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Efficient, Metal-Free Production of Succinic Acid by Oxidation of Biomass-Derived Levulinic Acid With Hydrogen Peroxide

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Materials

All materials were used as received. Levulinic acid (98%) and sulfuric acid (98%) were purchased from Sigma-Aldrich. 3M sulfuric acid was prepared by dilution of concentrated sulfuric acid (98%). Trifluoroacetic acid (99%), diethyl ether, and dichloromethane were purchased from Fischer Scientific. Hydrogen peroxide (30% aq) was purchased from Macron Chemicals.

Experimental Procedures

Oxidation of levulinic acid to succinic acid with hydrogen peroxide in 3M sulfuric acid



Levulinic acid (2.00 g, 17.2 mmol) was dissolved in 3M H_2SO_4 (20 mL) and 30% aq H_2O_2 (8 mL) was carefully added. The colorless solution was placed in an oil bath at 90 °C and stirred for 3.5 h. Additional 30% aq H_2O_2 (2.0 mL) was added, followed 20 min later by another aliquot of 30% aq H_2O_2 (2.0 mL). After 20 min the mixture was cooled to RT and a measured quantity of 1,4-dioxane was added as an internal standard. The ¹H NMR spectrum was measured and the yields were estimated as follows: succinic acid (48%), acetic acid (50%), formic acid (24%) and methanol (17%).

Oxidation of LA by hydrogen peroxide in TFA



Levulinic acid (2.00 g, 17.2 mmol) was dissolved in TFA (40 mL) and 30% aq H₂O₂ (2.0 mL) was carefully added. The flask was mounted with a water-cooled condenser and -78 °C volatiles trap, and the colorless mixture was placed in an oil bath at 90 °C and stirred for 20 min. Additional 30% aq H₂O₂ (8.0 mL) was added portionwise at a rate of 2 mL every 20 min. The reaction was allowed to stir a further 20 min after the final addition, at which point the LA had been completely consumed as indicated by ¹H NMR analysis. The mixture was cooled to room temperature and a measured amount of 1,4-dioxane was added as an internal standard. The ¹H NMR spectrum was measured and the yields were estimated as follows: succinic acid (62%), acetic acid (43%), 3-hydroxypropanoic acid (9%), and formic acid (45%). Methyl trifluoroacetate (45%) was obtained in the cold trap. The volatiles were evaporated to give a white solid (1.70 g) which was triturated with Et₂O (2 × 2 mL) to give succinic acid (1.22 g, 60%).

Scale-up of the oxidation of LA by hydrogen peroxide in TFA

Levulinic acid (10.00 g, 86.12 mmol) was dissolved in TFA (200 mL) and 30% aq H₂O₂ (10 mL) was carefully added. The flask was mounted with a water-cooled condenser and -78 °C volatiles trap, and the colorless mixture was placed in an oil bath at 90 °C and stirred for 20 min. Additional 30% aq H₂O₂ (40 mL) was added portionwise at a rate of 10 mL every 20 min. The reaction was allowed to stir a further 30 min after the final addition, at which point the LA had been completely consumed as indicated by ¹H NMR analysis. The volatiles were evaporated under reduced pressure to give a white solid. The crude product was triturated with 1:1 Et₂O/DCM (3 × 6 mL) to give succinic acid (6.00 g, 59%). In the cold trap, methyl trifluoroacetate was isolated as a colorless liquid (4.40 g, 40%).

NMR Spectra



Figure S1. ¹H NMR spectrum of succinic acid in D₂O.



Figure S2. ¹³C NMR spectrum of succinic acid in D₂O.