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Aerial oxidation of bisnaphthols to spironaphthalenones by a recyclable magnetic core-sell nanoparticle-supported TEMPO catalyst

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ABSTRACT

Aerial oxidative cyclization of bisnaphthols to their corresponding mixture of two isomeric spirans **3** and **4** has been carried out using a catalytic amount of magnetic core-shell nanoparticle-supported TEMPO (MNST) combined with a small amount of $FeCl_3{\cdot}6H_2O$. This catalytic system consistently has the advantages of moderate to good yields, low reaction times, mild and convenient conditions, simple experimental and work-up procedure, and of being environmentally benign and highly economic. The magnetically separable MNST catalyst makes it possible for it to be recovered and recycled for several times without significant loss of activity.

1. Introduction

Oxidation of bis(2-hydroxy-1-naphthyl)methanes as a subunit of calix[*n*]arenes (**i**) has been used for the preparation of spirodienones [1] (**ii**), which is an important reaction in the biosynthesis of certain plant products (Fig. 1) [2–4].

Abel, in 1892, reported the oxidation of bisnaphthols to spirodienones with Br_2 in alkaline solution [3]. The product was believed to be a peroxide, but on the basis of chemical evidence its structure was assigned as spirodienone [4,5]. Kasturi et al. perfectly studied the chemistry of spirodienone family [6]. According to Kasturi's reports, Abel's ketone derivatives have two sets of diastereomers which are assigned by the fact that one diastereomer, **3**, shows in its ^{1}HNM-R spectrum a doublet near δ6.1 ppm (vinylic H-3'); while for the other one, **4**, this hydrogen appears at about δ5.4 ppm, the up-field shift being due to the shielding effect of the μ-phenyl ring (Fig. 2) [7]. It has been reported that different oxidants give either one isomer (**3** or **4**) or a mixture of the two isomeric products. For example, hexacyanoferrate (in benzene and pyridine) [7], 2,4-di-*t*-butyl-6-phenylphenoxyl [8], 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) [9] and hydrogen peroxide/MoO_3 [10] give a mixture of two isomeric spiro products. Trichloroisocyanuric acid (TCCA) [11], potassium hypobromite and persulphate give **3** [7], whereas aerial oxidation in the presence of Ph_3Bi [12], periodic acid or its sodium salt, and (diacetoxyiodo)benzene in benzene is specific for **4** [8].

Most of these procedures have certain limitations, such as tedious procedure, long reaction time, harsh reaction conditions, poor yields and the use of toxic or expensive reagents (Fig. 2). In continuation of our research area for the oxidation of bisnaphthols [11,12], we were interested in the use of TEMPO as a catalyst. Based on literature survey and our previous experience, it was concluded that a suitable candidate might be 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) [a stable free nitroxyl radical], which has been used in many areas of synthetic organic chemistry as a safe, weakly toxic and highly efficient catalyst with the possible achievement of chemoselectivity in the oxidation processes [13–20]. TEMPO is quite an expensive reagent from which the separation of oxidation products requires lengthy work-up procedures. In order to fulfill the recovery problem, TEMPO has been immobilized

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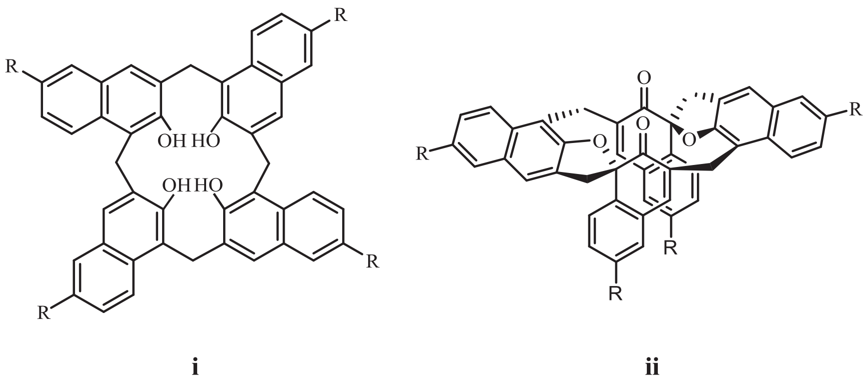
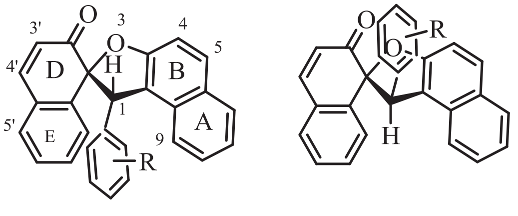


Fig. 1. Calix[*n*]arenes (i) and spirodienones (ii).

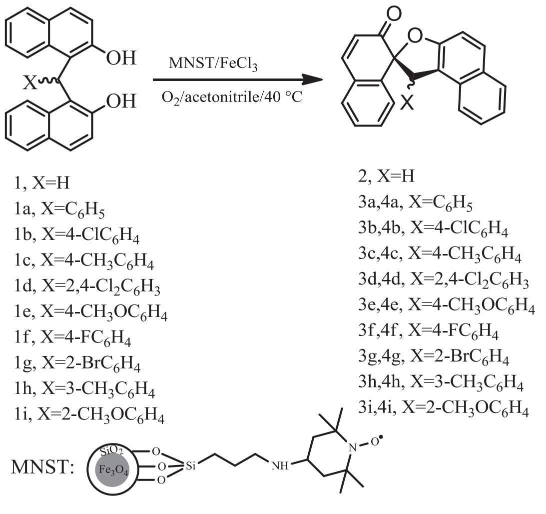


3 4

Fig. 2. Abel's ketone derivatives (**3** and **4**).

on either inorganic or organic supports such as silica [15], organic polymers [16], mesoporous silica [17], functionalized ionic liquids [18], and perfluoroalkyl systems with multiple triazole moieties [19].

Recently, a good strategy has been proposed by Karimi et al. for the aerial oxidation of alcohols using magnetic core-shell nanoparticle-supported TEMPO as a high activity catalyst, which is easily separated with an external magnetic field [20]. In addition, much attention has been paid to the use of molecular oxygen or air as a highly green oxidant [14,21,22]. Moreover, taking into account the fact that iron is an abundant inexpensive and environmentally friendly metal, iron chloride has attracted a great deal of attention in modern chemistry [23–25]. With the above consideration and the need for new and green procedures with minimum wastes, a key challenge for today's environment, we now report the aerial oxidative cyclization of bisnaphthols using MNST in the presence of $FeCl_3 \cdot 6H_2O$ (Scheme 1).



Scheme 1. Oxidation of bisnaphthols.

2. Results and discussion

At the outset, to optimize the reaction conditions, the aerial oxidation of bisnaphthol **1** was run using MNST in the presence of different transition metal salts, such as Fe (III), Mn (II), Cu (II), Co (II) as well as Nano–Fe_3O_4 as a co-catalyst in acetonitrile at 40 °C, with bubbling air into the reaction vessel (Table 1). As is clear from this Table, the best results were obtained with $FeCl_3 \cdot 6H_2O$ as a co-catalyst (Table 1, Entries 6-8). The amount of $FeCl_3 \cdot 6H_2O$ was optimized at 1 mol% in order to reduce the reaction time and to increase the product yield (Table 1, Entry 6).

Control tests in various solvents, such as acetonitrile, ethanol, acetone, dichloromethane and water showed that acetonitrile would be the best choice for the reaction to proceed. An additional experiment was also performed for three runs to test the reusability of the catalyst, using oxidation of bisnaphthol **1** as a model reaction. After each run, the catalyst was washed twice (2 × 10 ml) with hot ethanol and dried. The reused catalyst was found to be

Table 1
Aerial oxidation of bisnaphthol **1** in the presence of different co-catalysts.

Entry	Co-catalyst (mol%)	Time (h)	Yield[a] (%)
1	$CuCl_2 \cdot 4H_2O$ (1)	10	Trace
2	$Mn(OAc)_2 \cdot 4H_2O$ (1)	7	Trace
3	$Co(OAc)_2 \cdot 4H_2O$ (1)	10	Trace
4	M*(acac)$_2$ (1)	8	25
5	Nano–Fe_3O_4 (1)	10	–
6	$FeCl_3 \cdot 6H_2O$ (1)	3	80
7	$FeCl_3 \cdot 6H_2O$ (3)	15	60
8	$FeCl_3 \cdot 6H_2O$ (0.3)	8	45

M*: Co, Mn, Fe, Cu.

[a] Separated yields; Reaction conditions: bisnaphthol **1** (1 mmol), MNST (0.005 g, 0.001 mmol with respect to the TEMPO), co-catalyst, acetonitrile (20–25 ml), 40 °C, bubbling air.