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The aryl–aryl coupling reaction of 1-naphthol with $SnCl_4$ for 2,2′-binaphthol synthesis and its application to the biomimetic synthesis of binaphthoquinone isolated from *Plumbago zeylanica*

Iwao Okamoto, Hirohisa Doi, Eiichi Kotani and Tetsuya Takeya*

Showa Pharmaceutical University, 3-3165 Higashi-tamagawagakuen, Machida, Tokyo 194-8543, Japan

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Abstract—A simple method for the direct synthesis of 2,2′-binaphthols was developed, utilizing aryl–aryl coupling reaction via electron donor–acceptor complexes of 1-naphthols with $SnCl_4$. Heating of the complex in a sealed tube afforded the corresponding *o-o* coupling product in excellent yield. This method was utilized for a biomimetic synthesis of the binaphthoquinone, 3,3′-biplumbagin, isolated from *Plumbago zeylanica*. © 2001 Elsevier Science Ltd. All rights reserved.

The roots of the perennial herb *Plumbago zeylanica* (Plumbaginaceae) have long been used in a variety of medicinal applications in many Asian countries.[1] Several naphthoquinones have been isolated from this plant, including plumbagin (**1**), 3,3′-biplumbagin (**2**), elliptinone (**3**) and maritinone (**4**) (Fig. 1).[2] It is considered that the biogenetic pathway to the binaphthoquinones involves oxidative aryl–aryl coupling of 1-naphthols and subsequent oxidation of the resulting 2,2′-binaphthols.[3]

The oxidative aryl–aryl coupling reaction of naphthols and naphthol ethers is a useful reaction of fundamental importance in biomimetic or chemical synthesis of natural products and binaphthols used as chirality inducers.[4a,b] Although coupling reactions of 1-naphthols for preparation of 2,2′-binaphthols by means of chemical,[4c,d] electrolytic,[4e] thermal disproportionation[4f] and air oxidation[4g] reactions have been studied extensively, the numerous attempts usually showed poor selectivity and generated complex mixtures of dimeric, polymeric and quinonoid compounds. It is known that Lewis acids (inorganic acceptors) such as stannic chloride ($SnCl_4$; SC), form the corresponding σ-type[5] or π-type electron donor–acceptor (EDA) complexes [6] with some naphthoxy compounds (organic donors), and the complexes exhibit various colors. In addition, many studies on thermal and photochemical reactions via EDA complexes have been reported.[7] The EDA chemistry prompted us to devise a new method for 2,2′-binaphthol syntheses. We wish to report herein the aryl–aryl coupling reaction of 1-naphthols **5** via SC EDA complexes to afford 2,2′-binaphthols **6** and its application to the biomimetic synthesis of 3,3′-biplumbagin.

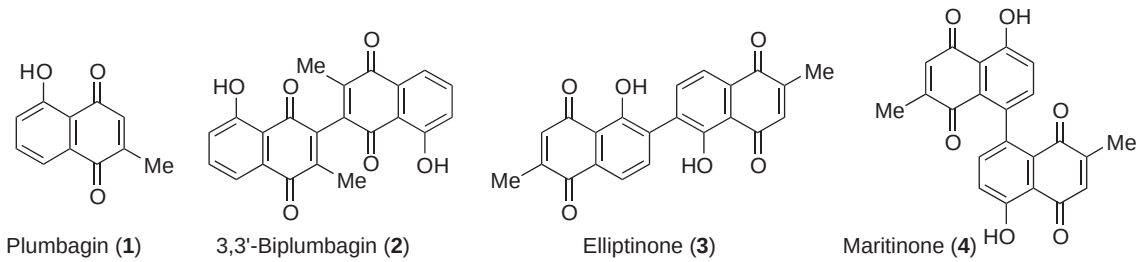

Figure 1.

Keywords: naphthalenes; coupling reactions; tin and compounds; biaryls.

* Corresponding author. Fax: +81-42-721-1579; e-mail: takeya@ac.shoyaku.ac.jp

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The reactions of 4,8-dimethoxynaphthols, **5a**[8a] and **5b**,[8b] which are intermediates for the synthesis of **2**, and the naphthol ethers **5c** and **5d** were examined and the results are shown in Table 1 and Scheme 1.

The addition of SC dissolved in the solvent to the solution of **5** immediately resulted in a yellow–green solution. This observation suggests the formation of the EDA complex of SC with each 1-naphthol **5**. Two new absorption bands were observed at 413 and 676 nm in the absorption spectra of the SC complex with **5a** in nitromethane.[5,6] The aryl–aryl coupling reaction of 1-naphthols **5** using SC did not proceed at room temperature, but the mixture changed into a deep-red colored solution with heating at 80–100°C, and the aryl–aryl coupling reactions proceeded. In the case of **5a**, the *o*-*o* coupled product **6a** was obtained in good yield at 80°C, and dehydrated dinaphthofuran **7a** was obtained at 100°C. The reaction can be carried out with SC in benzene, and the reaction in dichloromethane as the solvent gave an almost quantitative yield of the coupling product **6a**. The reaction of **5b** gave **6b** in excellent yield in nitromethane, but the yield was lower in dichloromethane. Both **5a** and **5b** reacted to give aryl–aryl coupled dimers. On the other hand, in the case of **5c** and **5d**, the corresponding naphthol ethers, the coupling product was not obtained under similar conditions, and entry 11 shows that prolonged reaction did not afford **6c** and gave **7a** in only 4% yield. These results show that the hydroxyl group in **5a**,**b** is important for the coupling reaction, in contrast with the previous report on the Scholl reaction.[9] We also used another Lewis acid and oxidant for the coupling reaction of **5a**. $TiCl_4$ in nitromethane gave the dinaphthofuran **7a**, and $AlCl_3$ in nitromethane gave a mixture of the coupling products in lower yield, while $AlCl_3$ in benzene or dichloromethane showed no reaction. Finally, the common oxidant Ag_2O in chloroform was used, but gave only a mixture of the coupling product and its oxidized quinone. These results shows that SC

Table 1. Aryl–aryl coupling reactions via the EDA complexes of 1-naphthols **5a**–**5d** with acceptor[a]

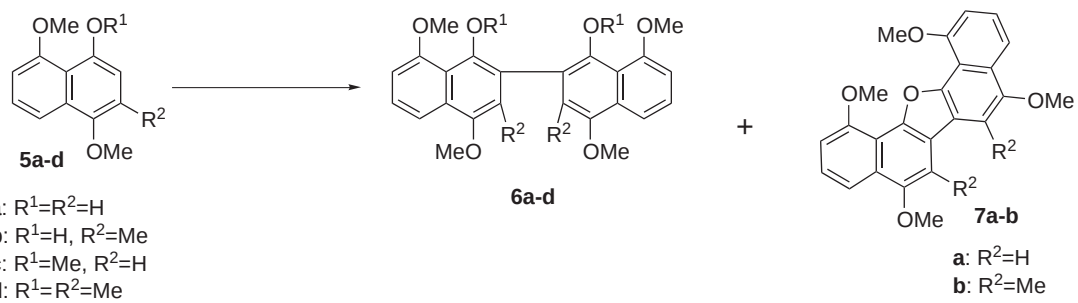
Entry	Substrate	Acceptor	Solvent	Temp. (°C)	R time (h)	Product (yield,[b] %)	Recovered **5** (%)
1	**5a**	–	CH_3NO_2	80	7	–	**5a** (100)
2	**5a**	–	CH_2Cl_2	100	24	–	**5a** (100)
3	**5a**	$SnCl_4$	CH_3NO_2	23	12	–	**5a** (100)
4	**5a**	$SnCl_4$	CH_3NO_2	80	1.5	**6a** (82)[c]	
5	**5a**	$SnCl_4$	CH_3NO_2	100	0.8	**7a** (60)[c]	
6	**5a**	$SnCl_4$	Benzene	100	24	**6a** (48), **7a** (4)	
7	**5a**	$SnCl_4$	CH_2Cl_2	100	24	**6a** (97)	
8	**5b**	$SnCl_4$	CH_3NO_2	100	6	**6b** (98)	
9	**5b**	$SnCl_4$	CH_2Cl_2	100	24	**6b** (12)	**5b** (74)
10	**5c**	$SnCl_4$	CH_2Cl_2	100	24	–	**5c** (84)
11	**5c**	$SnCl_4$	CH_2Cl_2	100	48	**7a** (4)	**5c** (77)
12	**5d**	$SnCl_4$	CH_2Cl_2	100	24	–	**5d** (97)
13	**5d**	$SnCl_4$	CH_2Cl_2	100	48	–	**5d** (93)
14	**5a**	$TiCl_4$	CH_3NO_2	100	0.5	**7a** (69)	
15	**5a**	$AlCl_3$	CH_3NO_2	100	24	**6a** (38), **7a** (17)	
16	**5a**	$AlCl_3$	Benzene	100	24	–	**5a** (100)
17	**5a**	$AlCl_3$	CH_2Cl_2	100	24	–	**5a** (83)
18	**5b**	Ag_2O	$CHCl_3$	23	0.5	**6b** (35[d])	

[a] General procedure: the acceptor (1.3 equiv.) was added to a solution of 1-naphthol **5** (1 mmol) in the solvent listed above (20 ml) and the mixture was stirred for 20 min at room temperature under normal laboratory light in an argon atmosphere. Then, the reaction mixture was heated in a sealed tube with stirring until disappearance of the 1-naphthol **5** except in the cases where the starting material was recovered. Similar results were obtained by carrying out the reactions in the dark.

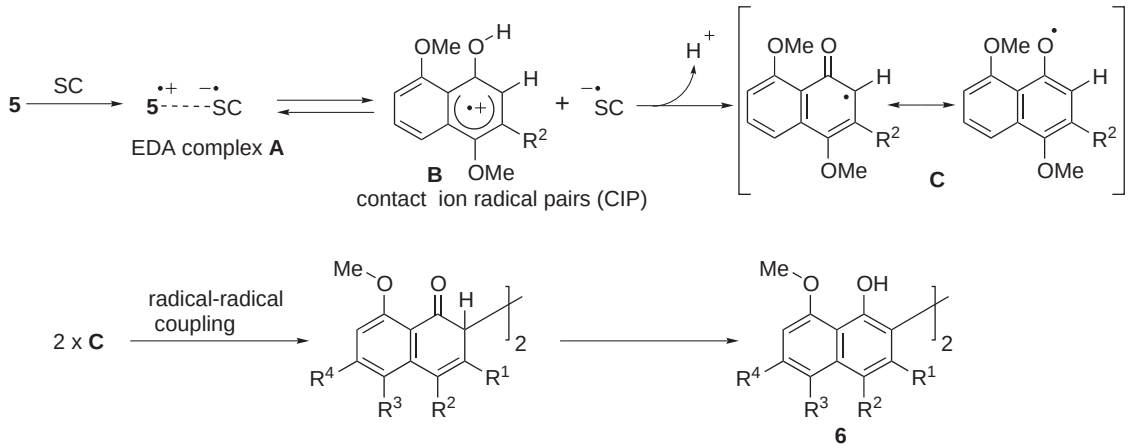
[b] All the yields recorded here are isolated yields.

[c] The structures of **6** and **7a** were elucidated by analyses of IR, ^1H and ^{13}C NMR spectra, with the aid of 2D NMR spectral analyses, and by transformation to the corresponding **2**.

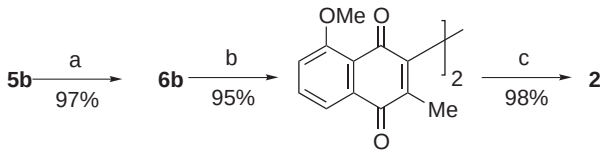
[d] The oxidized product, 5,5′-dimethoxy-2,2′-dimethyl-3,3′-bi-1,4-naphthoquinone, was obtained in 30% yield along with **6b** in 35% yield.



Scheme 1.



Scheme 2. Proposed mechanism for the formations of 2,2′-binaphthols **6**.



Scheme 3. Reagents: (a) $SnCl_4$ at 100°C in dichloromethane; (b) 65% HNO_3; (c) $MgBr_2 \cdot 6H_2O$.

or nitromethane can work as an electron acceptor or a dehydrogenation reagent in the aryl–aryl coupling reaction, and in non-oxidizing solvents such as dichloromethane or benzene, SC can work as both Lewis acid and oxidant.

A possible mechanism for the formation of **6** in the reaction of **5** with SC is as follows. It is unclear whether σ-type[5] or π-type[6] complexes were formed, but 1-naphthols **5** can form EDA complexes **A** with a 1:1 donor–acceptor ratio by the addition of SC, as shown in Scheme 2. Thermal dissociation of complex **A** into contact ion radical pairs of aryl radical cation **B** and stannic species is expected,[7] but the resulting radical cation itself does not seem to react because of the results listed in entries 10–13. Therefore, we suggest that deprotonation from **B** and the formation of the neutral radical **C** cause the coupling reaction to proceed in our system.

Finally, we have established a biomimetic synthesis of 3,3′-biplumbagin (**2**; mp 212–214°C) from the corresponding binaphthol **6b** through the reaction sequences mentioned (Scheme 3). Physical data for the synthetic compound **2** were identical with those of the natural product.[2]

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