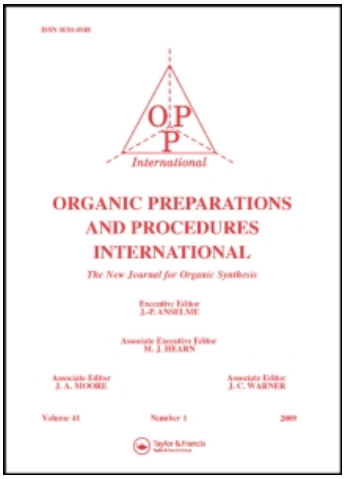

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OXIDATION OF FURFURALDEHYDES WITH SODIUM CHLORITE

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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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OXIDATION OF FURFURALDEHYDES WITH SODIUM CHLORITE

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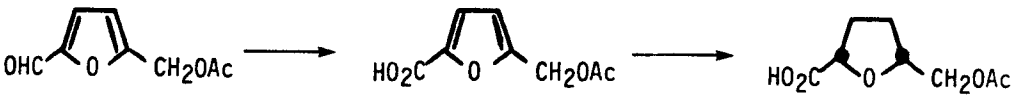
In connection with another project,[1] we required an effective route to 5-acetoxymethyl-cis-2-tetrahydrofuroic acid (3). This material should be readily prepared by the hydrogenation of 5-acetoxymethyl-2-furoic acid (2), which in turn could be obtained by the oxidation of 5-acetoxymethyl-2-furfuraldehyde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



1 2 3

a 90% yield from 5-hydroxymethyl-2-furfuraldehyde by the method of Karashima,[2] 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[3] 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[4] 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 α,β-unsaturated aldehyde to the carboxylic acid without attack on the hydroxyl group.[5] 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 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-Acetoxymethyl-2-furoic acid.- To a solution of 5-acetoxymethyl-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° to 32°, 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°), mp. 117.5-119°, lit.[6] 115°. 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 cm^{-1}. NMR (d_6 acetone): δ 2.03 (singlet, 3H), 5.00 (singlet, 2H), 6.92 (center of AB signal, 2H). No signal was observed at δ 4.50, the resonance attributed to the 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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