Novel two-phase oxidative cross-coupling of the two-component molecular crystal of 2-naphthol and 2-naphthylamine

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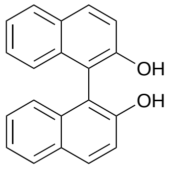
Two-phase reaction of a two-component molecular crystal of 2-naphthol and 2-naphthylamine suspended in aqueous Fe^{3+} solutions gives a cross-coupling product, 2-amino-2′-hydroxy-1,1′-binaphthalene, with good selectivity.

Solid-state organic reactions occurring in the ground state have attracted recent attention in organic synthesis.[1] For example, Toda *et al.* reported that a powdered mixture of 2-naphthol and $FeCl_3{\cdot}6H_2O$ gave 1,1′-bi-2-naphthol **1** in 95% yield.[2] We have developed a two-phase (solid–liquid) oxidative coupling reaction of 2-naphthol and 6-bromo-2-naphthol suspended in aqueous Fe^{3+} solutions which gives the corresponding 1,1′-bi-2-naphthols in up to 95% yield.[3] Here we report a novel oxidative cross-coupling reaction using a two-component molecular crystal composed of 2-naphthol and 2-naphthylamine *via* a similar solid–liquid process leading to 2-amino-2′-hydroxy-1,1′-binaphthalene **2**, which is a key catalytic ligand for asymmetric synthesis.[4] The present method is the first example of the ground-state reaction using two-component molecular crystals, in contrast to their known excited-state (photo)reactions.[5]

The molecular crystal **5** was obtained by the slow evaporation of an equimolar solution of 2-naphthol **3** and 2-naphthylamine **4** in methanol–acetone (1 : 1, v/v) at room temperature or by melting a 1 : 1 molar mixture of the component compounds followed by resolidification of the melt. Elemental analysis of **5** showed the composition of 2-naphthol and 2-naphthylamine present to be 1 : 1. The melting point of **5** is 127–129 °C which is higher than those of 2-naphthol (120–123 °C) and 2-naphthylamine (108–110 °C). Powder X-ray diffraction (PXD) results and the IR spectra of crystal **5** are quite different from those of the sum of the component compounds. All these results indicate the formation of a molecular compound between 2-naphthol and 2-naphthylamine. Particularly, the ν_{NH} absorptions at 3375, 3290 and 3170 cm^{-1} in the IR spectrum of 2-naphthylamine become two absorption bands at 3350 and 3260 cm^{-1} in the molecular compound **5** and the ν_{OH} absorption at 3250 cm^{-1} for 2-naphthol disappears in the spectrum of **5**. It can be deduced that the formation of the molecular compound was caused by hydrogen bonding between the OH and NH_2 groups.



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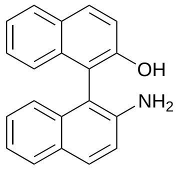

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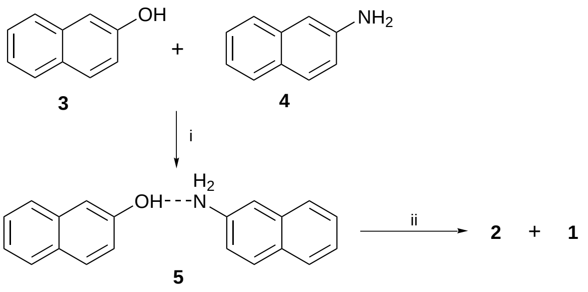

Scheme 1 *Reagents and conditions*: i, acetone–methanol, evaporation, room temp; ii, Fe^{3+}–H_2O, 55 °C

The oxidative coupling of 2-naphthol **3** reported previously was carried out using a suspension of the substrate in aqueous Fe^{3+} solution.[3] We applied this method to the synthesis of 2-amino-2′-hydroxy-1,1′-binaphthalene **2** *via* oxidative cross-coupling of molecular crystal **5**. In a typical run, a suspension of finely powdered **5** (2.87 g, 10 mmol) in water (50 ml) containing $FeCl_3{\cdot}6H_2O$ (10.80 g, 40 mmol) was stirred at 55 °C for 6 h under an argon atmosphere. After cooling, the solid material was collected quantitatively by filtration and washed with distilled water to remove Fe^{3+} and Fe^{2+}. The solid was chromatographed on an activated charcoal column (100 × 18 mm, 10 g of activated charcoal) using acetone as eluent. The eluent was evaporated and the residual solid was recrystallized from benzene to afford pure **2** (2.0 g, 70%) as colourless needles. Elemental analysis, IR, ^1H NMR and ^{13}C NMR data were consistent with the structure **2**. This procedure was also applied to the large-scale synthesis of **2**, using **5** (11.5 g, 40 mmol), $FeCl_3{\cdot}6H_2O$ (43.2 g, 160 mmol) and water (200 ml) at 55 °C for 6 h, to gave 7.15 g of **2** (65% isolated yield).

The selectivity and efficiency of the reaction under various conditions were also examined. The results obtained by the HPLC analysis of the products are summarized in Table 1. In a typical run carried out at 55 °C for 6 h (entry 1), the conversion of 2-naphthol **3** was quantitative and the yield of cross-coupling product **2** was highest. When the reaction was conducted at

Table 1 Oxidative cross-coupling of **5**

Entry	Fe^{3+} : **5**	*T*/°C	*t*/h	Conversion of **3** (%)	Yield (%)[a] **2**	**1**
1	4 : 1	55	6	100	82	14
2	4 : 1	55	3	98.0	79	13
3	4 : 1	room temp.	6	98.4	71	14
4	2.2 : 1	55	3	94.8	71	19
5[b]	4 : 1	55	3	97.0	63	19
6[c]	4 : 1	55	3	81.8	31	23
7[c]	4 : 1	55	3	77.2	42	30
8[c]	4 : 1	55	3	96.8	57	18
9[d]	4 : 1	55	5	100	39	39
10[e]	4 : 1	55	3	96.4	78	20

[a] Yields were obtained by HPLC and based on the amount of consumed **3**. [b] Ultrasound (25 KHz) was applied. [c] $Fe_2(SO_4)_3{\cdot}9H_2O$, $NH_4Fe(SO_4)_2{\cdot}12H_2O$ and $NH_4FeCl_4{\cdot}6H_2O$ were used as oxidants. [d] The reaction was conducted in the solid state. [e] **3** and **4** were added to aqueous $FeCl_3$ solution separately.

room temperature for 6 h (entry 3), the yield and the selectivity for the formation of **2** apparently decreased in comparison with those at 55 °C. At the lower molar ratio of $FeCl_3 \cdot 6H_2O$ to **5** (entry 4) the yields of **2** and **1** were unaltered. Under ultrasonic application (entry 5) no improvement of the yield and selectivity of the formation of **2** were observed. Although three other kinds of Fe^{3+} salts were also used as oxidants (entries 6, 7 and 8), the yield and the selectivity for the formation of **2** were poor in every case. A total solid-state reaction was carried out by grinding a mixture of $FeCl_3 \cdot 6H_2O$ and **5** (4 : 1) in a mortar at 55 °C for 5 h (entry 9), the conversion of 2-naphthol **3** was quantitative, but the yield and the selectivity of the formation of **2** were low. This is interpreted by the fact that with the progress of the reaction the powdered mixture became glassy, a state in which the original arrangement of the component molecules in the crystal lattice may be altered.

It is interesting to note that when the crystals of 2-naphthol **3** and 2-naphthylamine **4** were separately added to the solution of $FeCl_3 \cdot 6H_2O$ in water and the suspension was stirred at 55 °C for 3 h (entry 10), the yield of **2** was comparable to that obtained by the reaction of molecular **5** (entry 2). In order to clarify this phenomenon, a suspension of a mixture of 2-naphthol and 2-naphthylamine in water without the presence of oxidant was stirred at 55 °C for 1 h. The solid collected by filtration showed the same melting point and IR spectrum as those of **5**. It can be concluded that in the case of entry 10 the actual reacting species is molecular **5** and as a result it gave the same yield and selectivity of the product as those obtained from the reaction of **5**.

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References

1 F. Toda, *Synlett*, 1993, 303.
2 F. Toda, K. Tanaka and S. Iwata, *J. Org. Chem.*, 1989, **54**, 3007.
3 K. Ding, Y. Wang, L. Zhang, Y. Wu and T. Matsuura, *Tetrahedron*, 1996, **52**, 1005.
4 E. Carreira, R. A. Singer and W. Lee, *J. Am. Chem. Soc.*, 1994, **116**, 8837; E. Carreira, W. Lee and R. A. Singer, *J. Am. Chem. Soc.*, 1995, **117**, 3649; R. A. Singer and E. Carreira, *J. Am. Chem. Soc.*, 1995, **117**, 12360; H. J. Knolker and H. Hermann, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 341; D. J. Berrisford and C. Bolm, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1717.
5 H. Koshima and T. Matsuura, *Kokagaku*, 1995, **19**, 10; H. Koshima, Y. Chisaka, Y. Wang, X. Yao, H. Wang, R. Wang, A. Maeda and T. Matsuura, *Tetrahedron*, 1994, **50**, 13 617; H. Koshima, K. Ding and T. Matsuura, *J. Chem. Soc. Chem Commun.*, 1994, 2053; H. Koshima, K. Ding, Y. Chisaka and T. Matsuura, *Tetrahedron: Asymmetry*, 1995, **6**, 101; H. Koshima, K. Ding, Y. Chisaka, T. Matsuura, Y. Ohashi and M. Mukasa, *J. Org. Chem.*, 1996, **61**, 2352; H. Koshima, K. Ding, Y. Chisaka and T. Matsuura, *J. Am. Chem. Soc.*, 1996, **118**, 12 059.

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