

Supporting Information

Acid Monolayer Functionalized Iron Oxide Nanoparticles as Catalysts for Carbohydrate Hydrolysis

Myles Ikenberry^a, Leidy Pena^b, Daming Wei^a, Hongwang Wang^c, Stefan Bossmann^c, Trenton Wilke^a, Donghai Wang^b, Venugopal R. Komreddy^d, D. Paul Rillema^d, Keith L. Hohn^{*a}

^aDepartment of Chemical Engineering, Kansas State University, Manhattan, KS, USA

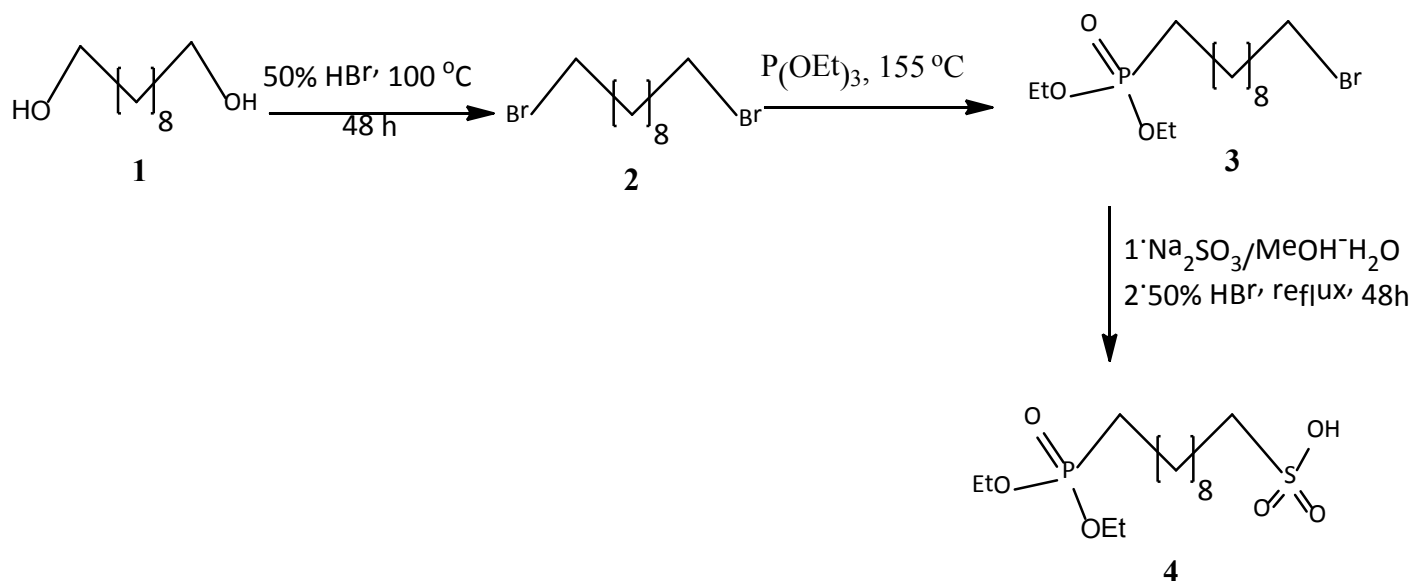
^bDepartment of Biological and Agricultural Engineering, Kansas State University, Manhattan, KS, USA

^cDepartment of Chemistry, Kansas State University, Manhattan, KS, USA

^dDepartment of Chemistry, Wichita State University, Wichita, KS 67260-0051206, USA

* 1016 Durland Hall, Manhattan, KS 66506-5102, USA, Fax: 785-532-7372; Tel: 785-532-4315 E-mail: hohn@ksu.edu

1.1 Complete reaction details for synthesis of 10-phosphono-1-sulfonodecane acid.



Scheme 1. Sequence of steps used to prepare diethyl(sulfonyldecyl)phosphonate (4).

1,10-Dibromodecane (2)

The intermediate compound, 1,10-dibromodecane, was synthesized by a modification of one previously published.¹ 1,10-butanediol (**1**) (16.0 g, 45.0 mmol), HBr (160 mL of 49 % HBr in H₂O) and water (80 mL) were added to a round-bottomed flask. The reaction mixture was stirred at 100°C for 48 h. After the reaction was complete, it was extracted with chloroform and the chloroform layer was washed with brine, followed by stirring over sodium bicarbonate. Then it was filtered and passed through Na₂SO₄. The obtained compound was purified by column chromatography on silica gel eluting with 3:1 cyclohexane/ethylacetate mixture to give 23.72 g (86 %) of 1,10-dibromodecane as a white crystals.

¹H NMR (δ, ppm, CDCl₃): 1.46 (m, 12H, CH₂)₆(CH₂CH₂Br)₂, 1.85 (m, 4H, -(CH₂CH₂Br)₂), 3.40 (t, 4H, -CH₂Br).

Diethyl (10-Bromodecyl) phosphonate (**3**)

Diethyl (10-Bromodecyl) phosphonate was synthesized following the procedure in reference 2. A 100-mL three-necked round-bottomed flask was charged with (20 g, 66 mmol) of 1,10-dibromodecane. A reflux condenser was attached and the system was purged with argon. The flask was heated to 155 °C in an oil bath, and then 2.38 mL (14.33 mmol) of triethyl phosphite was added dropwise via syringe over 8 h. The reaction was cooled to room temperature, and a white precipitate formed. The product was separated from the precipitate by filtration and purified by flash column chromatography with a gradient of neat hexane to 1:1 hexane/ethyl acetate yielding colorless oil 2.2 g, 44% yield. ¹H NMR (δ ppm, CDCl₃) 1.28-1.40 (unresolved coupling, eight CH₂ groups), 1.30 (t, J) 6.9 Hz, -OCH₂CH₃) combined integral 21.3H, 1.85 (m, 2H, PCH₂), 3.40(t, J) 6.9 Hz, 2H, BrCH₂-), 4.10 (m, 4H, -OCH₂CH₃).

Synthesis of diethyl(sulfonyldecyl)phosphonate (**4**)

The desired compound was synthesized following a report in the literature³. Diethyl(10-bromodecyl)phosphonate (2 g, 6.4 mmol) in 20 mL CH₃OH and a saturated solution of Na₂SO₃ (2.093 g, 16.4 mmol) in water were first refluxed for one hour and heated to 120 °C until

solvent were evaporated. The residue was then slurred with CH₃OH under reflux and then the hot solution was filtered. The filtrate containing the sodium salt was then evaporated and the residue was acidified with 80 mL 50% HBr and was refluxed for 48 h. The acid was allowed to evaporate slowly under reduced pressure yielding a pale-black powder yielding 1.32 g (81%).
¹H NMR (δ ppm, D₂O): 4.60 (q, -OCH₂CH₃-, 4H), 2.79 (t, -CH₂-SO₃, 2H), 1.64 (t, -CH₂PO-, 2H), 1.52 (t, -CH₂CH₃, 6H), 1.47 (p, -PCH₂CH₂-(CH₂)₆-CH₂CH₂S-, 4H), 1.21 ((-CH₂)₆-unresolved coupling, combined integral, 12H).

1.2 Turnover frequency of glucose and maltose production from starch hydrolysis

mol glucose (molH ⁺) ⁻¹ hr ⁻¹	Run 1	Run 2	Run 3
PSNPs	4.7	6.2	5.6
CSNPs	3.2	2.6	2.8
Amberlyst 15	0.6		
mol maltose (molH ⁺) ⁻¹ hr ⁻¹	Run 1	Run 2	Run 3
PSNPs	1.8	1.3	1.1
CSNPs	1.2	0.9	1.0
Amberlyst 15	0.2		

Table 1: Turnover frequency [mol product (mol H⁺)⁻¹ hr⁻¹] for three runs of 24 hour starch hydrolysis at 130°C.

1) Phenyl-Ring-Bearing Cationic Surfactants: Effect of Ring Location on the Micellar Structure, Swathi De, Vinod K. Aswal, and S.Ramakrishnan, *Langmuir* **2010**, *26*, 17882-17889.

2) Zirconium-Phosphonate Monolayers with Embedded disulfide Bonds, Xuejun Wang and Marya Lieberman, *Langmuir* **2003**, *19*, 7346-7353.

3) Tuning the Hydrophilic, Hydrophobic, and Ion Exchange Properties of Mesoporous TiO₂, Dereje Hailu Taffa, Murugavel Kathiresan and Lorenz Walder, *Langmuir* **2009**, *25*, 5371-5379.