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Aerobic oxidation of alkyl arenes and alcohols using cobalt(II) phthalocyanine as a catalyst in 1-butyl-3-methyl-imidazolium bromide

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Abstract

The aerobic oxidation of alkyl arenes and alcohols to the corresponding carbonyl compounds has been achieved using a catalyst and oxygen (0.1 atm) in an ionic liquid. Excellent yields were obtained under mild, easily obtainable conditions. Among the various metallophthalocyanine catalysts and ionic liquids examined, the best results were obtained with cobalt(II) phthalocyanine in 1-butyl-3-methylimidazolium bromide ([bmim]Br). These materials can be recycled and reused for several times without any significant loss of catalytic activity.

Keywords: Aerobic oxidation; Cobalt(II) phthalocyanine; 1-Butyl-3-methylimidazolium bromide; Alkyl arene; Alcohol

1. Introduction

Oxidation reactions are among the most important transformations in synthetic chemistry and offer important methodology for the introduction and modification of functional groups. During the last two decades, there has been spectacular development in the field and a large number of novel and useful oxidation reactions have been discovered.

The oxidation of alkyl arenes and alcohols to their corresponding carbonyl compounds is of significant importance in organic chemistry, both for fundamental research and industrial manufacturing. The worldwide annual production of carbonyl compounds is over 1×10^7 t and most of these are produced from the aerobic oxidation of alkyl arenes and alcohols [1–8].

Many bulk chemicals such as benzoic acid, terephthalic acid and isophthalic acid are manufactured by homogeneous liquid phase oxidations in air [9–11]. These processes are usually conducted at fairly severe temperatures (175–225 °C) and high air pressures (15–30 atm), in the presence of catalysts such as $Co(OAc)_2/Mn(OAc)_2$ and bromine, typically in the form of HBr, NaBr or tetrabromoethane in acetic acid. Due to the corrosive nature of these systems, the use of vessels lined with titanium or other expensive metal is necessary [12–14].

Phthalocyanines (Pcs) constitute a remarkably versatile and robust class of compounds with diverse technological applications [15–18]. Metallophthalocyanines (MPcs) have been used as efficient biomimetic catalysts for oxidation, reduction and other reactions of organic compounds [19–28]. However, to the best of our knowledge, the use of MPcs catalysts in ionic liquids for the aerobic oxidation of alkyl arenes and alcohols has not previously been reported.

Solvent effects have frequently been reported and analyzed in terms of solvent parameters, which can be used to predict the outcome of a reaction carried out in a particular solvent [29,30]. A change of solvent can have a drastic impact on the kinetics and/or thermodynamics of a chemical reaction due to differential stabilization of reagents, transition states or products by the solvent molecules [31–33]. Solvent effects on transition metal-catalyzed reactions may have major consequences for the activity and/or selectivity of a catalyst [34]. The use of a particular solvent can induce modifications in a catalytic cycle; or even suppress catalytic activity altogether.

Ionic liquids have been widely vaunted as greener solvents, suitable for a range of organic reactions and providing possibilities such as enhanced rate [35,36] greater reactivity [37], improved product recovery [38], secure catalyst immobilization [39,40], and ease of recycling [41,42].

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Herein we report on a continuation of our studies on the oxidation of alkyl arenes and alcohols [43–46], and the development of improved procedures for the synthesis of metallophthalocyanines [47–52], a simple and convenient method for the oxidation of primary and secondary benzylic hydrocarbons and alcohols under the neutral and mild reaction conditions using oxygen as the oxidant. The cobalt(II) phthalocyanine/[bmim]Br system has been studied for the oxidation of alkyl arenes and alcohols at 100 °C and 70 °C, respectively.

2. Experimental

2.1. Preparation of cobalt(II) phthalocyanine; general procedure

Cobalt(II) phthalocyanine was synthesized by a template method. Phthalic anhydride (26.50 g, 0.18 mol), urea (55.40 g, 0.92 mol), cobalt chloride (5.00 g, 0.05 mol) and ammonium molybdate (0.75 g, 3.80 mmol), were first ground together until a homogeneous powder was obtained. This powder was then placed in a beaker and irradiated in a microwave oven at high power for 5 min as previously reported [47]. The yield was 0.46 g, 81% of theory.

Characterization of cobalt(II) phthalocyanine: $C_{32}H_{16}CoN_8$ (571.46 g mol^{-1}): C, 67.28; H, 2.80; N, 19.6. Found: C, 67.30; H, 2.69; N, 19.47. IR (KBr): υ (cm^{-1}) 1598, 1515, 1458, 1419, 1327, 1283, 1160, 1118, 1089, 910, 871, 780, 756, 733. UV–vis (DMF): λ_{max} (nm) 658.0, 598.5.

2.2. Oxidation of alkyl arenes; general procedure

In a typical reaction, a mixture of alkyl arene (1 mmol) and cobalt(II) phthalocyanine (0.01 g, 5 mol%) was added in portions to a two-necked vial containing [bmim]Br (0.30 g, 1.37 mmol) and a magnetic stirring bar under oxygen at one atmospheric pressure. The vial was heated at 100 °C in a preheated oil bath. The progress of the reaction was followed by thin layer chromatography (TLC). Upon completion, the reaction mixture was extracted with *n*-hexane. Evaporation of the solvent gave a product of sufficient purity for most purposes. The yields were determined from the integrals of the ^1H NMR spectrum or by preparation of 2,4-dinitrophenylhydrazone derivatives of the products [45].

2.3. Oxidation of alcohols; general procedure

In a typical reaction, a mixture of alcohol (1 mmol) and cobalt(II) phthalocyanine (0.01 g, 5 mol%) was added in portions to a two-necked vial containing [bmim]Br (0.30 g, 1.37 mmol) and a magnetic stirring bar under oxygen at atmospheric pressure. The vial was heated at 70 °C in a preheated oil bath. The progress of the reaction was followed by TLC or gas chromatography (GC). Upon completion, the reaction mixture was extracted with *n*-hexane. Evaporation of the solvent gave a product of sufficient purity for most purposes.

2.4. Characterizations of products

All of the products of these reactions are known compounds. They were characterized from their IR and ^1H NMR spectra and by comparison of their melting points (or those of their DNP derivatives) with known compounds [45]. Most importantly, no over oxidized compounds were detected by ^1H NMR analysis in the crude products obtained from any of the reactions.

3. Results and discussion

In order to select the best solvent, we examined several ionic liquids including 1-butyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and 1-butyl-3-methylimidazolium hexafluorphosphate ([bmim]PF_6) and tetramethylguanidinium trifluoroacetate [49] (TMGT) in acidic (molar ratio of tetramethylguanidine (TMG):trifluoroacetic acid (TFA) = 1:1.5), basic (molar ratio of TMG:TFA = 1.5:1) and neutral (molar ratio of TMG:TFA = 1:1) conditions. Oxidation of fluorene to 9-fluorenone and benzoin to benzil were selected as model reactions. Test reactions were carried out by mixing cobalt(II) phthalocyanine (0.01 g, 5 mol%) with various ionic liquids (0.30 g) followed by addition of fluorene (0.17 g, 1 mmol) or benzoin (0.22 g, 1 mmol). As indicated in Table 1, [bmim]Br proved to be the best solvent for these reactions in terms of yield and easy work-up.

To evaluate the effect of molecular solvents, the aerobic oxidation of fluorine to 9-fluorenone and benzoin to benzyl were carried out using methanol, water, acetonitrile and xylene as solvents. As indicated in Table 1, the reactions were found to be very slow and the yields low (10–40%) even after 12–24 h. It is important to note that in water no reaction took place, even after 24 h. It is may be explained, due to insolubility of substrate in water.

The reason for the acceleration of these oxidation reactions in ionic liquids compared with molecular solvents may be that ionic liquid acts as both a phase transfer catalyst and a solvent. Moreover, this behaves macroscopically like non-coordinating, polar, aprotic solvents, and therefore can modify the reactivity of a catalyst precursor.

Table 1
Effects of the solvents on the aerobic oxidation of fluorene and benzoin using Co-Pc as a catalyst

Entry	Ionic liquid	Yield[a] (%)/time (h)	Yield[b] (%)/time (h)
1	[bmim]Br	91 (6)	92 (1)
2	[bmim]Cl	60 (6)	80 (1)
3	[bmim]PF_6	30 (6)	50 (1)
4	TMG/TFA 1:1	40 (6)	60 (1)
5	TMG/TFA 1:1.5	50 (6)	70 (1)
6	TMG/TFA 1.5:1	30 (6)	70 (1)
7	CH_3OH	10 (24)[c]	30 (12)
8	H_2O	0 (24)[c]	10 (12)
9	CH_3CN	0 (24)[c]	0 (12)
10	Xylene	10 (24)[c]	40 (12)

[a] Cobalt(II) phthalocyanine (0.01 g, 5 mol%); fluorene (1 mmol) at 100 °C.
[b] Cobalt(II) phthalocyanine (0.01 g, 5 mol%); benzoin (1 mmol) at 70 °C.
[c] The reaction is carried out at 70 °C.