemical Society, New York, N. Y., 1954, p. 78-O.

[10] L. F. Fieser, R. C. Clapp, and W. H. Daudt, *J. Am. Chem. Soc.*, **64**, 2052 (1942).

[11] W. B. Smith and H. G. Gilde, *ibid.*, **82**, 659 (1960).

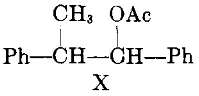
It appeared reasonable to suppose that the stereochemistry of such electrolytic hydroxylations might provide criteria for distinguishing between the two postulated mechanisms in eq. 3 and 4. Our working hypotheses were the following. If *trans*-stilbene were electrolytically hydroxylated *via* the epoxidation mechanism 3, the intermediate epoxide would in all probability undergo *trans* opening to form the inversion product,[12a] *erythro*-1-*O*-acetyl-1,2-diphenylethylene glycol (VII) (eq. 5), although *cis* opening to give the *threo*-epimer VIII or ring opening to give both VII and VIII could not be theoretically excluded.[12b] If the acetoxonium ion solvolysis mechanism 4 were applicable to *trans*-stilbene, however, electrolysis under moist conditions should, by analogy with the findings of Winstein,[13] produce a monoacetate of retained configuration, *threo*-1-*O*-acetyl-1,2-diphenylethylene glycol (VIII), whereas electrolysis in anhydrous acetic acid should afford[13] a diacetate of inverted configuration, *meso*-1,2-di-*O*-acetyl-1,2-diphenylethylene glycol (IX) (eq. 6). For comparison purposes, authentic samples of the products anticipated from each mechanism were synthesized independently. The *threo*-monoacetate VIII was prepared by the action of silver acetate and iodine[14] on *trans*-stilbene. The *erythro*-monoacetate VII and the *meso*-diacetate IX were obtained by the partial acetylation of *meso*-hydrobenzoin, prepared in turn by the sodium borohydride reduction of benzil.[15] *dl*-1,2-Di-*O*-acetyl-1,2-diphenylethylene glycol was obtained by acetylation of the above *threo*-monoacetate VIII.

VII (5)

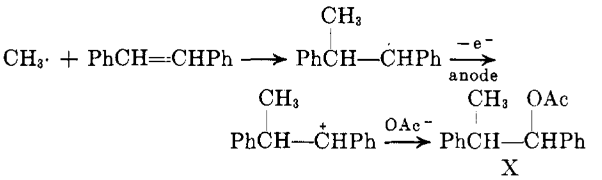


VIII IX (6)

Sodium acetate was electrolyzed in acetic acid containing *trans*-stilbene under anhydrous conditions, and the crude product was subjected to chromatographic separation. The pure products which could be characterized consisted of the *meso*-diacetate IX, a small quantity of the *threo*-monoacetate VIII, and a small quantity of *erythro*-1,2-diphenyl-1-propyl acetate (X, see below). None of the *erythro*-monoacetate VII was noted, although this was sought specifically using thin layer chromatography. The electrolysis was then repeated in acetic acid containing added water. Chromatographic separation of the crude product afforded primarily the *threo*-monoacetate VIII, small quantities of *dl*-1,2-di-*O*-acetyl-1,2-diphenylethylene glycol (by acetylation of VIII), and none of the *erythro*-epimer VII. In addition, considerable quantities of a mixture of *erythro*- and *threo*-1,2-diphenyl-1-propyl acetate (X) were isolated. It appeared probable that the latter ester arose by the reaction sequence illustrated in eq. 7.



$$\mathrm{Ph{-}\overset{CH_3}{C}H{-}\underset{X}{\overset{OAc}{C}}H{-}Ph}$$



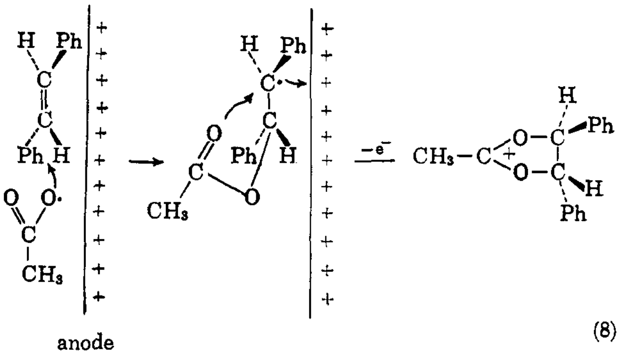
$$\mathrm{CH_3\cdot + PhCH{=}CHPh \longrightarrow Ph\overset{CH_3}{C}H{-}\dot{C}HPh \xrightarrow[\text{anode}]{-e^-}}$$

$$\mathrm{Ph\overset{CH_3}{C}H{-}\overset{+}{C}HPh \xrightarrow{OAc^-} Ph\overset{CH_3}{C}H{-}\overset{OAc}{C}HPh} \quad (7)$$

X

Since in the above electrolyses only the *threo*-monoacetate VIII was isolated and none of the *erythro*-epimer VII could be found, it was deemed essential to be certain that *erythro*-VII could not be converted into *threo*-VIII under the electrolysis conditions employed. An acetic acid solution of sodium acetate was accordingly electrolyzed in the presence of the *erythro*-monoacetate VII, and the crude product was examined for the *threo*-epimer VIII. None of the latter acetate was formed, and the *erythro*-epimer VII was recovered unchanged, except for a small amount of additional acetylation. Thus the *threo*-monoacetate VIII appeared to be an *original* product of the electrolysis in the presence of *trans*-stilbene and not to have been formed in any secondary process. These observations, involving the electrolysis of sodium acetate in the presence of *trans*-stilbene under anhydrous and moist conditions, are fully in accord with the predictions of mechanism 6, and appear to preclude the intervention both of the epoxide mechanism 5 and any alternative mechanism incapable of operating in a highly stereoselective manner.

The intimate details of the mode of formation of the cyclic acetoxonium intermediates in mechanism 4 and 6 are not completely clear at present. The addition of anodically produced acetoxy radicals to stilbene molecules in the bulk solution would appear unlikely, since Swarc[16] has estimated the acetoxy radical lifetime to be only 10^{-9}–10^{-10} second, and has suggested that such radicals react only in their original "cage" and not in the surrounding solution. If the *trans*-stilbene were adsorbed on the anode surface, however, it could conceivably be close enough to an acetoxy "cage" for the latter radical to add to it (eq. 8). Such anodic adsorption of dienes has been proposed by Smith and Gilde[8] to explain the stereochemistry of the addition products



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(12) (a) S. Winstein and R. B. Henderson, "*Heterocyclic* Compounds," Vol. 1, R. Elderfield, Ed., John Wiley and Sons, New York, N. Y., 1950, p. 27-32; (b) R. E. Parker and N. S. Isaacs, *Chem. Rev.*, **59**, 757 (1959).

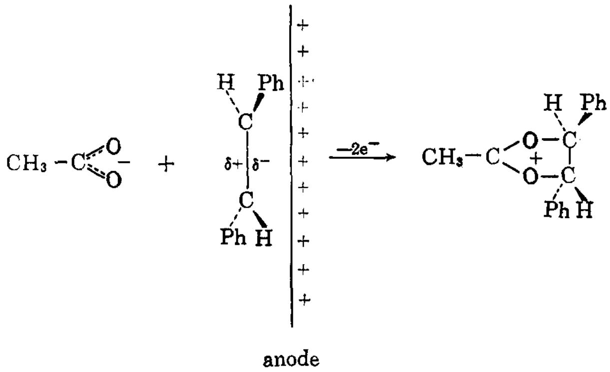
(13) S. Winstein, H. V. Mess, and R. E. Buckles, *J. Am. Chem. Soc.*, **64**, 2796 (1942); S. Winstein and R. M. Roberts, *ibid.*, **75**, 2297 (1953).

(14) R. B. Woodward and F. V. Brutcher, Jr., *ibid.*, **80**, 209 (1958).

(15) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1955, p. 175.

(16) L. Herk, M. Feld, and M. Swarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

of electrolytically produced radicals to conjugated dienes, and the fact that such addition products were found only in the anode compartment. Examples of the adsorption of uncharged aromatic compounds on electrode surfaces have also been reported,[17-20] and it has been proposed[18] that the adsorption of aryl amines on positively charged surfaces results from interactions between the π-electrons of the flatly held aromatic system and the metal. We presently have only preliminary experimental evidence that *trans*-stilbene is adsorbed on the anode surface during the above Kolbe electrolyses. When sodium acetate in acetic acid was electrolyzed in a cell powdered by a square wave generator (1 c.p.s.), the decay curve pattern (oscilloscope screen) resulting from interruption of the applied potential was significantly altered when *trans*-stilbene was present. These studies, however, are as yet incomplete. Another mechanism whereby the acetoxonium intermediate in eq. 6 might arise electrolytically from *trans*-stilbene is shown in eq. 9. Here the anodically adsorbed



(9)

olefin, polarized by the electrode as shown, is directly attacked at the positively polarized portion of its π-electron cloud by acetate ion, two electrons are expelled directly into the anode, and the acetoxonium intermediate is formed in one direct step. We have no experimental data, however, which distinguish between the two-step mechanism 8 and the one-step mechanism 9. Regardless, either process, each involving anodically adsorbed *trans*-stilbene, generates stereoselectively the required cyclic intermediate of eq. 6. So far as we are aware, electrolytic hydroxylations and acetoxylations of the above sort involving aryl-substituted alkenes have not been previously reported.

Experimental

Electrolysis of Sodium Acetate with 1,1-Diphenylethylene.—The electrolysis cell used in the following experiments was that which we have described earlier,[1] and the conditions for the following electrolyses were maintained as closely as possible to those described in our previous study.[1] Approximately 800 mg. of 1,1-diphenylethylene was added dropwise, at the rate of 1 drop per 10 min., to an electrolyzing (0.3 amp.) solution of sodium acetate (1.6 g.) in acetic acid (25 ml.). After about 4 hr. the crude product (*ca.* 0.7 g.), isolated as described earlier, was chromatographed on 50 g. of silicic acid using benzene, gradually enriched in ether, as eluant. Evaporation of the first 100 ml. of eluent left 35 mg. of clear oil, shown by its infrared spectrum to be unchanged 1,1-diphenylethylene. The next 300 ml. of eluent yielded 100 mg. of oil which appeared to be a mixture of starting material and the component in the next fraction. The next 400 ml. of eluent yielded 129 mg. of crystalline material. One recrystallization from a mixture of *n*-hexane and benzene yielded a white solid, m.p. 145–148°. The reported melting point for 1,1-di-*O*-acetyl-1,1-diphenylethylene glycol is 145–146°.[21] The infrared spectrum of the crystalline solid showed a strong carbonyl stretching band at 1731 cm.$^{-1}$, and three bands in the ester C–O stretching region at 1231, 1246, and 1252 cm.$^{-1}$. A 10-mg. portion of the crystalline material was hydrolyzed in alcoholic potassium hydroxide. The crude hydrolysis product, recrystallized from a mixture of *n*-hexane and benzene, had m.p. 119–121.5°. A mixture of this material with authentic 1,1-diphenylethylene glycol (m.p. 120–122°) showed no melting point depression (120–122°), and the infrared spectra of the two glycol samples were identical. The 1,1-di-*O*-acetyl-1,1-diphenylethylene glycol represented approximately 16% of the crude product. The final 500 ml. of eluent from the above chromatographic separation of the crude electrolysis product yielded 330 mg. of thick oil which crystallized on standing. This was recrystallized from a mixture of *n*-hexane and benzene, affording white crystals, m.p. 91–92.5°. The infrared spectrum showed an O–H stretching band at 3500 cm.$^{-1}$, a carbonyl stretching band at 1725 cm.$^{-1}$, and a strong band in the ester C–O stretching region at 1236 cm.$^{-1}$. The n.m.r. spectrum (Varian A60 n.m.r. spectrometer, tetramethylsilane internal standard, $CDCl_3$ solvent) contained a sharp band at 3.0, which shifted on warming, another band at 4.66, and a third at 1.98 p.p.m. A multiplet of bands appeared in the aromatic proton region between 7.15 and 7.5 p.p.m. This spectrum was consistent with 2-*O*-acetyl-1,1-diphenylethylene glycol, where the hydroxyl proton absorbed at 3.0, the identical methylene protons at 4.66, and the three acetate methyl protons at 1.98 p.p.m. This monoacetate had an identical infrared spectrum and showed no mixture melting point depression with a sample of the 2-*O*-acetyl-1,1-diphenylethylene glycol prepared below. The product represented approximately 46% of the crude material obtained from the above electrolysis.

The electrolysis was repeated using approximately 2 g. of 1,1-diphenylethylene, which was added in one batch to the electrolyzing solution of sodium acetate. Electrolysis was continued for approximately 8 hr., whereupon the crude product was isolated as before. The thick oil was chromatographed on 100 g. of silicic acid using a mixture of petroleum ether (b.p. 66–70°) and benzene (1:4) as eluent. The first 200 ml. of eluent yielded 70 mg. of clear liquid, which appeared to be homogeneous on thin layer chromatography. Its infrared spectrum showed no absorption bands attributable to functional groups. The hydrocarbon was purified by rechromatographing on neutral alumina (10 g.) using benzene–ether (100:2) as eluent. Evaporation of the first 25 ml. of eluent left 50 mg. of thin oil, presumably 2,2-diphenylbutane.

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.04; H, 8.68.

The remaining chromatography of the crude electrolysis product afforded various fractions of oily material from which little crystalline material separated. Thin layer chromatographic examination of these fractions indicated them to be impure, and to contain components in addition to the ones noted in the original electrolysis. Further attempts to obtain pure components from these fractions were abandoned.

1,1-Diphenylethylene Glycol.—This material was prepared, for comparison with the above electrolysis products, by the addition of dilute aqueous potassium permanganate to a chilled ethanol solution of 1,1-diphenylethylene, after the procedure of Clark and Owen.[22] The crude crystalline product was recrystallized from a mixture of *n*-hexane and benzene, affording sharp needles, m.p. 120–122. The reported melting point for 1,1-diphenylethylene glycol is 121°.[23]

2-*O*-Acetyl-1,1-diphenylethylene Glycol.—A few milligrams of the above 1,1-diphenylethylene glycol was treated with an excess of acetic anhydride in an equal volume of pyridine, and the resulting solution was allowed to stand at room temperature for 4 hr. The solution was treated with sufficient water to engender cloudiness and chilled; the crystalline material was collected. The product, recrystallized from a mixture of *n*-hexane and benzene, had m.p. 93–93.5°

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(22) M. F. Clark and L. N. Owen, *J. Chem. Soc.*, 315 (1949).

(23) P. Weidenkoff, *Ber.*, **39**, 2063 (1906).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.97; H, 6.32.

Electrolysis of Sodium Acetate with *trans*-Stilbene under Anhydrous Conditions.—Anhydrous glacial acetic acid was obtained by distilling the acid from acetic anhydride after a mixture of the two had been heated under reflux for 12 hr. Anhydrous conditions were maintained during the electrolysis, conducted otherwise as above, by sealing the electrolysis cell from the atmosphere with a calcium chloride tube. A magnetically stirred, ice-cooled, solution of anhydrous glacial acetic acid (20 ml.) and sodium acetate (2 g.) containing *trans*-stilbene (2 g., dried in a vacuum over phosphorus pentoxide) was electrolyzed (0.2 amp.) during a period of 29 hr. The electrolysis mixture was then evaporated to dryness under reduced pressure and the residue was added to a mixture of ether and water (100 ml., 1:1) and shaken vigorously. The ether layer was washed with water, dilute aqueous sodium bicarbonate, and again with water, then was dried and evaporated, leaving approximately 1.5 g. of crude product. The thin layer chromatogram (silica gel G), using ether and benzene (3:10) as eluent, showed three principal spots and three minor ones. The crude product was chromatographed on 100 g. of silicic acid using solvent mixtures of increasing polarity from 5% ligroin in benzene, through benzene, to 10% ether in benzene. Fractions (50-ml. each) were collected and evaporated to dryness under reduced pressure. The residues were examined by thin layer chromatography, and combined on the basis of their thin layer chromatographic behavior.

The first combined fraction (750 mg., 57.9%) gave a thin layer chromatogram displaying two spots with R_f values identical with those of 1,2-di-*O*-acetyl-1,2-diphenylethylene glycol and 1,2-diphenyl-1-propyl acetate, respectively. A portion (625 mg.) of the solid fraction was recrystallized from a mixture of benzene and *n*-hexane yielding first 40 mg. of white solid, m.p. 120–127°, and finally an additional 54 mg. of white solid, m.p. 87–97°. Both products were found to be mixtures by thin layer chromatographic examination. The solid having m.p. 120–127° was hydrolyzed by the procedure described above. The crude hydrolysis product was recrystallized from a mixture of *n*-hexane and benzene to yield 10 mg. of a white solid, m.p. 134–135°. The infrared spectrum of this solid was identical with that of authentic *meso*-hydrobenzoin (m.p. 135–136.5°).

The second combined fraction (172 mg., 13.3%) gave a thin layer chromatogram displaying two spots, the principal one corresponding in position and hue to that of 1,2-di-*O*-acetyl-1,2-diphenylethylene glycol. The product was recrystallized twice from petroleum ether (b.p. 56–70°), affording fine needles, m.p. 133–135°. The reported melting point for *meso*-1,2-di-*O*-acetyl-1,2-diphenylethylene glycol (IX) is 136–138°.[24] A mixture melting point of the above sample with an authentic specimen of the *meso*-diacetate IX (m.p. 135–136.5°) was 134–136.5°, and the infrared spectra of the two samples were identical.

Thin layer chromatographic examination of the third combined fraction (162 mg., 12.5%) revealed the presence of at least four components, one of which was the above *meso*-diacetate IX. The fourth combined fraction (211 mg., 16.3%) gave a thin layer chromatogram indicating again the presence of at least four components. One of the four spots on the chromatogram was identical in position and the hue with that of *threo*-1-*O*-acetyl-1,2-diphenylethylene glycol (VIII). No evidence of the presence of the epimeric *erythro*-monoacetate VII was found. These two epimers were found to separate cleanly upon thin layer chromatography, but that portion of the chromatogram which would contain the *erythro*-monoacetate spot was blank. All attempts to crystallize the *threo*-monoacetate from the original cuts making up this combined fraction failed, but one of these fractions, thought to be richest in the *threo*-epimer, afforded a small amount of waxy solid whose infrared spectrum was similar to that of the *threo*-monoacetate VIII, but contained one extraneous band in the methyl C–H stretching region at 2960 cm.$^{-1}$. We estimate that the *threo*-monoacetate VIII was present to the extent of less than 5% in the crude electrolysis product.

Electrolysis of Sodium Acetate with *trans*-Stilbene under Moist Conditions.—To an electrolyzing (0.4 amp.) glacial acetic acid solution (20 ml.) of *trans*-stilbene (2.7 g.) and sodium acetate (1 g.) was added dropwise over a period of 9 hr. 1.2 g. of water. The crude, partially crystalline electrolysis product (3.6 g.) was chromatographed on 100 g. of silicic acid in the manner described above, yielding three fractions after recombination as above on the basis of thin layer chromatography.

The first of these (1496 mg., 47.6%) was partially crystalline. It was recrystallized from ethanol and then from a mixture of *n*-hexane and benzene to yield a product having m.p. 105–106° and showing no mixture melting point depression with an authentic sample of *erythro*-1,2-diphenyl-1-propyl acetate (X, m.p 103–105°). The infrared spectra of the two samples were superimposable. Although some of the original fractions comprising this combined fraction were oils, their thin layer chromatograms contained single, sharply defined spots, identical in position and hue with those of either *threo*- or *erythro*-1,2-diphenyl-1-propyl acetate. The infrared spectra of these oils were almost identical with that of a mixture of the two epimers.

A thin layer chromatogram of the second combined fraction (343 mg., 10.9%) revealed the presence of four components. The principal one had a spot identical in position and hue with that of either *dl*- or *meso*-1,2-di-*O*-acetyl-1,2-diphenylethylene glycol. This material partially crystallized on prolonged standing and was recrystallized from a mixture of *n*-hexane and benzene, yielding a few milligrams of white solid, m.p. 90–110°. The thin layer chromatogram of this solid contained a single, cleanly defined spot, identical in position with that of 1,2-di-*O*-acetyl-1,2-diphenylethylene glycol. The infrared spectrum of the crude solid differed only slightly, with a few variations in band intensities and slight band shifts, from the spectrum of *dl*-1,2-di-*O*-acetyl-1,2-diphenylethylene glycol. The reported melting point for this racemic diacetate is 114–116°.[25] The diester represented less than 6% of the crude electrolysis product.

The third combined fraction (1306 mg., 41.5%) gave a thin layer chromatogram showing at least four spots. The principal spot was identical in all respects with that of *threo*-1-*O*-acetyl-1,2-diphenylethylene glycol (VIII). The crude material was rechromatographed on 100 g. of silicic acid using benzene as eluant. The first 900 ml. of eluent contained none of the monoacetate, and was discarded. The next 600 ml. of eluent left a thick oil (1124 mg.) which crystallized readily on seeding with a sample of authentic *threo*-monoacetate VIII. The thin layer chromatogram of this material contained one principal spot, identical in position with that of the *threo*-monoacetate, and two minor spots. The portion of the chromatogram corresponding to a spot for the *erythro*-monoacetate VII was blank. A portion (227 mg.) of the above crystalline material was recrystallized from a mixture of *n*-hexane and benzene, yielding 143 mg. of white solid, m.p. 85–87°. Its mixture melting point with authentic *threo*-1-*O*-acetyl-1,2-diphenylethylene glycol (m.p. 86–88°) was undepressed (85–87°), and the infrared spectra of the two samples were identical. The *threo*-monoacetate VIII represented approximately 20% of the crude electrolysis product.

Electrolysis of Sodium Acetate in the Presence of *erythro*-1-*O*-Acetyl-1,2-diphenylethylene Glycol.—This experiment was undertaken to establish whether or not the *erythro*-monoacetate VII, not found in the product mixtures from the above electrolyses, could survive the conditions of the reaction. The electrolysis was carried out as described above. A glacial acetic acid solution (20 ml.) of sodium acetate (1 g.) containing 0.57 g. of a mixture of *meso*-hydrobenzoin, the *erythro*-monoacetate VII, and the *meso*-diacetate IX was electrolyzed (0.4 amp.) for a period of 5 hr., after which a 2-ml. portion of the electrolysis mixture was withdrawn and evaporated to dryness in a vacuum desiccator over potassium hydroxide. The thin layer chromatogram of the residue contained spots corresponding to the *erthro*-monoacetate VII and the *meso*-diacetate IX, but did not contain a spot corresponding to *meso*-hydrobenzoin or to the *threo*-monoacetate VIII.

***threo*-1-*O*-Acetyl-1,2-diphenylethylene Glycol (VIII).**—The method used to prepare an authentic sample of the *threo*-monoacetate VIII was essentially that of Woodward and Brutcher.[14] A slurry of glacial acetic acid (100 ml.) containing *trans*-stilbene (5 g., m.p. 122–123°) and silver acetate (9.5 g.) was placed in a three-neck flask equipped with a reflux condenser, stirrer, and thermometer. Finally powdered iodine (6.7 g.) was added to the reaction mixture in small portions with vigorous stirring over a period of 30 min. at room temperature. When all of the iodine had been consumed, aqueous glacial acetic acid (10 ml., acid-water, 25:1) was added, and the reaction mixture was heated at 90–95° for 3 hr. with vigorous stirring, whereupon it was cooled, treated with an excess of sodium chloride, and filtered free

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(24) S. Winstein, *J. Am. Chem. Soc.*, **68**, 119 (1946).

(25) F. A. A. Elhafez and D. J. Cram, *ibid.*, **75**, 339 (1953).

of insoluble salts. There were washed with hot benzene, and the filtrate and washings were evaporated to dryness under reduced pressure. The residue was dissolved in ether (100 ml.) and the solution was washed with dilute ammonium hydroxide and with water. Evaporation of the dried ether solution left 6.5 g. (97.5%) of thick oil which crystallized on standing. After two recrystallizations from a mixture of *n*-hexane and benzene, the desired pure *threo*-monoacetate VIII was obtained as white crystals, m.p. 86–88°.

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 74.93; H, 6.21.

***dl*-1,2-Di-*O*-acetyl-1,2-diphenylethylene Glycol.**—A pyridine solution (5 ml.) of the above *threo*-monoacetate VIII (0.45 g.) was treated with 5 ml. of acetic anhydride, and the resulting solution was allowed to stand at room temperature for a period of 12 hr. The mixture was then evaporated under reduced pressure, yielding 0.5 g. of solid residue, m.p. 100–105°. After two recrystallizations from a mixture of *n*-hexane and benzene, the pure *dl*-diacetate was obtained, m.p. 116–117°. The reported melting point is 114–116°.[26]

***erythro*-1-*O*-Acetyl-1,2-diphenylethylene Glycol (VII) and *meso*-1,2-Di-*O*-acetyl-1,2-diphenylethylene Glycol (IX).**—The starting material, *meso*-hydrobenzoin, was prepared by the sodium borohydride reduction of benzil after the procedure of Fieser.[15] One recrystallization of the crude product from dilute ethanol yielded sufficiently pure product, m.p. 135–136.5°.

A pyridine solution (10 ml.) of *meso*-hydrobenzoin (1.1 g.) and acetic anhydride (0.6 ml., 1.2 equiv.) was allowed to stand at room temperature for a period of 2 hr., whereupon sufficient water was added to engender cloudiness. On standing in the cold room for 12 hr., a white solid crystallized from the turbid solution. The crystals were collected and the filtrate was acidified with dilute hydrochloric acid and extracted three times with ether. The extracts were washed with water, dried, and evaporated, affording 0.5 g. of thick oil. The original white solid (0.3 g., m.p. 128–131°) was recrystallized from a mixture of *n*-hexane and benzene, yielding white needles, m.p. 135–136.5°. The reported melting point for *meso*-1,2-di-*O*-acetyl-1,2-diphenylethylene glycol is 136–138°.[24] The crude oil extracted from the above aqueous filtrate was chromatographed on 100 g. of silicic acid using benzene, gradually enriched in ether, as eluent. The first 600 ml. of eluent was discarded. Evaporation of the next 700 ml. of eluent left 0.39 g. of white solid. This was recrystallized from a mixture of *n*-hexane and benzene, affording the pure *erythro*-monoacetate VII, m.p. 90–92°. The infrared spectrum showed a strong O–H stretching band at 3380 cm.$^{-1}$ in addition to two typical ester bands at 1732 (C═O) and 1239 cm.$^{-1}$ (C–O).

Anal. Calcd. for $C_{16}H_{16}O_3$: C, 74.98; H, 6.29. Found: C, 75.27; H, 6.43.

1,2-Diphenyl-1-propyl Acetate (IX).—1,2-Diphenyl-1-propanol was prepared in the customary manner by the action of phenylmagnesium bromide (20% excess) on hydratropaldehyde. The thin layer chromatogram of the crude product displayed two spots, with no spot corresponding to starting aldehyde, and its infrared spectrum showed an O–H stretching band at 3420 cm.$^{-1}$, and no carbonyl bands. The crude 1,2-diphenyl-1-propanol (10 g.) was added to a mixture of pyridine (10 ml.) and acetic anhydride (10 ml.), and the resulting solution was stirred at room temperature for a period of 18 hr., then was treated with an excess of chilled dilute sulfuric acid, extracted with ether, and processed in the usual fashion. The crude acetylation product was a thick oil, 11.4 g., which partially crystallized on standing. It was recrystallized once from petroleum ether (b.p. 66–70°), affording sharp rectangular crystals, m.p. 103–105°. The reported melting point for *erythro*-1,2-diphenyl-1-propyl acetate is 109–110°, and that for the *threo*-epimer is 38–39°.[25]

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Chlorination of Furfural in Concentrated Hydrochloric Acid

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Received September 25, 1963

Treatment of furfural with manganese dioxide or chlorine in hydrochloric acid to produce mucochloric acid yielded two unknown crystalline materials, one as an intermediate of the reaction and the other as a by-product. The intermediate was identified as β-chloro-β-formylacrylic acid and the by-product as α-chlorocrotonolactone.

When furfural is treated with manganese dioxide or chlorine gas in concentrated hydrochloric acid, the major product is mucochloric acid (III) which is the raw material for the synthesis of dichloromaleic acid.

Mucochloric acid has been produced by a variety of methods,[1,2] such as by the action of chlorine on furoic acid, treatment of furoic acid in hydrochloric acid with manganese dioxide, treatment of β,γ-dichlorofuroic acid with an excess of bromine water or with nitric acid, and by reaction of furfural with the reagents mentioned in the first paragraph. The mechanisms of these reactions are very complex since the process involves chlorination, oxidation, and opening of the furan ring. In this article, two unknown crystalline compounds were isolated, one from the initial stage of the reaction of furfural with manganese dioxide in hydrochloric acid and the other from the reaction of furfural with manganese dioxide or chlorine, and their structures were determined.

The reaction of furfural with manganese dioxide in concentrated hydrochloric acid is the most convenient way to prepare mucochloric acid on a laboratory scale A yield of nearly 75% was obtained by the method of Yanagida.[3]

In this process, the reaction can be considered to take place in two steps, the first below and the second above 10°. If the reaction is interrupted after the first step and extracted with ether, and the ether extract is distilled at reduced pressure, colorless crystals of m.p. 53–55° are obtained (compound A). If the reaction is allowed to proceed to completion, the mucochloric acid is separated by filtration, and the mother liquors are ether extracted, evaporation of the ether and distillation of the residue (105–115° at 4 mm.) yields a colorless liquid that crystallizes on standing, m.p. 25–27° (compound B). However, treatment of furfural with chlorine in hydrochloric acid is more convenient to obtain compound B in high yield.

Elementary analysis of compound A agreed with formula $C_4H_3O_3Cl$. Its infrared spectrum resembled that of mucochloric acid which exists not as the open-chain α,β-dichloro-β-formylacrylic acid but in the ring structure (III). The spectrum had bands at 1625

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[1] D. T. Mowry, *J. Am. Chem. Soc.*, **72**, 2535 (1950).

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[3] M. Yanagida, *J. Pharm. Soc. Japan*, **72**, 1383 (1952).