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### OXIDATION OF FURFURALDEHYDES WITH SODIUM CHLORITE

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tons a), 6.4 (s, 1H, proton b), 1.7 (s, 1H, proton c), 1.8 (s, 3H, protons d), 5.5 (s, 2H, protons d), 6.9-8 (m, 7H, ArH).

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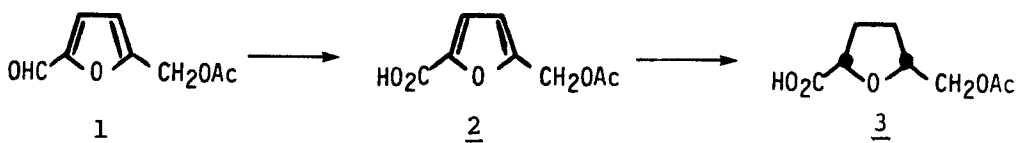
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#### OXIDATION OF FURFURALDEHYDES WITH SODIUM CHLORITE

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(02/13/84)

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In connection with another project,<sup>1</sup> we required an effective route to 5-acetoxymethyl-cis-2-tetrahydrofuroic acid (3). This material should be readily prepared by the hydrogenation of 5-acetoxymethyl-2-furoic acid (2), which in turn could be obtained by the oxidation of 5-acetoxymethyl-2-furfuraldehyde (1). However, oxidation of aldehyde 1, readily prepared in



a 90% yield from 5-hydroxymethyl-2-furfuraldehyde by the method of Karashima,<sup>2</sup> with oxidizing agents such as potassium permanganate did not give the desired carboxylic acid 2 but rather furan 2,5-dicarboxylic acid. Milder oxidizing agents such as aqueous alkaline silver oxide<sup>3</sup> resulted in oxidation of the aldehyde, accompanied by hydrolysis of the acetoxy group

to give 5-hydroxymethyl-2-furoic acid. Thus, a mild oxidizing agent was needed that would not cause hydrolysis of the acetoxy group.

Lindgren and Nilsson<sup>4</sup> earlier reported that a mixture of sodium chlorite and sulfamic acid (chlorine scavenger) oxidized aldehydes, including phenolic aldehydes, to carboxylic acids under mild conditions. Also sodium chlorite had proved far more selective than  $MnO_2$  for the oxidation of a hydroxyl-containing  $\alpha,\beta$ -unsaturated aldehyde to the carboxylic acid without attack on the hydroxyl group.<sup>5</sup> This reagent was applied to the oxidation of aldehyde 1 to give carboxylic acid 2 in high yields. To our knowledge, this is the first report of oxidation of aldehyde 1 to carboxylic acid 2 in the literature. The oxidation procedure was also used to convert furfuraldehyde to 2-furoic acid in 55% yield.

#### EXPERIMENTAL SECTION

NMR spectra were recorded on a Varian model T-60A spectrometer and chemical shifts are reported with respect to TMS as an internal standard. Infrared spectra were recorded on a Perkin-Elmer model 298 spectrometer, calibrated with polystyrene film at  $1601.4\text{ cm}^{-1}$ . Mass spectra were obtained with a Hitachi-Perkin-Elmer model RMU-6E spectrometer. Melting points were measured in open capillary tubes and are uncorrected.

5-Acetoxyethyl-2-furoic acid.— To a solution of 5-acetoxyethyl-2-furfuraldehyde (16.8 g, 0.10 mol) and sulfamic acid (9.7 g, 0.10 mol) in 600 ml of water was added a solution of sodium chlorite (Alfa Inorganics) (9.1 g, 0.10 mol) in 125 ml of water. The temperature of the solution rose from  $22^\circ$  to  $32^\circ$ , and the solution was stirred overnight. The aqueous solution was then extracted continuously with ether for two days. After drying, the ethereal extract was evaporated in vacuo to give a light yellow solid (18.3 g, 99%) which was recrystallized from petroleum ether (bp.  $60-90^\circ$ ), mp.  $117.5-119^\circ$ , lit.<sup>6</sup>  $115^\circ$ . TLC of the product exhibited one spot ( $R_f = 0.26$ ) on silica gel eluted with 3:1 hexane/ether.

IR (KBr pellet): 3100 (broad OH), 1730 (acetoxy C=O), 1695 (acid C=O),

1590 (aromatic), 1525, 1260, 1250, 1210, 1150, 1020, 935, 820, 720  $\text{cm}^{-1}$ . NMR ( $d_6$  acetone):  $\delta$  2.03 (singlet, 3H), 5.00 (singlet, 2H), 6.92 (center of AB signal, 2H). No signal was observed at  $\delta$  4.50, the resonance attributed to the  $\text{CH}_2$  group of 5-hydroxymethyl-2-furoic acid. MS (70 eV, m/e (relative intensity)): 184 (parent ion, 48.9), 142 (100), 125 (58.7), 97 (25.7), 79 (61.7), 43 (41.3).

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