

Tetrabutyl Phosphonium L-Alaninate Amino Acid ionic Liquids used as a Catalyst in Knoevenagel Condensation Reaction under Solvent Free Conditions

Aafaq A. Tantray and Santosh S. Terdale*

Ph. D Research Scholar, Savitribai Phule Pune University, Ganeshkhind, Pune, Maharashtra, India.

*Assistant Professor, Savitribai Phule Pune University, Ganeshkhind, Pune, Maharashtra, India.

E-mail: aafaqtantray@gmail.com, [sst@chem.unipune.ac.in](mailto:ssst@chem.unipune.ac.in)

Abstract— A simple, green and environmentally benign route has been developed for the Knoevenagel condensation of different aromatic aldehydes with active methylene compounds such as malononitrile and ethylcyanoacetate, were carried out in the presence of catalytic amount of amino acid ionic liquid namely Tetrabutyl phosphonium L-Alaninate. The remarkable advantages of the present method are mild reaction conditions, short reaction time, excellent yields and green aspects by avoiding toxic catalyst and hazardous solvent. Additionally, the ionic liquid was successfully reused without significant loss of activity.

1. INTRODUCTION

Ionic liquids (ILs) are commonly referred to as liquid salts that comprises of bulky organic cations and organic or inorganic anions with melting point below 100 °C and play a vital role as a substitute for volatile organic compounds (VOC), not only because of their low vapour pressures, but, more importantly, of their ability to act as catalysts [1-4]. ILs have distinctive properties such as negligible vapour pressure, non-volatility, non-flammability, chemical and thermal stability, high ionic conductivity, wide electrochemical potential window and solvation ability, because of which they were initially considered as green solvents [1-4]. The Knoevenagel condensation reaction of aldehydes with compounds containing active methylene compound as shown in (Scheme 1) is one of the best method in organic chemistry to obtain the functionalized alkenes. The condensation product is α,β -unsaturated carbonyl compound which can be used as key intermediate in organic synthesis. It finds a variety of applications in various fields such as synthesis of natural products, agriculture, therapeutic drugs, cosmetics, perfumes, polymers and light emitting materials etc. [5-9].

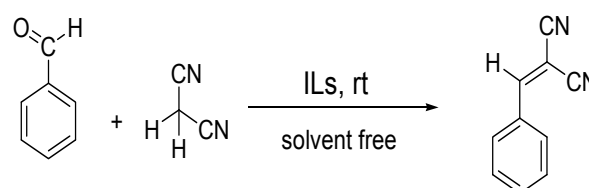
In this work, phosphonium based amino acid ionic liquid namely Tetrabutyl phosphonium L-Alaninate, [P₄₄₄₄][Alaninate], has been synthesized which was then tested for catalytic

activity in the synthesis of α,β -unsaturated carbonyl compounds under solvent free condition on the basis of Knoevenagel condensation reaction.

2. EXPERIMENTAL METHODS

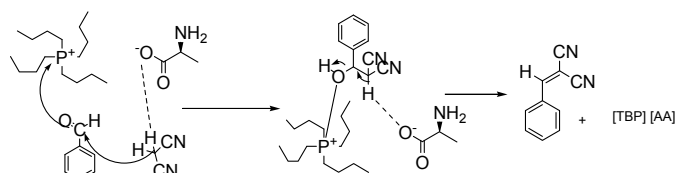
General procedures for the Knoevenagel condensation

A mixture of aldehyde (0.5 mmol) and active methylene compounds such as malononitrile (0.5 mmol), ethyl cyanoacetate (0.5 mmol) and tetrabutylphosphonium amino acid ionic liquid [P₄₄₄₄][Alaninate] (10 mol %) was taken in round bottom flask at room temperature under solvent-free condition. The mixture was stirred at room temperature with magnetic stirrer. The completion of the reaction was monitored by TLC and then, the reaction mixture was transferred into crushed ice and stirred for 30 min. The separated solid was filtered by using watman filter paper, washed with cold water thoroughly and then recrystallized from ethanol to get the pure product.



Scheme 1.

3. RESULTS AND DISCUSSION



Scheme 2. Mechanism for the Knoevenagel reaction.

A proposed mechanism of this reaction is summarized in Scheme 2. Firstly the carbonyl group of benzaldehyde get activated by the formation of hydrogen bonding with the amino acid anion. The second step involves the abstraction of acidic hydrogen from the active methylene group of malononitrile by the carboxylate group of amino acid. The next step involves the formation of carbanion as intermediate. The carbanion now makes the nucleophilic attack on the carbonyl carbon of aromatic aldehyde to form Knoevenagel product.

No product formation is detected for the blank reaction, which clearly shows that Knoevenagel condensation reaction is very difficult without catalyst. The results are shown in table 1. The results show that all the products were obtained in good yields in shorter reaction time, indicating that the [P₄₄₄₄][Alaninate] can be used as efficient catalyst for Knoevenagel reaction.

The comparison of the Knoevenagel condensation reaction carried out between malononitrile or ethyl cyanoacetate with various aromatic aldehydes, shows that more time is required in case of ethyl cyanoacetate than in case of malononitrile (table 1). This is due to the fact, the electron withdrawing power of cyanide group is much stronger than that of carbonyl / carboxylic group. Because of this the methylene group of malononitrile is more activated than ethyl cyanoacetate and reacts fast with aromatic aldehyde.

Table 1. Comparison of Knoevenagel condensation reaction between aromatic aldehyde (R₁) and malononitrile / ethyl cyanoacetate.

R ₁	products	Yield (%)	Time (min)
C ₆ H ₅ CHO		72	15
3-NO ₂ -C ₆ H ₅ CHO		61	2
3-NO ₂ -C ₆ H ₅ CHO		75	15

4. CONCLUSION

The use of AAIL as a catalyst provides a very efficient and convent methodology for Knoevenagel condensation reaction of aromatic aldehydes with a variety of active methylene compounds. The advantages are mild reaction conditions (room temperature), short reaction time (2-20 min), good yield of isolated products and reusability of the catalyst. Another advantage is the absence of organic solvent that makes it an approach towards the development of green chemistry.

5. ACKNOWLEDGEMENTS

Aafaq Ahmad Tantray gratefully acknowledges Savitribai Phule Pune University, Pune, Maharashtra, India for giving the Ph. D. fellowship.

REFERENCES

- [1] Kevin. J. F, Douglas R. M., J. Chem., 62 (2009) 309–321.
- [2] Martins M. A. P, Frizzo. C. P., Tier A. Z., Moreira D. N., N. Zanatta, Bonacorso H. G., Chem. Rev., 114 (2014) 1–70.
- [3] Vekariya. R. L., Journal of Molecular Liquids 227 (2017) 44–60.
- [4] Warke I. J, Patil K. J, Terdale S. S., J. Chem. Thermodynamics. 93 (2016) 101–114.
- [5] Fan. O, Yan. Z, Zhang-Min. L, Duan-Jian H. T. Korean J. Chem. Eng., 31, 8 (2014) 1377-1383
- [6] Iglesias, M. Gonzalez-Olmos, R. Cota, I. Medina .F. Chemical Engineering Journal. 162 (2010) 802–808.
- [7] Pippal, P. Singh, P. P. Orient. J. Chem. 33., 4 (2017) 1736-1743.
- [8] Leelavathi, P. Ramesh Kumar S., Journal of Molecular Catalysis A: Chemical., 240, (2005) 99–102.
- [9] Patil, S. S. Jadhav S. D., Deshmukh, M. B. Indian Journal of Chemistry, 54B (2013) 1172-1175.