

# **One-Pot Oxidative Cleavage of Cyclic Olefins for the Green Synthesis of Dicarboxylic Acids in Pickering Emulsions in the Presence of Phosphate Additives**

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## Experimental Section

### Chemicals

Aerosil®200 was a generous gift from Evonik Industries AG (Germany). Trimethoxy(octadecyl)silane (90%), Sodium hydrogenophosphate (98+%) and sodium dihydrogenophosphate (99%) were purchased from Aldrich (USA). (3-mercapto-propyl)trimethoxysilane (95%) was purchased from ABCR (Germany). Amberlite IRA-400 (Cl<sup>-</sup>) ion exchange resin and dodecyl trimethylammonium bromide (99%) were purchased from Alfa Aesar (USA). Tungstophosphoric acid, phosphoric acid and ammonium phosphate dibasic (>99%) were supplied by Acros (USA). Cyclohexene and cyclooctene (98%) were purchased from TCI (Japan). Hydrogen peroxide (50%) was procured from VWR International (France). DMSO-d<sub>6</sub> (99.8%) and CDCl<sub>3</sub> (99.8%) were purchased from Eurisotop (France) and were used for NMR analysis. All other chemical were purchased from Sigma-Aldrich and used without further purification. Millipore water (18.2 MΩ/cm; Simplicity 185) was used for preparing the particles and emulsions.

### Synthesis of functionalized C<sub>12</sub>-POM NPs, [C<sub>12</sub>][H<sub>2</sub>PO<sub>4</sub>] and [C<sub>12</sub>]<sub>2</sub>[HPO<sub>4</sub>]

The protocol for preparing C<sub>12</sub>-POM NPs was adapted from a previous study.<sup>1</sup> Briefly, dodecyltrimethylammonium bromide [C<sub>12</sub>][Br] (19.5 mmol) was dissolved in water (100 mL). An aqueous solution of [C<sub>12</sub>][Br] was eluted on a hydroxide ion exchange resin to obtain an aqueous solution of [C<sub>12</sub>][OH]. An aqueous solution of H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] (~6.5 mmol, 10<sup>-4</sup> M) was added dropwise (3 mL/min) to the aqueous [C<sub>12</sub>][OH] solution (3 × 10<sup>-4</sup> M) until pH 7 at 25 °C under dry Ar and vigorous magnetic stirring (1,500 rpm). The colourless precipitate of tri(dodecyltrimethylammonium) phosphotungstate formed within a few minutes was washed with water and lyophilized (Yield: 99%).

The protocols for preparing [C<sub>12</sub>][H<sub>2</sub>PO<sub>4</sub>] and [C<sub>12</sub>]<sub>2</sub>[HPO<sub>4</sub>] are the same than for C<sub>12</sub>-POM except that the aqueous solution of H<sub>3</sub>[PW<sub>12</sub>O<sub>40</sub>] is replaced by an aqueous solution of H<sub>3</sub>[PO<sub>4</sub>]. Molar ratios of 1:1 and 2:1 are used to obtain dodecyltrimethylammonium dihydrogen phosphate and di(dodecyltrimethylammonium) hydrogen phosphate, respectively. White precipitate are obtained, washed with water and lyophilized (Yield : 99% and 98% respectively).

### Synthesis of functionalized silica NPs (C<sub>18</sub>/C<sub>3</sub>SO<sub>3</sub>H)

The protocol for preparing C<sub>18</sub>/C<sub>3</sub>SO<sub>3</sub>H NPs was adapted from a previous study.<sup>2</sup> Briefly, trimethoxy(octadecyl)silane (16 mmol) and (3-mercaptopropyl)trimethoxysilane (4 mmol) were hydrolysed in a 100-mL water/ethanol (1:1 v/v) solution (pH 9.6) at room temperature overnight. The mixture was added dropwise to a suspension of Aerosil®200 (1 g / 50 mL water / 50 mL ethanol, pH 9.6), and was stirred for 24 h under reflux. After grafting, the suspension was cooled down and the white solid was filtered, washed with ethanol (3 x 30 mL) and acetone (30 mL), and dried overnight at 80 °C. The dried powder was grinded and the thiol groups were oxidized using 60-mL of an aqueous solution of H<sub>2</sub>O<sub>2</sub> (50 wt%). Acetonitrile was added dropwise until a homogeneous suspension was

obtained (3 to 4 mL). The reaction mixture was stirred at 40 °C for 24 h. After the synthesis, the powder was filtered, washed with ethanol and dried (Yield: 98%).

### Characterization of NPs

Thermogravimetric analysis (TGA) was carried out on a Q50 (TA Instrument, US) by heating the samples from room temperature to 900 °C at a rate of 10 °C/min under air atmosphere (100 mL(STP)/ min). The zeta potential of the samples was measured on a Zetasizer (Nano ZS ZEN 3600, Malvern, UK) equipped with a 4.0 mW He-Ne laser light source with a wavelength  $\lambda = 632.8$  nm. The measurements were performed by dispersing the nanoparticles in water at 25 °C in the presence of the additives at constant ionic strength (1.0 mS/cm). The acidity of the C<sub>18</sub>/C<sub>3</sub>SO<sub>3</sub>H NPs was measured using aliquots, where 50 mg of the NPs were stirred with NaCl (5.85 g / 20 mL ethanol / 30 mL water) at room temperature for 24 h. Then, the NPs were filtered off and the resulting solution was titrated with a 0.025 M NaOH solution using a pH-meter (Meterlab PHM250 Ion Analyzer, Radiometer Analytical).

### Preparation and characterization of emulsions

To generate Pickering emulsions, water (2.25 mL) and toluene (0.75 mL) were weighed before adding C<sub>12</sub>-POM and/or C<sub>18</sub>/C<sub>3</sub>SO<sub>3</sub>H NPs (50 mg each, 3.6 wt.%). The emulsification was performed using an Ultraturrax T10 basic at 20 °C and 11,500 rpm for a given time (IKA Works, Inc., Germany) in a 5-mL sealed container. To destabilize the emulsions, these were centrifuged at 4,000 rpm for 20 min using a Sigma 2-16PK apparatus.

The type of emulsion was inferred by observing the evolution of a drop of each emulsion when a volume of either oil or water was added (dilution test). Microphotographs were taken using a light microscope Standard 25 ICS (Carl Zeiss AG, Germany) coupled with an Axiocam ERc-5s camera (Carl Zeiss AG, Germany). The emulsions were diluted with the continuous phase before observation and several photographs were taken in different locations to acquire a general view of the droplets. The images were analysed with ImageJ software (National Institutes of Health, USA). The distribution function (log-normal, defined by eq 1) of droplet diameters was obtained by treatment of at least 250 individual droplets using OriginPro 8® software

$$y = \frac{A}{\sqrt{2\pi\omega d}} \exp \left[ -\frac{\left( \ln \frac{d}{d_m} \right)^2}{2\omega^2} \right] \quad (1)$$

where  $y$  is the density function,  $\omega$  is the polydispersity (the peak will be approximately symmetric when  $\omega$  is small),  $d_m$  is the median droplet diameter ( $d_m$  refers to the peak centre when the log-normal distribution is approximately symmetric), and  $A$  is the amplitude corresponding to the area under the integrated curve.

The emulsion stability was examined by the evolution in the emulsion volume fraction as a function of storage time at 60 °C to simulate the reaction conditions.

Finally, the pH of the emulsions was measured in the presence of the additives after stabilization using a pH-meter (Meterlab PHM250 Ion Analyzer, Radiometer Analytical). The pH was measured by adding 1 wt% emulsion in deionized water.






### Catalytic tests

In a typical catalytic test, toluene (0.75 mL) containing the given cycloalkene (2 mol/L) and water (2.25 mL) containing 1.2 equiv H<sub>2</sub>O<sub>2</sub> (2.4 mmol, 50%) was added to a 5-mL flask and placed in a thermoregulated Lauda RC6 water bath, followed by C<sub>12</sub>-POM and/or C<sub>18</sub>/C<sub>3</sub>SO<sub>3</sub>H NPs (50 mg each). The system was pre-emulsified using an Ultra-Turrax® (IKA T 25) at 11,500 rpm for 1 min. The reactor was sealed, heated at 65 °C for 4 h under stirring (500 rpm) to epoxidize the double bond. Then, another 3.5 equiv. H<sub>2</sub>O<sub>2</sub> (7 mmol, 50%) was added to the system, this was re-emulsified and the reaction was pursued at 80 °C for a given time (12 h for cyclohexene and 24 h for cyclooctene) under stirring (500 rpm). The composition of the organic and aqueous phases was analysed along the reaction by <sup>1</sup>H NMR after decantation. CDCl<sub>3</sub> and deuterated DMSO were used as solvents for each phase, respectively, whereas *n*-dodecane and *n*-dodecanol were used as internal standards. All the catalytic tests and analyses were carried out at least three times to ensure repeatability.

### References

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Table 1. Catalytic results for the oxidative cleavage of different cyclic alkenes using mixed C<sub>12</sub>POM + C<sub>18</sub>/C<sub>3</sub>SO<sub>3</sub>H NPs<sup>1</sup>

Substrate	Conversion (%)	Selectivity (%)		
		Epoxide	Diol	Diacid
	>99	1.0	20	72
	82	6.1	8.5	77
	65 (99)	24 (20)	43 (8)	37 (72)
	>99	2.0	25	61
	84	1.2	31	67

<sup>1</sup> Reaction conditions: 0.75 mL toluene (2 mol/L cyclic alkene), 2.25 mL H<sub>2</sub>O (1.2 equiv. H<sub>2</sub>O<sub>2</sub>), 50 mg C<sub>12</sub>-POM, 50 mg C<sub>18</sub>/C<sub>3</sub>SO<sub>3</sub>H, 2 equiv. Na<sub>2</sub>HPO<sub>4</sub> with respect to C<sub>12</sub>-POM, 60 °C, 500 rpm 4 h, followed by 3.5 equiv. H<sub>2</sub>O<sub>2</sub>, 80°C, 500 rpm, 12 h. <sup>2</sup> In parentheses, reaction conducted for 24 h.