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Synthesis of 1, 4-Dihydropyridine Derivatives using Fe [(L)proline]$_2$ as Catalyst

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ABSTRACT

A mixture of ethyl acetoacetate, benzaldehyde and ammonium acetate and in the presence of Fe [(L)proline]$_2$ were converted to 1,4-dihydropyridines with good yields. IR spectra Confirms formation complex of Fe [(L)proline]$_2$.

Key words: 1, 4-dihydropyridines, ammonium acetate, ethyl acetoacetate, Fe [(L) proline]$_2$.

INTRODUCTION

Chemical dihydropyridine reported by arthur hantzsch from 1882 years, he compounded]"-ketoester, aldehyde and ammohia that lead to forms of 1¡4-dihidropyridines where as reported many advantages of 1¡4-dihydropiridin ,and at this time identify as importance and vital in treatment of calcium antagonists[1], antitumours[2], antidiabetics[3], antagonists[4] and antivirals[5]. Recently a number of articles have published on the synthesis of 1, 4-dihydropyridines[6-13]. Heterogeneous catalysts have gained and have been widely used as a stable and an efficient catalyst for synthesis of organic compound.

We have synthesized of DHPs from ethyl acetoacetate, benzaldehyde, and ammonium acetate using Fe [(L)proline]$_2$ as catalyst (Scheme 1). Once the reaction goes to completion, the catalyst can be filtered, washed with warm ethanol, and reused without decrease in activity.

Previously, we have synthesized a number of heterocyclic compounds[14-19]. Although numerous methods are capable of affecting these synthesis has been previously reported. Zn [(L)proline]$_2$ has been used previously as a catalyst for synthesis of organic compound[20].

The comparison of IR spectra shows That in IR L- prolin spectra seeing NH And OH spectra . and was deleted Thes spectra in Fe [L-proline]2 Catalysors , and shows The Complex was formed between Fe and L - prolin , and in fact complex is similar To Zn [L- proline]2.

Therefore, we reported the development of an efficient, a facile method and green synthesis for 1, 4-DHPs by Fe [(L)proline]$_2$ as catalyst (Scheme 1). There is Fe [(L)proline]$_2$ as the catalyst were environmentally friendly, and easy separation.

General Procedure for the Preparation of the Fe [(L)proline]$_2$

A mixture of Triethylamine (1 ml) and L-proline (4 mmol) in methanol (10 ml) was added. After solubilization with heat, reaction mixture was stirred for 10 min and ferrous sulfate (2 mmol) was added. A white precipitate was readily formed and after 1 hour it was collected by filtration to give the desired complex. IR spectra confirm formation of Fe [(L)proline]$_2$, IR spectra fig 1 is for L-proline, IR spectra fig 2 is for ferrous sulfate and IR spectra fig 3 is for Fe [(L)proline]$_2$. Comparison of the spectra shows that loss some of signals and picks is sign for formation complex of Fe [(L)proline]$_2$.

General Procedure for the Preparation of diethyl 2, 6-dimethyl-4-phenylpyridine-3, 5-dicarboxylate

A mixture of ethyl acetoacetate (2 mol), benzaldehyde (1 mol) and ammonium acetate (1 mol) and Fe [(L)proline]$_2$ (% 10) in ethanol (20 ml was refluxed for 1.5 h. The obtained solid was filtered; the solid was washed with water and recrystallized using absolute ethanol.

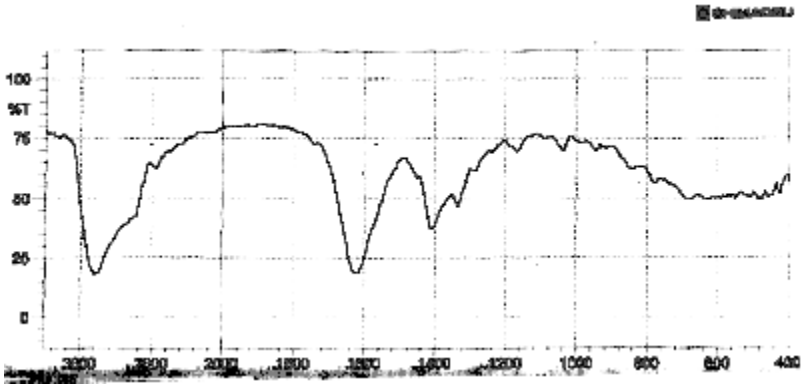


Fig. 1: IR spectra for L-proline

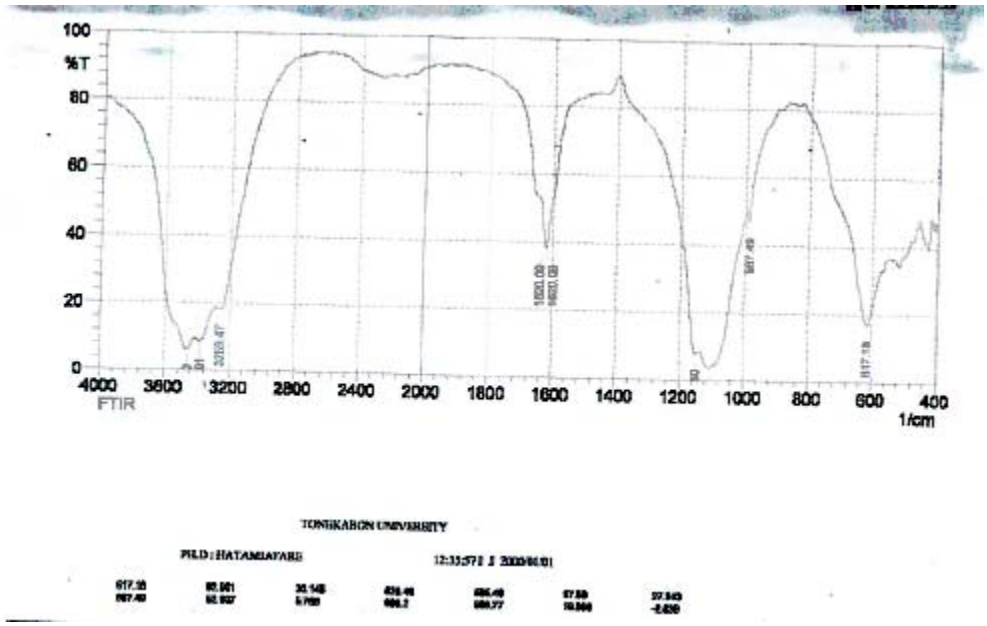


Fig. 2: IR spectra for ferrous sulfate

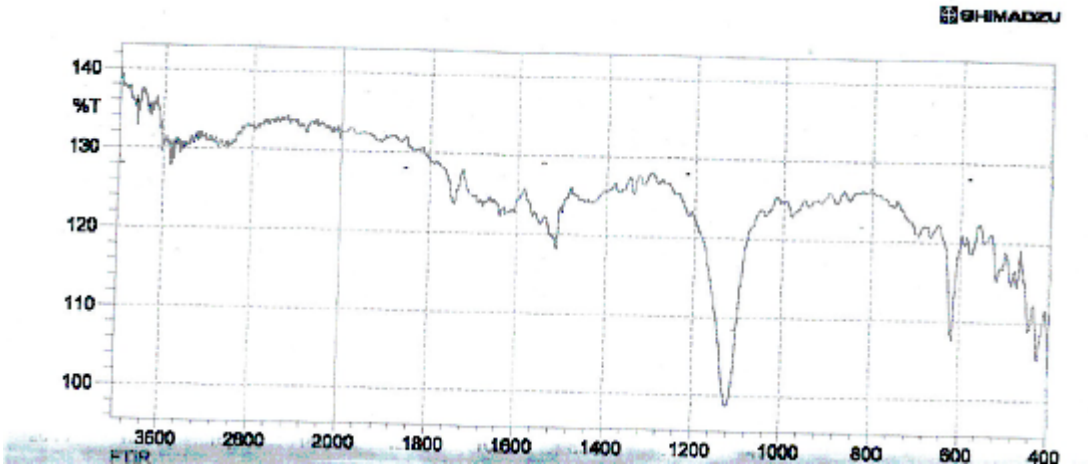
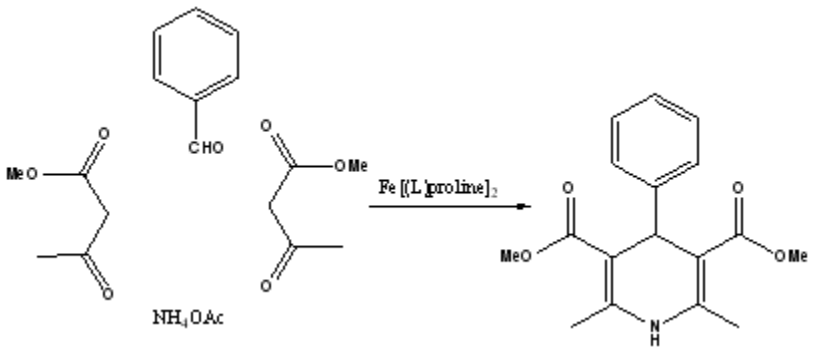


Fig. 3: IR spectra for Fe [(L)proline]$_2$



Scheme 1:

Spectral data for diethyl 2, 6-dimethyl-4-phenylpyridine-3, 5-dicarboxylate

Yellow crystals, Yield 91%, IR (KBr, cm^{-1}) ν: 3405, 3012, 2955, 1728. ^{1}H NMR (400MHz, $CDCl_3$) δ: 1.25 (t, 6H, $2CH_3$, *J* = 7. 4 Hz), 2.55 (s, 6H, $2CH_3$), 4.45 (q, 4H, $2CH_2O$, *J* = 7.4 Hz), 5.11 (s, 1H, CH), 7.23-7.80(m, 5H, H_{arom}) 8.88 (s, 1H, NH).

RESULTS AND DISCUSSION

Herein, we report Fe [(L)proline]$_2$ as catalyst that could provide an efficient, environmentally friendly, easy separation, high yield, green synthesis and simple route for the synthesis of 1,4-DHPs.

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