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[Bmim]PF_6/$RuCl_3 \cdot xH_2O$: a novel and recyclable catalytic system for the oxidative coupling of β-naphthols

Jhillu S. Yadav,* Basi V. S. Reddy, Kamakolanu Uma Gayathri and Attaluri R. Prasad

Division of Organic Chemistry, Indian Institute of Chemical Technology, Hyderabad 500 007, India. E-mail: yadav@iict.ap.nic.in; Fax: +91-40-27160512

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2-Naphthols readily undergo oxidative coupling in the presence of $RuCl_3 \cdot xH_2O$ in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim]PF_6) ionic liquid under aerobic conditions to afford binaphthols in excellent yields with high selectivity. The β-naphthols show enhanced reactivity in ionic liquids, thereby reducing reaction times and improving the yields significantly. The recovered ionic liquid containing ruthenium catalyst can be reused in three to four successive runs with a gradual decrease in activity.

Binaphthols are widely used as chiral auxiliaries in asymmetric synthesis.[1] Enantiomerically pure binaphthols can be easily obtained from their racemates by a number of methods including classical resolution *via* crystallization of diastereomeric derivatives, formation of inclusion crystals with chiral host molecules, deracemization of recemates with copper complexes of chiral amines or enzymatic hydrolysis of esters.[2] A simple and direct method for the preparation of binaphthols is the oxidative coupling of 2-naphthols using $FeCl_3$, $Mn(acac)_3$, $K_3Fe(CN)_6$ and Cu(II) amine complexes as coupling agents.[3–5] However, most of these methods suffer from the use of stoichiometric amounts of reagents, the production of large amounts of heavy metal wastes and the need for high temperatures. Recently, several catalytic processes, using chiral diamine copper complexes, copper sulfate–alumina, $VO(acac)_2$, methylrhenium trioxide as the catalysts[6,7] and molecular oxygen as the primary oxidant, have also been reported for this conversion. Many of these methods require long reaction times, high temperature reaction conditions and complicated preparation of catalysts. Therefore, it is of synthetic importance to find a convenient and efficient reagent for the catalytic coupling of 2-napthols in which molecular oxygen can be effectively used for the facile regeneration of the reagent in a catalytic cycle.

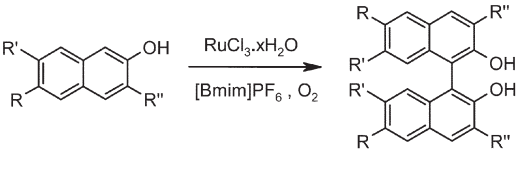
In recent times, ionic liquids have emerged as green solvents with desirable properties such as a wide liquid range, tunable polarity, high thermal stability, negligible vapor pressure and easy recycling.[8] They are referred to as 'designer solvents' as their properties such as hydrophilicity, hydrophobicity, Lewis acidity, viscosity and density can be altered by the fine-tuning of parameters such as the choice of organic cation, inorganic anion and the length of the alkyl chain attached to the organic cation. These structural variations offer flexibility to the chemist to devise the ideal solvent, catering to the needs of any particular process. Consequently, ionic liquids are being used as recyclable solvents for the immobilization of transition metal based catalysts, Lewis acids and enzymes.[9] As a result of their green credentials and potential to enhance reaction rates and selectivities, ionic liquids are finding increasing applications in organic synthesis.[10]

In view of the emerging importance of ionic liquids as green solvents, we herein report a simple and efficient method for the preparation of binaphthols from 2-naphthols using a catalytic amount of $RuCl_3 \cdot xH_2O$ immobilized in the hydrophobic [bmim]PF_6 ionic liquid under aerobic conditions. Thus, treatment of β-naphthol with 10 mol % of $RuCl_3 \cdot xH_2O$ in 3 mL of [bmim]PF_6 under an oxygen atmosphere afforded binaphthol in 93% yield (Scheme 1).

The oxidative coupling reactions of 2-naphthols are relatively faster and more efficient in ionic liquids than in conventional solvents. The efficiency of various catalysts and solvents has been examined in the oxidative coupling of 2-naphthol and the results are presented in the Table 1.

Among the various catalysts studied, $RuCl_3 \cdot xH_2O$ and CuCl–TMEDA were found to be efficient in terms of conversion and reaction rates. When compared to chorobenzene, toluene and CCl_4, [bmim]PF_6 ionic liquid was found to give the best results. A first generation ionic liquid (*i.e.*, [bmim]-$FeCl_4$ prepared from 1.0 equiv. of [bmim]Cl and 2.0 equiv. of $FeCl_3$) also afforded binapthol in 87% yield. However, metallic nitrates such as $Cu(NO_3)_2$ and $Fe(NO_3)_3$ gave lower yields when compared to metal halides. In contrast, the reactions with $RuCl_3$ are more efficient in ionic liquids than in organic media.

Encouraged by the results obtained with 2-naphthol and 10 mol % $RuCl_3 \cdot xH_2O$ under aerobic conditions, we turned our attention to various 2-naphthols. Interestingly, 6-bromo-2-naphthol, 7-methoxy-2-naphthol and 3-(methoxycarbonyl)-2-naphthol underwent oxidative coupling to give the corresponding substituted binaphthols under these reaction conditions. In the case of 6-bromo-2-naphthol, the coupling was completed within 4.0 h whereas 7-methoxy-2-naphthol required a longer reaction time (6 h) to achieve complete conversion. However, in the case of 3-(methoxycarbonyl)-2-naphthol, the coupling product was obtained in relatively low yield (Table 2, entry c). It should be noted that air or oxygen was essential for the coupling of 2-naphthol in the presence of $RuCl_3 \cdot xH_2O$ since the product was obtained in only 45% yield under nitrogen atmosphere. Furthermore, the oxidative coupling of phenol did not take place, but 2,4-dimethylphenol and 4-chloro-3,5-dimethylphenol selectively oxidized to their ortho-ortho coupled products under similar conditions (Table 2, entries e and f).



Scheme 1

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Table 1 Conversion of β-naphthol to binaphthol using various catalysts and solvents

Entry	Catalyst	Solvent	Reaction time[a] /h	% Yield[b]
a	5 mol % $RuCl_3{\cdot}xH_2O + O_2$	CCl_4	8.0	45
b	10 mol % $RuCl_3{\cdot}xH_2O + O_2$	Toluene	6.5	71
c	10 mol % $RuCl_3{\cdot}xH_2O + O_2$	Chlorobenzene	7.0	75
d	10 mol % $RuCl_3{\cdot}xH_2O + O_2$	[bmim]PF_6	5.0	93
e	10 mol % $FeCl_3 + O_2$	[bmim]PF_6	6.0	78
f	20 mol % CuCl + TMEDA + O_2	[bmim]PF_6	4.5	89
g	[bmim]Cl/$FeCl_3$(1 equiv./2 equiv.)	–	6.0	87
h	[bmim]Cl/$Cu(NO_3)_2$ (1 equiv./2 equiv.)	–	6.0	73
i	[bmim]Cl/$Fe(NO_3)_3$ (1 equiv./2 equiv.)	–	6.0	75

[a] All reactions were performed at 27 °C. [b] Yield refers to the pure product after purification.

The coupling reactions proceed much faster and more efficiently with 10 mol % $RuCl_3{\cdot}xH_2O$ in ionic liquids under aerobic conditions. This is probably due to the increased solubility of oxygen in the ionic liquid. Compared to conventional solvents, the solubility of gases in ionic liquids is generally high.[11] This is another advantage of the use of ionic liquids for hydrogenation or aerobic oxidation reactions. In addition, the recovery of the catalyst is extremely simple in ionic liquids when compared to organic solvents. Since binaphthols were fairly soluble in ionic phase, they could be easily separated by simple extraction with toluene. Recrystallization of the crude products in toluene afforded pure binaphthols. The advantage of the use of ionic liquids as reaction media is that these molten salts can be easily recovered on work-up. The remaining ionic liquid was thoroughly washed with toluene and reused in three to four subsequent runs with a gradual decrease in activity. For example, the treatment of 2-naphthol with 10 mol % $RuCl_3{\cdot}xH_2O$ in [bmim]PF_6 afforded binaphthol in 93%, 89%, 85% and 79% yields over four cycles. Although the yields decreased in runs carried out using recovered ionic liquid, the products obtained were of the same purity as in the first run. Thus, the combination of $RuCl_3{\cdot}xH_2O$ and [bmim]PF_6 ionic liquid was found to be the most efficient catalytic system for the oxidative coupling of 2-naphthols.[12] Since similar yields and selectivity were also obtained using an air and moisture stable ionic liquid [bmim]BF_4, 1-butyl-3-methylimidazolium hexafluorophophate [bmim]PF_6 can be adequately replaced by [bmim]BF_4.

In summary, we describe a simple and efficient catalytic process for the oxidative coupling of 2-naphthols to their corresponding binaphthols using a catalytic amount of $RuCl_3{\cdot}xH_2O$ immobilized in air- and moisture-stable [bmim]PF_6 ionic liquid under aerobic conditions. The simple experimental and product isolation procedures combined with ease of recovery and reuse of this novel catalytic system is expected to contribute to the development of a green strategy for the preparation of binaphthols.

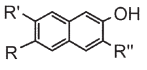
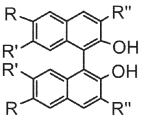
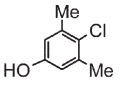
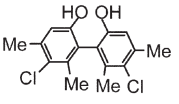
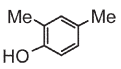
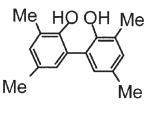
Experimental

Melting points were recorded on Buchi R-535 apparatus and are uncorrected. IR spectra were recorded on a Perkin–Elmer FT-IR 240-c spectrophotometer using KBr optics. ^1H, ^{13}C NMR spectra were recorded on a Gemini-200 spectrometer in $CDCl_3$ using TMS as internal standard. Mass spectra were recorded on a Finnigan MAT 1020 mass spectrometer operating at 70 eV. CHN analyses were recorded on a Vario EL analyzer.

General procedure

A mixture of the 2-naphthol (1 mmol) and $RuCl_3{\cdot}xH_2O$ (10 mol %) in 1-butyl-3-methylimidazolium hexafluorophosphate (3 mL) was stirred under an atmosphere of air or oxygen at room temperature for the appropriate time. After completion of the reaction, as indicated by TLC, the product was extracted

Table 2 Oxidative-coupling of 2-naphthols and phenols using $RuCl_3$/[bmim]PF_6

Entry	Substrate (**1**)	Product[a] (**2**)	Reaction time/h	% Yield[b]
				
a	R = R′ = R″ = H (**1a**)	R = R′ = R″ = H (**2a**)	5.0	93
b	R = Br; R′ = R″ = H (**1b**)	R = Br; R′ = R″ = H (**2b**)	4.0	91
c	R = R′ = H; R″ = COOMe (**1c**)	R = R′ = H; R″ = COOMe (**2c**)	7.5	60
d	R = H; R′ = MeO; R″ = H (**1d**)	R = H; R′ = MeO; R″ = H (**2d**)	6.0	90
e			9.0	49
f			8.5	57

[a] All products were characterized by ^1H NMR, IR and mass spectroscopy. [b] Isolated and unoptimized yields.

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with toluene or ether (3 × 10 mL). The combined organic extracts were concentrated *in vacuo* and the resulting product was recrystallized in toluene to afford the pure binaphthol. The remaining ionic liquid was further washed with ether and recycled in subsequent reactions. The spectroscopic data including IR, NMR, mass spectra and melting point of products were identical to those of authentic samples.

Product characterisation data

1,1′-Binaphthyl-2,2′-diol (2a). Solid, m.p. 218–219 °C (lit.[3b] 214–216 °C). IR (KBr): υ 3475, 3381, 3033, 1616, 1590, 1500, 1465, 1459, 1380, 1215, 1179, 1145, 1123, 825, 750 cm^{-1}. ^1H NMR ($CDCl_3$, 200 MHz): δ 5.05 (br s, 2H, OH), 7.16 (d, $J = 9.0$ Hz, 2H), 7.33 (ddd, $J = 8.5$, 7.0 and 1.5 Hz, 2H) 7.37 (ddd, $J = 8.0$, 7.0 and 1.5 Hz, 2H) and 7.40 (d, $J = 9.0$ Hz, 2H), 7.90 (d, $J = 8.0$ Hz, 2H), 7.99 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (50 MHz, $CDCl_3$, proton decoupled): δ 111.0, 117.8, 124.0, 124.2, 127.4, 128.4, 129.4, 131.3, 133.5, 152.8. Anal. calcd for $C_{20}H_{14}O_2$ (286.329): C, 83.90; H, 4.93; found: C 83.71; H 4.99.

6,6′-Dibromo-1,1-binaphthyl-2,2′-diol (2b). Solid, m.p. 206–207 °C (lit.[3b] 208–209 °C). IR (KBr): υ 3503, 3439, 1620, 1593, 1505, 1389, 1357, 1321, 1224, 1175, 1147, 937, 887, 825 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 5.01 (br s, 2H, OH), 6.92 (d, $J = 8.4$ Hz, 2H), 7.35 (dd, $J = 9.0$ and 2.1 Hz, 2H), 7.39 (d, $J = 8.4$, 2H) 7.85 (d, $J = 9.0$, 2H), 8.05 (br s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled): δ 111.0, 118.0, 119.0, 125.9, 130.5, 130.9, 130.7, 131.3, 132.4, 153.0. Anal. calcd for $C_{20}H_{12}Br_2O_2$ (444.121): C 54.09; H, 2.72; Br, 35.98; found: C 54.21; H, 2.65; Br, 35.79.

3,3′-Bismethoxycarbonyl-1,1′-binaphthyl-2,2′-diol (2c). Solid, m.p. 275–277 °C (lit.[7b] m.p. 276–278 °C). IR (KBr): υ 3480, 3360, 3035, 1607, 1595, 1359, 1240, 1130, 1021, 820 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 3.56 (s, 6H), 5.05–5.20 (br s, 2H, OH), 6.45 (d, $J = 2.8$ Hz, 2H), 7.05 (dd, $J = 5.6$ and 2.8 Hz, 2H), 7.20 (d, $J = 5.6$ Hz, 2H), 7.75 (d, $J = 5.6$ Hz, 2H), 7.84 (d, $J = 5.6$ Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, proton decoupled): δ 55.1, 103.5, 110.0, 115.0, 116.0, 125.0, 130.0, 131.0, 135.0, 153. 5, 158.0. Anal. calcd. for $C_{24}H_{18}O_6$ (402.40): C 71.64; H, 4.51; found: C 71.51; H, 4.63.

7,7′-Dimethoxy-1,1′-binaphthyl-2,2′-diol (2d). Solid, m.p. 149–150 °C (lit.[3d] 151–152 °C). IR (KBr): υ 3350, 1605, 1505, 1450, 1415, 1360, 1260, 1210, 1135, 830 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 3.29 (s, 6H), 6.20 (d, $J = 3.0$ Hz, 2H), 6.60 (dd, $J = 3.0$, 8.0 Hz, 2H), 6.80 (d, $J = 9.0$ Hz, 2H), 7.27 (br s, 2H, OH), 7.40 (d, $J = 9.0$ Hz, 2H), 7.43 (d, $J = 8.0$ Hz, 2H). EI-MS:m/z: 347 ($M+1$, 40%), 346 (M^+, 100%), 314 (15%), 287 (10%), 157 (15%), 145 (18%), 121 (12%), 113 (23%), 107 (30%). Anal. calcd. for $C_{22}H_{15}O_4$ (346.38): C 76.29; H, 5.24; found: C 76.15; H 5.36.

2,2′-Dihydroxy-5,5′-dichloro-4,4′,6,6′-tetramethyl biphenyl (2e). Solid, m.p. 195–197 °C. IR (KBr): υ 3519, 1396, 1205, 1027, 821 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.20 (s, 6H), 2.25 (s, 6H), 5.15 (br s, 2H, OH), 6.53 (s, 2H). Anal. calcd. for $C_{16}H_{16}Cl_2O_2$ (311.206): C 61.75; H, 5.18; Cl, 22.78; found: C 61.59; H 5.31; Cl, 22.93.

2,2′-Dihydroxy-3,3′,5,5′-tetramethyl biphenyl (2f). Solid, m.p. 131–132 °C (lit.[12a] 132–133 °C). IR (KBr): υ 3526, 1391, 1209, 1031, 827 cm^{-1}. ^1H NMR (200 MHz, $CDCl_3$): δ 2.23 (s, 6H, Me), 2.26 (s, 6H, Me), 4.60 (br s, 2H, OH), 6.62 (s, 4H, Ar–H). Anal. calcd. for $C_{16}H_{18}O_2$ (242.316): C 79.31; H, 7.49; found: C 79.46; H 7.66.

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