

Ionic Liquid Ethyl Ammonium Nitrate (EAN): An Efficient Catalyst for the Synthesis of Dipyrromethane under Room Temperature

Sagar R. Kande¹, Uddhav N. Chaudhar^{2*}

¹P.G. Department of Chemistry, New Arts, Commerce and Science College, Shevgaon, Ahmednagar, Maharashtra, India

²Department of Chemistry, Kalikadevi Arts, Science & Commerce College, Shirur (Ka.), Beed, Maharashtra, India

ABSTRACT

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A simple, convenient efficient and eco friendly one-pot synthesis of dipyrromethane derivatives using ionic liquid i.e. ethyl ammonium nitrate by the reaction of aromatic aldehydes and pyrrole was reported. Short reaction time, room temperature solvent free reaction condition, high yields and environmental friendliness are the main advantages of this method.

Keywords: Dipyrromethane, Aromatic aldehydes, solvent free

I. INTRODUCTION

The development of a chemical reaction which eliminates to reduce the hazardous products through the chemical reaction is known as the green chemistry [1-2]. In order to achieve this goal various synthetic organic chemists are working in this area for the development of efficient transformation reaction. Environment friendly catalyst and solvent free reactions these are the important aspects for the synthesis in an organic chemistry [3-5]. High yield, low reaction cost and eco-friendly these the main advantages of the solvent free reactions. In this context, several organic chemists are in this field of green chemistry to develop the best route in the

organic reactions using solvent-free reaction conditions at room temperature [6-8].

Several porphyrins and porphyrin analogues which are widely used in several areas were synthesized by using the dipyrromethanes as a starting compound. It is also well known that the pyrrole chemistry is closely associated with the natural products [9-11]. In this regard several efforts have been taken by the researchers to develop the dipyrromethanes using aldehydes and pyrrole [12-15]. Moreover, the reported methods till this date are having several disadvantages like expensive catalyst, toxic solvent, long reaction time etc.

Thus the present work deals with the successful synthesis of substituted dipyrromethanes using ionic liquid i.e. ethyl ammonium nitrate (EAN) by the

reaction of aromatic aldehydes and pyrrole. The results show the improved the quantum efficiency of the reaction.

II. EXPERIMENTAL

All solvents and chemicals which are used in this reaction are of analytical grade quality without any purification and were produced from sigma-aldrich. The progress of the reaction was monitored through thin layer chromatography using silica gel coated aluminium sheets. Melting points were measured by an open capillary tube method and are uncorrected. ^1H NMR was carried out Bruker AMX-500 MHz spectrometer at 500MHz. IR spectra recorded from KBr disk on the Nicolet Nexus FTIR 670 spectrophotometer.

Typical procedure for the synthesis of dipyrromethane derivatives using EAN as a catalyst at room temperature-

The mixture of aromatic aldehyde (1mmol), pyrrole (2mmol) and 7mmol% EAN was taken in a round bottom flask and stirred it for 30 minutes on magnetic stirrer. The progress and completion of the reaction was monitored through thin layer chromatography using silica gel coated aluminium sheets. Recrystallization method was used to purify the product using ethyl alcohol as a solvent to get products (3a-k). All the compounds were synthesized, characterized and compared using their data in literature.

Spectroscopic Data for representative and newly synthesized compounds is listed below:

3a: Pale yellow solid, m.p. 96-99°C; ^1H NMR (500 MHz) δ : 6.71 (s, 1H), 6.03 (s, 2H), 5.95 (q, $J=3.3$ Hz, 2H), 7.75 (t, $J=3.3$ Hz, 2H), 6.80-6.90 (m, 5H, ArH), 8.05 (s, 2H, NH); IR (KBr) ν : 3355, 3105, 1605, 1495, 1507, 1305, 997, 690, 670 cm^{-1} .

3d: Light Yellow solid, m.p. 121-123°C; ^1H NMR (500 MHz) δ : 3.24 (s, 6H), 4.93 (s, 1H), 6.20 (s, 2H), 5.92 (q, $J=3.1$ Hz, 2H), 7.11-7.22 (m, 4H), 8.40 (s, 2H, NH); IR (KBr) ν : 3386, 3102, 1706, 1594, 1560, 1512, 1259, 988, 764 cm^{-1} .

3g: Light brown solid, m.p. 174-177°C; ^1H NMR (500 MHz) δ : 6.63 (t, $J=3.1$ Hz, 3H), 7.23 (q, $J=3.4$ Hz, 2H), 7.11 (d, $J=2.3$ Hz, 2H), 8.23 (q, $J=2.3$ Hz, 2H), 8.49 (t, $J=6.9$ Hz, 1H), 8.30 (d, $J=8.1$ Hz, 1H), 8.50 (s, 2H, NH); IR (KBr) ν : 3242, 2944, 1752, 1746, 1344, 1352, 988, 659 cm^{-1} .

3k: Light yellow solid, m.p. 84-86°C; ^1H NMR (500 MHz) δ : 3.95 (s, 2H), 6.12 (s, 2H), 5.94 (q, $J=3.1$ Hz, 2H), 7.01 (q, $J=2.5$ Hz, 2H), 8.10 (s, 2H, NH); IR (KBr) ν : 2995, 3113, 1614, 1511, 1395, 1112, 997, 823, 691 cm^{-1} .

III. RESULTS AND DISCUSSION

The dipyrromethane derivatives were synthesized by the condensation of mixture of aromatic aldehyde (1mmol), pyrrole (2mmol) and 7mmol% EAN as a catalyst. The products (3a-k) obtained were purified by recrystallization method using ethyl alcohol as a solvent. Several lewis, bronsted acids and ionic liquids were studied were by different researchers till this date. The EAN gives remarkable results during the synthesis of dipyrromethanes derivatives at room temperature. The effect of the catalyst concentration was also studied. The 7 mmol% was observed as an optimum concentration of the catalyst for the successful formation of the product. It is also observed that the aromatic aldehyde with electron withdrawing group shows the enhanced yield. In this regard the EAN acts as an efficient reaction for this green reaction.

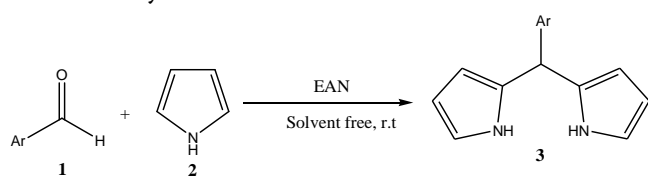
Table 1**Effect of the catalyst concentration**

Entry	EAN (mmol%)	Yield ^b
1	3	82.3
2	7	91.2
3	10	86.4
4	15	83.4
5	20	79.9

Note- Bold values indicate optimized condition

a Reaction condition: 1a(1mmol) and 2(2mmol), rt

b Isolated yield

**Scheme 1: Synthesis of dipyrromethane derivative****Table 2****EAN catalyzed synthesis of dipyrromethane -**

Entry	Aldehydes (1)	% Yield ^a
3a		93.3
3b		89.2
3c		83.7
3d		88.4
3e		86.3
3f		81.5
3g		89.4
3h		81.5
3i		88.6

3i		88.6
4j		90.5
3k		87.7

Isolated Yields.**IV. CONCLUSION**

In conclusion we have developed an eco-friendly protocol for the synthesis of dipyrromethane derivatives by using aromatic aldehydes and pyrrole in the presence of EAN as a catalyst. Short reaction time, low cost, high reaction yield and room temperature reaction these are the advantages of this procedure.

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VI. REFERENCES

- [1]. S.A.R. Mulla, A. Sudalai, M.Y. Pathan, S.A. Siddique, S.M. Inamdar, S.S. Chavan and R.S. Reddy, RSC Adv., 2012, 2, 3525.
- [2]. H. Xiang, L. Zhou, Y. Feng, J. Cheng, D. Wu and X. Zhou, Inorg. Chem., 2012, 51, 5208.
- [3]. M. Ak, V. Gancheva, L. Terlemezyan, C. Tanyeli and L. Toppare, Eur. Polym. J., 2008, 44, 2567.
- [4]. S. Verma, S. Kumar, S.L. Jain and B. Sain, Org. Biomol. Chem., 2011, 9, 6943.
- [5]. H. Mori, T. Tanaka, N. Aratani, B. S. Lee, P. Kim, D. Kim and A. Osuka, Chem. Asian J., 2012, 7, 1811.

- [6]. R. Sharma, A.K. Pandey and P.M.S. Chauhan, *Synlett.*, 2012, 23, 2209.
- [7]. C.D. Gabbutt, B.M. Heron, C. Kilner and S.B. Kolla, *Dyes and Pigments*, 2012, 94, 175.
- [8]. J. Jaratjaroonphong, S. Tuengpanya, R. Saeeng, S. Udompong and K. Srisook, *Eur. J. Med. Chem.*, 2014, 83, 561.
- [9]. E.A. Mikhalitsyna, V.S. Tyurin, S.E. Nefedov, S.A. Syrbu, A.S. Semeikin, O.I. Koifman and I.P. Beletskaya, *Eur. J. Inorg. Chem.*, 2012, 14, 5979.
- [10]. Y. Wu, J. Feng, H. Gao, X. Feng and L. Jiang, *Adv. Mater.* 2019, 31, e1800718.
- [11]. J.H. Clark, *Acc. Chem. Res.* 2002, 35, 791.
- [12]. J.K. Laha, S. Dhanalekshmi, M. Taniguchi, A. Ambroise and J.S. Lindsey, *Organic Process Research & Development* 2003, 7, 799.
- [13]. B. Temelli and C. Unaleroglu, *Tetrahedron* 2006, 62, 10130.
- [14]. A.S. Amarasekara, *Chem. Rev.* 2016, 116, 6133.
- [15]. L.M. Kantam, A. Ravindra, C.R.V. Reddi, B. Sreedar and B.M. Choudary, *Adv. Synth. Catal.* 2006, 348, 569.