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Short Communication

Highly efficient oxidation of diphenylmethane to benzophenone employing a novel ruthenium catalyst with *tert*-butylhydroperoxide under mild conditions

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ABSTRACT

The ruthenium complex Ru(bpbp)(pydic) (bpbp = 2,6-bis(1-phenylbenzimidazol-2-yl), pydic = pyridine-2,6-dicarboxy acid) has been synthesized and tested in the selective oxidation of diphenylmethane to benzophenone utilizing *tert*-butylhydroperoxide as the terminal oxidant. The influence of various reaction parameters such as temperature, catalyst amount and nature of solvent on the activity and selectivity was evaluated. Diphenylmethane was converted with 94% conversion and 100% selectivity to benzophenone under the optimized reaction conditions, in which the turnover number (TON) of catalyst reached 94,000. Moreover, a plausible reaction mechanism through redox ruthenium species was proposed.

1. Introduction

The selective oxidation of C–H bonds is one of the most challenging transformations both in academia and industry [1–3]. As a model of benzylic C–H oxyfunctionalization, the oxidation of diphenylmethane to benzophenone is gathering much attention, as benzophenone is a key intermediate for the synthesis of pharmaceuticals, insecticides, photo initiators, perfumes and also ultraviolet curing agents [4–6]. The oxidative process using stoichiometric quantities of oxidizing agents like $KMnO_4$, SeO_2 and CrO_3 has gradually been eliminated due to the generation of large amount of waste [7–11]. Therefore, the discovery of new catalysts using clean oxidants such as H_2O_2 or *tert*-butylhydroperoxide (TBHP) is gathering much attention.

So far, various transition metal-based catalysts have been intensively investigated toward the oxidation of diphenylmethane [12–15]. Kishore and Rodrigues reported the oxidation of diphenylmethane catalyzed by Cu–MgAl ternary hydrotalcites at 65 °C with TBHP, which took 24 h to achieve benzophenone with 95% yield [16]. Mesoporous vanadium oxide was used for the homogeneous oxidation of diphenylmethane with TBHP, but low conversion (about 40%) was observed using acetic acid as solvent at 60 °C [17]. The catalytic activities of other heterogeneous catalysts such as Ag/SBA-15 [18], CrSBA-15 [19], MnO_2 [20], and chromium-exchanged zeolite (Cr_E-ZSM-5) [21] toward the oxidation of diphenylmethane were examined using TBHP as a terminal oxidant. Most of the above mentioned catalytic systems suffer from disadvantages such as low efficiency, high reaction temperature, and long reaction time. Hydrogen peroxide is an environmental benign oxidant, which theoretically generates only water as a by-product [22–24]. Bolm reported the oxidation of saturated hydrocarbons to alcohols and ketones with aqueous H_2O_2 in acetonitrile at room temperature in the presence of iron catalysts [25]. However, compared with TBHP used in the oxidation of diphenylmethane, lower conversion of diphenylmethane but excellent selectivity toward benzophenone could be obtained by a Mn Schiff base complex [26], nickel-coordinated organic nanotubes (Ni-ONTs) [27] and chromium containing mesoporous MCM-41 molecular sieves (CrMCM-41) [28] in combination with hydrogen peroxide.

Thus, the development of a catalytic system for the oxidation of C–H bonds is highly desirable and challenging. Ruthenium complexes with nitrogen-based ligands have been intensively investigated in order to develop catalysts for organic oxidation processes and to simulate the mechanism of bioorganic oxidation [29]. We reported an efficient oxidation process of alcohols catalyzed by ruthenium porphyrins in the presence of molecular oxygen [30]. Nishiyama first reported the asymmetric epoxidation by one kind of ruthenium complex based on bis(oxazolinyl) pyridine, the ruthenium-(pyridinebisoxazoline)(pyridinedicarboxylate) complex [Ru(pybox)(pydic)] [31]. Inspired by the efficiency of Nishiyama's catalyst in epoxidation reactions, we adopted the introduction of 2,6-bis(1-phenylbenzimidazol-2-yl) pyridine as the counterpart to synthesize a new catalyst with dual closed meridional stereotopes around an active metal. With diphenylmethane as model substrate, herein we report a highly efficient procedure for benzylic C–H bond

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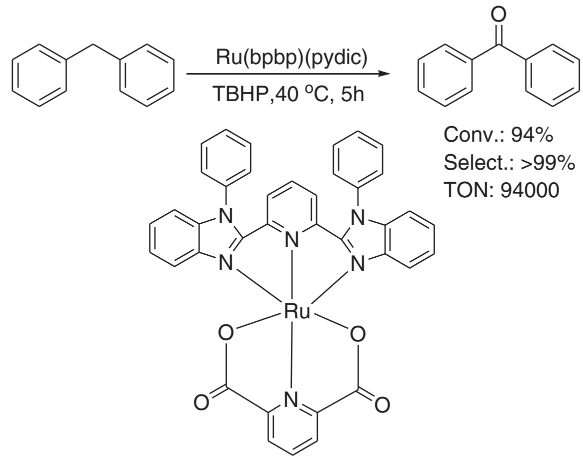

Ru(bpbp)(pydic)

Scheme 1. Oxidation of diphenylmethane to benzophenone catalyzed by Ru(bpbp)(pydic).

oxidation by using a novel ruthenium complex Ru(bpbp)(pydic) as catalyst in the presence of TBHP (Scheme 1). This catalyst proved to be efficient with an extremely high TON (94,000) and excellent selectivity toward benzophenone.

2. Experimental

2.1. Reagents and methods

Chemicals were of analytical grade and purchased from Aldrich without further purification unless indicated. Solvents were of analytical purity and used as received. Mass spectra were obtained on a Shimadzu LCMS-2010A. Elemental analyses were carried out with an Elementar vario EL elemental analyzer. ^{1}H NMR was recorded on a Bruker AVANCE 400 spectrometer (500 MHz). IR spectra were recorded on a Bruker 550 FT-IR spectrometer. UV spectra were recorded on a Shimadzu UV-2450 spectrophotometer.

2.2. Synthesis of the ruthenium complex

The ligand 2,6-bis(1-phenylbenzimidazol-2-yl) pyridine (bpbp) was synthesized according to previous procedures [32].

Ru(bpbp)(pydic):bpbp (444 mg, 0.96 mmol), [Ru(*p*-cymene)Cl_2]$_2$ (300 mg, 0.48 mmol), pyridine-2,6-dicarboxy acid (160 mg, 0.96 mmol) and NaOH (40 mg, 1.0 mmol) were dissolved in EtOH/H_2O (2: 1, 30 mL). The whole reaction mixture was refluxed at 80 °C under N_2 atmosphere. The solvent was reduced to 7 mL after reaction for 2 h. After filtering, the dark violet precipitate was collected (194 mg, 0.34 mmol, yield: 70%). Calc. for $C_{38}H_{24}N_6O_4Ru$: C, 62.55; H, 3.32; N, 11.52. Found: C, 62.41; H, 3.42; N, 11.45%; IR (KBr)/cm^{-1}: 3441, 3056, 1656, 1499, 1467, 1436, 1396, 1318, 1161, 1075, 1011, 768, 736, 697, 579, 476; ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.56–8.59 (d, 5H), 8.36–8.40 (d, 3H), 7.77 (s, 6H), 7.65(s, 4H) 7.03(s, 2H), 6.91–6.93 (s, 2H), 6.41–6.45 (d, 2H).

2.3. Catalytic oxidation of diphenylmethane

The catalytic oxidation of diphenylmethane was carried out in a magnetically stirred glass reaction tube fitted with a reflux condenser. A typical procedure was as follows: diphenylmethane (1 mmol), Ru(bpbp)(pydic) (1×10^{-4} mmol), and 0.2 mmol naphthalene (inert internal standard) were solved in ethyl acetate (3 mL) solution. The reaction tube containing this mixture was heated to 40 °C in an oil bath under vigorous stirring, and then the aqueous TBHP (70% in H_2O, 3 mmol) was slowly dropped in. Product samples were drawn at regular time intervals and analyzed by GC and GC–MS.

The procedure for the large scale oxidation of diphenylmethane to benzophenone was: diphenylmethane (10 mmol, 1.68 g) and Ru(bpbp)(pydic) (1×10^{-3} mmol, 0.732×10^{-3} g) were added into a reactor. The reactor containing this mixture was heated to 40 °C in an oil bath under vigorous stirring, and then the aqueous TBHP (70%, 30 mmol) was slowly dropped in. The mixture was stirred for 5 h. After extraction with *n*-hexane, the crude product was chromatographed on silica gel (eluent: *n*-hexane/ethyl acetate, 1/1, v/v). Pure benzophenone (8.5 mmol, 1.546 g) was obtained with the yield of 85% by removing solvent.

3. Results and discussion

3.1. Effects of solvents

Table 1 shows the effect of solvents on oxidation of diphenylmethane with TBHP over Ru(bpbp)(pydic). After much experimentation on optimizing solvent, it was found that the use of a less-polar solvent like toluene, benzotrifluoride and dichloromethane afforded benzophenone in low yields (entries 1–3). High polar and protic solvents like methanol, ethanol and water were demonstrated to be inefficient (entries 4–6). Higher yield of benzophenone was obtained using aprotic solvents like acetonitrile and acetone (entries 7–9). Gratifyingly, the maximum diphenylmethane conversion of 94% was obtained with the aprotic solvent ethyl acetate (entry 9). Further investigation reveals the amount of ethyl acetate could also influence the oxidation (entry 10), presumably due to a lower concentration of the reactant originating from the increased amount of solvent.

3.2. Effects of reaction temperature

Fig. 1 shows the influence of the reaction temperature on the oxidation of diphenylmethane. The conversion of diphenylmethane was little influenced by the temperature. For example, 85% of diphenylmethane was converted to benzophenone when the reaction was carried out at 30 °C. When increasing the temperature to 60 °C, 95% conversion was obtained. Higher temperature was unfavorable for the selectivity toward benzophenone as shown in Fig. 1. When the reaction was conducted at 50 °C or 60 °C, phenylbenzoate was observed through Bayer–Villiger oxidation of benzophenone in the presence of TBHP and Ru(bpbp)(pydic).

3.3. Effects of the amount of TBHP

Fig. 2 shows various amounts of the oxidant employed for the diphenylmethane oxidation catalyzed by Ru(bpbp)(pydic). The oxidation was tracked with different molar ratios of oxidant/substrate

Table 1
Oxidation of diphenylmethane catalyzed by Ru(bpbp)(pydic) with TBHP.[a]

Entry	Solvent	Conv. (%)[b]	Selectivity (%)[b]
1	Toluene	35	98
2	Benzotrifluoride	46	>99
3	Dichloromethane	43	96
4	Methanol	28	>99
5	Ethanol	25	>99
6	Water	26	>99
7	Acetone	63	>99
8	Acetonitrile	86	>99
9	Ethyl acetate	94	>99
10[c]	Ethyl acetate	83	>99

[a] Diphenylmethane (1 mmol), catalyst (1×10^{-4} mmol), solvent (3 mL), TBHP (3 mmol), 40 °C, 5 h.
[b] Determined by GC.
[c] Solvent (5 mL).