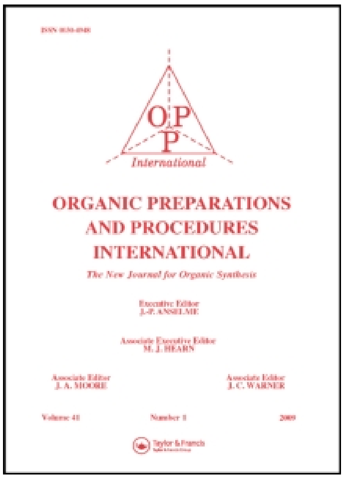

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# NEW CHEMICAL CONVERSIONS OF 5-HYDROXYMETHYLFURFURAL AND THE ELECTROCHEMICAL OXIDATION OF ITS DERIVATIVES

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# NEW CHEMICAL CONVERSIONS OF 5-HYDROXYMETHYLFURFURAL AND THE ELECTROCHEMICAL OXIDATION OF ITS DERIVATIVES

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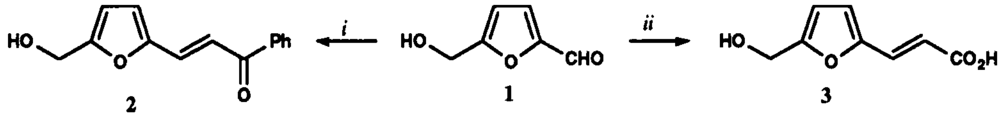
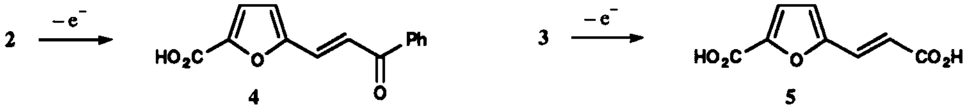
5-Hydroxymethylfurfural (**1**) reacts with carbonyl compounds such as acetone,[1b] anthrone[2] and barbituric acid.[3] We previously reported the electrochemical oxidation of **1** at the nickel oxide/hydroxide electrode[5] and now describe the application of this electrode to 5-hydroxymethylfurfurylideneacetophenone (**2**) and 5-hydroxymethyl-2-furanacrylic acid (**3**). Compound **2** was obtained by the addition of acetophenone to **1** in methanol in the presence of catalytic amount of aqueous potassium hydroxide. This reaction was also carried out in water, in the presence of sodium hydroxide; both methods gave **2** in good yields (82% and 80% respectively). 5-Hydroxymethyl-2-furanacrylic acid had previously been obtained by the Perkin condensation with acetic anhydride[1a] or the Wittig-Horner reaction with Horner reagent[4] with **1**. We have obtained **3** in 55% yield by the Knoevenagel reaction of **1** with malonic acid in pyridine, in the presence of piperidine.

5-Hydroxymethylfurfurylideneacetophenone (**2**) was oxidized electrochemically at the nickel oxide-hydroxide anode in a solution of potassium hydroxide in acetonitrile-water to give 5-(2-benzoyl)-vinyl-2-furancarboxylic acid (**4**) in 72% yield. 5-Hydroxymethyl-2-furanacrylic acid (**3**) could also be oxidized at the nickel oxide-hydroxide electrode in aqueous sodium hydroxide to yield 5-carboxy-2-furanacrylic acid (**5**) in 67% yield. The IR and $^1H$ NMR spectra and elemental analyses confirmed the structure of compounds **2-4**.



*i)* Acetophenone, KOH, $H_2O$, MeOH; *ii* $CH_2(CO_2H)_2$, piperidine, pyridine



## EXPERIMENTAL SECTION

All solvents (POCh) were distilled and dried prior to use. Acetophenone (REACHIM) was used as received. Spectra were recorded on a SPECORD 75 (IR), and a BRUCKER 200 MHz ($^1H$ NMR) spectrometers. The electrolyses were performed on power supply ZT-980-2M, Unitra-CEMI. 5-Hydroxymethylfurfural has been synthesized by a literature procedure.[6] The nickel oxide/hydroxide-electrode was prepared following a published procedure.[7]

**Synthesis of 5-Hydroxymethylfurfurylideneacetophenone (2). Method A.**- 5-Hydroxymethylfurfural (0.01 mol, 1.26 g) and acetophenone (0.01 mol, 1.2 mL) were dissolved in 2 mL of methanol; 15% aqueous potassium hydroxide (0.17 mL) was added and the mixture was stirred for 3.5 hrs at a room temperature. The mixture was then acidified with 10% acetic acid to precipitate the yellow solid. Recrystallization from benzene gave 1.87 g (82%) of yellow crystals, mp 97-99°.

**Method B.**- 5-Hydroxymethylfurfural (4 mmol, 0.52 g) and acetophenone (4.1 mmol, 0.5 g) were suspended in 10 mL of water and 0.4 mL of 1N aqueous sodium hydroxide. After 2 hrs of stirring at room temperature, the mixture was acidified with 1N hydrochloric acid until pH 5. The precipitate was collected and the filtrate was extracted with ethyl acetate and dried over anhydrous $MgSO_4$. After removal of the solvent, the residue was combined with the precipitate and recrystallized from hexan-ethyl acetate (5:1) to afford 0.73 g (80%) of **2**, mp 97-99°, identical to the sample above.

UV (EtOH): λmax 350 nm; ε max 25270, IR (KBr): 3840 (OH), 1680 (C=O), 1660 (C=C), 1600, 1560, 1380 (Carom) $cm^{-1}$.

$^1H$ NMR ($CDCl_3$): δ 1.92 (s, OH), 4.69 (s, $CH_2$),6.42 (d, $J$ = 3.3 Hz, =CH-CH=) ,6.67 (d, $J$ = 3.3 Hz, =CH-CH=),7.44 and 7.55 (quadruplet, $J$ = 15.3 Hz, CH=CH),7.51 (dd, $J$ = 1.5 and 7.5 Hz, ArH), 7.56 (t, $J$ = 1.4 Hz, ArH), 8.10 (dd, $J$ = 1.4 and 7.4 Hz, ArH)

*Anal.* Calcd. for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30. Found: C, 73.42; H, 5.28

**Synthesis of 5-Hydroxymethyl-2-furanacrylic acid(3).**- 5-Hydroxymethylfurfural (0.015 mol, 1.89 g), malonic acid (0.03 mol,3.12 g) and piperidine (0.1 mL) were dissolved in 6 mL of pyridine. The mixture was heated at 90° for 3.5 hrs, then was poured onto ice and 1N aqueous hydrochloric acid was added until pH 4. The mixture was then extracted with ether (5x100 mL); the etherical layer was evaporated and the dark brown was residue crystallized from *n*-butanol-toluene (1:1) to give 1.39 g (55%) of yellow crystals, mp 138-141° , lit.[1a] 139°.

IR(KBr): 3300 (OH), 2950 (OH acid), 1680 (C=O), 1620 (C=C) $cm^{-1}$.

$^1H$ NMR($CD_3COCD_3$): δ 4.78 (s, $CH_2$), 6.17 (s, OH), 6.45 (d, $J$ = 3.2 Hz, =CH-CH=), 6.78 (d, $J$ = 3.2 Hz, =CH-CH=), 6.27 and 7.48 (quadruplet, $J$ = 15.3 Hz, CH=CH), 13.25 (broad s, COOH).

**Electrosynthesis of 5-(2-Benzoyl)-vinyl-2-furancarboxylic Acid (4).**- The electrolysis has been carried out in a divided, H-shaped cell at the nickel oxide/hydroxide anode[5,7] and stainless steel cathode. 5-Hydroxymethylfurfurylideneacetophenone (0.005 mol, 1.14 g) was dissolved in 0.2 M solution of potassium hydroxide in acetonitrile-water (1:1), and the mixture was placed in the anodic cell and 100 mL of 0.2 M solution of potassium hydroxide in acetonitrile-water (1:1) was placed in the cathodic cell. The reaction was carried out at constant current density of 5 mA /$cm^2$ at a room temperature for 5 hrs. Then, the anodic mixture was evaporated to remove acetonitrile, the residue was extracted with ether (3x100 mL) and the aqueous layer was acidified with 1N hydrochloric acid up to pH 3 to yield 0.85 g (72%) of **4** as yellow crystals, mp. 188-190°.

IR(KBr): 2940 (OH acid), 1700 (C=O), 1660 (C=C), 1610, 1500, 1320 cm$^{-1}$.

$^1$H NMR($CD_3COCD_3$): δ 7.13 (d, *J* = 3.7 Hz, =CH-CH=), 7.33 (d, *J* = 3.7 Hz, =CH-CH=),7.52 (dd, *J* = 1.5 and 7.2 Hz, ArH), 7.61 (t, *J* = 1.6 Hz, ArH), 7.65 and 7.75 (quadruplet, *J* = 15.6 Hz, -CH=CH-), 8.18 (dd, *J* = 1.5 and 6.9 Hz, ArH), 13.38 (broad s, -COOH).

*Anal.* Calcd. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.60; H, 4.26

**Electrosynthesis of 5-Carboxy-2-furanacrylic Acid (5).**- 5-Hydroxymethyl-2-furanacrylic acid (0.004 mol, 0.67 g) was electrolyzed at the nickel oxide/ hydroxide anode and stainless steel cathode, in H-shaped divided cell in 1 M aqueous sodium hydroxide at a room temperature, at a constant current density of 5 mA/cm$^2$ and lasted 4 hrs. Then, the anodic mixture was acidified with 1N hydrochloric acid up to pH 3 to give 0.49 g (67%) of **5**, mp 175-178°.

IR(KBr): 2950 (OH acid), 1690 (C=O), 1620 (C=C), 1600, 1570, 1390 (CH furan ring) cm$^{-1}$.

$^1$H NMR($CD_3COCD_3$): δ 6.47 and 7.47 (quadruplet, *J* = 15.6 Hz, -CH=CH-), 7.02 (d, *J* = 3.2Hz, =CH-CH=), 7.32 (d, *J* = 3.2 Hz, =CH-CH=), 13.61 (v broad s, 2H, COOH).

*Anal.* Calcd. for $C_8H_6O_5$: C, 52.75; H, 3.30. Found: C, 52.68; H, 3.27

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