

## INFLUENCE OF THE SOLVENT CONDITION FOR THE SYNTHESIS OF THE $\beta$ -DIKETIMINES LIGANDS

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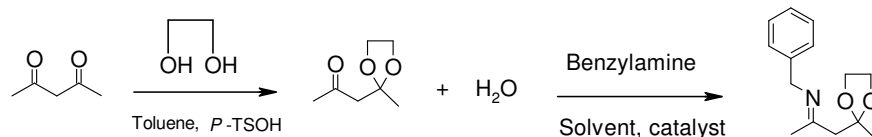
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### ABSTRACT

A general synthesis for preparation of  $\beta$ -diketimines has been developed. The method reported here demonstrates the use of solvent for conversion of ethylene glycol monoketal to  $\beta$ -diketimines. The reaction can be performed with  $\text{CH}_2\text{Cl}_2$  without catalyst providing.



**Keywords:** Synthèses,  $\beta$ -diketimines ligands, Solvent, Catalyst

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### INTRODUCTION

In recent years, a significant amount of attention have been concentrated on the design and synthesis of polydentate ligands<sup>1,2</sup>, attempting to generate novel coordination environments, stabilizing particular oxidation, states and preparing robust catalysts<sup>3,4</sup>.

The chemistry of  $\beta$ -diketimines represents an active investigation area in organic<sup>5,6</sup> or organometallic chemistry, due to their high catalytic activity and polymer synthesis<sup>7,8</sup>. These compounds have been used as ligand for the complex formation with a variety of transition metal<sup>9,10</sup> and they have found immense analytical applications, for example in extracting traces of metals. These ligands are particularly useful as they can be prepared in high yields, crystallize easily and offer various coordination modes, thus have the ability to stabilize low oxidation state compounds<sup>11</sup>.

### EXPERIMENTAL

All experiments were carried out under a room temperature. All substrates were used without further purification. NMR spectra were recorded on a AMX 300 MHz spectrometer.

#### 2,4-pentanedione-2,2-(ethylene glycol) Monoketal (2)

This procedure was slightly modified from that given in the literature. A mixture of 2,4-pentandione (5g, 49.93mmol), ethylene glycol (3.09g, 49.93mmol), and *p*-toluenesulfonic acid (0.19mg, 0.99mmol) in toluene (15mL) was placed in a three necked round bottom flask equipped with magnetic stirrer and a dream-stark apparatus was used to remove the water continuously from the homogenous reaction mixture. The solution was refluxed in toluene for 2h, then evaporated in vacuo to afford **monoketal 2** (yellow dark oil, 85%). <sup>1</sup>H NMR, <sup>13</sup>C NMR.

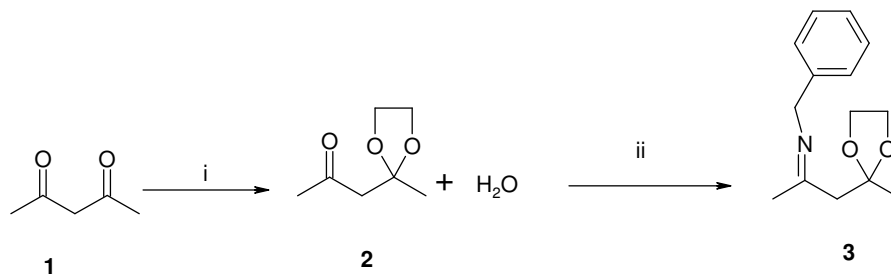
#### Benzyl-[1-methyl-2-(2-methyl-[1,3]dioxolan-2-yl)-ethylidene]-amine (3)

To a solution of monoketal (0.1g, 0.86mmol) in  $\text{CH}_2\text{Cl}_2$  (5mL) was added benzylamine (0.093g, 0.86mmol) at room temperature. The reaction mixture was heated at reflux for 6h after, the solvent was evaporated at reduced pressure to afford **3** (viscous oil, 62%). <sup>1</sup>H NMR ( $\text{CDCl}_3$ )  $\delta$  ppm 7.29 (m, 5H), 3.97

(m, 4H), 2.77 (s, 2H), 2.22 (s, 3H), 1.41 (s, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ ppm 206.00, 191.09, 107.63, 100.30, 64.42, 52.31, 31.45.

## RESULTS AND DISCUSSION

The desired β-diketimines ligand was prepared in two step standard condensation route (scheme1). Method reported here demonstrates the influence of solvent, time and catalyst in the yield of the reaction.



Scheme-1: General synthesis of the β-diketimine

Reagents : (i) ethylene glycol, toluene, P-TSOH, (ii) benzylamine, solvent, or benzylamine, CH<sub>2</sub>Cl<sub>2</sub>, P-TSOH.

First the dean stock reaction of 2,4-pentanedione with substituted ethylene glycol in toluene using *P*-TSOH as catalyst, turned out useful in the synthesis of monoketal ethylene glycol **2** in good yield. The water generated by the reaction was removed by azeotropic distillation promoting the formation product minimizing hydrolysis of the Schiff base.

In general, monoketals were prepared through condensation of carbonyl compounds with catechol catalysed by protonic or Lewis acid catalysts such as phosphorus pentoxide, trimethylsilyl chloride<sup>12</sup>, phosphorus trichloride<sup>13</sup>, super acid<sup>14</sup>, *p*-toluenesulfonic acid<sup>15,16</sup>. However, some of the previously reported have various disadvantages. For example trimethylsilyl chloride and phosphorus trichloride are poisonous, expensive and unstable. Moreover, they could not be recycled due to the difficulty in purification. The use of *p*-toluenesulfonic acid as homogenous catalyst in the liquid phase regenerates the catalyst as solid heterogeneous systems when the reaction is carried out. This catalyst exhibits high activities for the reaction.

The β-diketimine was prepared by the condensation of the ethylene glycol monoketal of 2,4-pentanedione with 1eq of benzylamine in the presence of solvent. The mixture was refluxed for the specific periods. The reaction process was monitored by NMR analysis. The influence of solvent, the amount of catalyst and reaction time on the yield of product were investigated in order to find out the optimum reaction condition as shown in Table 1.

Table-1: Influence of solvent for the β-diketimine preparation

Solvent X (h)	Toluene (% yield)	THF (% yield)	CH <sub>2</sub> Cl <sub>2</sub> (% yield)	CH <sub>2</sub> Cl <sub>2</sub> + <i>p</i> - toluenesulfonic acid 2% (% yield)
1	30	35	57	57
3	31	55	57	56
6	32	55	62	56
21	41	59	62	57

The experimental observation reported herein shows that a solvent plays an important role in the yield reaction. Whatever the reaction time of monoketal with benzylamine in toluene gave the desired product

at low yield. According to THF solvent used, the yields of products obtained were improved with reaction time. The optimum yield reaction was obtained after 21h stirring.

The yields are good from the  $\beta$ -diketimine when the  $\text{CH}_2\text{Cl}_2$  are used as solvent, the reaction worked very well and the optimum yield was obtained after 6h of mixture. This condensation is preferable to the typical acid-catalysed condensation of monoketal in  $\text{CH}_2\text{Cl}_2$ . The latter method gave mixtures of product. In conclusion the optimum reaction condition was obtained in the presence of  $\text{CH}_2\text{Cl}_2$  at 6 h stirring without catalysts.

### CONCLUSION

In summary, the reaction of monoketal with benzylamine and  $\text{CH}_2\text{Cl}_2$  solvent represents a practical and cheap method for the preparation for the  $\beta$ -diketimines ligand. The reaction procedure is simple and efficient.

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