Pergamon

Tetrahedron Letters 41 (2000) 10061–10064

TETRAHEDRON
LETTERS

Reduction of 1,1′-binaphthyls to octahydro-1,1′-binaphthyl derivatives with Raney Ni–Al alloy in aqueous solution

Hui Guo and Kuiling Ding*

*Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
354 Fenglin Lu, Shanghai 200032, China*

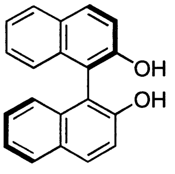
Received 19 May 2000; revised 23 June 2000; accepted 4 July 2000

Abstract

Reduction of BINOL, BINAM and NOBIN with Raney Ni–Al alloy in dilute NaOH aqueous solution results in the formation of H_8-BINOL, H_8-BINAM and H_8-NOBIN in 60–86% isolated yields with 97.5–99% enantiomeric excesses. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: binaphthyls; octahydrobinaphthyls; reduction; Ni–Al; chiral.

Optically active 1,1′-bi-2-naphthol (BINOL, **1**), 1,1′-bi-2-naphthylamine (BINAM **2**), 2-amino-2′-hydroxy-1,1′-binaphthyl (**3**, NOBIN), and their derivatives have found many applications, ranging from chiral ligands of catalysts for asymmetric reactions,[1] to hosts for molecular recognition,[2] to being intermediates for the synthesis of chiral materials.[3] Very recent research showed that the chiral catalysts derived from 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthol (H_8-BINOL) **4** and 5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-bi-2-naphthylamine (H_8-BINAM) **5** exhibit higher efficiency and enantioselectivity for asymmetric reactions than those prepared from their parent ligands (e.g. **1** and **2**), due to the steric and electronic modulation in the binaphthyl backbone.[5]



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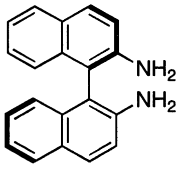

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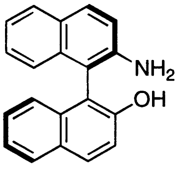

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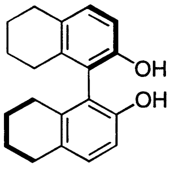

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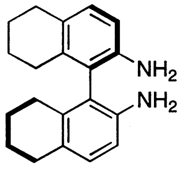

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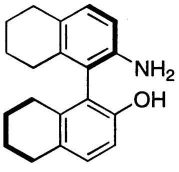

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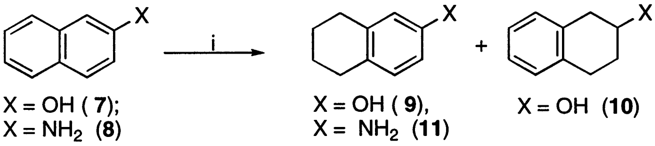
* Corresponding author. Fax: 86-21-6416-6128; e-mail: kding@pub.sioc.ac.cn

PII: S0040-4039(00)01799-8

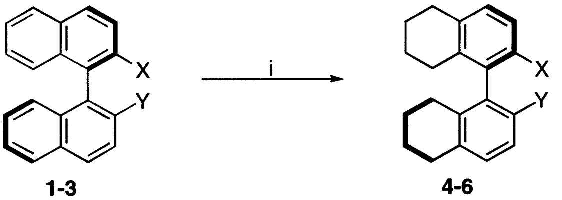
It has been reported that **4** and **5** can be obtained by partial hydrogenation of the corresponding binaphthyls **1** and **2** in the presence of PtO_2 in an autoclave.[2,4b] Recently Tashiro et al. reported that a Raney Ni–Al alloy in dilute aqueous alkaline solution possesses very strong reducing ability and can be used for the dechlorination of chlorobiphenyls without the use of any organic solvents.[5] Of interest is that one of the phenyl rings could be reduced as well if the concentration of the alkaline solution was adjusted at 1–0.5% levels. In the present work, we would like to report a readily available protocol for the preparation of H_8-binaphthyls **4**–**6** through the partial reduction of the corresponding binaphthyls **1**–**3** with Raney Ni–Al alloy in dilute aqueous alkaline solution.



Scheme 1. *Reagents and conditions*: (i) Raney Ni–Al alloy, NaOH–H_2O, 90°C; isolated yields for **9**: 51%; **10**: 35%; **11**: 84%

The classical hydrogenation of naphthols with Raney Ni catalysis is usually carried out under very high hydrogen pressure and special care must be taken to avoid contact with air in the preparation of the catalyst.[6] Obviously, this protocol is not practical for a laboratory preparation. With the inspiration of Tashiro's finding, we investigated the possibility of the reduction of naphthyl derivatives by using Raney Ni–Al alloy in dilute aqueous alkaline solution. Accordingly, 2-naphthol (**7**) and 2-naphthylamine (**8**) were submitted for reduction. It was found that both **7** and **8** could be efficiently partially reduced with Raney Ni–Al alloy in 0.5% aqueous NaOH solution at 90°C (Scheme 1). In the case of **7**, both the 5,6,7,8- and 1,2,3,4-positions are hydrogenated, the ratio of two isomers (**9** versus **10**) being ~2:1. However, the reduction of **8** takes place specifically at the 5,6,7,8-carbon atoms and gives 5,6,7,8-tetrahydro-2-naphthylamine (**11**) in 84% isolated yield.

With these results in hand, we then examined the reduction of the 1,1′-binaphthyl derivatives **1** and **2** (Scheme 2). We were pleased to find that both **1** and **2** are hydrogenated under the experimental conditions mentioned above. The conversions of the starting materials were completed in 6 and 16 h, respectively. Considering the poor solubility of **2** in the reaction medium, the addition of isopropanol was found to facilitate the process of the reduction (100% conversion of **2** within 9 h). H_8-BINOL (**4**) and H_8-BINAM (**5**) were obtained in 60% and 86% isolated yields, respectively. The configurational stabilities of compounds during the reaction were checked with **2** yielding **5** (> 99% ee) with complete retention of configuration, whereas



Scheme 2. *Reagents and conditions*: (i) Raney Ni–Al alloy, NaOH–H_2O–*i*-PrOH, 50–90°C; isolated yields and enantiomeric excesses for **4**: 60%, up to 97.5% ee; **5**: 86%, >99% ee; **6**: 75%, >99% ee

reduction of **1** was accompanied by partial racemization (giving H_8-BINOL of 91.8% ee). Decreasing the reaction temperature to 50°C improved the enantiomeric excess of **4** up to 97.5%. This phenomenon was probably caused by partial racemization of the starting material under basic conditions because ditetrallyl units are more configurationally stable than binaphthyl units.[2] Fortunately, recrystallization of **4** with 97.5% ee from heptane yielded its enantiopure form with >99% enantiomeric excess.

Enantiopure NOBIN (**3**) was recently found to be an excellent chiral ligand for asymmetric reactions[7] and its synthesis has been well developed.[8] Its octahydrogenated derivative should be an interesting compound for asymmetric induction as well. Accordingly, the reduction of **3** was also carried out under the experimental conditions mentioned above and it was found that H_8-NOBIN (**6**) could be obtained in 75% isolated yield with >99% ee (Scheme 2).[9] The application of chiral ligands derived from **6** to asymmetric catalysis will be reported in an alternative report.[10]

In conclusion, we have demonstrated a convenient preparation of some important chiral inducers, H_8-binaphthyls **4**–**6**, through the partial reduction of corresponding binaphthyls **1**–**3** using commercially available Raney Ni–Al alloy in dilute aqueous alkaline solution. This protocol provides a readily available procedure for the selective reduction of naphthyls and possesses advantages of simple manipulation, mild reaction conditions and low cost of the reagent.

Acknowledgements

We thank the National Natural Science Foundation of China, Chinese Academy of Sciences, Major Basic Research Development Program of China (Grant No. G2000077506), and Science and Technology Commission of Shanghai Municipality for financial support of this work.

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9. A typical procedure for reduction of reduction of **3** to **6**: A 500 mL flask was charged with Raney Ni–Al alloy (2.5 g), water (200 mL) and (*R*)-NOBIN (356 mg, 1.25 mmol) in isopropanol (30 mL), to which aqueous NaOH solution (1%, 200 mL) was gradually added over 1 h under stirring at 90°C. The reaction process was monitored by TLC. After stirring for 7 h at 90°C, the reaction mixture was cooled to room temperature. The insoluble materials were filtered off with Celite and the solids washed with ethyl acetate. The filtrate was neutralized with 2N HCl to pH$\sim$7 and then exacted with ethyl acetate and dried over $MgSO_4$. After the removal of the solvent, the residue was submitted to column-chromatographic separation on silica gel with petroleum ether/ethyl acetate (5/1) as eluent to give (*R*)-**6** (275 mg, 75% yield) as a white solid with >99% ee (determined by HPLC on a Chiralcel OJ column with 93:7 hexane/isopropanol as eluent, 0.7 mL min^{-1}, t_R: 10.57 min; t_S: 13.94 min). Mp 156–158°C; $[\alpha]_D^{20}$: 103.6 ($c=1.0$, THF); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02 (d, 1H, $J=8.2$ Hz), 6.96 (d, 1H, $J=8.2$ Hz), 6.81 (d, 1H, $J=8.4$ Hz), 6.65 (d, 1H, $J=8.3$ Hz), 4.60 (br, 1H), 3.35 (br, 2H), 2.77–2.70 (m, 4H), 2.38–2.11 (m, 4H), 1.78–1.64 (m, 8H); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 150.6, 142.5, 137.1, 136.5, 130.4, 129.9, 129.7, 127.9, 122.1, 118.3, 113.3, 112.6, 29.3, 29.2, 27.2, 26.9, 23.3, 23.2, 23.1, 23.0; FT-IR (KBr pellet): 3406, 2934, 2861, 1615, 1482, 1457, 1285, 815 cm^{-1}; EIMS (m/z): 293 (M^+, 100%). Anal. calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.81; H, 7.96; N, 4.61.
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