



Green, selective and swift oxidation of cyclic alcohols to corresponding ketones



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ABSTRACT

Cyclohexanol oxidation to cyclohexanone is an important reaction in both organic chemistry and industry. We propose here an efficient, eco-friendly, and general method for oxidizing five- to eight-membered cyclanols used as model substrates, with aqueous hydrogen peroxide (H₂O₂) in the presence of tungstic acid (H₂WO₄) as a catalyst and an ammonium-based ionic liquid (IL) as a co-catalyst under organic solvent-free conditions. Cyclohexanol was found to be the most reactive of the four tested cyclanols. In addition, the role of the IL as a phase transfer catalyst was confirmed by the use of Aliquat 336 and the kinetic of the reaction was significantly improved under microwave or ultrasonic activation, leading to excellent yields in only a few minutes.

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1. Introduction

The oxidation of alcohols to their corresponding carbonyl compounds is an important functional transformation in organic synthesis [1]. Among them, cyclohexanone is an excellent solvent widely used in coating processes [2]. Currently the industrial production of cyclohexanone is based on three main processes: (1) the nitric acid oxidation of cyclohexanol [3,4], (2) the two-step process of cyclohexane oxidation by nitric acid [5,6] and (3) the hydrogenation of phenol [7,8]. The two latter processes suffer, respectively, from the generation of a significant amount of cyclohexane by-products, and from the use of an energy-intensive process for the hydrogenation reaction. As regards the cyclohexanol oxidation route, wide use is made of stoichiometric amounts of inorganic oxidants under high temperature in particular chromium(VI) reagents,

and environmentally harmful solvents, namely chlorinated hydrocarbons [9].

In the context of Green Chemistry [10], the importance of developing efficient, eco-friendly, highly selective, economical and safe processes in both academia and industry represents a real challenge for the chemistry of the 21st century [11–13]. In accordance with the twelve principles of Green Chemistry, the best oxidants are molecular oxygen or air, but a major limitation of their use is, in many cases, the low selectivity of the associate processes, and the limiting activation of metal catalysts can reduce the opportunities offered by O₂ [14]. In this context, aqueous hydrogen peroxide, H₂O₂, also represents an ideal reactant, with its ability to oxidize organic compounds with a high atom efficiency of 47%, leading to H₂O molecules as the only theoretical co-product [15]. Additionally, it is relatively cheap (<500 US dollar ton⁻¹ (35% H₂O₂)) and about 3 million metric tons are produced annually, mainly for use as bleach [15].

Numerous works on the oxidation of alcohols by H₂O₂ are reported in the literature [14,16,17]. In many cases, tungstate complexes are chosen as catalysts to produce to carboxylic acids [18], aldehydes [19,20] or ketones [21,22]. Recently, Chen et al. have explored the effects of the 1-methyl-3-octylimidazolium chloride

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ionic liquid ([C₈mim]Cl) on the selective oxidation of cyclohexanol to cyclohexanone in the presence of WO₃ catalyst (0.6 mol%) [23]. Based on COSMO-RS (CONductor-like Screening MOdel for Real Solvents) calculations, the authors showed that hydrophobic ionic liquids (ILs) tend to be more suitable for the reaction than polar ILs, especially those with a long alkyl chain (e.g., octyl chain).

In recent years, the use of room-temperature ionic liquids (RTILs) as reaction medium has become increasingly attractive [24–26]. The reason is that these ionic solvents display interesting physicochemical properties and can be used advantageously to replace volatile organic solvents (low vapor pressure, air and moisture stabilities, high polarity, etc.). Moreover, ILs display very considerable potential for the improvement of chemical processes, and for the enhancement of reaction rates in organic chemistry [27,28].

In our previous work, we especially studied the effect of different hydrophobic bis(trifluoromethylsulfonyl)imide-based ILs ([NTf₂]⁻) in the epoxidation of cyclic olefins by H₂O₂ in the presence of a Mn-porphyrin as catalyst [29,30]. It is their low viscosity and chemical stability under oxidation conditions which prompted us to choose them [29–33].

In the present study, we reported the application of these hydrophobic ILs in the oxidation of cyclohexanol to cyclohexanone by H₂O₂, in the presence of metal salts as catalysts. We paid particular attention to the study of the role of each reagent, to better understand the reaction mechanism and to optimise the reaction in terms of efficiency and eco-friendliness. In this context, we investigated the use of ultrasound and microwave as activation methods having major consequences, such as a reduction in reaction time and in energy consumption. The novelty of our contribution lies in the unique combination of the metal salt with a quaternary ammonium-based co-catalyst, under non-conventional activation conditions, to assist an oxidation reaction.

2. Materials

2.1. Materials

1-Methylpyrrolidine, 1-ethylpiperidine, 1-methylimidazole, pyridine, 1-octylchloride, 1-octylbromide, activated charcoal NORIT[®], Celite[®] 545, hydrogen peroxide (30%: wt% solution in water), cyclohexanol (98%), sodium tungstate dehydrate (99%) were purchased from Acros, magnesium sulfate from Chimie-Plus Laboratoires, tungstic acid (99%), cyclopentanol (99%), cycloheptanol (99%), cyclooctanol (99%) and Aliquat[®] 336 from Sigma-Aldrich, bismuth(III) sulfate (99%) from Alfa Aesar, iron(II) sulfate (99%) and iron(III) nitrate nonahydrate (99%) from Prolabo, dichloromethane and ethyl acetate from Carlo Erba Reagents, LiNTf₂ from Solvionic. Chemicals were used without further purification.

¹H NMR spectra were recorded in CDCl₃ (Euriso-Top, Saint Aubin, France) at 23 °C using a Bruker DRX300 spectrometer, at 300 MHz and 75.5 MHz for ¹H and ¹³C, respectively. Chemical shifts (δ) are reported in ppm relative to tetra-methylsilane (TMS).

Gas chromatography was performed on a GC8000series gas chromatograph from Fisons Instruments using a flame-ionization detector (250 °C) and equipped with an HP1 capillary column (dimethylpolysiloxane, 50 m × 0.32 mm × 0.52 μm) from Agilent technologies. The program used an isothermal temperature of 45 °C for 14 min, and then a 30 °C min⁻¹ ramp for 2 min and at last, an isothermal temperature of 100 °C for 2 min. The 4 μL samples were injected at 275 °C for GC analyses.

Ultrasound was generated by a digital Sonifier[®] S-250D from Branson (*P*_{elec,1} = 11.5 W and *P*_{elec,2} = 22.9 W). A 3 mm diameter

tapered microtip probe operating at a frequency of 20 kHz was used and its acoustic power in water (*P*_{acous,1} = 0.787 W mL⁻¹ and *P*_{acous,2} = 1.26 W mL⁻¹) was determined by calorimetry according to previous work [31].

Microwave irradiations were performed by means of a MicroSynth reactor (35 cm × 35 cm × 35 cm cavity) from Milestone. Temperature was measured and controlled with an optic fiber thermometer (ATC-FO).

2.2. Ionic liquids syntheses and characterizations

Methyloctylpyrrolidinium ([C₈mpyr]Br, [C₈mpyr][NTf₂]), ethyloctylpiperidinium ([C₈epip][NTf₂]), octylpyridinium ([C₈py][NTf₂]) and methyloctylimidazolium ([C₈mim]Cl, [C₈mim]Br, [C₈mim][NTf₂]) based ILs (formula given in Table 1) were synthesized, purified and characterized (¹H and ¹³C NMR, FTIR, UV-visible, mass spectrometry, cyclic voltammetry, water content, viscosity and density measurements) as described previously [29,30].

Synthesis of [Aliquat][NTf₂] from Aliquat 336 (Fig. 1): Aliquat 336 (2.27 g, 5.6 mmol, 1 equiv.) was added to a solution of LiNTf₂ (1.69 g, 5.9 mmol, 1.1 equiv.) in distilled water (50 mL). The mixture was stirred at room temperature under argon for 5 h and extracted with CH₂Cl₂ (3 × 20 mL). The combined organic phases were then washed with water (2 × 10 mL) and with a saturated sodium chloride solution (2 × 10 mL), and then dried over MgSO₄. After filtration, the resultant mixture was stirred for 2 h with activated charcoal. Filtration on celite to remove charcoal and evaporation under reduced pressure (rotary evaporator, 2 × 10⁻³ bar) afforded the colourlessness desired [Aliquat][NTf₂] (Fig. 1b, 2.74 g, 76%).

¹H NMR (C₂₇H₅₄O₄N₂F₆S₂, δ ppm, CDCl₃, 300 MHz): δ 0.82 (9H, m, 3 CH₃), 1.28 (30H, m, 15 CH₂), 1.58 (6H, m, 3 CH₂), 2.91 (3H, m, 1 CH₃), 3.12 (6H, m, 3 CH₂); ¹³C NMR (δ ppm, CDCl₃, 75.5 MHz): δ 15.0 (2 C), 15.1, 23.3, 23.6, 23.7, 26.9, 27.2 (2 C), 30.0–30.55 (9 C), 32.7, 32.9, 33.9, 49.4, 62.9 (2 C), 63.9, 121.0 (2 C, J_{C-F} = 321.2 Hz).

2.3. Optimized cyclohexanol oxidation with Aliquat 336

Cyclohexanol (1.04 mL, 10 mmol, 1 equiv.), tungstic acid (58.9 mg, 0.24 mmol, 2.4 mol%), Aliquat 336 (275 mg, 0.68 mmol, 6.8 mol%) and 30% hydrogen peroxide (2.04 mL, 20 mmol, 2 equiv.) were introduced into a glass tube. The mixture was stirred at 90 °C for 30 min. Then, the organic phase was extracted with ethyl acetate (3 × 2 mL) and cyclohexane (2 × 2 mL). The combined organic phases were dried with MgSO₄ and analysed by gas chromatography (GC). The same procedure was used from the other substrates: cyclopentanol (0.91 mL, 10 mmol, 1 equiv.), cycloheptanol (1.20 mL, 10 mmol, 1 equiv.) and cyclooctanol (1.32 mL, 10 mmol, 1 equiv.).

Cyclohexanone: C₆H₁₀O, δ ppm, CDCl₃, 300 MHz): δ 1.73 (2H, m, 1 CH₂), 1.86 (4H, m, 2 CH₂), 2.36 (4H, m, 2 CH₂); **Cyclopentanone** (C₅H₈O, δ ppm, CDCl₃, 300 MHz): δ 1.97 (4H, m, 2 CH₂), 2.16 (4H, m, 2 CH₂); **Cycloheptanone** (C₇H₁₂O, δ ppm, CDCl₃, 300 MHz): δ 1.49–1.81 (8H, m, 4 CH₂), 2.49 (4H, m, 2 CH₂); **Cyclooctanone** (C₈H₁₄O, δ ppm, CDCl₃, 300 MHz): δ 1.28–1.72 (6H, m, 3 CH₂), 1.88 (4H, m, 2 CH₂), 2.41 (4H, m, 2 CH₂).

2.4. Microwave assisted cyclohexanol oxidation with Aliquat 336

Cyclohexanol (1.04 mL, 10 mmol, 1 equiv.), tungstic acid (58.9 mg, 0.24 mmol, 2.4 mol%), Aliquat 336 (275 mg, 0.68 mmol, 6.8 mol%) and 30% hydrogen peroxide (2.04 mL, 20 mmol, 2 equiv.) were introduced into a 50 mL quartz reactor equipped with a 15 bar pressure cap. The mixture was stirred, under microwave irradiation at 90 °C for 2.5 min (*P* = 80 W). After stopping the microwave

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