

## Aliquat 336 catalysed Knoevenagel condensation at room temperature

Kyadare G. N.

Department of chemistry Degloor college, Degloor SRTMU Nanded

Email - [ganesh.chem@rediffmail.com](mailto:ganesh.chem@rediffmail.com)

### ABSTRACT:

*Knoevenagel condensation of aromatic aldehydes with active methylene compounds malononitrile, proceeds smoothly in the presence of Aliquat 336 as catalyst at room temperature without solvent, to produce products of good purity and in high yields. The reactions occur at room temperature giving excellent yields of the products. All the reactions were performed under mild reaction conditions, shorter reaction time and in high yields. All the synthesized compounds were characterized by IR, <sup>1</sup>HNMR, Mass.*

**KEYWORDS:** Knoevenagel condensation, active methylene compounds, Aliquat 336.

### 1. INTRODUCTION:

The Knoevenagel condensation of aldehydes with active methylene compounds is an important and widely employed method for carbon-carbon bond formation in organic synthesis(1) There have been several modifications of the reaction such as the Doebner modification, Hantzsch pyridine synthesis, the Feist-Benary furan synthesis and the Gewald reaction, all contain a step of Knoevenagel reaction with numerous applications in the synthesis of fine chemicals,(2) hetero Diels-Alder reactions(3) and in synthesis of carbocyclic as well as hetero- cyclic(4) compounds of biological significance. The reactions are usually catalysed by bases(5) such as amines, ammonia or sodium ethoxide in organic solvents. Lewis acids,(6) surfactants,(7) zeolites(8) and heterogeneous catalysts(9) have also been employed to catalyse the reactions. Similarly, the use of ionic liquids(10) pave a new path for such organic synthesis. The use of environmentally benign solvents like water(11) and solvent-free reactions represent very powerful green chemical technology procedures from both the economical and synthetic point of view. They not only reduce the burden of organic solvent disposal, but also enhance the rate of many organic reactions. Therefore, efforts have been made to perform the Knoevenagel condensation in aqueous medium as well as in the absence of solvents(12) which are usually catalysed by Lewis acids,(12a) or base(12e,f)and require drastic conditions.(12b-d) Some of these reactions are performed on solid supports, promoted by infrared,(13a) ultrasound or microwave(13b,c) heating.

Aliquat 336 is a water insoluble quaternary ammonium salt made by the methylation of tri octyl / decyl amine, which is capable of forming oil soluble salts of anionic species at neutral or slightly alkaline pH. Aliquat 336 is a versatile and affordable cation source for an entirely new family of hydrophobic ionic liquids.(14) It can form salts with anions over a wider pH range than primary, secondary or tertiary amines. For this reason Aliquat 336 finds application in environments from acid to slightly alkaline pH. It is used as a phase transfer catalyst(15)

Here in the present work we have attempted to discover the role of Aliquat336 as a catalyst in Knoevenagel reaction .We are successful in a one pot protocol for the synthesis of 3,4 dimethoxybenzylidene malanonitrile by just stirring the equimolar mixture of malanonitrile, 3,4-dimethoxybenzaldehyde, in presence of catalytic amount of Aliquat336 .The structure of the derivative was confirmed based on the spectral data .

### 2. MATERIALS & METHOD:

Aldehydes , malononitrile & Aliquat336 were procured from Sd-fine chem. All melting points were determined in open capillaries on Kumar's melting point apparatus. <sup>1</sup>H NMR spectra were recorded on Mercury Plus Varian in CDCl<sub>3</sub> at 400 MHz using TMS as an internal standard. IR spectra were recorded on a Perkin-Elmer FTIR using KBr discs. Mass spectra were recorded on Micromass Quattro II using electrospray Ionization technique, showing (m+1) peak as a base peak. The test for the purity of products and the progress of the reactions were accomplished by TLC on Merck silica gel plates. General procedure : Synthesis of 3,4-Dimethoxy-benzylidene malononitrile. In a 100 ml round bottom flask 1 mmole of malanonitrile (0.066gm) is warmed 5 min on magnetic stirrer and mixed with 1 mmole of benzaldehyde 0.166gm alongwith catalytic amount of Aliquat336 and warmed on mechanical stirrer for 3 minutes and then 5 ml water is added to get yellow solid .The completion of reaction checked by T.L.C. The reaction mixture was poured on ice contained a beaker to obtain the product .The solidified substance was filtered and recrystallized from ethanol.

### 3. RESULT & DISCUSSION:

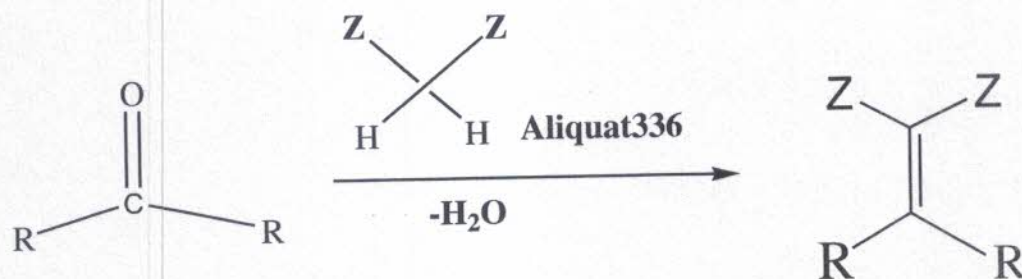
  
Dr. Anil Chidrawar

IC Principal

A.V. Education Society's  
Degloor College, Degloor Dist.Nanded



Here in the present work we have attempted to discover the role of Aliquat336 as a catalyst in Knoevenagel reaction. We are successful in a one pot protocol for the synthesis of 3,4 dimethoxybenzylidene malanonitrile by just stirring the equimolar mixture of malanonitrile, 3,4-dimethoxybenzaldehyde, in presence of catalytic amount of Aliquat336. The structure of the derivative was confirmed based on the spectral data.



In this reaction the carbonyl compound is an aldehyde or a ketone. The catalyst is usually a weakly basic amine. The active hydrogen component has the following for  $Z-CH_2-Z$  or  $Z-CHR-Z$  such as diethyl malonate, Meldrum's acid, ethyl acetoacetate or malonic acid, or cyanoacetic acid.  $Z-CHR_1R_2$  such as nitromethane, where  $Z$  is an electron withdrawing functional group.  $Z$  must be powerful enough to facilitate deprotonation to the enolate ion even with a mild base. Using a strong base in this reaction would induce self-condensation of the aldehyde or ketone.

#### 4. ANALYSIS:

Molecular Formula =  $C_{12}H_{10}N_2O_2$

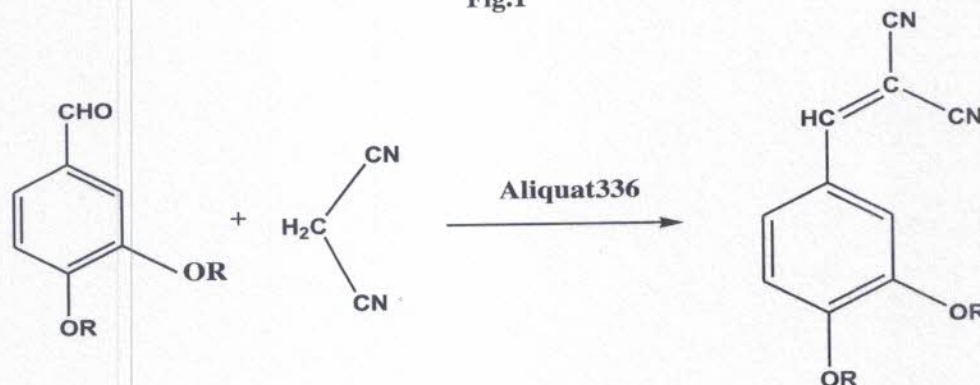
Molecular Weight 214.23 = Exact Mass 214 = Molecular Composition Calculated found

C 67.3% 67.28% O 4.75% 4.71% N 13.08% 13.05%

<sup>1</sup>H NMR:  $\delta$  ppm 7.14-7.87(m, 3H, Ar), 3.85(s, 3H, OMe), 3.86(s, 3H, OMe), 6.88(s, 1H, CH)

IR (KBr): (cm<sup>-1</sup>) 3080-3030 (C-H); 3050.83 (Ar C-H); 2235-2215 (CN); 1604±3 (C=C); 1160.03 (O-CH<sub>3</sub>)

Fig.1



#### 5. CONCLUSION:

Thus, we have successfully synthesized 3,4 dimethoxy benzylidene malanonitrile by using Aliquat 336 Knoevenagel condensation reaction. A highly efficient and simple method has been described for the catalysed synthesis of this compound, The present condensation completes with the principle of green chemistry.

#### REFERENCES:

1. Jones, G. *In Organic Reactions*; Wiley: New York, (1967); Vol. 15, pp 204-599
2. Fleming, I., Eds.; *Pergamon Press: Oxford*, (1991); Vol. 2, pp 341-394.
3. Tietze, L. F.; Saling, P. *Synlett* (1992), 281-282; (b) Borah, H. N.; Deb, M. L.; Boruah, R. C.; Bhuyan, P. J. *Tetrahedron Lett.* (2005), 46, 3391-3393.
4. Tietze, L. F. *Chem. Rev.* (1996), 96, 115-136.
5. Ayoubi, S. A.-E.; Texier-Boullet, F.; Hamelin, J. *Synthesis* (1994), 258-260; (b) Binev, I. G.; Binev, Y. G.; Stamboliyska, B. A.; Juchnovski, I. N. *J. Mol. Struct* (1997), 435, 235-239; (c) Brufola, G.; Fringuelli, F.; Piermatti, O.; Pizzo, F. *Heterocycles* (1997), 45, 1715-1721.
6. Prajapati, D.; Lakhok, K. C.; Sandhu, J. S.; Ghosh, A. C. *J. Chem. Soc., Perkin Trans. 1* (1996), 959-



960. \* Dist. Nanded.
7. Bose, D. S.; Narsaiah, A. V. *J. Chem. Res. (S)* (2001), 36–38.
  8. Reddy, T. I.; Verma, R. S. *Tetrahedron Lett*(1997), 38, 1721–1724.
  9. Kubota, Y.; Nishizaki, Y.; Ikeya, H.; Saeki, M.; Hida, T.; Kawazu, S.; Yoshida, M.; Fujii, H.; Sugi, Y. Micro- porous Mesoporous Mater.(2004), 70, 135–149; (b) Ben- nazha, J.; Zahouilly, M.; Boukhari, A.; Hol, E. A. *J. Mol. Catal. A: Chem*(2003), 202, 247–252.
  10. Harjani, J. R.; Nara, S. J.; Salunkhe, M. M. *Tetra- hedron Lett.* (2002), 43, 1127–1130; (b) Khan, F. A.; Dash, J.; Satapathy, R.; Upadhyaya, S. K. *Tetrahedron Lett.* (2004), 45, 3055–3058.
  11. (a) Li, C. J.; Chan, T. H. *Organic Reactions in Aqueous Media*; John Wiley and Sons: New York, (1997), 1–189; (b) Lindstrom, U. M. *Chem. Rev.*(2002), 102, 2751–2772.
  12. Thakur, A. J.; Prajapati, D.; Gogoi, B. J.; Sandhu, J. S. *Chem. Lett.* (2003), 32, 258–259; (b) Bigi, F.; Conforti, M. L.; Maggi, R.; Piccinno, A.; Sartori, G. *Green Chem.* (2001), 3, 101–104; (c) Hangarge, R. V.; Sonwane, S. A.; Jarikotc,
  13. D. V.; Shingarce, M. S. *Green Chem.* (2001), 3, 310–312; (d) Kaupp, G.; Naimi-Jamal, M. R.; Schmeyers, J. *Tetra- hedron* (2003), 59, 3753–3760; (e) Cao, Y.-Q.; Dai, Z.; Zhang, R.; Chen, B.-H. *Synth. Commun.* (2004), 34, 2965– 2971; (f) Jin, T.-S.; Zhang, J.-S.; Wang, A.-Q.; Li, T.-S. *Synth. Commun.* (2004), 34, 2611–2616.
  14. (a) Obrador, E.; Castro, M.; Tamariz, J.; Zepeda, G.; Miranda, R.; Delgado, F. *Synth. Commun.* (1998), 28, 4649– 4663; (b) Ayoubi, S. A.-E.; Texier-Boullet, F. *J. Chem. Res. (S)* (1995), 208–209; (c) Xu, X.-M.; Li, Y.-Q.; Zhou, M.-Y.; Tan, Y.-H. *Chin. J. Org. Chem.* (2004), 24, 184– 186.
  15. J. Mikkola; P. Virtanen; R. Sjöholm, *Green Chem.*, 8, 250, (2006).
  16. K. Sato; M. Aoki; *Science*, 281, 1646, (1998).

  
**Dr. Anil Chidrawa,**  
I/C Principal  
A.V. Education Society's  
Degloor College, Degloor Dist. Nanded