Scientific Research and Essay Vol.4 (11), pp. 1201-1204, November, 2009
Available online at http://www.academicjournals.org/SRE
ISSN 1992-2248 © 2009 Academic Journals

Full Length Research Paper

A mechanochemical reaction for highly efficient preparation of 1, 1´-bi-2-naphthol from 2-naphthol

Keivan Shayesteh[1,2]*, Jafarsadegh Moghaddas[1], Mohammad Haghighi[1] and Gholamhasan Imanzadeh[3]

[1]Sahand University of Technology, Chemical Engineering Department, Tabriz, Iran.
[2]Chemical Engineering Group, the University of Mohaghegh Ardabili, Ardabil, Iran.
[3]Chemistry Group, the University of Mohaghegh Ardabili, Ardabil, Iran.

Accepted 31 August, 2009

In this paper, different mechanochemical methods for production of 1, 1´-Bi-2-naphthol from oxidative coupling 2-naphthol in presence of $FeCl_3$ were compared. The first were designed and a vibration mill as a new device for this reaction was manufactured. Our results were compared to the works of Toda et al. (1989) and Rasmussen et al. (1997) who reported other mechanochemical systems. It was found that our proposed method has a higher yielding with low reaction time. In our proposed device, there is a possibility to change the vibration frequency from 0 to 4000 rpm and the results of the effect of different frequencies on reaction progress were presented accordingly. This method was developed for the oxidative coupling of other phenols such as anthrone and 2,3-dihydroxy-1,4-naphthylene.

Key words: 1,1´-Bi-2-naphthol production, oxidative coupling of phenols, mechanochemical reaction, vibration mill.

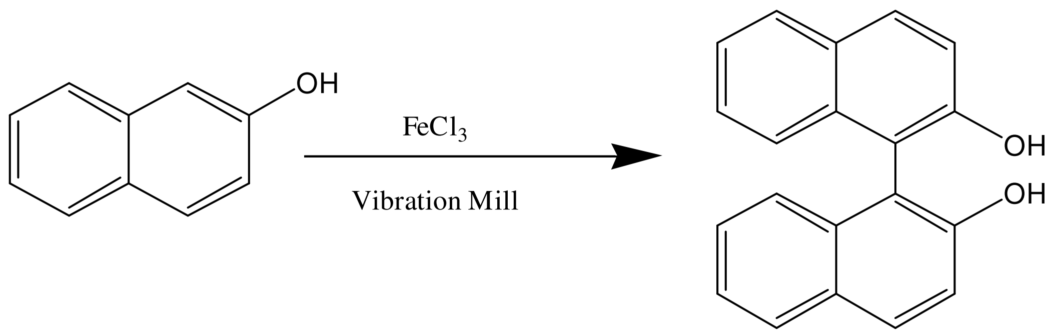
INTRODUCTION

Naphthols are used in making of dyes, pigments, fluorescent whiteners, tanning agents, especially in special medicines, antioxidants and antiseptics. Naphthol structure is found in transition-metal catalysts particularly in the form of 1,1´-bi-2-naphthol which is composed of two naphthol rings connected at one carbon site on each ring. Optically active 1,1´-bi-2-naphthol is widely used in asymmetric synthesis of rearrangements, epoxidations and reductions (Kelemen et al., 1982; Chen et al., 2001; Pandey, 2006; Noyori, 2002).

Mechanochemical processes use mechanical energy to activate substances by developing their structural changes. Solid state reactions can be classified as mechanochemical processes, if the reactants are vigorously mixed by external mechanical energy (Dybkov, 2002; Kaupp, 2009). Mechanical milling increases solid state reaction rates by generating clean and fresh surfaces, increasing defect density and reducing the size of particles (Sheibani et al., 2008; Bruckmann et al., 2008). In the simplest case, the reactions are done by grinding grinding of reactants using a mortar and pestle. Toda et al. (1989) studied the reaction of oxidative coupling 2-naphthol 1 by this method. Results indicated that reaction time and yield of reaction are 2 h and 95%, respectively (Toda et al., 1989). Ball mills are other methods that are used in solid state reactions, usually when a longer reaction time is required. Rasmussen et al. (1997) investigated this reaction using the ball mill. Their results indicated that the reaction time and yield were 1 h and 87%, respectively (Rasmussen et al., 1997; Rodriguez et al., 2007). In cases where higher energy is necessary, vibratory mill is more efficient (Krycer and Hersey, 1980). The special type of this mill is known as “High-Speed Vibration Mill" or “HSVM", the main parts of which consist of a stainless steel capsule and milling balls. These parts are rapidly vibrated at a speed of about 3000 rpm (Dachille and Roy, 1960).

So far there are not any reports in the literature on the oxidative coupling of 2-naphthol under the vibration mill. For this reason, herein, we report the mechanochemical oxidative coupling reaction of 2-Naphthol with $FeCl_3$ using the vibration mill in different frequencies (Scheme 1). The main difference between our proposed device and ball mill lies in their movement mechanism. Movement of ball mill is in rotational form while vibration mill moves in a

*Corresponding author. E-mail: K_shayesteh2000@yahoo.com. Fax: +984515512904.



1

2

Scheme 1. Oxidative coupling of 2-Naphthol in a vibration mill.

linear forward and backward direction. Rotational speed of ball mill should be limited to a certain amount at high speed because the centrifugal force of the ball is equal to its weight at that speed and hence it will stick to the wall of the ball mill. This speed of the ball mill causing this phenomenon is referred to as "critical speed". The operational speed is about 70% of critical speed (Walas, 1990). Based on the above reasons, we introduced a vibration mill for eliminating of the ball mill's problem. Consequently, we can conclude that the mechanical energy given to reactants from the balls in a vibration mill is higher than the ball mill.

Experimental

All chemical materials were purchased from Fluka Company. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were recorded on Bruker 400 Spectrospin. IR spectra were recorded on Buck-Scientific 500 instrument. The melting points were determined in open capillaries with a Stuart melting point apparatus and are uncorrected.

The vibration mill was made and optimized by the authors according to Figure 1. This device can work up to 4000 rpm equal to 70 Hz with the frequency being adjusted by an inverter. Digital Tachometer Nicety–TC802 was used for calibrating the number of vibration at a given frequency. The capsule with a diameter of 2 cm and a length of 5 cm and a ball with a diameter of 9 mm were made of non-abrasive stainless steel. The reaction takes place in the capsule.

General procedure

Synthesis of 1,1´-Bi-2-naphthol under the vibration mill

1.7 mmol of 2-naphthol and 3.4 mmol of $FeCl_3.6H_2O$ both in powder form were premixed together and then transferred into the reactor which was vigorously shaken by vibration mill for a designated time. After completion of the reaction that is monitored by TLC, the reaction mixture was quenched with dilute HCl and extracted with CH_2Cl_2. Then the solvent was removed under vacuum and the crude coupling product was crystallized from toluene. The structure of the product was characterized by comparing its melting point, ^{1}H NMR, ^{13}C NMR and IR spectra with the authentic compound.

Characterization of phenols

The synthesized 1,1´-bi-2-naphthol was characterized by melting point determination, Infrared and NMR studies. In addition, based on proposed procedure, oxidative coupling reactions of anthrone and 2, 3-dihydroxy-1, 4-naphthylene was investigated. Characterizations of these phenols are:

1,1´-bi-2-naphthol (2): mp. 214 - 211°C, lit. mp. 216 - 218°C (Rasmussen et al., 1997); IR (KBr, □cm^{-1}): 3492, 3417, 1591, 1508, 1496, 1384, 1318 and 1115. ^{1}H NMR (300 MHz, $CDCl_3$): 7.50 (d, J = 6.6 Hz, 1H), 7.42 (d, J = 6.6 Hz, 1H), 6.89 (m, 2H), 6.85 (m, 1H), 6.79 (s, 1H), 6.96 (d, J = 2.6 Hz, 1H), 4.60 (s, 1H) ^{13}C NMR ($CDCl_3$, 75 MHz), 151.11, 132.4, 130.4, 128.6, 127.4, 127.1, 123.2, 123.0, 116.7 and 109.8.

Bianthrone (4): Mp. 260 - 262°C, lit. mp. 256 - 260°C (Dabestani, 1995); IR (KBr, cm^{-1}): 3059, 2882, 1660, 1593, 1313, 1168 and 785. ^{1}H NMR (300 MHz, $CDCl_3$): 7.45 (dd, J = 2.7 Hz, J = 4.0 Hz, 2H), 6.93 (dd, J = 2.7, J = 4.0 Hz, 4H), 6.37 (dd, J = 5.2, J = 4.0 Hz, 2H), 4.27 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): 181.8, 138.8, 136.2, 133.9, 132.7, 131.2, 127.4, 126.8 and 125.5.

Bi (2,3-dihydroxy-1,4-naphthylene) (6): IR (KBr, cm^{-1}): 3387, 3059, 1691, 1514, 1344, 1241, 1156 and 851. ^{1}H NMR (300 MHz, d_6-DMSO): 10.99 (s, 1H), 8.39 (s, 1H), 7.64 (d, J = 5.6, 1H), 7.32 (s, 1H), 6.94 7.15 (m, 2H), 6.80 (d, J = 5.8, 1H).

RESULTS AND DISCUSSION

The effects of different vibration frequencies on the yield of 2-naphthol coupling reaction were studied. We found that the applied frequency of the vibration mill had a significant effect on the yield of this reaction. Based on the results of Table 1, it can be inferred that in frequencies lower than 20 Hz, the efficiency of this method is unfavorable, while by increasing the frequency, the rate of reaction are increased, therefore we can obtain 100% conversion in lower time.

These results encouraged us to investigate the oxida-

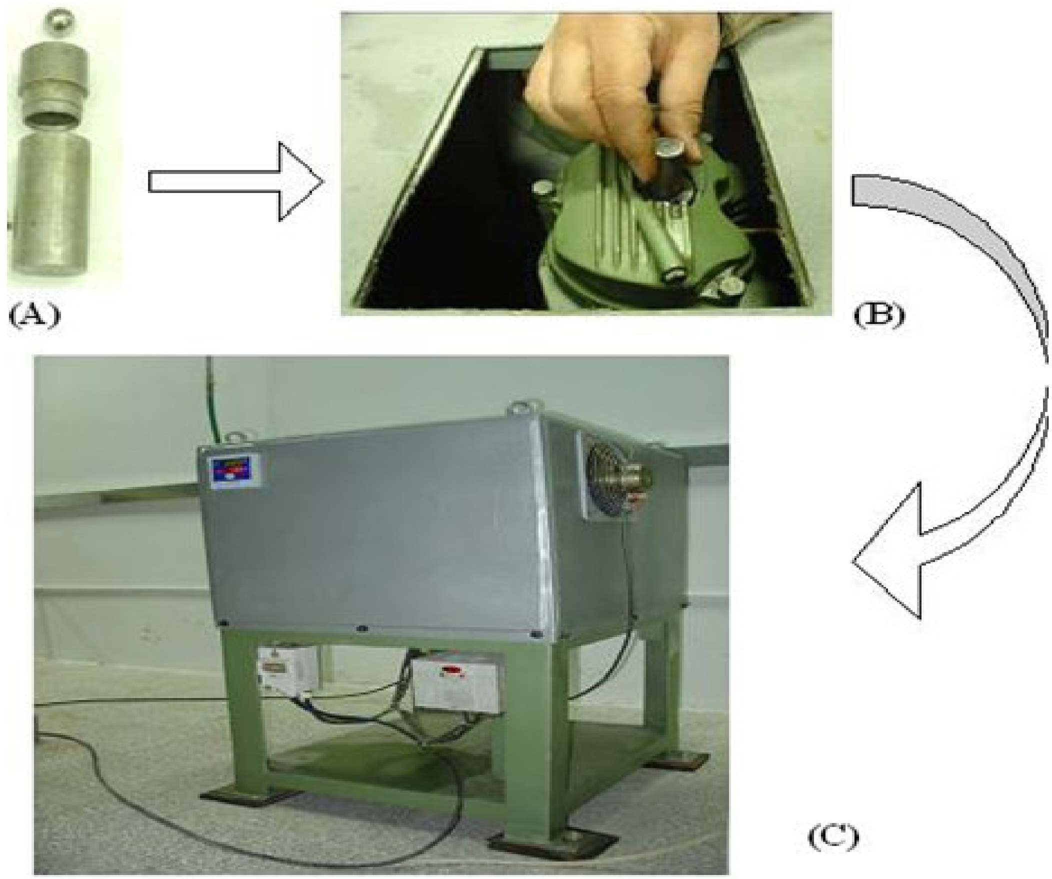


Figure 1. (a) Reaction chamber and ball, (b) Reactor holder, **(c)** Vibratory mill device.

Table 1. Effect of vibration frequencies on rate and reaction yield of coupling reaction of 2-naphthol.

Frequency(Hz)	10	15	20	30	50	60	70
Reaction time(min)	60	60	30	12	8	7	7
Conversion (%)[a]	Less than 10	30	100	100	100	100	100

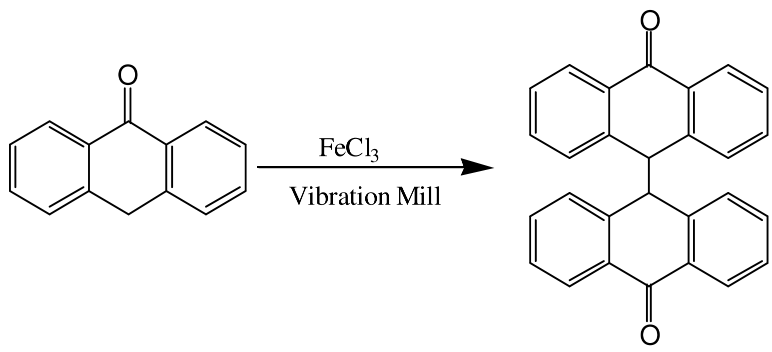
[a]Conversion of 2-naphthol. The 2-naphthol and $FeCl_3$-$6H_2O$ were used at a molar ratio of 1:2, respectively at room temperature. The total weight of the reactants was 1.19 gr.

tive coupling of anthrone 3 and 2, 3-dihydroxynaththalene 5 to corresponding products under the same reaction conditions. When a fine powdered of compound 3 and $FeCl_3$-$6H_2O$ at a molar ratio of 1:2 was vigorously shaken by the vibration mill at 30 Hz for 20 min, the oxidative coupling product 4 was obtained in 90% isolated yield (Scheme 2).

We also repeated this reaction on compound 5 under the same conditions, that surprisingly, bi (2, 3-dihydroxy-1, 4-naphthylene) 6 was obtained from oxidative coupling of 2, 3-dihydroxy-1, 4-naphthylene 5 after 15 min. The product 6 with 94% isolated yield was prepared (Scheme 3).

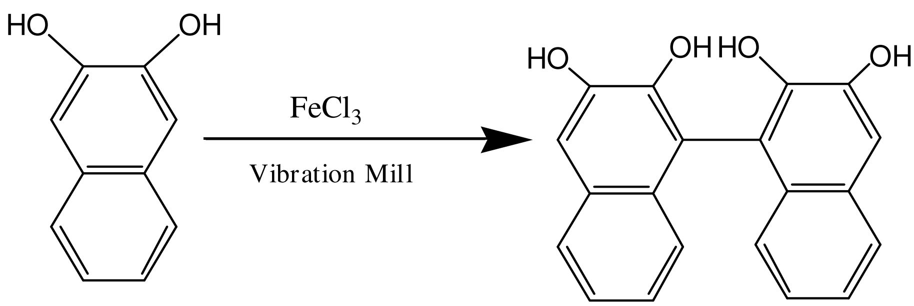
Conclusion

In this work, we designed and manufactured a vibration mill as a new device for oxidative coupling reaction of 2-naphthol by $FeCl_3.6H_2O$ in solid state. The importance of vibration method is the completion of reaction in lower reaction time. The needed time to consume all of 2-naphthol in both Toda et al. (1989) and Rasmussen et al. (1997) methods is equal to two and one hour, respectively, while we obtained 100% conversion in 12 min on operation condition of 30 Hz. According to Table 1, we even obtained a conversion of 100% at less than 12 min. This study indicated that the vibration mill method has a



3 4

Scheme 2. Oxidative coupling of anthrone in a vibration mill at 30 Hz.



5 6

Scheme 3. Oxidative coupling of 2, 3-dihydroxy-1, 4-naphthylene in a vibration mill at 30 Hz.

better performance in comparison to other commonly used methods such as ball mill and mortar and pestle. This is due to higher mechanical energy given to reactants by vibration mill as was mentioned earlier. Thismethod was developed for the oxidative coupling of other phenols such as anthrone and 2,3-dihydroxy-1,4-nap-hthylene. We believe that the vibration mill increases solid state reaction rates by generating clean and fresh surfaces and reducing the size and increasing the surface area of particles.

REFERENCES

Bruckmann A, Krebs A, Bolm C (2008). Organocatalytic reactions: effects of ball milling, microwave and ultrasound irradiation. Green Chem. 10: 1131-1141.

Chen R, Qian C, Vries JG (2001). Asymmetric epoxidation of α,β-unsaturated ketones catalyzed by chiral ytterbium complexes. Tetrahedron Lett. 42: 6919-6921.

Dabestani R, Ellis K J, Sigman ME (1995). Photodecomposition of anthracene on dry surfaces: products and mechanisms. J. Photochem. Photobiol., A. 86: 231-239.

Dachille F, Roy R (1960). High-pressure Phase Transformations in Laboratory Mechanical Mixers and Mortars. Nature. 186: 34-71.

Dybkov VL (2002). Reaction Diffusion and Solid State Chemical Kinetics. Ipms Publications, Kyiv.

Kaupp G (2009). Mechanochemistry: the varied applications of mechanical bond-breaking. Cryst. Eng. Comm. 11: 388-403.

Kelemen J, Moss S, Sauter H, Winkler T (1982). Azo—hydrazone tautomerism in azo dyes. II. Raman, NMR and mass spectrometric investigations of 1-phenylazo-2-naphthylamine and 1-phenylazo-2-naphthol derivatives. Dyes Pigm. 3: 27-47.

Krycer I, Hersey JA (1980). A comparative study of comminution in rotary and vibratory ball mills. Powder Technol. 27: 137-141.

Noyori R (2002). Asymmetric Catalysis: Science and Opportunities, Nobel Lecture. Angew. Chem., Int. Ed. Engl. 41: 2008-2022.

Pandey SK (2006). BINOL: A Versatile Chiral Reagent. Synlett. 19: 3366-3367.

Rasmussen MO, Axelsson O, Tanner D (1997). A Practical Procedure for the Solid- Phase Synthesis of Racemic 2, 2´-Dihydroxy- 1, 1´-Binaphthyl. Synth. Commun. 27: 4027-4030.

Rodriguez B, Bruckmann A, Rantanen T, Bolm C (2007). Solvent-Free Carbon-Carbon Bond Formations in Ball Mills. Adv. Synth. Catal. 349: 2213-223.

Sheibani S, Ataie A, Heshmati-Manesh S (2008). Kinetics Analysis of Mechano-chemically and Thermally Synthesized Cu by Johnson–Mehl–Avrami Model. J. Alloys Compd. 1: 447-453.

Toda F, Tanaka K, Iwata S (1989). Oxidative Coupling Reactions of Phenols with $FeCl_3$ in the Solid State. J. Org. Chem. 54: 3007-3009.

Walas SM (1990). Chemical Process Equipment: Selection and Design. Butterworth- Heinemann, Boston.