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# Solvent-Free Knoevenagel Condensation over Iridium and Platinum Hydroxyapatites[1]

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**Abstract**—The Knoevenagel condensation between various aldehydes (benzaldehyde, *p*-methoxybenzaldehyde and 1-naphthaldehyde) and esters (ethylcyanoacetate, ethylacetoacetate and diethylmalonoester) was carried out under solvent-free condition in the presence of iridium or platinum hydroxyapatites as a catalyst.

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The Knoevenagel condensation is an important reaction forming carbon-carbon double bond. Some important end products or intermediates such as pharmaceuticals, perfumes, polymers etc. are synthesized by this reaction [1–3]. The reaction is usually catalyzed by bases such as ammonia, primary and secondary amines [4], quaternary ammonium salts [5], Lewis acids [6–9], and catalytic acid-base sites [10] etc. and often carried out under homogeneous condition. Such condition requires organic solvents and use of these organic solvents has always been concerned due to their hazardousness and associated environmental pollution. For the standpoint of sustainable environment and minimizing pollution, solvent-free heterogeneous catalysts have been receiving increasing attention. Since, these heterogeneous catalysts not only avoid the use of organic solvents but also suppress side reactions such as self condensation, oligomerisation etc. resulting in better selectivity and product yield [11]. In recent years, therefore, the use of heterogeneous catalysts [12–15], their recovery and reusability are very much sought after in industry.

We synthesized and characterized several hydroxyapatites and used them for various studies, including their catalytic activities [16]. Recently, we have also reported the use of nickel hydroxyapatite as a heterogeneous catalyst for the Knoevenagel condensation of benzaldehyde with malononitrile [17]. The use of fluorapatite as a heterogeneous catalyst for the Knoevenagel condensation has earlier been reported in the literature [18]. Based on these evidences, we envisioned that iridium and platinum hydroxyapatites (**IrHAp** and **PtHAp**) which we had synthesized for other studies as mentioned earlier could also be extended as a heterogeneous catalyst for the Knoevenagel condensation and the results of this study are communicated herewith.

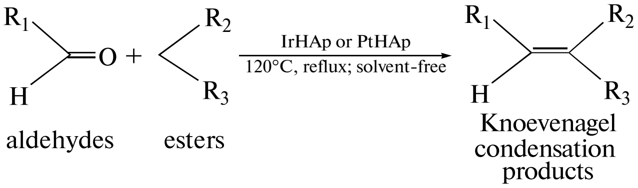
## EXPERIMENTAL

An equimolar quantity (2.0 mmol) of aldehyde and ester was taken in a round-bottom flask and then IrHAp or PtHAp catalyst was added. The mixture was refluxed at 120°C with continuous stirring using a magnetic stirrer. The products (**3a–3i**) were extracted with chloroform, then the catalyst was removed by simple filtration and the extract was evaporated. The products were purified by recrystallization and/or chromatography and identified by NMR $^1$H spectroscopy.

## RESULTS AND DISCUSSION

In the present study, we report the Knoevenagel condensation between various aldehydes, namely benzaldehyde (**1a**), *p*-methoxybenzaldehyde (**1b**) and 1-naphthaldehyde (**1c**) and esters, namely ethylcyanoacetate (**2a**), diethylmalonoester (**2b**) and ethylacetoacetate (**2c**) under solvent-free condition in the presence of IrHAp or PtHAp as a catalyst (Scheme).

The Knoevenagel condensation between various aldehydes and esters and their products



| | | |
|---|---|---|
| **1a**: $R_1$ = Ph | **2a**: $R_2$ = CN; $R_3$ = COOEt | **3a–3i** |
| **1b**: $p$-MeO–$C_6H_4$– | **2b**: $R_2$ = $R_3$ = COOEt | |
| **1c**: 1-naphthyl | **2c**: $R_2$ = COMe; $R_3$ = COOEt | |

**Scheme.**

Each one of the reactions was carried out twice but by varying the amounts of catalyst as 0.05 and 0.100 g. For example, the reaction of **1a** with **2a** was carried out

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[1] The article is published in the original.

**Table 1.** Synthesis of various alkenes by Knoevenagel condensation using IrHAp

| Aldehyde | Ester | Product | Amount of catalyst, g | | | |
|---|---|---|---|---|---|---|
| | | | 0.050 | | 0.100 | |
| | | | Yield, % | Time, min | Yield, % | Time, min |
| Benzaldehyde (**1a**) | **2a** | **3a** | 62 | 60 | 95 | 60 |
| *p*-Methoxybenzaldehyde (**1b**) | **2a** | **3b** | 42 | 90 | 68 | 90 |
| 1-Naphthaldehyde (**1c**) | **2a** | **3c** | 30 | 240 | 42 | 240 |
| Benzaldehyde (**1a**) | **2b** | **3d** | 65 | 30 | 97 | 30 |
| *p*-Methoxybenzaldehyde (**1b**) | **2b** | **3e** | 53 | 120 | 82 | 120 |
| 1-Naphthaldehyde (**1c**) | **2b** | **3f** | 25 | 240 | 34 | 240 |
| Benzaldehyde (**1a**) | **2c** | **3g** | 61 | 60 | 92 | 60 |
| *p*-Methoxybenzaldehyde (**1b**) | **2c** | **3h** | 48 | 120 | 78 | 120 |
| 1-Naphthaldehyde (**1c**) | **2c** | **3i** | 22 | 240 | 38 | 240 |

**Table 2.** Synthesis of various alkenes by Knoevenagel condensation using PtHAp

| Aldehyde | Ester | Product | Amount of catalyst, g | | | |
|---|---|---|---|---|---|---|
| | | | 0.005 | | 0.100 | |
| | | | Yield, % | Time, min | Yield, % | Time, min |
| Benzaldehyde (**1a**) | **2a** | **3a** | 65 | 60 | 91 | 60 |
| *p*-Methoxybenzaldehyde (**1b**) | **2a** | **3b** | 40 | 90 | 65 | 90 |
| 1-Naphthaldehyde (**1c**) | **2a** | **3c** | 25 | 240 | 40 | 240 |
| Benzaldehyde (**1a**) | **2b** | **3d** | 55 | 30 | 95 | 30 |
| *p*-Methoxybenzaldehyde (**1b**) | **2b** | **3e** | 58 | 120 | 70 | 120 |
| 1-Naphthaldehyde (**1c**) | **2b** | **3f** | 23 | 240 | 31 | 240 |
| Benzaldehyde (**1a**) | **2c** | **3g** | 56 | 60 | 90 | 60 |
| *p*-Methoxybenzaldehyde (**1b**) | **2c** | **3h** | 45 | 120 | 70 | 120 |
| 1-Naphthaldehyde (**1c**) | **2c** | **3i** | 21 | 240 | 33 | 240 |

in the presence of 0.05 and 0.100 g of IrHAp as catalyst and respectively 62 and 95% of yields of product **3a** (Table 1) were obtained. Similarly, the reaction of **1a** with **2a** was carried out in the presence of 0.05 and 0.100 g of PtHAp as catalyst and respectively 91 and 65% of yields of product **3a** (Table 2) were obtained. The same reactions were carried out under similar reaction conditions without IrHAp or PtHAp and it did not give any product. These results confirm the necessity of IrHAp or PtHAp as catalyst for the proposed condensation reaction. The percentage yields of other condensation products (**3b**–**3i**) are given in Tables 1 and 2.

0.100 mg of IrHAp catalyzed reactions of **1a** with **2a**–**2c** gave products **3a**, **3d** and **3g** with excellent yields of 95, 97 and 92% respectively, whereas 0.050 mg of IrHAp catalyzed reactions of **1a** with **2a**–**2c** gave products **3a**, **3d** and **3g** with moderate yields of 62, 65 and 61%, respectively. Similarly, 0.100 mg of IrHAp catalyzed reactions of **1b** with **2a**–**2c** gave products **3b**, **3e** and **3h** with moderate to good yields of 68, 82 and 78% respectively, whereas 0.050 mg of IrHAp catalyzed reactions of **1b** with **2a**–**2c** gave products **3b**, **3e** and **3h** with moderate yields of 42, 53 and 48% respectively. Finally, 0.100 mg of IrHAp catalyzed reactions of **1c** with **2a**–**2c** gave products **3b**, **3e** and **3h** with poor yields of 42, 34 and 38% respectively, whereas 0.050 mg of IrHAp catalyzed reactions of **1c** with **2a**–**2c** gave products **3b**, **3e** and **3h** with poorest yields of 30, 25 and 22% respectively.

**Table 3.** Comparison of IrHAp and PtHAp catalyzed Knoevenagel condensation of **1a** with **2a** for the yield of product **3a** with other heterogeneous catalysts

| Catalyst | Amount of catalyst, g | Time, min | Yield, % |
|---|---|---|---|
| IrHAp | 0.100 | 60 | 95 |
| IrHAp | 0.050 | 60 | 62 |
| PtHAp | 0.100 | 60 | 90 |
| PtHAp | 0.050 | 60 | 65 |
| Flourapatite [18] | 1.25 | 30 | 14 |
| Flourapatite [18] | 1.25 | 90 | 45 |
| NiHAp [17] | 0.083 | 1200 | 55 |
| Zeolite (Znβ) [1] | 0.100 | 360 | 72 |
| $AlPO_4/Al_2O_3$ [19] | 3.00 | 60 | 74 |
| Resin [20] | 0.100 | 300 | 87 |
| Zeolite [21] | 0.106 | 480 | 70 |
| $ZnCl_2$ [22] | 0.136 | 90 | 86 |

Similar trend was also observed with PtHAp catalyzed reactions of **1a** with **2a**–**2c**, **1b** with **2a**–**2c** and **1c** with **2a**–**2c**. 0.100 mg of IrHAp catalyzed reactions of **1a** with **2a**–**2c** gave products **3a**, **3d** and **3g** with excellent yields of 91, 95 and 90% respectively, whereas 0.050 mg of IrHAp catalyzed reactions of **1a** with **2a**–**2c** gave products **3a**, **3d** and **3g** with moderate yields of 65, 55 and 56% respectively. Similarly, 0.100 mg of IrHAp catalyzed reactions of **1b** with **2a**–**2c** gave products **3b**, **3e** and **3h** with moderate to good yields of 65, 70 and 70% respectively, whereas 0.050 mg of IrHAp catalyzed reactions of **1b** with **2a**–**2c** gave products **3b**, **3e** and **3h** with moderate yields of 40, 58 and 45% respectively. Finally, 0.100 mg of IrHAp catalyzed reactions of **1c** with **2a**–**2c** gave products **3b**, **3e** and **3h** with poor yields of 40, 31 and 33% respectively, whereas 0.050 mg of IrHAp catalyzed reactions of **1c** with **2a**–**2c** gave products **3b**, **3e** and **3h** with poorest yields of 25, 21 and 23% respectively.

In general, IrHAp catalyzed reactions gave somewhat higher yields than PtHAp catalyzed reactions (Tables 1 and 2). Overall, both IrHAp and PtHAp catalyzed reactions were very efficient towards the reactions of **1a** with **2a**, **2b** and **2c** which gave the products, respectively, **3a**, **3d** and **3g** with excellent yields.

A literature survey was done on the yields reported for Knoevenagel condensation reaction of **1a** with **2a** to give **3a** by various heterogeneous catalysts. The summary of the literature values of yields are given in Table 3. It was observed that PtHAp or PtHAp catalyst was found to be better than other heterogeneous catalyst in the sense that it required a meagre quantity to provide a maximum yield. For example, a large amount of fluorapatite catalyst (1.25 g, > 1 mmol) was required to produce 45% yield of product **3a** [16]. However, only a small quantity of IrHAp or PtHAp catalyst (0.100 g, < 0.1 mmol) is required for producing over 90% yield of the same product, **3a**.

We have demonstrated the efficiency of IrHAp and PtHAp as catalysts for the Knoevenagel condensation between various aldehydes (**1a**–**1c**) and esters (**2a**–**2c**). The reactions were carried out by refluxing at 120°C under solvent-free conditions. IrHAp and PtHAp can be a good alternative to the existing homogeneous catalyst as well as many other heterogeneous catalysts.

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