

Aqueous biphasic catalysis with polyoxometalates: Oximation of ketones and aldehydes with aqueous ammonia and hydrogen peroxide

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Supplemental Information

Experimental

Materials. The organic substrates were from commercial sources (Aldrich, Fluka) and were used without further purification. $\text{Na}_{12}[\text{WZn}_3(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]$ was prepared according to the published literature procedure (Tourné, C. M.; Tourné, G. F.; Zonnevijlle, F. *J. Chem. Soc. Dalton Trans.* **1991**, 143-151).

Oximation reaction procedures. 5 mmol substrate, 14 mmol 30 % aqueous H_2O_2 and 1 mL of a 0.01 M solution of $\text{Na}_{12}[\text{WZn}_3(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]$ dissolved in water were placed in a 50 mL round bottomed flask at room temperature and vigorously stirred with a magnetic stirrer. An aqueous solution of 25 % NH_4OH was added dropwise at a rate of 0.3 mL/h by syringe pump (Aitecs, SEP-10S). The total amount of ammonia added was 16 mmol and the total reaction time was 6 h. After six hours the stirring was discontinued, effectively quenching the reaction. The organic phase was immediately analyzed by GLC (HP 6890) using a 30 m 5% phenylmethyl silicone capillary column with an ID of 0.32 mm and 0.25 μm coating (Restek 5MS); products were identified using reference standards or when necessary by GC-MS (HP 5973) with the same column and. The decomposition of hydrogen peroxide to molecular oxygen was measured using a gas burette. Reactions carried out using self-assembled $\text{Na}_{12}[\text{WZn}_3(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]$ were carried out in the same way except that instead of using purified $\text{Na}_{12}[\text{WZn}_3(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]$ a ~ 0.01 M solution of $\text{Na}_{12}[\text{WZn}_3(\text{H}_2\text{O})_2(\text{ZnW}_9\text{O}_{34})_2]$ was prepared by mixing 0.019 mol (6.27 g) $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 0.005 mol (1.49 g) $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 0.016 mol 70% HNO_3 in 100 mL H_2O .