Pergamon

Tetrahedron Letters, Vol. 37, No. 26, pp. 4459-4462, 1996

0040-4039/96 $15.00 + 0.00

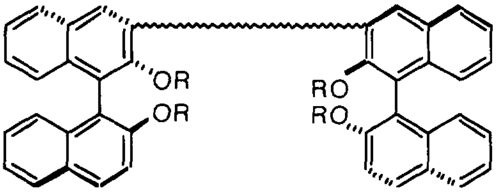
PII: S0040-4039(96)00876-3

SYNTHESIS OF A BIS-(BINAPHTHOL)

Chao-Jun Li,* Dong Wang and William T. Slaven IV
Department of Chemistry, Tulane University, New Orleans, LA 70118, USA

Summary. *A bis-(binaphthol) was prepared by using 3-iodo-1,1'-bi-2-naphthol dimethyl ether and bis(tributylstannyl)acetylene via the Stille reaction.* Copyright © 1996 Elsevier Science Ltd

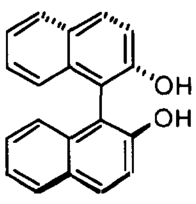
Previously, we proposed the synthesis of binapthol-based polymers and oligomers as novel conducting materials, as hosts for molecular recognitions, and as chiral ligands for asymmetric catalysis. Recently, we have prepared a binaphthol-based polymer.[1] However, in order to control and fine-tune the properties of these materials, it is important to control the size of the molecules being generated.[2] The molecular distribution of these material could have a critical influence on their properties. Here we report a synthesis of a novel binaphthol dimer (**1**), a potential useful chiral ligand, by using 3-iodo-1,1'-bi-2-naphthol dimethyl ether and bis(tributylstannyl)acetylene *via* the Stille coupling reaction.[3]



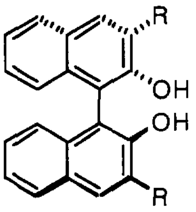
1

1,1'-Bi-2-naphthol (BINOL, **2**) is an important chiral auxiliary and a ligand for many asymmetric transformations.[4] Recently, its 3,3'-disubstituted derivatives **3** were synthesized[5] and used as chiral catalysts,[6] through complexation with Lewis acids, in a variety of reactions. These compounds have also been used widely in molecular recognition studies.[7] The preparation and synthetic utilities of the unsymmetrical, 3-substituted derivatives **4** have also been explored recently by Snieckus and others.[8,9]

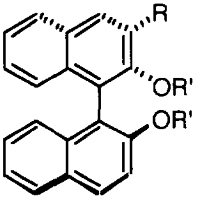
In an effort to prepare binaphthol based-oligomers, a key obstacle we encountered is the selective mono-iodination of binaphthol. Using Snieckus lithiation-iodination[9] reaction led to a mixture of the starting material, mono-iodination and di-iodination products, in which the mono-iodination compound often consists the minor product. To improve the yield of the mono-iodination compound by changing the ratio of lithiation reagents or reaction conditions was not successful, with either predominant formation of bis-iodination product or recovered starting material being observed in each case. On the other hand, we found that the Snieckus lithiation-iodination is very effective in generating bis-iodination products.



2



3

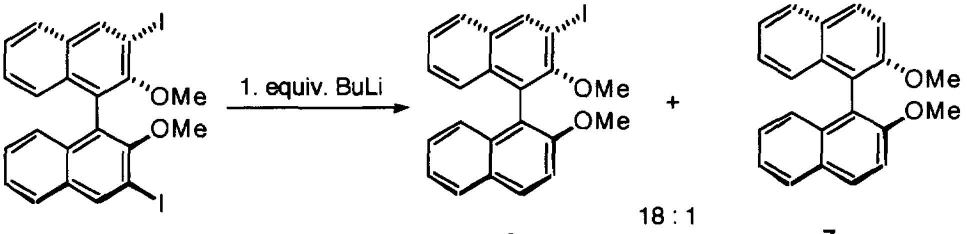


4

R=Me, Br, Cl, CH(OH)Ph, SPh
R'=MOM, SEM

After many failures in preparing the mono-iodo BINOl derivative, we decided to examine de-iodination of the readily accessable bis-iodo derivative **5**. This lead us to the developing of a very efficient method for the preparation of mono-iodobinaphthol derivatives through highly selective mono-de-iodination of bis-diiodobinaphthol (Scheme 1).[10] The reaction gave virtually a single product, the one we desired, each time we ran the reaction.

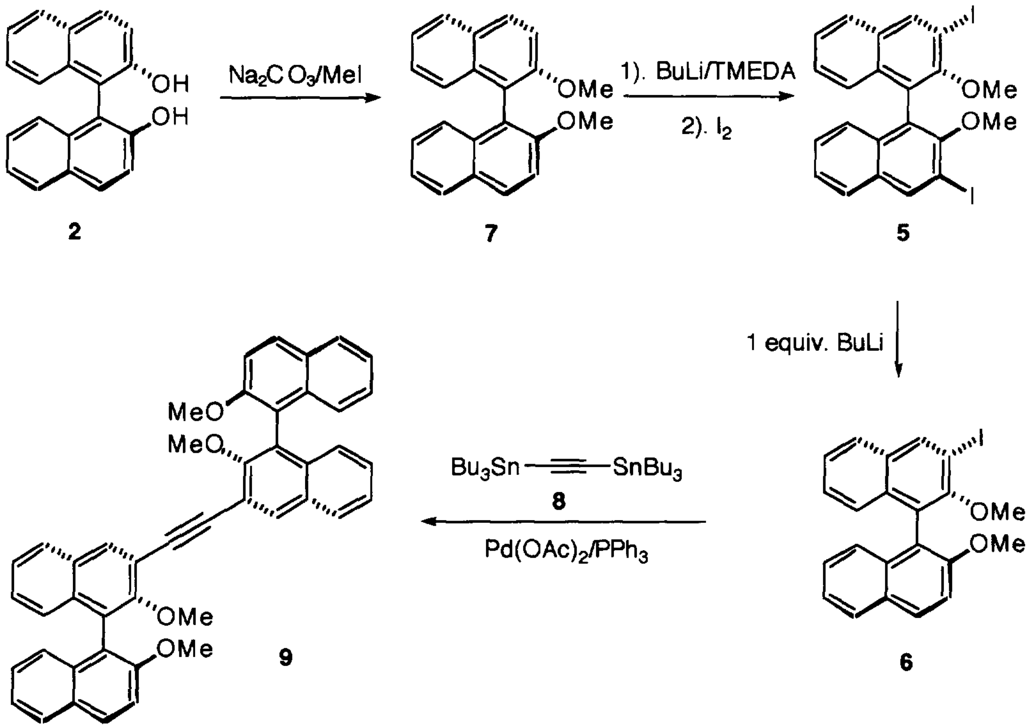
Scheme 1



5 **6** **7**

The success of this highly selective mono-diiodination gave us ready access of the proposed bis-binaphthol derivative (Scheme 2). Thus, binaphthol (S- isomer) (**1**) is methylated in 78-80% yield by reaction with methyl iodide and sodium carbonate.[11] Following the literature procedure, 3,3'-diiodo derivative **5** was obtained in 76% yield from BINOL dimethyl ether (**7**) by reaction with butyllithium in the presence of tetramethylethylenediamine (TMEDA) followed by quenching with iodine. Treatment of the di-iodo compound **5** with one equivalent of butyl lithium at -78°C lead to the formation of the mono iodo-binaphthol derivative **6** in 73% isolated yield (the yield discrepancy is primarily due to isolation loss), together with 6-7% recovered starting material. The formation of a minute amount of compound **7** (ca. 5%) was due to the dilithiation of **5**. Finally, reaction of the mono-iodo derivative **6** with bis-(tributylstannyl)acetylene (**8**), catalyzed by palladium and triphenylphosphine,[12] produced the bis-(binaphthol) ($[\alpha]$= -120, C=0.5, $CHCl_3$) derivative in 66% after column chromatography. The potential application of this novel bis-binaphthol derivative (as well as other bis-binaphthol derivatives) as a ligand for asymmetric synthesis is under investigation.

Scheme 2



Acknowledgment: We gratefully acknowledge support by Tulane University and the Department of Energy, and from the Center for Photoinduced Processes funded by the National Science Foundation and the Louisiana Board of Regents. High-resolution mass spectra were gratefully provided by Dr. D. A. Grimm of Tulane University's Coordinated Instrumentation Facility. We thank Profs. H. F. Chow and T. L. Chan of

Chinese University of Hong Kong for informing us about their research related to this work and Prof. H. Ensley for helpful discussion.

References:

1. Li, C. J.; Wang, D.; Slaven, IV, W. T.; McPherson, G.; John, V. T.; Premachandran, R. *manuscript in preparation.*
2. Tour, J. *Chem. Rev.* **1996**, *96*, 537.
3. For reviews, see: Stille, J. F. *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508; Scoot, W. J.; McMurry, J. E. *Acc. Chem. Res.* **1988**, *21*, 47.
4. For reviews, see: Whitesell, J. K. *Chem. Rev.* **1989**, *89*, 1581; Narasaka, K. *Synthesis* **1991**, 1; Noyori, R. *Chem. Soc. Rev.* **1989**, *18*, 187.
5. Cram, D. J.; Helgeson, R. C.; Peacock, S. C.; Kaplan, L. J.; Domeier, L. H.; Moreau, P.; Koga, K.; Mayer, J. M.; Chao, Y.; Siegel, M. G.; Hoffman, D. H.; Sogah, G. D. Y. *J. Org. Chem.* **1978**, *43*, 1930; Maruoka, K.; Itoh, T.; Shirasaki, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310; Wong, M. S.; Nicoud, J. F. *J. Chem. Soc., Chem. Commun.* **1994**, 249; see also refs 3, 4 and 7.
6. For examples, see: Maruoka, K.; Itoh, T.; Shirasaka, T.; Yamamoto, H. *J. Am. Chem. Soc.* **1988**, *110*, 310; Maruoka, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1989**, *111*, 789; Maruoka, K.; Banno, H.; Yamamoto, H. *J. Am. Chem. Soc.* **1990**, *112*, 7791; Maruoka, K.; Hoshino, Y.; Shirasaka, T.; Yamamoto, H. *Tetrahedron Lett.* **1988**, *29*, 3967; Kazlauskas, R. J. *J. Am. Chem. Soc.* **1989**, *111*, 4953; Seebach, D.; Beck, A. K.; Roggo, S.; Wonnacott, A. *Chem. Ber.* **1985**, *118*, 3673.
7. Lingenfelter, D. S.; Helgeson, R. C.; Cram, D. J. *J. Org. Chem.* **1981**, *46*, 393.
8. Hovorka, M.; Gunterova, J.; Zavada, J. *Tetrahedron Lett.* **1990**, *31*, 413.
9. Cox, P. J.; Wang, W.; Snieckus, V. *Tetrahedron Lett.* **1992**, *33*, 2253 and refs are cited therein.
10. Li, C. J.; Wang, D.; Slaven, IV, W. T. *Submitted for publication.* Procedure: To a mixture of **5** (0.62 g, 1.1 mmol) in 30 mL THF was added n-BuLi (0.73 mL, 1.6 M, 1.17 mmol) dropwise at -78°C under N_2. After stirring for 1 h at -78°C, saturated aqueous NH_4Cl solution (10 mL) was added, and the reaction mixture was warmed to room temperature. The organic layer was separated, and the aqueous phase was extracted with methylene chloride (3x). The combined organic layer was dried over magnesium sulfate and concentrated. The residue was purified by flash chromatography on silica gel (eluent: hexane/methylene chloride from 4:1 to 3:1) to give the monoiodo compound **6** (0.35 g, yield 73%). $[\alpha]$= -54.6(C=0.5, $CHCl_3$).
11. Kelly, T. R.; Whiting, A.; Chandrakumar, N. S. *J. Am. Chem. Soc.* **1986**, *108*, 3510.
12. Cummins, C. H. *Tetrahedron Lett.* **1994**, *35*, 857.

(*Received in USA* 4 *April* 1996; *revised* 30 *April* 1996; *accepted* 2 *May* 1996)