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Electrochemical Methoxylation of Cinnamic Acid and Its Derivatives

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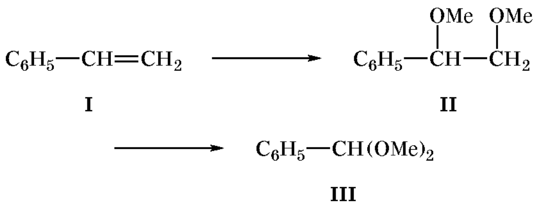
Abstract—Electrochemical methoxylation of cinnamic acid is accompanied by decarboxylation and yields 1,1,2-trimethoxy-2-phenylethane through formation of γ-truxillic acid in the initial stage. Under the same conditions methyl cinnamate and cinnamamide give rise to hydrodimerization and reduction products. The results show that introduction of electron-acceptor substituents into the β-position of the aliphatic chain of styrene hinders methoxylation.

In the recent time a considerable attention is given to electrochemical methoxylation since methoxy derivatives obtained in such a way are key compounds in numerous organic syntheses [1]. Methoxylation of styrene (**I**) initially gives 1,2-dimethoxy-1-phenylethane (**II**), and the subsequent electrolysis results in cleavage of the C–C bond with formation of benzaldehyde dimethyl acetal (**III**) as final product [2] (Scheme 1).

Scheme 1.

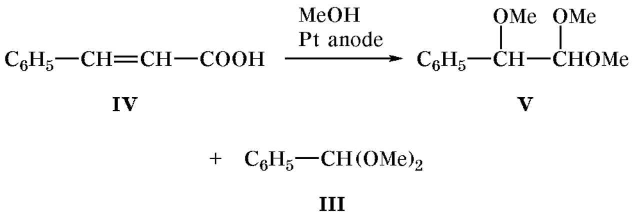


$$C_6H_5{-}CH{=}CH_2 \longrightarrow C_6H_5{-}\underset{|}{\overset{OMe}{C}}H{-}\overset{OMe}{C}H_2 \longrightarrow C_6H_5{-}CH(OMe)_2$$

The goal of the present work was to examine the effect of substituents in the aliphatic chain of styrene on the methoxylation process. We have performed electrochemical methoxylation of cinnamic acid and its methyl ester and amide under conditions reported in [2] for methoxylation of styrene. The electrolysis was carried out in a diaphragmless electrolyzer in the galvanostatic mode at 60–65°C using a 0.1 M solution of KF in methanol as supporting electrolyte.

In the electrolysis of cinnamic acid (**IV**), after passing 1.93×10^5 C/mol of electricity, the major product was 1,1,2-trimethoxy-2-phenylethane (**V**) (yield 96%, according to the GLC data); further electrolysis led to formation of benzaldehyde dimethyl acetal (**III**) (4%, GLC; Scheme 2).

Scheme 2.



$$C_6H_5{-}CH{=}CH{-}COOH \xrightarrow[\text{Pt anode}]{\text{MeOH}} C_6H_5{-}\overset{OMe}{C}H{-}\overset{OMe}{C}HOMe + C_6H_5{-}CH(OMe)_2$$

After passing 6.76×10^5 C/mol of electricity, the ratio of 1,1,2-trimethoxy-2-phenylethane (**V**) and benzaldehyde dimethyl acetal (**III**) was 54:46 (GLC).

Cinnamic acid, like diphenylacrylic acid [3], is classed with so-called "anomalous" carboxylic acids which lose two electrons at an anode, yielding carbocation **A**. Methoxide ions **B** are generated at a cathode. These species combine in the bulk solution to give methoxystyrene **C**. Methoxylation of the latter at the double C=C bond, as in the case of unsubstituted styrene, leads to formation of the primary product, 1,1,2-trimethoxy-2-phenylethane (**V**). The reaction mechanism can be illustrated by Scheme 3 [4, 5]. It should be noted that at a graphite anode γ-truxillic acid (**VI**) is formed as intermediate product (Scheme 4); it is known [6] that no dimerization occurs in solution. After passing 0.96×10^5 C/mol

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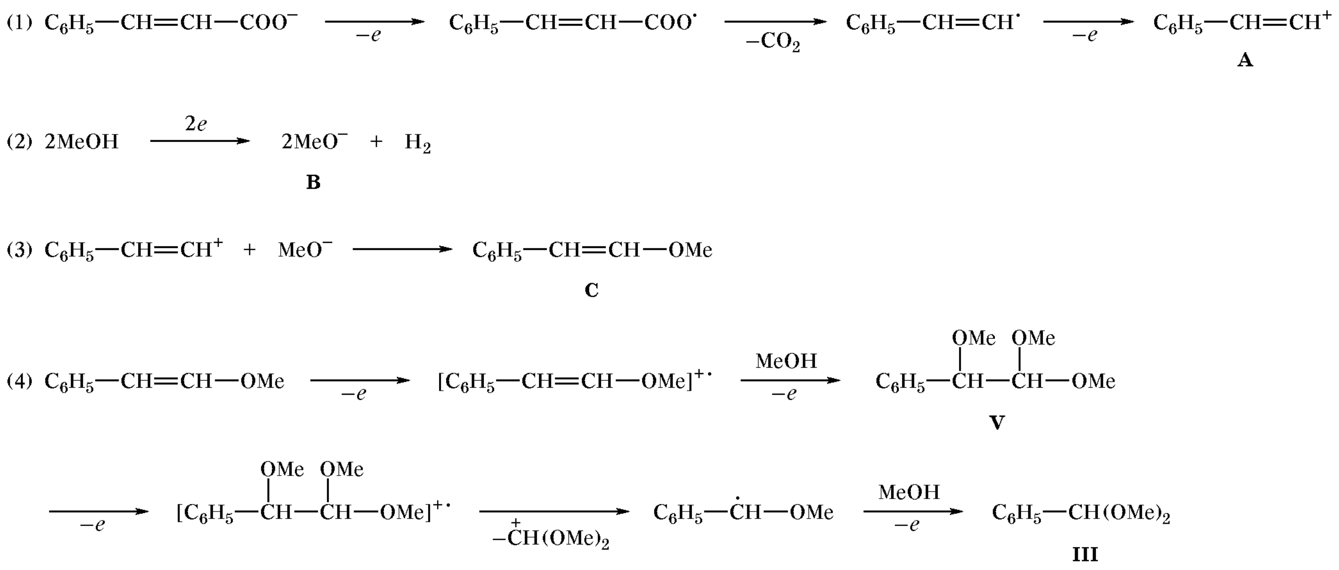
Scheme 3.



(1) $C_6H_5{-}CH{=}CH{-}COO^- \xrightarrow[-e]{} C_6H_5{-}CH{=}CH{-}COO^{\bullet} \xrightarrow[-CO_2]{} C_6H_5{-}CH{=}CH^{\bullet} \xrightarrow[-e]{} \underset{\mathbf{A}}{C_6H_5{-}CH{=}CH^+}$

(2) $2MeOH \xrightarrow{2e} \underset{\mathbf{B}}{2MeO^-} + H_2$

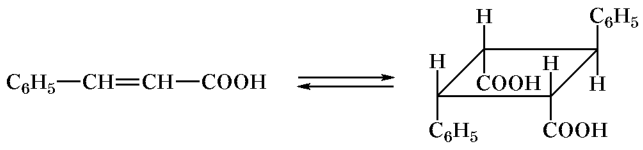
(3) $C_6H_5{-}CH{=}CH^+ + MeO^- \longrightarrow \underset{\mathbf{C}}{C_6H_5{-}CH{=}CH{-}OMe}$

(4) $C_6H_5{-}CH{=}CH{-}OMe \xrightarrow[-e]{} [C_6H_5{-}CH{=}CH{-}OMe]^{+\bullet} \xrightarrow[-e]{MeOH} \underset{\mathbf{V}}{C_6H_5{-}\overset{OMe}{CH}{-}\overset{OMe}{CH}{-}OMe}$

$\xrightarrow[-e]{} [C_6H_5{-}\overset{OMe}{CH}{-}\overset{OMe}{CH}{-}OMe]^{+\bullet} \xrightarrow[-\overset{+}{C}H(OMe)_2]{} C_6H_5{-}\dot{C}H{-}OMe \xrightarrow[-e]{MeOH} \underset{\mathbf{III}}{C_6H_5{-}CH(OMe)_2}$

of electricity, the yield of γ-truxillic acid was 63%, calculated on the reacted cinnamic acid. γ-Truxillic acid gradually disappears, and it is not detected by the end of the process. Acid **VI** is converted into cinnamic acid on heating, and the latter undergoes further transformations.

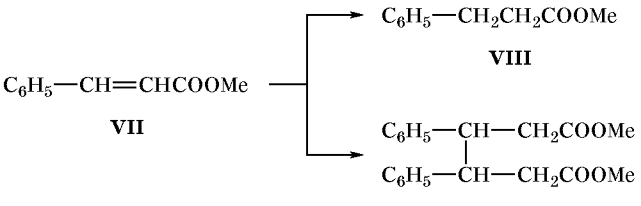
Scheme 4.



VI

Methyl cinnamate and cinnamamide showed a different behavior under analogous conditions. In both cases no methoxylation products were obtained, but reduction of the double bond occurred with formation of monomeric and dimeric products. The electrolysis of methyl cinnamate **VII** afforded 61% of ester **VIII** and 23% of diester **IX** (Scheme 5).

Scheme 5.



IX

After passing 1.93×10^5 C/mol of electricity, the yield of dimeric product **IX** was 23% at a stainless steel cathode, 16% at a zinc cathode, and 8% at a copper cathode. By electrolysis of cinnamamide (**X**) we obtained only product **XI** as a result of reduction of the double bond (Scheme 6).

Scheme 6.

$$\underset{\mathbf{X}}{C_6H_5{-}CH{=}CHCONH_2} \longrightarrow \underset{\mathbf{XI}}{C_6H_5{-}CH_2CH_2CONH_2}$$

The yield of the reduction and dimerization products descreases when the reaction is carried out in a diaphragm electrolyzer.

Our results led us to conclude that introduction of electron-acceptor groups into the β-position of the side chain of styrene molecule hampers methoxylation of the double C=C bond. This conclusion is consistent with the assumption that electrolytic methoxylation of cinnamic acid begins only after elimination of the carboxy group which is a fairly strong electron acceptor.

EXPERIMENTAL

The electrolysis was carried out in a 200-ml diaphragmless sealed cell equipped with an electrode assembly (platinum or graphite anode as a 50 × 15-mm plate and two cathodes each as a 50 × 15-mm stainless steel plate; anode-to-cathode distance 3 mm), reflux condenser, and magnetic stirrer. GLC analysis was performed on an LKhM-8MD chromatograph with a heat-conductivity detector. The ^{1}H NMR spectra were recorded on a Varian VXR-300 spectrometer (300 MHz) in deuterated solvents. The IR spectra were obtained on a Specord 75IR spectrometer in mineral oil.

Cinnamic acid was of pure grade; KF of pure grade was dried in a desiccator over P_2O_5 prior to use. Methanol (from NZSP) contained 99.5% of the main substance and was used without additional purification. Methyl cinnamate was synthesized by the procedure reported in [7].

Electrochemical methoxylation of cinnamic acid (IV). The electrolytic cell was charged with 6.9 g (0.04 mol) of cinnamic acid, 0.43 g (0.005 mol) of KF, and 125 ml of methanol. The electrolysis was carried out at 60–65°C under vigorous stirring at a current density of 0.1 A/cm^2 (0.5 A); 1.93×10^5 C $\times$ mol^{-1} (2F/mol) of electricity was passed. When the reaction was complete, the solvent was distilled off under reduced pressure (water-jet pump), and the residue was treated with a 10% solution of KOH to remove unchanged cinnamic acid. The aqueous layer was extracted with benzene (2×30 ml), and the extract was acidified with hydrochloric acid to isolate 5 g of unreacted cinnamic acid. The benzene extract was evaporated under reduced pressure to obtain 2 g (80% on the reacted cinnamic acid or 22% on the total amount of cinnamic acid) of 1,1,2-trimethoxy-2-phenylethane (**V**), bp 98–100°C (6 mm), n_D^{20} = 1.4912. IR spectrum, ν, cm^{-1}: 1720, 1620, 1450. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.18 s (3H, OCH_3), 3.25 s (3H, OCH_3), 3.45 s (3H, OCH_3), 4.15 d (1H, CH), 4.35 d (1H, CH), 7.28 m (5H, H_{arom}). Only the ^{1}H NMR and mass spectra of **V** were given in [2, 8].

After passing 6.76×10^5 C/mol (7F/mol) of electricity, the conversion of cinnamic acid was 100%. According to the GLC data, a mixture of 1,1,2-trimethoxy-2-phenylethane (**V**, 54%) and benzaldehyde dimethyl acetal (**III**, 46%) was formed. After appropriate treatment, we isolated 2.9 g (33%) of compound **V** and 2.45 g (28%) of **III**, bp 80–82°C (6 mm), n_D^{20} = 1.5095 [2]. Analogous results were obtained when the electrolysis was carried out at a graphite anode.

γ-Truxillic acid (VI). The electrolysis was carried out as described above using a graphite anode; 0.96×10^5 C/mol (1F/mol) of electricity was passed. γ-Truxillic acid was separated by filtration; yield 1.5 g (22%), colorless needles, mp 227–229°C (from methanol) [9]. Removal of the solvent left 4.5 g of unchanged cinnamic acid and 0.9 g (30%) of compound **V**.

Electrochemical reduction of methyl cinnamate (VII). *a. In a diaphragmless cell.* The electrolytic cell was charged with 6.5 g (0.04 mol) of methyl cinnamate, 0.43 g (0.005 mol) of KF, and 125 ml of methanol. The conditions were the same as above. When 1.93×10^5 C/mol (2F/mol) of electricity was passed, most part of the solvent was distilled off. Crystalline product **IX** was filtered off and recrystallized from methanol. The yield of dimer **IX** was 2 g (23%), colorless crystals with mp 174–175°C. IR spectrum, ν, cm^{-1}: 1720, 1600, 1450. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm): 2.4 m (4H, CH_2), 3.25 t (2H, CH), 3.62 s (6H, OCH_3), 7.28 m (5H, H_{arom}).

The residue was extracted with benzene, the extract was evaporated, and the residue was distilled under reduced pressure to isolate methyl 3-phenylpropionate (**VIII**). Yield 3.5 g (61%), bp 118–120°C (6 mm), n_D^{20} = 1.4991. IR spectrum, ν, cm^{-1}: 3600–3400, 1720, 1650, 1600, 1450. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.5 t (2H, CH_2), 2.9 t (2H, CH_2), 3.25 d (1H, CH), 3.65 s (3H, OCH_3), 7.28 m (5H, H_{arom}).

b. In a diaphragm cell. Methyl cinnamate, 4 g (0.025 mol), and $LiClO_4$, 1 g (0.01 mol), were dissolved in 150 ml of methanol. A 120-ml portion of that solution was placed in the cathode space, and the remaining 30-ml portion, in the anode space. The electrolysis was carried out at a current strength of 0.75 A (cathode current density 0.1 A/cm^2) and was terminated when 1.93×10^5 C/mol (2F/mol) of electricity was passed. From the catholyte we isolated 1.3 g (32%) of methyl 3-phenylpropionate (**VIII**) and 0.5 g (7%) of dimer **IX**. We failed to perform electrolysis using potassium fluoride as supporting electrolyte because of too high resistance of the system.

Electrochemical reduction of cinnamamide (X). The procedure was the same as described above for reduction of methyl cinnamate (**VII**). From 6 g (0.04 mol) of compound **X** we obtained 3.5 g (60%) of 3-phenylpropionamide (**XI**) as colorless crystals with mp 103–105°C (from water) [9].

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