Research article Available online www.ijsrr.org ISSN: 2279–0543

International Journal of Scientific Research and Reviews

Recent Advances in Rate Acceleration of Baylis-Hillman Reaction

Dandamudi V. Lenin*

School of Chemical Sciences, Central University of Gujarat, Gandhinagar, India.
E-Mail: lenindv@cug.ac.in; Phone: +91-934955719.

ABSRACT :

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.

***Corresponding Author:**

Dandamudi V. Lenin

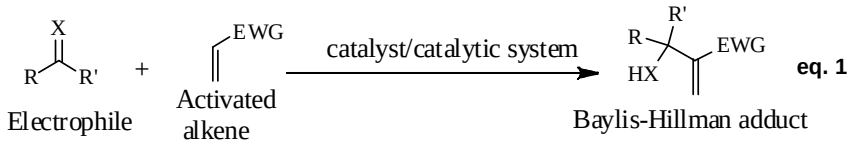
School of Chemical Sciences, Central University of Gujarat,

Gandhinagar, India.

E-Mail: lenindv@cug.ac.in; Phone: +91-934955719.

INTRODUCTION

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



R = alkyl, aryl, hetero-aryl, *etc.*
R' = H, COOR, alkyl, *etc.*
X = O, *N*-Ts, *N*-CO_2R, *N*-$PO(R)_2$, *etc.*

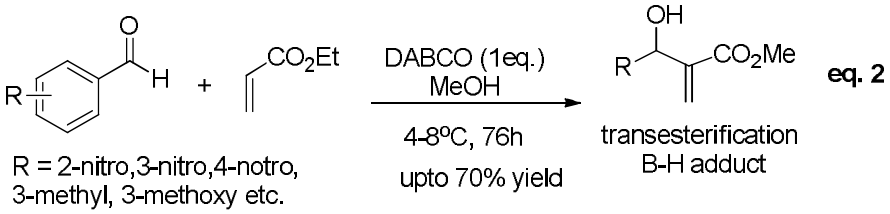
catalyst / catalytic system = *tert*-amines, phosphines, Lewis acids, *etc.*

EWG (Electron Withdrawing Group) = COOR, COR, CHO, CN, $PO(OEt)_2$, SO_2Ph, SO_3Ph, SOPh, *etc.*

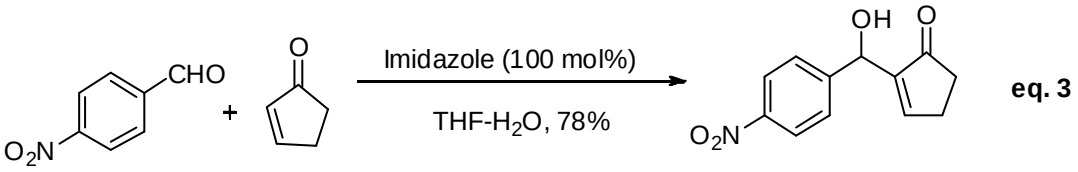
The Baylis–Hillman reaction is a very slow reaction and it requires a several days for completion. Toovercome this problem many efforts has been made with respect to three essential components *i.e.* electrophiles, activated alkene and catalytic source. Recent advances in this strategy for the rate acceleration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

RATE ACCELERATION OF THE BAYLIS-HILLMAN REACTION

Amaranteand co-workers[5]very recently reporteda remarkable rate acceleration of the Baylis–Hillman reaction between benzaldehyde (1eq.) with of ethyl acrylate (10eq.) in the presence of DABCO(1eq.) in excess of methanol (63eq.) at 4-8^oC for 76h. They also observed transesterification of Baylis-Hillman alcohols in moderate to good yield (eq. 2).

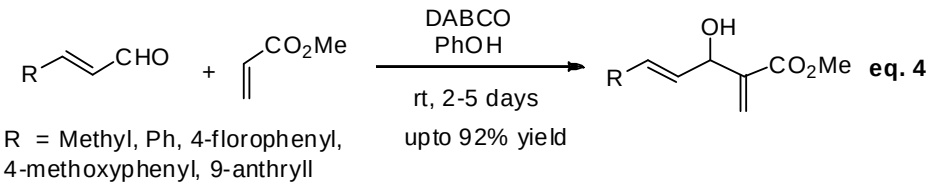


Huimin and co-workers[6]have observedthe considerable rate acceleration of Baylis–Hillman reaction of cyclopent-2-enone and 4-nitrobenzaldehyde in the presence of imidazole on microreactor. Moreover, for the first time reported the rate acceleration approximately 4-5.2fold under electric field (eq. 3).



eq. 3

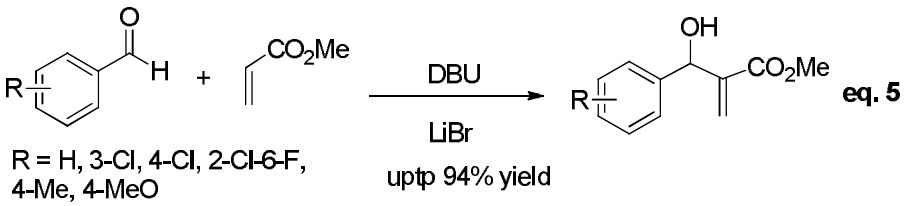
Recently Kim and co-workers[7] reported the rate acceleration of Baylis-Hillman reaction between various α, β–unsaturated aldehydes and methyl acrylate in the presence of proton donor (eq.4).



R = Methyl, Ph, 4-florophenyl, 4-methoxyphenyl, 9-anthryll

eq. 4

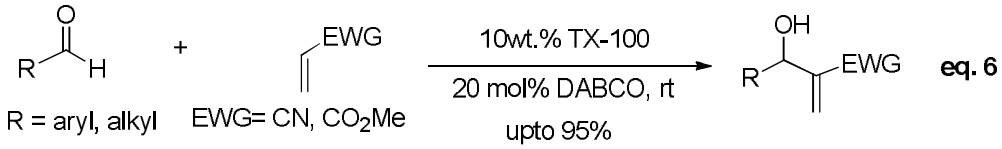
Mamaghani and co-workers[8] reported the rate acceleration of the Baylis–Hillman reaction in the presence of catalytic amount of lithium bromide and DBU in solvent free condition (eq.5).



R = H, 3-Cl, 4-Cl, 2-Cl-6-F, 4-Me, 4-MeO

eq. 5

Chaskar and co-workers[9] 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).

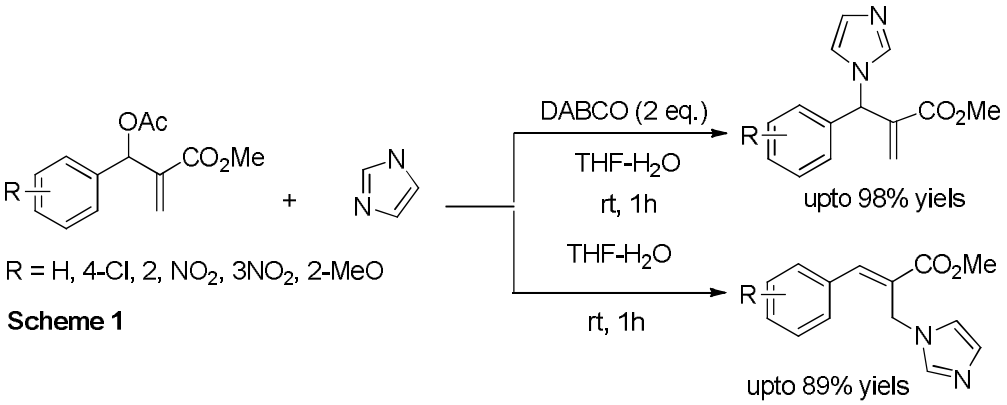


R = aryl, alkyl EWG= CN, CO_2Me

eq. 6

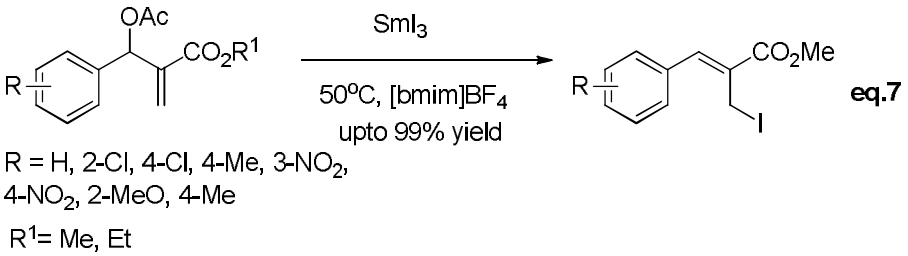
RATE ACCELERATION OF BAYLIS-HILLMAN ADDUCTS

Zhang and co-workers[10] 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).



Scheme 1

Zhang and co-workers[11]reported SmI_3-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).



eq.7

ACKNOWLEDGEMENTS

LDV thankful for financial support from CUG pilot project and UGC tart up grant.

REFERENCE

1. (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 AcetatesEur.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 derivativesusing 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; DevendarB,2008; Lenin DV,2010, SaradaDS**,** 2004; Raju JR, 2007; Rao JS, 2004; Roy, S, 2010; SatyanarayanaT, 2005; (n) Ciganek, E. in *Organic Reactions*: (Ed. L. A. Paquette) Wiley: New York. **1997**: Vol. *51*. pp 201.

2. SinghV, BatraS,; Advances in the BayliseHillman reaction-assistedsynthesis of cyclic frameworks, Tetrahedron, 2008; 64, 4511.
3. BaylisAB, Hillman MED, German patent 2155113, 1972;Chem. Abstr. 1972;*77*, 34174.
4. Hillman MED, BaylisAB, U. S. Patent 3743669, 1973.
5. Amarante GW,Carpanez AG,CoeihoF, J.OnthetandemMorita-Baylis-Hillman/transesterificationprocesses. MechanisticinsightsfortheroleofproticsolventsMol.Structure. 2018; 1154, 83.
6. HuiminM, JunY, Li Q, Juan Q,Rate Acceleration of the Baylis-Hillman Reactionwithin Microreactors, Chin.J.Chem. 2011; 29, 2385.
7. KimJN, KimKH, LeeHS, KimYM, Bull.KoreanChem.Soc. Remarkable Rate Acceleration of Baylis-Hillman Reaction of Notoriousα,β-Unsaturated Aldehydes Catalyzed by Proton Donor, 2011;32(3), 1087.
8. MamaghaniM, RadmogadamK,BadrianA,. Rate acceleration of Baylis-Hillman reaction with lithium bromide and 1,8-diazabicyclo[5.4.0]undec-7-ene in silvent free nedium. Asian. J. Chemistry. 2006;18(2), 840.
9. ChaskarA, PawarB, PadalkarV, PhatangareK, NirmalkarS, Miceller media accelerated Baylis–Hillman reaction, Catal.Sci.Technol. 2011; 1, 1641.
10. ZhangY, LiJ, WangX, Remarkable rate acceleration of water-promotednucleophilic substitution of Baylis–Hillman acetate: a facileand highly efficient synthesis of *N*-substituted imidazole, Tett. Lett. 2005; 46, 5233.
11. ZhangY-m, Liu Y-k, Xu D-q, XuZ-y, Remarkable rate acceleration of SmI3-mediated iodination ofacetates of Baylis-Hillman adducts in ionic liquid:facile synthesis of (*Z*)-allyl iodides,J. Zhejiang Univ Science B, 2006, 7(3), 193.