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Concentrated solar radiation aided energy efficient protocol for oxidation of alcohol using biodegradable task specific ionic liquid-choline peroxydisulfate

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ABSTRACT

An eco-friendly and energy efficient protocol for selective oxidation of alcohols to aldehydes/ketones has been developed by using Choline Peroxydisulfate under concentrated solar radiation (CSR). Choline and peroxydisulfate based biodegradable oxidizing task specific ionic liquid (TSIL) ChPS was synthesized, characterized, and evaluated. The oxidizing property shows excellent performance as an effective oxidant. Comparative energy calculations between conventional and CSR method show, CSR method is superior alternative pathway with high energy conservation method (~90%). Incorporation of biodegradable ionic liquid and renewable energy source, makes the present protocol environmentally benign and energy efficient.

1. Introduction

Environmental awareness is expanding day by day in chemical research and industry, challenge for the sustainable environment calls for clean reactions that are designed to be energy efficient and inherently safe. Till today, energy conservation is one of the most ignored principles of the green chemistry. In order to develop an environmental benign reaction, it is necessary that any process in addition of being high yielding and simple, it should have a minimum energy consumption with involvement of a renewable source of energy (Clark, 1999). Use of solar radiations for heating reaction mass may overweigh the direct conversion of electricity into heat, ultimately reducing the overall energy efficiency.

Now a day's use of solar energy and ionic liquids are the booming areas in the field of green chemical research. Solar energy represents the largest energy flow entering the terrestrial ecosystem. Around 50% of the total solar energy reaching at the earth's surface is in the form of "visible light" (An Assessment of Solar Energy Conversion Technologies and Research Opportunities. GCEP Energy Assessment Analysis Summer, 2006). Though the sunlight is free, it is variable and intermittent. The potential of this resource is enormous making it a crucial component of a renewable energy portfolio aimed towards reduction of the global emissions of greenhouse gasses. The application of concentrated solar energy to carry out organic reactions has been reported earlier for various photochemical reactions such as cycloadditions, Diels-Alder reactions, Paterno-Buchi (Pohlmann et al., 1997), synthesis of 2-aminothiophenes by solar thermal energy (Mekheimer et al., 2008), and Juglone (Pohlmann et al., 1997), photocatalytic reaction of 2-propanol using high flux solar radiations. Wentworth and Chen (1994), chemical reactions in a solar furnace (Levy et al., 1992), chemical reaction using concentrated solar energy (Levy et al., 1992), solar light induced photocatalytic oxidation of benzyl alcohol (Ruther et al., 2003), evaluation of photo contribution to a chemical reaction using concentrated solar energy (Wentworth et al., 1990).

Ionic liquids (Wasserscheid and Welton, 2007) (ILs) are an important class of green medium and have gained overwhelming interest over the past few years in organic chemistry field as an environmental friendly or "green" alternatives to the conventional molecular solvents. Its success as environmental benign solvents or catalysts is described in numerous reactions, such as Diels-Alder reactions (Fischer et al., 1999), Friedel Crafts reaction (Earle et al., 1998; Xiao and Malhotra, 2005), and esterification (Xing et al., 2005; Zhu et al., 2003). ILs polarity can be adjusted by a suitable

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choice of cation/anion; they are able to dissolve a wide range of organic, inorganic and organometallic compounds; ILs are often composed of weakly coordinating anions and therefore have a potential to be highly polar.

Since few decades selective oxidation of alcohols to carbonyl compounds is a key aspect in the industrial production of many medicines, vitamins, dyes and perfumery compounds (Backvall, 2004). An oxidation is one of the important reactions. It is always desirable to find a new oxidizing agent. Traditional oxidizing reagents such as CrO_3 (Zhao et al., 1998), Pyridinium Dichromate (PDC) (Hunsen, 2005), 2,2,6,6-Tetramethylpiperidinyloxy (TEMPO) (Okada et al., 2014), Oxalyl chloride, Tetrapropylammonium Perruthenate (TPAP) (Ley et al., 1994), periodic acid and halide compounds such as Iodine (Gogoi and Konwar, 2005), Pyridinium Chloro Chromate (PCC), and IBX-tetrabutylammonium bromide (Shukla et al., 2003). have been introduced in oxidation of alcohols to aldehyde, which are costly, hazardous and generates massive amounts of heavy metal waste. Some novel catalytic systems are used in presence of sun light and ionic liquids for the oxidation of alcohol to aldehyde such as, CAN in Bronsted acid ionic liquids (Hajipour et al., 2011), in protic ionic liquids (pyridinium nitrate) (Shi et al., 2011), photoactive VO@g-C_3N_4 (Verma et al., 2016), nanosized zinc peroxide (Verma et al., 2011a; Verma and Jain, 2014), mesoporous silica supported oxo-vanadium Schiff base (Verma et al., 2013a, 2011b), Pd-grafted Ti cluster (Verma et al., n.d.), thiourea dioxide with TBHP (Verma et al., 2013b), and dispersed palladium nanoparticles grafted onto nanocrystalline starch (Verma et al., 2013c). Due to environmental concern of pollution by metal oxidants and by considering the perspective of 12 principles of green chemistry, we have designed, synthesized and characterized recently reported environmental benign biodegradable and biocompatible oxidizing Task Specific Ionic Liquid (bio-TSIL) choline persulfate (ChPS) (Deshpande et al., 2015; Gadilohar et al., 2016, 2015, 2014; Ghorpade et al., 2015; More et al., 2014).

Thus as a part of our ongoing research on the development of green solvents in the organic synthesis as well as development of energy efficient processes (Deshpande et al., 2015; Gadilohar et al., 2016, 2015, 2014; Ghorpade et al., 2015; More et al., 2014) here we report oxidizing activity of ChPS (Gadilohar et al., 2014) by using concentrated solar radiations (CSR) for selective oxidation of primary and secondary alcohols to the corresponding carbonyl compounds (Scheme 1). The present work avoids over oxidation of aldehyde to acid as well as offer excellent yields of desired products in shorter period. The comparison of energy calculations of CSR method with the conventional method for the oxidation of alcohols shows that the CSR method is more efficient as compared to the conventional method (CONV).

2. Experimental

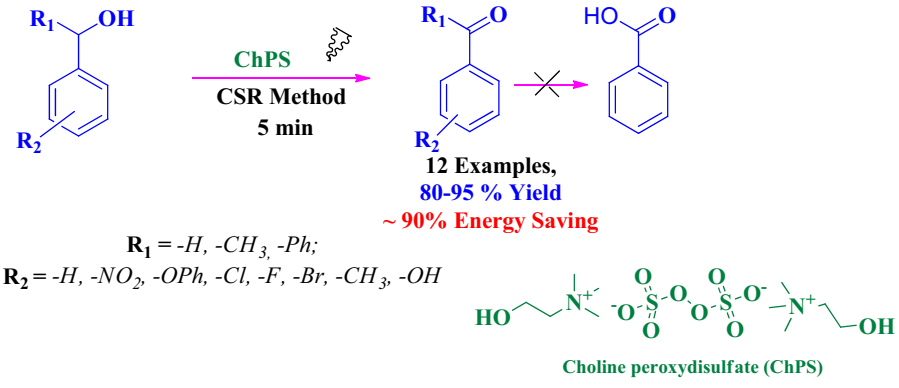
2.1. Materials and method

All reagents choline chloride, potassium peroxydisulfate and benzyl alcohol derivatives were purchased from M/s. S. D. Fine Chemicals Ltd, Mumbai, India. Reagents were used as they are received without further purification. All the solvents were purchased from commercial sources and were distilled prior to use. All melting points/boiling points are uncorrected and are presented in degrees Celsius. IR spectra were recorded on a JASCO-FT/IR-4100 LE with attenuated total reflection (ATR) method. ^1H & ^{13}C NMR spectra were recorded on Varian 400 MHz mercury plus spectrometer, and chemical shifts are expressed in δ ppm using TMS as an internal standard. Mass spectral data were obtained using a micromass - Q - TOF (YA105) spectrometer. GC–MS analysis was done on a Hewlett Packard GCD-1800 MS system. ESI-MS was carried out using Varian Inc, USA, 410 Prostar Binary LC with 500 MS IT PDA Detectors.

2.2. Experimental set-up for CSR method using Fresnel lens

The Fresnel lens is mounted on a frame which is held along the sides rigidly by two arms which are themselves fixed to pivots on another frame. The length of the arms is such that the perpendicular distance between the lens and the pivots is equal the focal length of the lens: the line joining these pivots is the *travel axis*. The second frame is pivoted about an axis perpendicular to the travel axis and this is the *helical axis*. The point of intersection of both axes is the stationary focus of the system. The device (Fig. 1) can be used to hold the focus of a Fresnel lens at a fixed point while rotating the lens about a single axis to track the sun. The device is composed of a frame for the Fresnel lens that is capable of rotating about two perpendicular axes, both of which pass through its focal point. The whole assembly is arranged so that one of the axes is directed parallel to the axis of the Solar Helix (mentioned above). We will call this the *helical* axis. This is the axis about which the rotation occurs. The angular position of the lens about the other axis (which we will call the *travel* axis) is fixed at the beginning of each day and not changed thereafter. The Sun can now be tracked with 0.04° accuracy by adjusting the angular position about the helical axis.

To align the helical axis along the Solar Helix, the whole assembly is mounted on a base which is inclined at the latitude angle θ w. r.t the horizontal and positioned so that the face of the Fresnel lens is southwards (for Northern Hemisphere mounting). At the beginning of each day, the lens is adjusted about the travel axis and then



Scheme 1. Oxidation of alcohols using ChPS under CONV and CSR condition.