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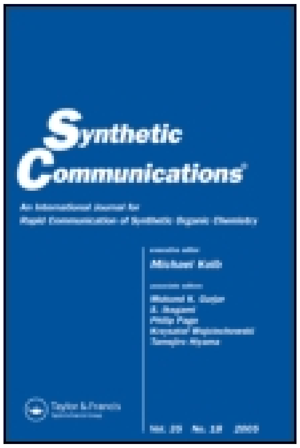

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A New and Efficient Method for the Synthesis of 2,2′-Dibromo-1,1′-binaphthyl Under Microwave Irradiation

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A New and Efficient Method for the Synthesis of 2,2′-Dibromo-1,1′-binaphthyl Under Microwave Irradiation

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ABSTRACT

A very simple and efficient method to prepare 2,2′-dibromo-1,1′-binaphthyl via two-step procedure from β-naphthol in good yield under microwave irradiation is described.

The most well-known example of an axially chiral ligand is the diphosphine, 2,2′-*bis*(diphenylphosphino)-1,1′-binaphthyl (BINAP), a C_2-symmetric triaryldiphosphine. The synthesis and first application of which were reported by Noyori and Takaya in 1980,[1] this ligand

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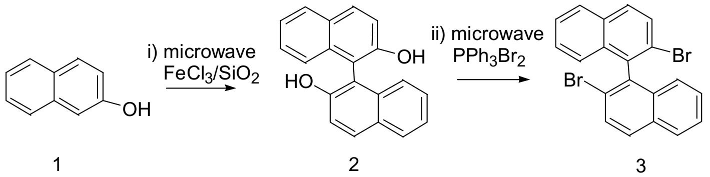
is very effective in inducing asymmetry by intra-complex steric interactions between the bulkyl triarylphosphine system and the reactants bound to the metal. Its application in asymmetric catalysis has been reviewed in 1990[2] and 1992[3] and subseqently its use has been well documented in numerous textbooks. Optically pure BINAP was obtained by stereospecific transformation of optically active 2,2′-dibromo-1,1′-binaphthyl. The phosphine is also synthesized by the optical resolution of (±) BINAP. The procedure is the best preparative-scale synthesis of both enantiomers of BINAP in an optically pure starting from accessible reacemic 2,2′-dibromo-1,1′-binaphthyl. We have been working in developing new synthetic methods for the preparation of substituted 2,2′-dibromo-1,1′-binaphthyl only using microwave irradiation from β-naphthol.

Excellent reviews have been published on various aspects of microwave-assisted chemistry.[4] These reviews were highlight microwave-assisted rapid organic transformating of particular importance in organic chemistry and pharmaceutical chemistry and discussed some of the most recently disclosed applications to medicinal and combinational chemistry.[5] Microwave technique has been widely used for many organic reactions, such as Diel–Alder, esterification, etherification, oxidation, hydrolysis, cyclization, claisen, Reformatsky, Knoevenagel, and Bischler Napieraski reactions.[6] Microwave irradiation produces efficient internal heating transfer (in situ heating), resulting in even heating throughout the sample, as compared with the wall heat-transfer that occurs under an oil bath is applied as an energy source.[7]

In this article, we reported a new, rapid, practical, and high-yielding method for the total preparation of 1,1′-binaphthalene-2,2′-diol (BINOL) and 2,2′-dibromo-1,1′-binaphthyl via microwave irradiation respectively (Sch. 1).

The classical approach to give 1,1′-binaphthalene-2,2′-diol (BINOL) relies on the oxidative coupling of β-naphthol. A number of mild oxidants have been reported to facilitate this reaction, in particular, Fe (III), Cu (II) salts.[8] BINOL also can be obtained by oxidative coupling



Scheme 1.

of 2-hydroxynaphthalane in the presence of transition metal complexes, such as $FeCl_3 \cdot 6H_2O$.[9] However, the classical methods need longer times and complexed work-up procedures. Carrying out reactions using microwave heating of β-naphthol and ferric chloride ($FeCl_3 \cdot 6H_2O$) under solvent-free conditions, has major advantages of shorter reaction times and afford the BINOL in more excellent yields. Although Villemin and Sanvaget[10] have reported that microwave irradiation acceleted greatly the addition of naphthol with $FeCl_3 \cdot 6H_2O$ without solvent, the results are difficult to reproduce when the reactions are conducted with small samples. In this report, we improved the method by the addition of silical gel. It has the advantages of facile work-up procedures, and the good results is easy to reproduce. The results for prepared the BINOL listed in Table 1. It is worth mentioning that in the absence of silica gel the yield is poor.

The 2,2′-dibromo-1,1′-binaphthyl is a useful and versatile building block for the synthesis of BINAP. It has been prepared by the reaction triphenylphosphinebromine complex with BINOL. However, the bromination reaction involves the use of high bath temperature (340°C) and long reaction times to obtain the 2,2′-dibromo-1,1′-binaphthyl in appropriate yields.[11] To our surprise, the use of microwave technology has not been decribed in relation to the type of bromination reaction. Using microwave irradiation, we obtain the title compound in good yield. Microwave irradiation by 10 min at 800 W of power of a mixtures of BINOL, triphosphine, and bromine yields over 50% of 2,2′-dibromo-1,1′-binaphthyl. At 800 W and an additional 10 min of irradiation, the

Table 1. Synthesis of BINOL under microwave irradiation.

Entry	Ratio of reagents[a]	Power (W)	Time (s)	Yield[c] (%)
1	1/2	200	60	70
		250	120	85
2	1/2.2	250	120	89
3	1/2.5	250	60	92
		200[b]	60	48
4	1/3	250	60	93
5	1/3.5	250	60	92
6	1/4	250	60	96

[a] The weight ratio of β-naphthol and ferric chloride ($FeCl_3 \cdot 6H_2O$).
[b] No silica gel.
[c] Isolated yield.

best yields increase to 60%. It is important that the last trace of acetonitrile is removed at a bath temperature of 200°C before microwave irradiation. From the results of a comparative study of the synthesis of the 2,2′-dibromo-1,1′-binaphthyl by the classical method and microwave irradiation, it is clear that the reaction time is reduced from several hours to only a few minutes by using microwave irradiation, indicating that microwaves plays an important role in the rate enhancement.

In conclusion, BINOL and 2,2′-dibromo-1,1′-binaphthyl promoted by microwave irradiation was a facile, high yield and rapid reaction with easy purification that could be as a path for synthesis of these title compounds.

EXPERIMENT

All commercially available regeant β-naphthol, ferric chloride ($FeCl_3 \cdot 6H_2O$), triphosphine, bromine, silica gel (200–300 mesh) were used as received from the suppliers. The acetonitrile was cautiously distilled from phophorus pentoxide. All of the products are known compounds and were identified by comparison of their spectral data (IR, ^{1}H NMR, ^{13}C NMR). Melting points were obtained in a modified Koffler apparatus and were uncorrected. Microwave assisted reactions were carried out using a Galanz microwave oven model WP800SL23 of variable radiofrequency.

1,1′-Binaphthalene-2,2′-diol (BINOL) (2). The premixed mixture of β-naphthol, ferric chloride ($FeCl_3 \cdot 6H_2O$), and silica gel (200–300 mesh) which was placed in a flask inside an modified household Galanz microwave oven for the specified time at the power of 200 W or 250 W (see Table 1). After the reaction mixture is cooled, the crude product was directly purified via flash chromatography, using acetone/petroleum ether as the eluting solvent, yielding the title compound BINOL in high yield. M.p. 217–218°C.

2,2′-Dibromo-1,1′-binaphthyl (3). A 250 mL three-necked, round-bottomed flask is equipped with an efficient mechanical stirrer, thermometer, and a droping funnel. The flask is charged with 24 g (91.5 mmol) of triphenylphosphine and 50 mL of dry acetonitrile. the solution is stirred and cooled in an ice bath and 15.5 g (5 mL, 96.9 mmol) of bromine is added dropwise over a period of 10 min. Then 12 g (42 mmol) of 1,1′-binaphthalene-2,2′-diol (BINOL) is added to the solution. The viscous slurry is stirred at 60°C for 30 min. After all the acetonitrile has been removed, the reaction was carried out in microwave oven and irradiation for the special time (10–20 min) at its full power of 800 W. On completion of the reaction, as determined by TLC (hexane:benzene, 4:1). The reaction mixture is added 100 mL Celite with stirring. The mixture is extracted with three 50 mL portions of a boiling 1:1 mixture of a benzene and hexane. The combined extracts are evaporated to give an orange-yellow viscous crude product. Recrystallization from ethanol affords the pure 2,2′-dibromo-1,1′-binaphthyl as yellow, fine crystals (10.4 g, 60% yield). M.p. 185°C (Lit.[11] M.p. 180°C).

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