

Selective synthesis of 1,1'-binaphthalene derivatives by oxidative coupling with TiCl_4

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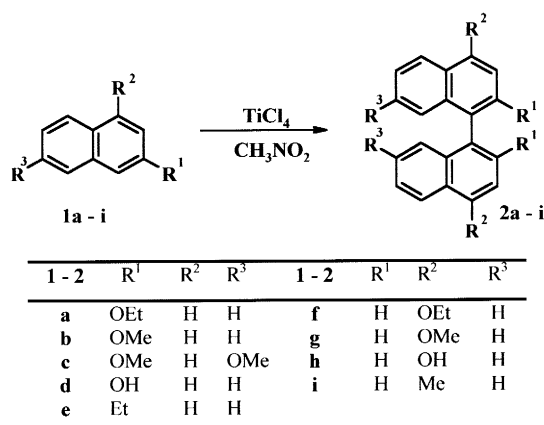
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Abstract

Oxidative coupling of naphthalene compounds with TiCl_4 in nitromethane under mild conditions gives symmetrical 1,1'-binaphthyls in good yields. The method is particularly useful when applied to substrates with electron donating groups. © 2000 Elsevier Science Ltd. All rights reserved.

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The biaryl substructure is a central building block in a very large number of natural products, such as polyketides, terpenes, lignanes, coumarins, flavonoids, tannins, and many alkaloids.¹ Homochiral 1,1'-binaphthalene derivatives have successfully been utilized as chiral inducers for highly stereoselective reactions because of their axial dissymmetry and molecular flexibility.² Therefore, it is essential to



Scheme 1.

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Table 1
Oxidative coupling of naphthalene compounds **1** into 1,1'-binaphthyls **2**

run	Reactant 1	Reaction conditions			Yield 2 (%) ^{a,b}	Recovered 1 (%) ^a
		TiCl ₄ (equiv.)	Temp. (°C)	Reaction time (h)		
1	1a	0.5	20	18	40	60
2		1	20	18	75	25
3		1	50	1.7	75(45)	25
4		2	50	0.8	95(70)	5
5	1b	1	20	18	65	35
6		2	50	1	>95(60)	-
7	1c	1	20	18	55(40)	45
8	1d	1	40	4.5	>90(60)	-
9	1e	1	20	48	60(33)	40
10	1f	1	20	18	75	- ^c
11		2	20	1	>95(85)	-
12	1g	1	20	18	60(45)	- ^d
13	1h	1	20	18	-	100
14		1	40	1.5	- ^e	40
15	1i	1	20	48	55(30)	45

^a Determined by NMR

^b The number in brackets corresponds to the yield of **2** isolated after column chromatography

^c 25 % of naphthoquinone was also formed

^d 40 % of naphthoquinone was also formed

^e complex mixture

establish simple and convenient methods for the preparation of 1,1'-binaphthalene derivatives. Several procedures have been developed for this purpose, and the most straightforward method for the construction of binaphthyl skeletons is the oxidative coupling of corresponding naphthalene derivatives. A variety of oxidants, e.g. FeCl₃,³ Cu²⁺- and Fe³⁺-doped MCM-41 aluminosilicate,⁴ Cu(II)-amine complexes,⁵ or Mn(acac)₃⁶ have been utilized as coupling reagents. The reactions were carried out in organic solvents,⁷ in aqueous Fe³⁺ solution,⁸ or in the solid state without solvent,⁹ sometimes accelerated by microwave¹⁰ or ultrasound irradiation.¹¹ Recently, Schreier et al. reported the oxidative coupling of phenolic compounds catalyzed by horseradish peroxidase.¹² Some Lewis acids such AlCl₃, ZrCl₄, SnCl₄, or SbCl₃ are reported¹³ to be effective catalysts to produce biaryls from aromatic compounds via aromatic radical cations. The latter reaction is known as the Scholl reaction,¹⁴ usually giving mixtures of isomeric biaryls.

In this paper, we report the coupling reaction of naphthalene derivatives using the relatively weak Lewis acid TiCl₄ as oxidant. The reaction proceeds regioselectively in nitromethane under milder conditions compared to those initially used in the Scholl reaction (Scheme 1).

Some factors which may influence the yield of the reaction were examined and are summarized in

Table 1. A typical experimental procedure is as follows: at 5°C and under an argon atmosphere, the dropwise addition of TiCl_4 (number of equivalents is indicated in Table 1) to nitromethane (50 mL) gave a bright yellow complex. To this complex, a solution of **1** (0.020 mol) in nitromethane (20 mL) was slowly added at room temperature. The resulting dark brown mixture was stirred and heated if necessary for the time indicated. The mixture was hydrolyzed with cold water and extracted with dichloromethane (3×50 mL). The combined organic layers were washed with water and dried over MgSO_4 . After removal of the solvent under reduced pressure, the resulting product was first checked by ^1H NMR (Bruker AC 300 spectrometer) and then purified by flash chromatography on silica gel (heptane:ethyl acetate). Analytical data of binaphthyls **2a–i** were identical to data reported in the literature.

As can be seen in Table 1 runs 3, 4, and 6, the yield of coupling product **2** is higher if the reaction is conducted at 50°C instead of room temperature and the rate of the reaction increases significantly. When the molar ratio of oxidant (Ti^{4+}) to substrate **1** is changed from 2:1 to 1:2, the yield of reaction decreases significantly (runs 3, 5, 10 vs 4, 6, 11). The naphthalene compounds substituted in 1-position by an alkoxy or an hydroxy substituent ($\text{R}^2=\text{OMe}$, OEt , OH) lead, beside to the coupling product, to a significant quantity of naphthoquinone (runs 10, 12) or to an unidentifiable product mixture (run 14). In the case of alkyl substituted substrates **1e** or **1i**, the rate of the reaction is slower (runs 9, 15).

By contrast, all attempts to couple compounds without electron donating substituents like naphthalene or 1-chloronaphthalene were unsuccessful even at higher temperature. In other solvents such as trifluoroacetic acid, the reaction gave little conversion (about 20%) and required a very long reaction time (one week).

In conclusion we have described for the first time the oxidative coupling of naphthalene derivatives mediated by a Ti^{4+} –nitromethane complex, which provides efficient and regioselective means for preparation of 1,1'-binaphthyls substituted by electron donating groups. A mechanistic study is now in progress in our laboratory.

References

1. For leading references on both the synthesis and natural occurrence of biaryls, see: Bringmann, G.; Walter, R. *Angew. Chem., Int. Ed. Engl.* **1990**, 29, 977–991.
2. (a) Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. *Synthesis* **1992**, 503–517. (b) Noyori, R. *Asymmetric Catalysis in Organic Synthesis*; Wiley & Sons: New York, 1994. (c) Zimmer, R.; Suhrbier, J. *J. Prakt. Chem.* **1997**, 339, 758–762.
3. (a) Deussen, H.-J.; Fredericksen, P.; Bjornholm, T.; Bechgaard, K. *Org. Prep. Proced. Int.* **1996**, 28, 484–486. (b) Tong-Shuang, L.; Hui-Yun, D.; Bao-Zhi, L.; Brij, B. T.; Sheng-Hui, L. *J. Chem. Soc., Perkin Trans. 1* **1999**, 291–293.
4. Armengol, E.; Corma, A.; Garcia, H.; Primo, J. *Eur. J. Org. Chem.* **1999**, 1915–1920.
5. Nakajima, M.; Miyoshi, I.; Kanayama, K.; Hashimoto, S. *J. Org. Chem.* **1999**, 2264–2271.
6. Yamamoto, K.; Fukushima, H.; Okamoto, Y.; Hatada, K.; Nakazaki, M. *J. Chem. Soc., Chem. Commun.* **1984**, 1111–1112.
7. (a) Noji, M.; Nakajima, M.; Koga, K. *Tetrahedron Lett.* **1994**, 35, 7983–7984. (b) Kantam, M. L.; Santhi, P. L. *Synth. Commun.* **1996**, 26, 3075–3079. (c) Sakamoto, T.; Yonehara, H.; Pac, C. *J. Org. Chem.* **1997**, 62, 3194–3199.
8. Ding, K.; Wang, Y.; Zhang, L.; Wu, Y.; Matsuuara, T. *Tetrahedron* **1996**, 52, 1005–1010.
9. Nakajima, M.; Hashimoto, S.-I.; Noji, M.; Koga, K. *Chem. Pharm. Bull.* **1998**, 46, 1814–1815.
10. Toda, F.; Tanaka, K.; Iwata, S. *J. Org. Chem.* **1989**, 54, 3007–3009.
11. Villemain, D.; Sauvaget, F. *Synlett* **1994**, 435–436.
12. Schmitt, M. M.; Schüler, E.; Braun, M.; Häring, D.; Schreier, P. *Tetrahedron Lett.* **1998**, 39, 2945–2946.
13. Tanaka, M.; Nakashima, H.; Fujiwara, M.; Ando, H.; Souma, Y. *J. Org. Chem.* **1996**, 61, 788–792, and references cited therein.
14. Scholl, R.; Seer, C.; Weitzenböck, R. *Ber. Dtsch. Chem. Ges.* **1910**, 43, 2202.