Bismuth (III) Triflate: A Mild, Efficient Promoter for the Synthesis of Trisubstituted Alkenes through Knoevenagel Condensation

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ABSTRACT

In this work, smooth efficient and eco-friendly two component coupling method is reported for the synthesis of Knoevenagel Condensation product in presence of Bi(OTf)$_3$ catalyst under solvent free condition. Catalyst has participated in condensation between substituted aldehydes (aromatic and hetero-aromatic) and active methylene compounds (ethyl cyanoacetate, malononitrile and cyanoacetamide) effectively to generate an excellent yield of the product. Bi(OTf)$_3$ catalyst is stable, inexpensive and easily available was used for four times in this reaction without loss of catalytic activity.

**Keywords:** Knoevenagel Condensation, Different aldehydes, Various active methylene compounds, Bi(OTf)$_3$, Heterogeneous Catalyst.

INTRODUCTION

The Knoevenagel reaction first reported in 1890 by Emil Knoevenagel which is an Aldol type condensation is extensively applied to the formation of the carbon–carbon double bond in synthetic organic chemistry. This important methodology has been used to produce different $\alpha,\beta$-unsaturated acids like cinnamic acid. This reaction is assisted for the production of such compounds which have immense biological significance that is therapeutic activity and drug discovery. In addition these compounds are used for production of polymers, cosmetics, perfumes and natural products. Malononitrile, ethyl cyanoacetate, cyanoacetamide are active methylene compounds and usually used in the string
of carbon-carbon double bond formation in organic transformation.\(^6\)

A large no of methods for the synthesis of Knoevenagel Condensation products has been reported because of their immense biological activity and synthetic viewpoint. Bases such as amines (piperidine and N methyl piperidine), metal alkoxides, metal hydroxide and pyridine catalyzed Knoevenagel condensation reaction in either solvent free or organic solvents were reported.\(^{10}\) Ammonium salts\(^{10}\) and amino acids\(^{10}\) were also used to construct this condensation product. These catalysts are homogeneous and very effective to increase the reaction rate but some disadvantages of these catalysts were (a) toxic to human\(^{11}\) (b) difficult to separate from the reaction mixture because of homogeneity and can’t be recycled and (c) neutralization was required at the end of the process. In many published papers green methodology was used to develop the Knoevenagel condensation product.\(^{12,13}\) Analysis of the literature reveals that many Lewis acid catalysts for Knoevenagel condensation were used compared to bases as catalysts in huge numbers to overcome the above difficulties. Some Lewis acid catalysts such as TiCl\(_4\),\(^{14}\) MgO,\(^{15}\) Al\(_2\)O\(_3\),\(^{16}\) ZnCl\(_2\),\(^{17}\) LaCl\(_3\),\(^{18}\) and NbCl\(_5\)\(^{19}\) were used to construct this reaction in presence of hazardous organic solvents in few cases. Heteropoly acid catalyst Na\(_2\)H\([\text{PW}_{12}O_{40}]\)\(^{20}\) was used to create the Knoevenagel Condensation product to improve the methodology in solvent free medium.\(^{21}\) Knoevenagel Condensation in green solvents like ionic liquids\(^{22,23}\) and water\(^{22,26}\) was documented in literature in different conditions in presence of different catalyst. Now a days solvent free technique is more popular because it maintains the green reaction conditions. Solvent free reaction is more attractive if it is carried out by using readily available non toxic and inexpensive reagent. Scientists are very interested in using Lewis acids like lanthanide triflate because they have certain characteristics.\(^{23}\) Lanthanide triflates are used as an alternative to conventional Lewis acids because of the following advantages like low toxicity, high catalytic activity, air tolerance and reusability.\(^{24}\) However large scale synthesis of this catalyst is inadequate because they are costly, so cheap and efficient catalysts are required to develop this reaction. Bismuth (III) triflate shows remarkable catalytic activity like lanthanide triflate in an organic transformation.\(^{25}\) Bi\((\text{OTf})_3\) is very cheap compare to lanthanide triflate and can be prepared in large scale by the reaction between Bi\(_2\)O\(_3\) and triflic acid.\(^{26}\) This catalyst was successfully used to synthesize the Substituted 2-Alkenylfurans in nitro methane solvent\(^{27}\) and 2-aryl-1-arylmethyl benzimidazole derivatives in water.\(^{28}\)

So my aim was to search an environmentally benign catalyst to build up a scheme for the synthesis of Knoevenagel Condensation products and for this purpose herein, I explore a scheme in presence of Bismuth (III) triflate catalyst under solvent free condition.

**EXPERIMENTAL**

Chemicals were purchased from SRL India and Spectrochem Pvt. Ltd. \(^1\)H and \(^13\)C NMR spectra were recorded on a Bruker 300 MHz instrument. From Aldrich chemical company NMR solvents CDCl\(_3\), DMSO-\(d_6\) and TMS as the internal standard were purchased. Electrical melting point apparatus were used to determine the melting point. Perkin Elmer Spectrophotometer was used to study FT-IR spectra. Thin layer chromatography was used to monitor the reaction. For recrystallisation, distilled ethyl acetate-petroleum ether was used as solvents.

**General procedure**

An active methylene compound 2 (2.2 mmol), aldehyde 1 (2 mmol) and Bi(OTf)\(_3\) (0.10 mmol) were taken and mixed in a 50 mL Erlenmeyer flask with a condenser containing ice water circulation and it was heated in an oil bath at 80°C with a specific time period. The reaction was monitored by TLC time to time. After the complete conversion of the reaction indicated by brown spot in TLC then the crude product was cooled and diluted with 10 mL water stirred and filtered. After the separation of organic portion the crude product was crystallized from minimum volume of distilled ethylacetate-petroleum ether to get pure product. All \(^1\)H-NMR and \(^13\)C-NMR spectral data of all known compounds (3a-u) were checked with the data of authentic known compounds.

**Selected characterization data for synthesized compounds**

**Ethyl-(E)-2-cyano-3-(4-methoxyphenyl)-2-propenoate (3b)**

White color solid, FT-IR (KBr, cm\(^{-1}\)): 3417, 2990, 1718, 1582, 1264 and 1181, \(^1\)H-NMR (300 MHz, CDCl\(_3\)) \(\delta\): 8.17 (s, 1H, =CH), 8.01 (dd, 2H, C\(_6\) and C\(_5\) protons), 7.01 (dd, 2H, C\(_6\) and C\(_5\) protons), 4.37 (q, 2H,
TABLE 1. Mixture of the substrate and reagent under different conditions to focus the feasibility of the catalyst in solvent free condition at changeable temperature and it was noticeable that reaction was warmed with different amount of Bi(OTf)₃ catalyst, solvent, time and yield; a model reaction had been chosen for this purpose. Initially 4-methoxybenzaldehyde (2 mmol) and ethyl cyanoacetate (2.2 mmol) were taken as model substrate and reagent under different conditions to focus the feasibility of the catalyst in solvent free medium at suitable temperature.

\[
\begin{align*}
n &\text{Reaction} & \text{Yield} \\
\text{Bi(OTf)₃ (mol)} & \text{Solvent} & \text{Yield (\\%)} \\
0.1 & \text{MeCN} & 84.3 \\
0.2 & \text{MeCN} & 84.4 \\
0.3 & \text{MeCN} & 84.5 \\
0.4 & \text{MeCN} & 84.6 \\
0.5 & \text{MeCN} & 84.7 \\
0.6 & \text{MeCN} & 84.8 \\
0.7 & \text{MeCN} & 84.9 \\
0.8 & \text{MeCN} & 85.0 \\
0.9 & \text{MeCN} & 85.1 \\
1.0 & \text{MeCN} & 85.2 \\
1.1 & \text{MeCN} & 85.3 \\
1.2 & \text{MeCN} & 85.4 \\
1.3 & \text{MeCN} & 85.5 \\
1.4 & \text{MeCN} & 85.6 \\
1.5 & \text{MeCN} & 85.7 \\
1.6 & \text{MeCN} & 85.8 \\
1.7 & \text{MeCN} & 85.9 \\
1.8 & \text{MeCN} & 86.0 \\
1.9 & \text{MeCN} & 86.1 \\
2.0 & \text{MeCN} & 86.2 \\
\end{align*}
\]

\[\text{Bi(OTf)₃ (mol)} = C_{4}H_{7}N_{2}O_{5} (\\%)\text{: C: 60.31; H: 2.53; N: 21.10; Found: C: 60.20; H: 2.41; N: 20.93.}\]

\[\text{2-(4-Chlorophenylmethylene) malononitrile (3n)}\]
White color solid, FT-IR (KBr, cm⁻¹): 2221, 1578, 1484, 1408, 1215 and 1091. ¹H-NMR (300 MHz, CDCl₃) δ: 7.85 (td, 2H, C₂ and C₆ protons), 7.52 (td, 2H, C₅ and C₆ protons), 1³C-NMR (75 MHz, CDCl₃) δ: 158.2, 141.1, 131.9, 130.1, 129.3, 113.4, 112.4, 112.6, 84.3, Analytical calculation for C₇H₆ClN₂ (\\%): C: 69.76; H: 4.68; N: 16.27; Found: C: 69.63; H: 4.52; N: 16.15.

\[\text{(E)-2-Cyano-3-phenyl-2-propenamide (3s)}\]
White color solid, FT-IR (KBr, cm⁻¹): 3088, 3161, 1691, 1595 and 1371. ¹H-NMR (300 MHz, CDCl₃) δ: 8.32 (s, 1H, -CH), 7.95-7.91 (m, 2H, Ar protons), 7.56-7.45 (m, 2H, Ar protons), 6.42 (brs, 2H, CONH₂), 1³C-NMR (75 MHz, CDCl₃) δ: 162.2, 154.0, 133.1, 131.6, 130.8, 129.2, 116.8, 103.2, Analytical calculation for C₉H₇N₂ (\\%): C: 69.76; H: 4.68; N: 16.27; Found: C: 69.63; H: 4.52; N: 16.15.

\[\text{RESULT AND DISCUSSIONS}\]
In order to investigate the effect of catalyst, solvent, time and yield; a model reaction had been chosen for this purpose. Initially 4-methoxybenzaldehyde (2 mmol) and ethyl cyanoacetate (2.2 mmol) were taken as model substrate and reagent under different conditions to focus the feasibility of the catalyst in solvent free medium at suitable temperature.

Scheme 1. Study of optimization of Knoevenagel Condensation product in presence of Bi(OTf)₃

The reaction was performed systematically and results were shown in Table 1. Mixture of the reaction was warmed with different amount of Bi(OTf)₃ (BT) catalyst in solvent free condition at changeable temperature and it was noticeable that the product yield depends on the amount of BT.
catalyst and as well as temperature. The reaction sluggish without catalyst in solvent less condition
at 80°C and no yield was isolated when 10 mol% of
BT catalyst was used at room temperature although
reaction was continually monitored for 6 h (Entry 1,
Table 1). When the mol% of the catalyst was varied
from 1 to 10, the yield of the product gradually
increased. 5 mol% of the catalyst at 80°C gave only
60% yield of the product (Entry 4, Table 1). Increasing
the amount of the catalyst from 5 to 10 mol% resulted
in a drastic increase of the yield to 90% (Entry 6, Table
1). More over in presence of 10 mol% of catalyst at
90°C no improved yield was observed (Entry 7, Table
1). More than 10 mol% of the catalyst that means 15
and 20 mol% of the catalyst at 80°C did not improve
the yield of the product (Entries 8 and 10, Table 1) and
at comparatively high temperature (90°C) no better result was observed (Entries 9 and 11, Table 1). So I
came to the point that only 10 mol% of catalyst was
adequate to complete the reaction at 80°C (Entry 6,
Table 1) with excellent yield of the product.

**Table 1: Study of the optimization condition of the**
**Knoevenagel Condensation in different mol% of**
**Bi(OTf)₃ catalyst**

| Entry | BT(mol%) | Conditions            | Time (h) | Yield(%) |
|-------|----------|-----------------------|----------|----------|
| 1     | 0        | Oil bath 80°C, solvent free | 6        | 25       |
| 2     | 10       | Room temp, solvent free  | 6        | 00       |
| 3     | 2.5      | Oil bath 80°C, solvent free | 6        | 30       |
| 4     | 5.0      | Oil bath 80°C, solvent free | 6        | 60       |
| 5     | 7.5      | Oil bath 80°C, solvent free | 6        | 75       |
| 6     | 10       | Oil bath 80°C, solvent free | 6        | 90       |
| 7     | 10       | Oil bath 90°C, solvent free | 6        | 88       |
| 8     | 15       | Oil bath 80°C, solvent free | 6        | 90       |
| 9     | 15       | Oil bath 90°C, solvent free | 6        | 90       |
| 10    | 20       | Oil bath 80°C, solvent free | 6        | 88       |
| 11    | 20       | Oil bath 90°C, solvent free | 6        | 90       |

*Reaction Conditions: p-methoxy benzaldehyde (2 mmol) and
ethylcyanoacetate (2.2 mmol), *Isolated Yield.

**Table 2: Study of solvent effect for the formation of**
**Knoevenagel compound at 80°C**

| Entry | Solvent(5mL) | Conditions       | Time (h) | Yield(%) |
|-------|--------------|-----------------|----------|----------|
| 1     | THF          | Oil bath 80°C   | 6        | 30       |
| 2     | Toluene      | Oil bath 80°C   | 6        | 35       |
| 3     | DMSO         | Oil bath 80°C   | 6        | 45       |
| 4     | MeCN         | Oil bath 80°C   | 6        | 40       |
| 5     | EtOH         | Oil bath 80°C   | 6        | 50       |
| 6     | Aqueous EtOH | Oil bath 80°C   | 6        | 55       |
| 7     | H₂O          | Oil bath 80°C   | 6        | 68       |
| 8     | none         | Oil bath 80°C   | 6        | 90       |

*Reaction conditions: p-methoxy benzaldehyde (2 mmol),
ethylcyanoacetate (2.2 mmol) and 10 mol% of BT catalyst,
*Isolated Yield.

Then I have studied the influence of the solvent effect on Knoevenagel condensation
product catalyzed by 10 mol% of BT using the model
substrate 4-methoxy benzaldehyde and reagent
ethylcyanoacetate at 80°C temperature and the
results were shown in Table 2. In presence of less
polar solvent (Entries 1 and 2, Table 2) the yield was
very low even after 6 h of the continuous heating of
the reaction mixture. Polar aprotic solvent increases
the yield slightly (Entries 3 and 4, Table 2) but the
reaction gave moderate yield in polar protic solvent
(Entries 5, 6 and 7, Table 2). Under solvent free
condition 90% yield of the product was determined,
so I can conclude that BT catalyst worked well under
solvent less condition (Entry 8, Table 2) than protic
solvent to generate high yield of the condensation
product. In solvent free condition the substrates and
reagents are very close to each other and that’s why
high yield was observed under this conditions.

**Scheme 2. Synthesis of Knoevenagel Condensation**
**Product in presence of BT catalyst under solvent free**
**condition at 80°C**

From the analysis of the reported data in
Table 3, I can say that electron pulling group like NO₂,
Cl, Br present in the aromatic aldehyde increases
the electrophilicity of the aldehyde group and then
enol form of the active methylene compound
reacted with the aldehyde group smoothly and it was
reflected in the yield of the products. Temperature
was required to complete the dehydration step
of the reaction. Electron donating group like
OMe, NMe₂ gave slightly lower yield because of
lower electrophilicity of aldehyde group (Entries
2 and 10, Table 3). However, all the substrates
reacted very fine and produce excellent yields of
the products. Beside this, it was also observed
that when 4-bromobenzaldehyde was reacted
separately with three different active methylene
compound then different time was required to
complete the reaction so the reactivity order is
malononitrile>ethyl cyanoacetate>cyanoacetamide
of three active methylene compounds. Lewis
acid catalysed mechanism was reported in many
previously published papers. Here Bi (III) acts as a Lewis acid catalyst which polarizes the aldehyde group by the formation of Lewis acid-Lewis base complex and beside this, catalyst helps to generate the nucleophilic activity of the active methylene compound by enolisation and then nucleophilic addition to aldehyde take place rapidly. In recent published paper where they shown the mechanism of the reaction.39 I have represented here the details mechanism in Scheme 3 like that paper. In the previous published paper the products configuration was Trans.31 According to this information all the products obtained through this methodology were Trans in nature.

Table 3: BT catalysed Knoevenagel Condensation

| Entry | Aldehyde(R₁), (1) | Methylene Comp. R₂(2) | Product (3) | Time (h) | Yield(%) | Melting Point(°C) | Ref |
|-------|------------------|-----------------------|-------------|----------|----------|------------------|-----|
| 1     | 4-Cl-C₆H₄        | CO₂CH₂CH₃             | 3a          | 4.5      | 92       | 86-87            | 29  |
| 2     | 4-OMe-C₆H₄       | CO₂CH₂CH₃             | 3b          | 6.0      | 90       | 82-84            | 30  |
| 3     | 4-OH-3OMe-C₆H₄   | CO₂CH₂CH₃             | 3c          | 5.5      | 85       | 98-99            | 31  |
| 4     | C₆H₅              | CO₂CH₂CH₃             | 3d          | 5.0      | 84       | 50-59            | 31  |
| 5     | 4-OH-C₆H₄         | CO₂CH₂CH₃             | 3e          | 6.0      | 86       | 170-171          | 31  |
| 6     | 4-NO₂-C₆H₄       | CO₂CH₂CH₃             | 3f          | 5.0      | 88       | 167-169          | 29  |
| 7     | 2-NO₂-C₆H₄       | CO₂CH₂CH₃             | 3g          | 5.0      | 82       | 96-98            | 29  |
| 8     | 2-O-Me-C₆H₄      | CO₂CH₂CH₃             | 3h          | 6.0      | 80       | 70-71            | 30  |
| 9     | 3-OH-C₆H₃         | CO₂CH₂CH₃             | 3i          | 6.0      | 86       | 82-84            | 32  |
| 10    | 4-N,NMe₂-C₆H₄    | CO₂CH₂CH₃             | 3j          | 6.0      | 82       | 121-122          | 31  |
| 11    | 4-Br-C₆H₄        | CO₂CH₂CH₃             | 3k          | 4.5      | 88       | 85-86            | 31  |
| 12    | 2-Furanyl        | CO₂CH₂CH₃             | 3l          | 5.0      | 86       | 92-93            | 32  |
| 13    | 4-OH-C₆H₄        | CN                    | 3m          | 4.0      | 90       | 183-184          | 33  |
| 14    | 4-Ci-C₆H₄        | CN                    | 3n          | 3.5      | 92       | 160              | 159-161 |
| 15    | 2-NO₂-C₆H₄       | CN                    | 3o          | 4.0      | 85       | 136-138          | 137-138 |
| 16    | 4-Br-C₆H₄        | CN                    | 3p          | 3.5      | 88       | 153-154          | 153-155 |
| 17    | 2-cinnamyl       | CN                    | 3q          | 4.0      | 88       | 128              | 126-128 |
| 18    | 3-Br-C₆H₅        | CONH₂                 | 3r          | 5.5      | 85       | 133-134          | 135  |
| 19    | C₆H₅              | CONH₂                 | 3s          | 5.0      | 85       | 82-83            | 37  |
| 20    | 4-Br-C₆H₅        | CONH₂                 | 3t          | 5.5      | 88       | 223-224          | 222-224 |
| 21    | 2-cinnamyl       | CONH₂                 | 3u          | 5.0      | 85       | 136-137          | 135-137 |

Recycling experiment of the catalyst always gets importance in industrial method and for this purpose an experiment was carried out to check the reusability of the catalyst in the present work. After complete conversion of the reaction the isolated crude product was incubated in 10 mL of water then stirred and filtered. Then aqueous layer was dried and regenerated catalyst was reused for next reaction under the same reaction condition. It was observed that no loss of efficiency of the catalyst even after using four times in the reaction and it is clearly represented graphically in Figure 1.
CONCLUSION

In outline, it is clear that catalyst proves it efficiency and effectiveness towards the synthesis of trisubstituted alkene and provides a new synthetic methodology. Catalyst is inexpensive, easily obtainable and shows its eco friendly behavior. Moreover, the protocol offers some advantages with operational simplicity, clean reaction conditions, high yields with three different active methylene compounds under solvent less condition and causes less environmental pollution which makes the method more useful and interesting.

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Conflict of Interest
No conflict of interest regarding this article.

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