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A Novel Two – Phase Oxidative Coupling of 2 – Naphthols Suspended in Aqueous Fe^{3+} Solutions

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Abstract: The oxidative coupling of 2 – naphthols suspended in aqueous Fe^{3+} solutions gives corresponding 1,1' – bi – 2 – naphthols in the yields of 91 – 95%. This reaction can be also effectively applied to the large – scale synthesis of 1,1' – bi – 2 – naphthol. It was suggested that the oxidation occurred at the surface of the crystalline 2 – naphthols *via* a solid – liquid process.

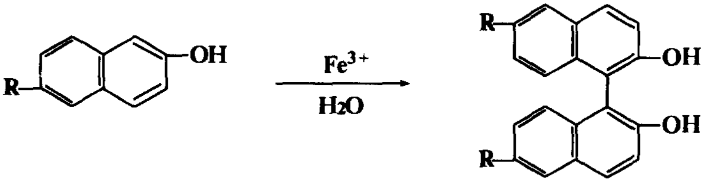
INTRODUCTION

1, 1' – Bi – 2 – naphthol derivatives have been widely used in asymmetric synthesis as chirality inducers.[1] Because the enantiomerically pure binaphthols can be easily obtained from their racemates by a number of methods, including classical resolution via crystallization of diastereoisomeric derivatives,[2] formation of inclusion crystals with chiral host molecules,[3] deracemization of racemates with copper complexes of chiral amines[4] or enzymatic hydrolysis of esters,[5] it is essential to establish a simple and convenient method for the preparation of racemic 1,1' – binaphthol derivatives. Several procedures have been developed for this purpose.[6] For example, two molecules of 2 – naphthol **1** can be coupled by using Fe^{3+}, Cu^{2+} or Mn^{3+} as the oxidants to produce binaphthol **2**. In all cases, the reactions were carried out in organic media. F. Toda and his coworkers reported a solid – state oxidative coupling procedure for the preparation of binaphthol derivatives and found that the reaction proceeds faster and more efficiently in the solid state than in solution.[7] In this paper, we describe a novel synthetic method for 1,1' – bi – 2 – naphthols **2(a – b)** *via* oxidative coupling of 2 – naphthols **1(a – b)** suspended in aqueous Fe^{3+} solutions.

RESULTS AND DISCUSSION

Synthesis of 1,1′-Bi-2-naphthols **2**

From synthetic point of view, chemists always expect an organic reaction to proceed effectively and selectively under mild conditions without need of special reagents. As we noted in the introduction, the syntheses of 1,1′-bi-2-naphthols were usually performed in organic media by the oxidative coupling of corresponding 2-naphthols. However, in such a case the reactions sometimes give quinones as byproducts.[7] Recently we found that the coupling reaction of 2-naphthols suspended in aqueous Fe^{3+} solution procceeds much faster and more efficiently than in homogeneous solution.



1(a-b)
a: R = H; b: R = Br

2(a-b)

Scheme 1

As a typical run, a suspension of powdered 2-naphthol **1a**(1.0 g, 7 mmol) in water (20 mL) containing $FeCl_3 \cdot 6H_2O$ (3.8 g, 14 mmol) was stirred at 50 ℃ for 1 h under air atmosphere. The crude product **2a** was separated quantitatively by filtration and washed with distilled water to remove Fe^{3+} and Fe^{2+}. Recrystallization of the product from toluene gave pure **2a** as white needles in 95% yield. Its melting point, IR and ^1H NMR data were identical to

Table 1. Coupling oxidation of 2-naphthol 1a in water media.

Oxidants	Fe^{3+}: **1a**	Temp.(℃)	Time (h)	Yield of **2a** (%)
$FeCl_3 \cdot 6H_2O$	2:1	50	1	95
$FeCl_3 \cdot 6H_2O$	1:1	50	1	90
$FeCl_3 \cdot 6H_2O$	1:2	50	1	85
$FeCl_3 \cdot 6H_2O$	1:2	50	1	80*
$FeCl_3 \cdot 6H_2O$	2:1	r.t.	55	90
$FeCl_3 \cdot 6H_2O$	1:4	50	24	40
$NH_4FeCl_4 \cdot 6H_2O$	2:1	50	1	95
$Fe(NO_3)_3 \cdot 9H_2O$	2:1	50	1	95
$Fe_2(SO_4)_3 \cdot 9H_2O$	4:1	50	3	96
$Fe_2(SO_4)_3 \cdot 9H_2O$	4:1	50	1	75
$NH_4Fe(SO_4)_2 \cdot 12H_2O$	2:1	50	3	92
$NH_4Fe(SO_4)_2 \cdot 12H_2O$	2:1	50	1	80

* The reaction was conducted under N_2 atmosphere.

those of literature and a commercial 1,1′-bi-2-naphthol sample. Considering the insolubility of 2-naphthol in water, we suggest that the reaction occurs at the surface of crystalline 2-naphthol *via* a solid-liquid process.

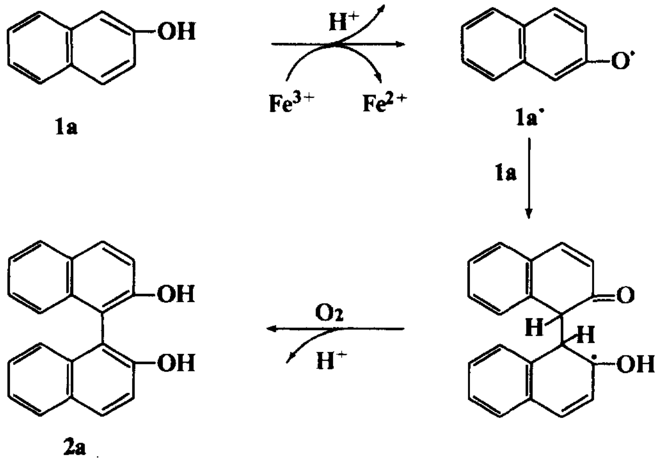
Some factors which may influence the yield of the reaction were also examined and summarized in Table 1. It was found that the oxidative coupling of **1a** in aqueous $FeCl_3$ solution gives **2a** in high yields, which are comparable to those of solid-state reaction.[7] Contrarily, heating of a solution of **1a** and $FeCl_3 \cdot 6H_2O$ (1:2 molar ratio) in 50% aqueous methanol under reflux for 2 h gave **2a** in 60% yield.[7] It is apparent that the reaction in aqueous suspension is more efficient than in homogeneous solution. Several kinds of other Fe^{3+} salts were also used as the oxidants. In every case, the reaction proceeds effectively. When the molar ratio of oxidants (Fe^{3+}) to 2-naphthol were altered from 2:1 to 1:2, the yield of reaction ranged from 95% to 85%. The reaction also occurred at room temperature, but the rate decreased significantly. When the reaction was conducted at r.t. for 55 h, the yield of coupling product was 90%.

In the case of 6-bromo-2-naphthol **1b**, the coupling reaction did not proceed at room temperature. Increasing the reaction temperature (70 ℃) and prolonging the reaction time (17 h) result in the coupling product **2b** in 91% yield.

The present reaction can be also applied to large-scale synthesis of **2a**. For example, a reaction using **1a**(14.4 g, 100 mmol), $FeCl_3 \cdot 6H_2O$ (54.1 g, 200 mmol) and water(200 mL) gave 13.0 g of pure **2a**(91% yield) after recrystallization of the crude product from toluene. Because the reaction was carried out with an aqueous suspension of the substrates under mild conditions and gave oxidative coupling products in excellent yields, it provided a convenient and economic route for the synthesis of 1,1′-bi-2-naphthols.

Mechanism Remarks

F. Toda reported that the coupling reaction of 2-naphthol **1a** by $FeCl_3$ in the solid state was caused by one electron oxidation of **1a** to the radical species **1a**˙ which underwent dimerization followed by releasing two protons to give 1,1′-bi-2-naphthol **2a**.[7] However in the solid state it is very difficult for two radicals to dimerize because of the control of the crystal lattice.[8] It is noteworthy that in the present system when the molar ratio of the oxidant (Fe^{3+}) to 2-naphthol **1a** is 1:2, the coupling reactions both under the air and under nitrogen atmosphere give 1,1′-bi-2-naphthol **2a** in the yields of 85% and 80% respectively. We also found that the reaction proceeds very slow in the presence of a catalytic amount of $FeCl_3$. For example, when the molar ratio of **1a** to $FeCl_3$ was 4:1 and the reaction was conducted at 50 ℃ for 24 h under the air, the yield of **2a** was only 40%. This result shows that the oxidation of Fe^{2+} to Fe^{3+} under the air in water is not so efficient as that in the solid state.[7] All the facts mentioned above imply that the formation of one molecule of **2a** only consumes one equivalent of Fe^{3+}, which suggests that the radical species **1a**˙ resulted from one electron oxidation of **1a** with Fe^{3+} adds to another neutral **1a** to form a new C-C bond and generate carbinyl radical followed by elimination of H˙ which may be further oxidated by O_2 present in the air or nitrogen (without further purification) to release H^+, to regain the aromatic state (Scheme 2). In the system of present study, Fe^{3+} cations homogeneously dispersing in water can readily contact with the surface of crystalline 2-naphthol to undergo one electron oxidation. Because the radical species **1a**$^{\bullet}$ formed in this way is situated in an environment with extremely high concentration of **1a**, it quickly combines with another 2-naphthol molecule to form the coupling product. Therefore the reaction in water media exhibits higher speed and efficiency than that in homogeneous solution.



Scheme 2

CONCLUSION

In conclusion we have presented a novel two-phase oxidative coupling of 2-naphthols suspended in aqueous Fe^{3+} solutions. It provides a convenient and economic procedure for the synthesis of 1,1'-bi-2-naphthols. The solid-liquid phase synthesis has also provided a new synthetic methodology.

EXPERIMENTAL SECTION

General

Unless stated otherwise, all reagents and chemicals were obtained commercially and used without further purification. 6-Bromo-2-naphthol **1b** was prepared following the literature procedure.[9] Melting points were measured using a WC-1 microscopic apparatus and are uncorrected. Elemental analyses were determined on a Carlo Erba 1106 Elemental Analysizer. IR spectra were recorded on a Shimadzu 435 Spectrophotometer in KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were taken on a Bruker AC-80 Spectrometer in $CDCl_3$ with TMS as an internal standard ($\delta = 0$ ppm).

Synthesis of 1,1'-Bi-2-naphthols **2**

*1,1'-Bi-2-naphthol (***2a***).* To a solution of $FeCl_3 \cdot 6H_2O$ (3.8 g, 14 mmol) in distilled water (20 mL) was added powdered 2−naphthol **1a** (1.0 g, 7 mmol) at room temperature, and the suspension was stirred at 50 ℃ for 1 h. After cooling, the resulting solid was separated by filtration and washed with distilled water for three times to remove Fe^{3+} and Fe^{2+}. The crude product was dried at room temperature *in vacuo* and recrystallized from toluene (10 mL) to give pure 1,1′−bi−2−naphthol **2a** as white needles (0.95 g, 95% yield): m.p. 216−218 ℃ (lit.[6h] m.p. 214−216 ℃). IR: 3475, 3380, 3030, 1615, 1591, 1510, 1466, 1458, 1380, 1214, 1174, 1145, 1123, 821, 815, 750 cm^{-1}. ^{1}H NMR: δ 4.00(s, 2H), 7.00−7.48 (m, 8H), 7.80−8.00 (m, 4H). ^{13}C NMR: δ 111.0, 117.8, 124.0, 124.2, 127.4, 128.4, 129.4, 131.3, 133.5, 152.8. Anal. calcd. for $C_{20}H_{14}O_2$: C, 83.90; H, 4.93%. Found: C, 83.68; H, 4.91%.

*6,6′−Dibromo−1,1′−bi−2−naphthol (***2b***).* Following the procedure mentioned above, the suspension was stirred at 70 ℃ for 17 h. Recrystallization of the crude product from toluene gave 6, 6′ −dibromo−1, 1′ −bi−2−naphthol **2b** as white crystals in 91% yield: m. p. 202−205 ℃ (lit.[6h] m.p. 208−209 ℃). IR: 3501, 3440, 1619, 1590, 1500, 1387, 1355, 1320, 1220, 1170, 1150, 932, 880, 820 cm^{-1}. ^{1}H NMR: δ 5.26 (s, 2H), 6.93(d, 2H, J=8.9), 7.24−7.42(m, 4H), 7.95(d, 2H, J=8.0), 8.01(d, 2H, J=2.0). ^{13}C NMR: δ 111.0, 118.0, 119.0, 125.9, 130.5, 130.7, 130.9, 131.3, 132.4, 153.0. Anal. calcd. for $C_{20}H_{12}Br_2O_2$: C, 54.09; H, 2.72%. Found: C, 53.70; H, 2.63%.

Large−scale synthesis of **2a**. To a 500−mL Bunsen flask were added **1a** (14.4 g, 100 mmol), $FeCl_3 \cdot 6H_2O$ (54.1 g, 200 mmol) and distilled water (200 mL), and the mixture was stirred vigorously with a magnetic stirrer at 50 ℃ for 3 h. The reaction mixture was cooled to room temperature and filtered. The filtered solid was washed with distilled water and re−crystallized from toluene to give colourless **2a** (13.0 g, 91% yield).

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