Green synthesis, Characterization of Derivatives of 1, 1'-binaphthalene]-2, 2'-diol

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Abstract

BINOL (1, 1'-bi-2-naphthol) is used as a chiral ligand for many asymmetric reactions. In this a green chemistry approach was used for the preparation of BINOL by the oxidative coupling of 2-naphthol using Cu-Montmorillonite, a green material. Results obtained were compared with conventional method i.e., the $FeCl_3$ catalyzed oxidative coupling of 2-naphthol. The physical characterization includes % yield, M.P., etc, parameters were measure for newly synthesized derivative were characterized by FTIR and ^{1}HNMR ^{13}CNMR, XRD etc spectral methods and bioactivity of the newly synthesized derivatives will studied.

***Keywords*:** BINOL, oxidative coupling, 2-naphthol, Cu- Montmorillonite.

Introduction:

Green Chemistry is defined as invention, design, development and application of chemical products and processes to reduce or to eliminate the use and generation of substances hazardous to human health and environment. Prime focus for chemists now is to develop synthetic methods that are less polluting i.e., to design green chemical transformation. The chemical process should be such that it doesn't cause permanent damage to the environment. Therefore ways to minimize the damage caused by raw materials and process should be done. Though it is expensive but it leads to environment friendly condition. Natural aluminosilicates like clays and zeolites are solid acids that are used to substitute liquid acids in chemical transformation. (Gates 2003) Among these clays and modified clays are gaining interest due to their versatile properties.(Balogh and Laszlo, 1993; Benesi and Winquest, 1978; Theng, 1974; Vaccari, 1999) The most common modified clays applied in organic synthesis are K-10 and KSF montmorillonites. Their physicochemical properties are sameas that of the natural clays but their BET surface areas are different. Developments of clay catalyzed reactions are important in green chemistry point of view and they produce less hazardous waste products. Clay minerals as such or after modification/treatment can be used are solid acid catalyst. It exhibits both Bronsted as well as Lewis acidity, hence finds application in a wide range of organic transformations. (Cativiela et al. 1993; Cseri et al., 1995).Montmorillonite (MMT) having chemical formula$Al_2Ci_4O_{10}(OH)_2nH_2O$ and have variable moisture content. The crystalline structure of MMT consists of multiple layers and each layer made up of one octahedral alumina sheet sandwiched between two tetrahedral silica sheets1, 1'-bi-2-naphthol (BINOL) has become an important chiral auxiliary for asymmetric synthesis and due to its high degree of utility various synthetic approaches have been developed. Generally for BINOL synthesis transition metals have been used as catalysts or oxidants. For the transition metal-catalyzed and promoted reactions, the most frequently employed

metals are Fe (III) and Cu (II), though oxidations utilizing Mn (III), Ti (IV) and (V) have also been reported. There have been some known methods for the oxidative coupling of 2-naphthols using

$FeCl_3$, $K_3Fe(CN)_6$, $Mn(AcAc)_3$, $CuCl(OH)$, $CuSO_4(Al_2O_3)$ and Cu(II) - amine complexes as coupling reagents. In addition to solution-phase oxidation with $FeCl_3$ and Cu (II)/amine complexes, a number of metal complexes have been immobilized on solid supports for use in this reaction. Although such supported reagents offer some advantages with regard to ease of isolation of products, typically high volumes of organic solvents have been used for this oxidation reaction. (Between 10–20mL of either xylene or chlorobenzene per millimole of 2- naphthol), which are not at all a green chemistry approach. Solvent less systems have also been reported, one of them is preparation of BINOL by heating of a powdered mixture of $FeCl_3$ and 2-naphthol both with and without microwave irradiation.

Experimental

A mixture of 2-naphthol (2.88 g) and iron (III) chloride (0.7 g) with 2 drops of water in an agate (or porcelain) mortar pestle was grinded for about 20minutes. The mixture was allowed to stand for about 2 hrs with a little grinding now and then. The mixture was transferred with water (40 ml) into a 100 ml beaker and boiled for 10-15 minutes. The mixture was cooled and the solid was filtered, washed with boiling water (10 ml), dried and recrystallized from toluene. m.p. 214-217 ^oC. In the present work a mechanical method, grinding, melt of 2-naphthol with copper montmorillonite clay was attempted for the coupling reaction. Result obtained was also compared with the product formed by the procedure suggested elsewhere .Cu-Montmorillonite was prepared by slurring montmorillonite clay (1.5g) with 0.5M aqueous solution of $Cu(CH_3CO_2)_2$ at room temperature and stirred for 2hrs. It was left overnight and then filtered and washed with water. It was dried in oven for 2hrs and solid yellow colored Cu- montmorillonite clay was obtained.2-naphthol and Cu-montmorillonite clay was heated separately till molten state obtained. It was then grinded together in molten state. 1,1'-bi-2-naphthol was obtained. It has been checked with thin layer chromatography (TLC) with the authenticated BINOL prepared and its melting point.

2.1 Synthesis of 1, 1'-binaphthalene]-2, 2'-diyl diacetate (II)

1,1'-binaphthalene]-2,2'-diol mixed with the pinch of zinc dust and 5 ml of acetic acid heated strongly for the period of 1 Hr. in the round bottom flask yielded the 1,1'-binaphthalene]-2,2'-diyl diacetate (II) which is recrystallized by suing redistilled ethyl alcohol. The product II dried and conversion monitored by TLC technique. The yield of product found to be 83%.

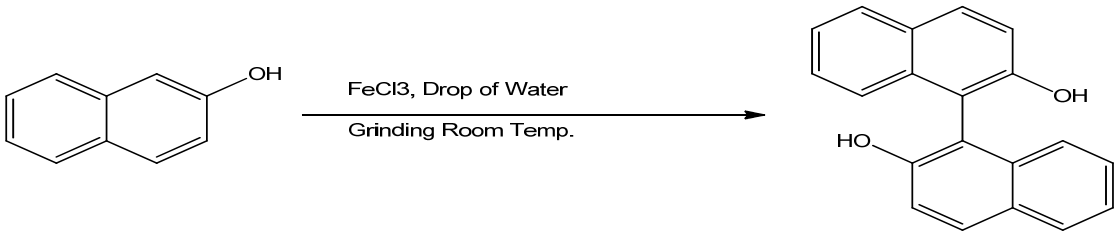
2.2 Synthesis of 2, 2'-bis ((phenyldiazenyl) oxy)-1, 1'-binaphthaleneIII)

The extra pure 1,1'-binaphthalene]-2,2'-diol coupled benzyldiazonium chloride in a slightly acidic medium and heated strongly for the period of 2 Hrs.in the round bottom flask using water condenser to yielded the 2,2'-bis((phenyldiazenyl)oxy)-1,1'-binaphthalene (III) .This is then recrystallized by suing redistilled ethyl alcohol. The product III dried and conversion monitored by TLC technique. The yield of product found to be 8o%.

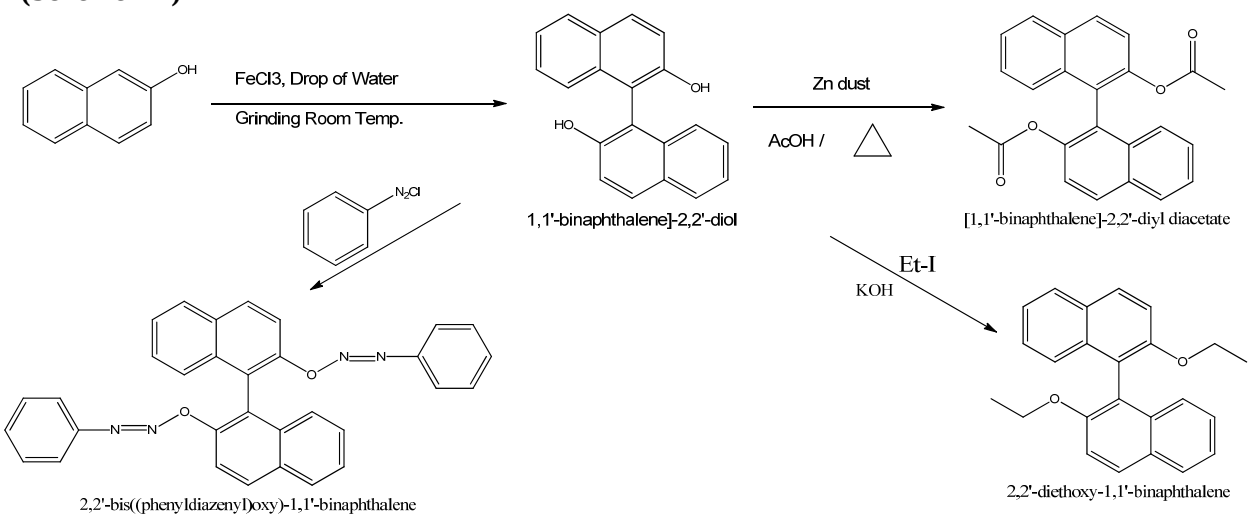
2.3 Synthesis of 2, 2'-diethoxy-1, 1'-binaphthalene (IV)

The extra pure 1,1'-binaphthalene]-2,2'-diol(I) is mixed with ethyl iodide with few Drops of alkaline KOH medium and heated strongly for the period of about 2 Hrs. in the round bottom flask using water condenser to yielded the Synthesis of 2,2'-diethoxy-1,1'-binaphthalene (IV) .This is then recrystallized by suing redistilled ethyl alcohol. The product IV dried and conversion monitored by TLC technique. The yield of product found to be 8o%.

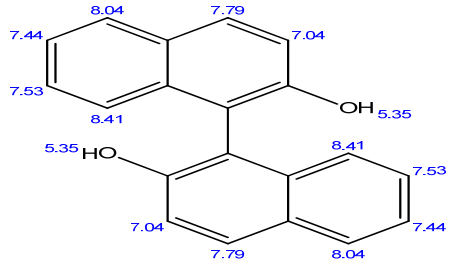
(Scheme –I)



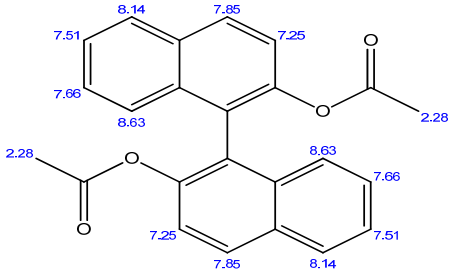
(Scheme –II)



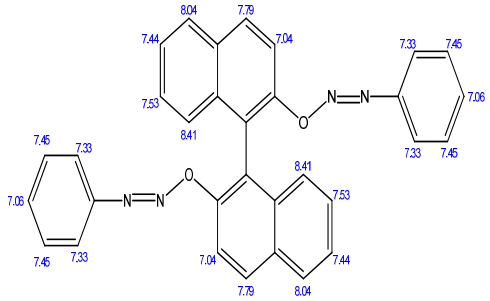
Characterization^{1}*HNMR*



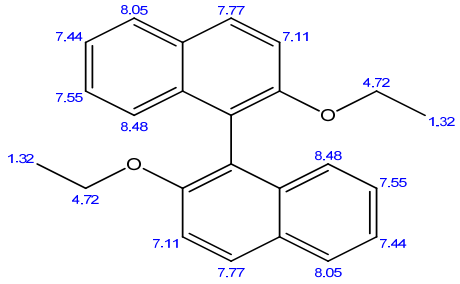
I (1, 1'-binaphthalene]-2, 2'-diol)



II (1, 1'-binaphthalene]-2, 2'-diyl diacetate)



III (2, 2'-bis ((phenyldiazenyl) oxy)-1, 1'-binaphthalene)



IV (2, 2'-diethoxy-1, 1'-binaphthalene)

Results and Discussion

The diffractograms of reaction mixture Cu- montmorillonite clay and 2-naphthol showed similar pattern with that of $FeCl_3$ and 2-naphthol, indicating similar nature of reaction products. Results from the FTIR

showed an appearance of peaks in the Cu-montmorillonite and 2-naphthol around 3300 cm^{-1} similar to that of 2-naphthol and $FeCl_3$ reaction mixture, which were very much different from the FTIR spectra of Cu-montmorillonite. This indicated similarity of reaction products. The product was also compared with the BINOL prepared from standard reflux method with the FTIR spectra. The yield of reaction is 3g about 90% efficient method easily available catalyst Reaction is performed with simple grinding at room temperature without any solvent Work up of the reaction involves aqueous medium. The newly synthesized compound I, II, III, and IV will be characterized with different spectral methods like 13CMR, XRD etc and their bioactivity study is under process. Literature survey show large numbers of bioactivity of the binol and its derivatives functions like *endo* and *ecto* parasiticide. It could be concluded from the compound obtained by green synthesis were characterized by FTIR and ^{1}HNMR^{13}CNMR, XRD etc spectral methods. It is better to prevent waste than to treat or clean up waste after it is formed. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. Substances and the forms of the substance used in chemical reaction should be chosen so as to minimize the potential of chemical accidents, including releases, explosions, and fires. Wherever practicable, synthetic methodologies should be designed to use and generate substances that posses little or no toxicity to human health and the environment. The use of auxiliary substances (e.g. solvents, separation agents *etc*.) should be made unnecessary wherever possible and, innocuous when use Chemical products should be designed to preserve efficacy of function while reducing toxicity. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure. Unnecessary derivatization (blocking group, protection/deportation, and temporary modification of physical/chemical processes) should be avoided whenever possible. A raw material feedstock should be renewable rather than depleting whenever technically and economically practical. Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances. Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into innocuous degradation product.

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References

[1] A. I. Vogel, *Textbook of Practical Organic Chemistry,* Fifth Edition, 1989 York, 1968, 39-41.
[2] Rosini, C.; Franzini, L.; Raffaelli, A.; Salvadori, P. Synthesis and Applications of Binaphthylic C2-Symmetry Derivatives as Chiral Auxiliaries in Enantioselective Reactions. Synthesis 1992, 503.
[3] Holy, P.; Belohradsky, M.; Zavada, J. A Novel One-Pot Conversion of2-Naphthols into 1,10-Binaphthalene-2,20-diols. Synth.Commun.1996,26, 2597.
[4] Dewar, M.J.S.; Nakaya, T. Oxidative Coupling of Phenols. J. Am.Chem. Soc. 1968, 90, 7134.
[5] Doussot, J.; Guy, A.; Ferroud, C. Selective Synthesis of 1,10- Binaphthalene Derivatives by Oxidative Coupling with TiCl4. Tetrahedron Lett.2000, 41, 2545.
[6] Hwang, D.-R.; Chen, C.-P.; Uang, B.-J. Aerobic Catalytic OxidativeCoupling of 2-naphthols and Phenols by VO(acac)2. Chem. Commun.1999, 1207.

[7] Deussen, H.-J.; Frederiksen, P.; Bjørnholm, T.; Bechgaard, K. AFacile Large Scale Preparation of Racemic 2,20-Dihydroxy- 1,10-binaphthyl. Org. Prep. Proced.Int. 1996, 28, 484.

[8] (a)Smrcina, M.; Polakova, J.; Vyskocil, S.; Kocovsky, P. Synthesis ofEnantiomerically Pure Binaphthyl Derivatives. Mechanism of theEnantioselective, Oxidative Coupling of Naphthols and Designing aCatalytic Cycle.J. Org. Chem. 1993, 58, 4534; (b) Noji, M.;Nakajima, M.; Koga, K. A New Catalytic System for AerobicOxidative Coupling of 2-Naphthol Derivatives by the Use of CuCl-Amine Complex: A Practical Synthesis of Binaphthol Derivatives.Tetrahedron Lett. 1994, 35, 7983; (c) Nakajima, M.; Miyoshi, I.;Kanayama, K.; Hashimoto, S.; Noji, M.; Koga, K. Enantioselective

[9] Synthesis of Binaphthol Derivatives by Oxidative Coupling of NaphtholDerivatives Catalyzed by Chiral Diamine-Copper Complexes. J. Org.Chem. 1999, 64, 2264.

[10] Li, T.-S.; Duan, H.-Y.; Li, B.-Z.; Tewari, B.; Li, S.-H. Novel OxidativeCoupling of 2-naphthols to 1,10-bi-2-naphthols Catalyzed by SolidLewis Acids using Atmospheric Oxygen as Oxidant. J. Chem. Soc.Perkin Trans. 1 1999, 291.

[11] Sakamoto, T.; Yonehara, H.; Pac, C. Efficient Oxidative Coupling of2-Naphthols Catalyzed by Alumina-Supported Copper(II) Sulfate UsingDioxygen as Oxidant. J. Org. Chem. 1994, 59, 6859; (b) Sakamoto, T.;Yonehara, H.; Pac, C. Catalytic

[12] Activities of CuSO4/Al2O3 inDehydrogenation of Arenes by Dioxygen.J. Org. Chem. 1997, 62, 3194.

[13] Armengol, E.; Corma, A.; Garcia, H.; Primo, J. A Highly SelectiveSynthesis of 1,10-Bi-2-naphthol by Oxidative Coupling of Naphthol on2072 LOVE AND BILLSDownloaded by [Moskow State UnivBibliote] at 10:10 05 February 2014Mesoporous Fe, Cu/MCM-41 Aluminosilicates. Eur. J. Org. Chem.1999, 1915.

[14] Nakajima, M.; Hashimoto, S.; Noji, M.; Koga, K. Aerobic OxidativeCoupling of 2-Naphthol Derivatives Catalyzed by a Copper-AmineComplex without Solvent. Chem. Pharm. Bull. 1998, 46, 1814.

[15] Villmin, D.; Sauvaget, F. Dry Synthesis Under Microwave Irradiation:A Rapid and Efficient Coupling of Naphthols. Synlett 1994, 435.

[16] Comprehensive Practical Organic Chemistry, V K Ahluwalia, Renu Aggarwal. Pg-48.