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Recent Advances in Rate Acceleration of Baylis-Hillman Reaction

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ABSTRACT :

The Baylis-Hillman reaction is a carbon-carbon bond forming reaction between activated alkene and carbon electrophile under the influence of a tertiary amine catalyst. It provides a multifunctional molecule usually known as Baylis-Hillman adducts. This article highlights the recent advances in the rate acceleration of Baylis-Hillman reaction.

KEYWORDS: Carbon-carbon bond forming reaction, carbon electrophile, activated alkenetertiary amine.

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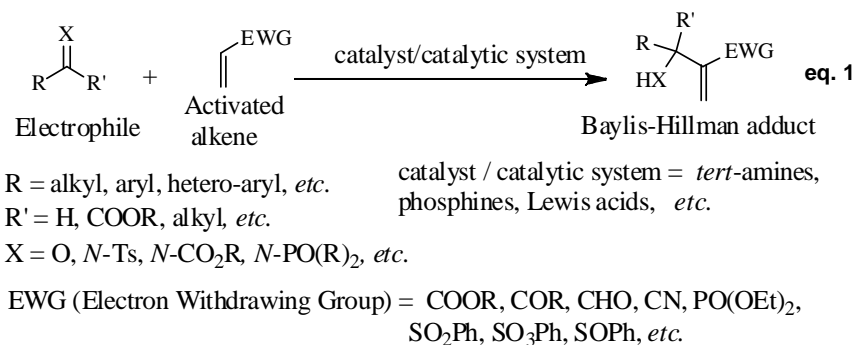
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INTRODUCTION

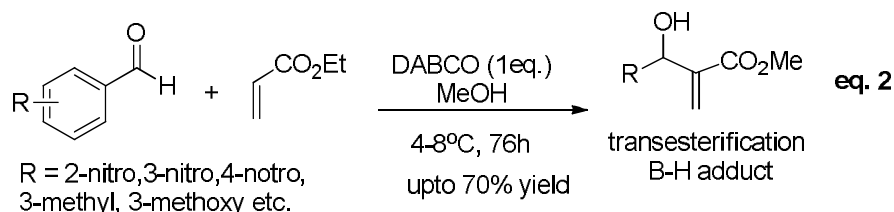
Baylis-Hillman reaction^{1,2} is one of the important carbon-carbon bond forming reaction in organic chemistry. It is a coupling reaction between activated alkenes and electrophiles in the presence of a tertiary amine catalyst (eq. 1). This reaction was discovered^{3,4} in 1973 by two American chemists A. B. Baylis and M. E. D. Hillman.



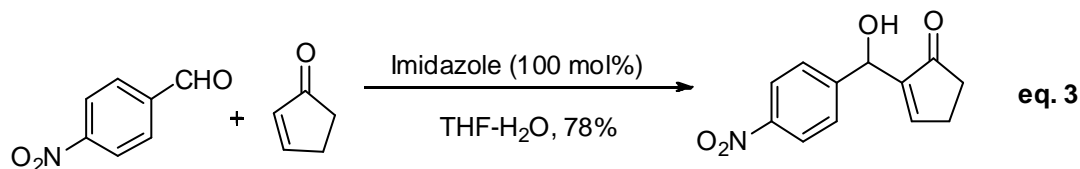
The Baylis–Hillman reaction is a very slow reaction and it requires several days for completion. To overcome this problem many efforts have been made with respect to three essential components *i.e.* electrophiles, activated alkene and catalytic source. Recent advances in this strategy for the rate acceleration of the Baylis–Hillman reaction have discussed in this article.

RATE ACCELERATION OF THE BAYLIS-HILLMAN REACTION

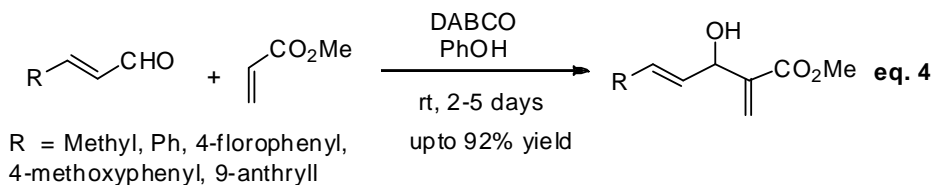
Amarante and co-workers⁵ very recently reported a remarkable rate acceleration of the Baylis–Hillman reaction between benzaldehyde (1eq.) with ethyl acrylate (10eq.) in the presence of DABCO (1eq.) in excess of methanol (63eq.) at 4–8°C for 76h. They also observed transesterification of Baylis-Hillman alcohols in moderate to good yield (eq. 2).



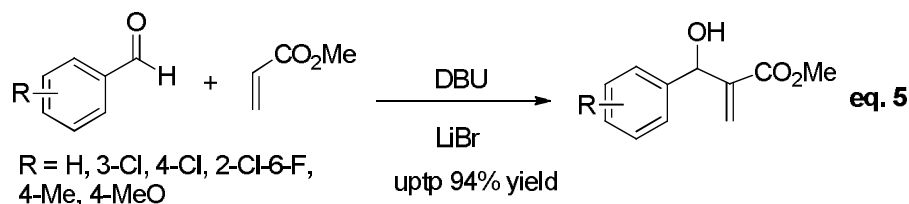
Huimin and co-workers⁶ have observed the considerable rate acceleration of Baylis–Hillman reaction of cyclopent-2-enone and 4-nitrobenzaldehyde in the presence of imidazole on microreactor. Moreover, for the first time reported the rate acceleration approximately 4–5.2 fold under electric field (eq. 3).



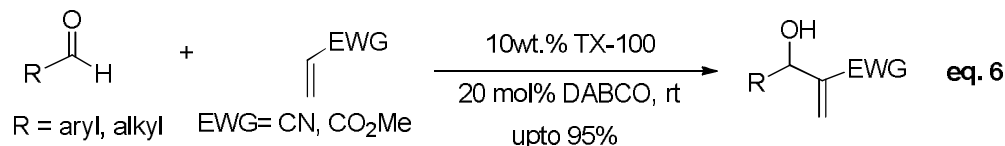
Recently Kim and co-workers⁷ reported the rate acceleration of Baylis-Hillman reaction between various α , β -unsaturated aldehydes and methyl acrylate in the presence of proton donor (eq.4).



Mamaghani and co-workers⁸ reported the rate acceleration of the Baylis-Hillman reaction in the presence of catalytic amount of lithium bromide and DBU in solvent free condition (eq.5).

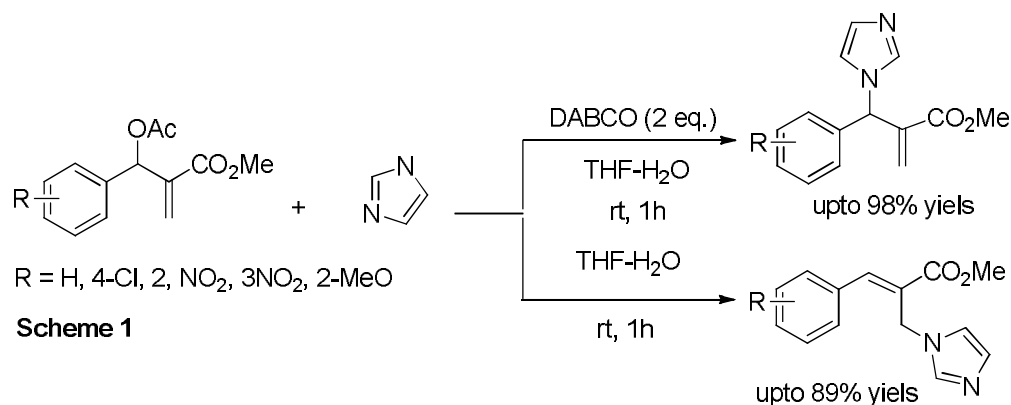


Chaskar and co-workers⁹ reported that triton X-100 aqueous micelle accelerates the Baylis-Hillman reaction of aryl aldehydes and acrylonitrile or ethyl acrylate in the presence of DABCO in good yield (eq.6).

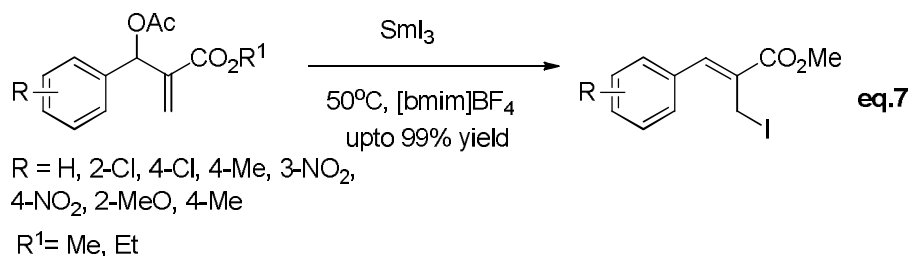


RATE ACCELERATION OF BAYLIS-HILLMAN ADDUCTS

Zhang and co-workers¹⁰ reported the remarkable rate acceleration of Baylis-Hillman adducts in nucleophilic substitution in the presence of aqueous THF solution without any additional reagents for the synthesis of N-substituted imidazole in excellent yield (Scheme 1).



Zhang and co-workers¹¹ reported SmI₃-mediated iodination of Baylis-Hillman adducts in ionic liquid with remarkable rate acceleration for the synthesis of (Z)-allyl iodides in excellent yields (eq. 7).



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REFERENCE

- (a) Basavaiah D, RaoAJ, SatyanarayanaT, Recent Advances in the Baylis-Hillman Reaction and Applications, *Chem. Rev.* 2003; 103, 811. (b) Basavaiah D, Reddy BS, Badsara,SS,Recent Contributions from the Baylis-Hillman Reaction to Organic Chemistry, *Chem. Rev.* 2010;110, 5447. (c) Basavaiah D, Devendar B, LeninDV, Satyanarayana T,Recent Contributions from the Baylis-Hillman Reaction to Organic Chemistry, *Synlett*, 2008; 411. (d) Basavaiah D, Lenin DV, A Facile Synthesis of Substituted Indenones and Piperidine-2,6-diones from theBaylis–Hillman Acetates*Eur.J.Org.Chem*, 2010; 5650. (e) Basavaiah D, Reddy RJ, Lenin DV, The Baylis – Hillman Adducts as Valuable Source for One-Pot Multi-StepSynthesis: A Facile Synthesis of Substituted Piperidin-2-ones,*Helv.Chimica.Acta*, 2010; 1180. (f) Basavaiah D, LeninDV, A simple protocol for the synthesis of a piperidine-2,6-dione frameworkfrom Baylis–Hillman adducts, *Tetrahedron.Lett*, 2009; 50, 3538. (g) BasavaiahD, LeninDV, Veeraraghavaiah G,

- Synthesis of substituted maleimide derivatives using the Baylis–Hillman adducts, *Curr. Science*, 2011;101 (7), 888. (h) Lenin DV, *I.J.C.R.T*, Baylis-Hillman reaction: A novel opportunity to the synthetic organic chemistry, 2018;6, 550. (i) Lenin DV, Baylis-Hillman reaction in organic chemistry, *W.J.P.R*, 2018, 7(6), 641. (j) Lenin DV, Rate acceleration of Baylis-Hillman reaction, *I.J.C.S*, 2018;2(2), 86. (k) Lenin DV, Intramolecular Baylis-Hillman reaction, *I.J.C.S*, 2018; 2(2), 53; (l) Lenin DV, *I.J.E.S.M*, Non-amine catalyzed Baylis-Hillman reaction, 2018;7(5),70. (m) PhD thesis, University of Hyderabad, Rao AJ, 2003; Aravindu K, 2010; Devendar B, 2008; Lenin DV, 2010, Sarada DS, 2004; Raju JR, 2007; Rao JS, 2004; Roy, S, 2010; Satyanarayana T, 2005; (n) Ciganek, E. in *Organic Reactions*: (Ed. L. A. Paquette) Wiley: New York. **1997**: Vol. 51. pp 201.
2. Singh V, Batra S,; Advances in the Baylis-Hillman reaction-assisted synthesis of cyclic frameworks, *Tetrahedron*, 2008; 64, 4511.
 3. Baylis AB, Hillman MED, German patent 2155113, 1972; Chem. Abstr. 1972;77, 34174.
 4. Hillman MED, Baylis AB, U. S. Patent 3743669, 1973.
 5. Amarante GW, Carpanez AG, Coeifo F, J. On the tandem Morita-Baylis-Hillman/transesterification processes. Mechanistic insights for the role of protic solvents *Mol. Structure*. 2018; 1154, 83.
 6. Huimin M, Jun Y, Li Q, Juan Q, Rate Acceleration of the Baylis-Hillman Reaction within Microreactors, *Chin. J. Chem.* 2011; 29, 2385.
 7. Kim JN, Kim KH, Lee HS, Kim YM, Bull. Korean Chem. Soc. Remarkable Rate Acceleration of Baylis-Hillman Reaction of Notorious α,β -Unsaturated Aldehydes Catalyzed by Proton Donor, 2011;32(3), 1087.
 8. Mamaghani M, Radmogadam K, Badrian A, Rate acceleration of Baylis-Hillman reaction with lithium bromide and 1,8-diazabicyclo[5.4.0]undec-7-ene in solvent free medium. *Asian. J. Chemistry*. 2006;18(2), 840.
 9. Chaskar A, Pawar B, Padalkar V, Phatangare K, Nirmalkar S, Micellar media accelerated Baylis–Hillman reaction, *Catal. Sci. Technol.* 2011; 1, 1641.
 10. Zhang Y, Li J, Wang X, Remarkable rate acceleration of water-promoted nucleophilic substitution of Baylis–Hillman acetate: a facile and highly efficient synthesis of *N*-substituted imidazole, *Tett. Lett.* 2005; 46, 5233.
 11. Zhang Y-m, Liu Y-k, Xu D-q, Xu Z-y, Remarkable rate acceleration of SmI₃-mediated iodination of acetates of Baylis-Hillman adducts in ionic liquid: facile synthesis of (*Z*)-allyl iodides, *J. Zhejiang Univ Science B*, 2006, 7(3), 193.