ELECTROCHEMICAL OXIDATION OF 1-ALKENYLARENES TO GIVE BENZALDEHYDE DIMETHYL ACETALS

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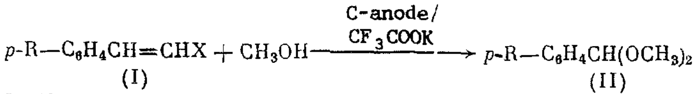
The electrochemical oxidation of 1-alkenylarenes (AA) such as styrene and α-methylstyrene in a diaphragmless electrolyzer with a graphite anode in methanolic $NaClO_4$ at 20°C and AA concentration above 3 moles/liter leads to the dimerization of these substrates and formation of 1,4-dimethoxy-1,4-diarylbutanes or 1,4-diaryl-1,3-butadienes as the major products [1].

We have found that the direction of the electrochemical oxidation is fundamentally altered upon the electrolysis of styrene, propenylbenzene, p-propenyltoluene, and stilbene in methanolic potassium or sodium trifluoroacetate at 55-60°C and a much lower concentration of the AA achieved by the gradual addition of the substrate to the electrolyte. All other conditions were analogous. The selective conversion of the AA to benzaldehyde dimethyl acetals occurs in this case.



$$\underset{(I)}{p\text{-}R{-}C_6H_4CH{=}CHX} + CH_3OH \xrightarrow{\text{C-anode}/CF_3COOK} \underset{(II)}{p\text{-}R{-}C_6H_4CH(OCH_3)_2}$$

$R = H, CH_3, X = H, CH_3, C_6H_5$ (I); $R = H$ (IIa), CH_3 (IIb).

A constant current of 0.8 A (the current density on the anode was 150 mA/cm^2) was passed through a solution of 4 mmoles CF_3CO_2K in 20 ml dry methanol at constant 55-60 °C in a diaphragmless electrolyzer with a graphite anode (the core diameter was 8 mm) and iron cathode consisting of a 10-mm-wide steel plate initially for 30 min with the concurrent addition of a solution of 1.93 g p-propenyltoluene (I, $R = X = CH_2$) in 10 ml methanol, and then for 165 min only with stirring of the electrolyzate maintained at 55-60°C. At the end of the electrolysis, the current passed was 7055 coulombs (5.5 F/mole I). The reaction mixture was then evaporated and the residue was diluted with pentane. The pentane layer was separated and evaporated. Trichloroethylene was added as an internal standard and PMR spectroscopy was used to determine the amount of acetal (IIb) formed relative to the intensity of the signal of the acetal group at 5.38 ppm. The yield of (IIb) was found to be 1.82 g (78%). The current yield was 55%. The 2,4-dinitrophenylhydrazone derivative of (IIb) had mp 234°C (from ethanol) [2]. Found: C, 55.99; H, 4.18; N, 18.68%. Calculated for $C_{14}H_{12}N_4O_4$: C, 55.84; H, 4.02; N, 18.61%. PMR spectrum of (IIb) (δ, ppm): 2.35 s (3H, CH_3), 3.35 s (6H, CH_3O), 5.38 s (1H, CH), 7.25 m (4H, C_6H_4).

Acetal (IIa) was obtained by analogy from styrene in 42% yield, from propenylbenzene in 47% yield, and from stilbene in 33% yield. The 2,4-dinitrophenylhydrazone derivative of (IIa) had mp 237°C (from ethanol) [2]. Found: C, 54.78; H, 3.72%. Calculated for $C_{13}H_{10}N_4O_4$: C, 54.57; H, 3.52%. PMR spectrum of (IIa): 3.45 s (6H, CH_3O), 5.45 s (1H, CH), 7.35 br. s (5H, C_6H_5). The yields of (IIa) and (IIb) were not optimized.

LITERATURE CITED

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2. Organic Chemistry Laboratory Textbook [Russian translation], Mir, Moscow (1979), p. 327.

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