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ONE POT SYNTHESIS OF HIGHLY FUNCTIONALIZED TETRAHYDROPYRIDINES UTILIZING NANO-TICL2/ CELLULOSE AS BIODEGRADABLE AS WELL AS ECO-FRIENDLY CATALYST

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ABSTRACT:

Nano-TiCl2/cellulose was used as an efficient and biodegradable Lewis acid catalyst for the synthesis of highly functionalized tetrahydropyridines by one-pot multi component reactions of amines and aldehydes with β-ketoester. The catalyst was prepared via reaction of nano-cellulose and TiCl4 and characterized by Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), powder X-ray diffraction (XRD), energy dispersive X-ray spectroscopy (EDX), X-ray fluorescence techniques (XRF) and transmission electron microscopy (TEM). Simple methodology, eco-friendly catalyst, clean procedure, easy work-up and high yields are some of the important advantages of this protocol.

***Keywords*: NMR, PPI, FT-IR, Morphology, propylene.**

1. INTRODUCTION:

Tetrahydropyridines (THPs) and their derivatives have potent pharmaceutical properties as antiemetic and antipsychotic agents, anticance and antimalarial. THPs have been used as drugs in the treatment of diseases such as alzheimer (GTS-21) and central nervous system (CNS) disorders (RO-10-5824). Alkyl-1-aryl4-(arylamino)-2,6-di-aryl-1,2,5,6-tetrahydro-pyridine-3-carboxylates are some important densely substituted tetrahydropyridines. These compounds are synthesized via one-pot reaction of p-substituted anilines, p-substituted aldehydes and alkyl acetoacetate. Recently, these compounds have been synthesized in the presence of InCl3, BDMS, L-proline/TFA, TBATB, I2, CAN, ZrOCl2·8H2O, ZrCl4, p-TsOH·H2O, Fe(NO3)3·9H2O, FeCl3/SiO2, amberlite IRA400-Cl resin/I2/KI, HOAc, BF3.SiO2, nano-silica sulfuric acid, NiFe2O4@SiO2 and BF3 [4]. Considering the new trends of science and technology towards using natural materials such as cellulose, the research efforts on green and eco-friendly methods have become popular and desirable. Cellulose is one of the most abundant natural carbon based biopolymers containing free OH groups with nucleophilic character. Cotton is a natural, cheap and readily available source of cellulose. In this work,

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we have investigated preparation of nano-cellulose from cotton and synthesis of nano-TiCl2/cellulose by bonding TiCl4 to OH groups of D-glucose units in nano-cellulose. Herein, we introduce nano-TiCl2/cellulose as a new, biodegradable, inexpensive and eco-friendly bio-based catalyst for the synthesis of alkyl-1-aryl-4-(arylamino)-2,6-di-aryl-1,2,5,6-tetrahydropyridine-3-carboxylates.

2. RELATED STUDY:

All compounds were purchased from Merck chemical company and used without any additional purification. A refrigerated centrifuge (Appendorf Centrifuge 5417R) was used for preparation of nano-cellulose. FT-IR spectra were run on a Bruker, Equinox 55 spectrometer. A Bruker (DRX400 Avance) NMR was used to record the 1H NMR and 13C NMR spectra. Melting points were determined by a Buchi melting point B-540 B.V.CHI apparatus and were uncorrected. X-ray diffraction pattern was obtained by PAN alytical X'Pert Pro MPD, powered by a Philips PW3040/60 X-ray generator and fitted with an X'Celerator detector and a Cu Kα anode (λ = 1.5418 Å) in the 2θ range from 5-80°. Field emission scanning electron microscopy (FESEM) was obtained on a Mira 3-XMU. Elemental analysis were performed using Costech ECS 4010 CHNS-O analyzer. Quantitative elemental information (EDS) of nanoTiCl2/cellulose was measured by EDS instrument, Phenom pro X. Optical rotation was determined by OGAW Polarimeter (OSK 7822). XRF analysis was carried out using BRUKER, S4 EXPLORER instrument.

Preparation of nano-cellulose from cotton. Cotton fibers were washed with distilled water several times and dried in an air-circulated oven at 100 ± 2 °C until constant weight. Then, they were chopped to an approximate length of 5-10 mm. The fibers were then treated with a 17.5 w/v NaOH solution at 100 °C for 12 h under mechanical stirring. This treatment allowed purifying cellulose by removing other constituents like lignin, hemicellulose, wax, organic acids, etc. present in the fibres. Subsequently, fibres were filtered and washed with distilled water until the alkali was completely eliminated. It was then bleached with 100 ml of 1:1 dilution of 3.5% w/v sodium hypochlorite solution at 80 °C for 3 h under mechanical stirring. The resulting alpha cellulose was hydrolyzed partially using 65% sulfuric acid aqueous solution with a cotton-to-acid weight ratio of 1-10 at 45 ℃. After 1 h, the obtained suspension was diluted with water five-fold to stop the hydrolysis reaction. The suspension was centrifuged at 12,000 rpm to separate nano-cellulose from acid solution. Washing with water and centrifuging were repeated four to five times to remove any remaining free acid.

3. PROPOSED METHODOLOGY:

In a well-ventilated system, TiCl4 (5 ml) was added dropwise to the mixture of nano-cellulose (5 g) in chloroform (20 ml). The mixture was stirred for one hour at room temperature. The resulted suspension was

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filtered, washed with chloroform and dried at room temperature. General Procedure for Synthesis of THPs Firstly, a mixture of para-substituted anilines (2 mmol) and ethyl acetoacetate (1 mmol) was heated while stirring at 80 °C for 30 min in the presence of nano-TiCl2/cellulose (0.03 g). Then, the para-substituted benzaldehyde (2 mmol) was added and the final mixture was heated at 80 °C. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was dissolved into hot ethanol and filtered off for separation of catalyst. By adding water to filtrate, the product was appeared as a pure solid in high yields.

The particle size of nano-cellulose and nanoTiCl2/cellulose were investigated by field emission scanning electron microscopy (FESEM) and transmission electron microscopey (TEM) in which the dimensions of catalyst was achieved below 50 nm (Fig. 1). Comparison of nano-TiCl2/cellulose with nanocellulose and TiCl4 was achieved by FT-IR spectra (Fig. 2). C-O-Ti stretching band is appeared in 828 cm-1 in FT-IR spectrum of nano-TiCl2/cellulose. Presence of Ti and Cl in catalyst was approved by EDS analysis data (Fig. 3). The percentage of Ti and Cl in TiCl4 are 25.24 and 74.76, respectively. Thus, the amounts of Ti and Cl in EDS data (Ti: 20.3%, Cl: 14.9%) showed the absence of any no reacted TiCl4 in catalyst. So, XRF analysis of nano-TiCl2/cellulose was performed to determine its elemental component. To obtain the Ti:Cl ratio in nano-TiCl2/cellulose using XRF analysis, Killo Counts Per Seconds (KCPS) values of elements in catalyst were compared with KCPS values of the same elements in pure samples, NaCl and TiO2. Through this comparison, the amounts of Ti and Cl were obtained 12.02 g (0.25 mol) and 14.3 g (0.4 mol), respectively. Thus, the ratio of Ti:Cl in catalyst is approximately 1:2. The X-ray diffraction (XRD) patterns of nanoTiCl2/cellulose and nano-cellulose are compared in Figure. According to this comparison, signals in 2Θ, 20.55 and 34.63, can prove the bonding of Ti to cellulose backbone. According to the above mentioned data, we have proposed a structure for nano-TiCl2/cellulose (Fig). This catalyst does not need special precautions for preparation, handling or storage, and can be stored at an ambient temperature for months without losing its catalytic activity. In continuation of our efforts about application of the supported Lewis acids in organic synthesis, we have used nano-TiCl2/cellulose for preparation of highly functionalized tetrahydropyridines.

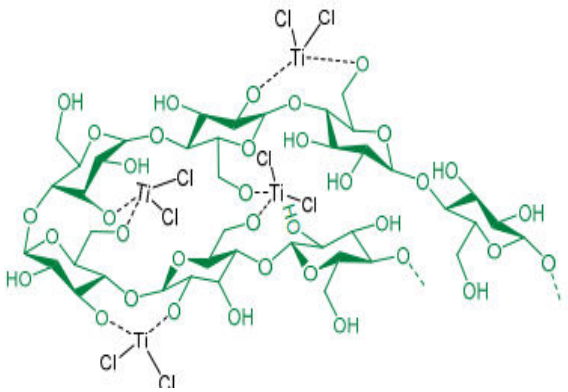

Fig.3.1. Proposed structure of TiCl4/nano-cellulose.

5. CONCLUSION:

We have developed a simple and efficient method for the synthesis of highly substituted tetrahydropyridines by one-pot multi-component reactions under solvent-free conditions using nano-TiCl2/cellulose as a green, cheap and biodegradable solid acid catalyst. Environmentally benign conditions, clean synthesis, easy work-up, high yields, solvent-free condition and medium reusability of catalyst are some advantages of this novel methodology.

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