The Baylis–Hillman reaction: a novel source of attraction, opportunities, and challenges in synthetic chemistry†

Deevi Basavaiah,* Kalapala Venkateswara Rao and Raju Jannapu Reddy

Received 30th October 2006
First published as an Advance Article on the web 23rd March 2007
DOI: 10.1039/b613741p

The Baylis–Hillman reaction is a successful, useful, and atom-economical carbon–carbon bond forming reaction, which has grown from an obscure level to the level of high synthetic popularity due to its operational simplicity and also due to the enormous applications of the Baylis–Hillman adducts in organic synthesis. In this *tutorial review*, we briefly describe the way this reaction has grown to its present heights and the opportunities, attractions, and challenges the reaction offers with respect to its asymmetric and intramolecular versions, and mechanistic aspects.

1. Introduction

Carbon–carbon bond formation is one of the most fundamental reactions in organic chemistry and, therefore, has been and continues to be one of the challenging and fascinating areas in synthetic organic chemistry. Selective construction of carbon–carbon bonds at required places in a situation, where there are a number of competing sites for formation of several carbon–carbon bonds, is the present-day requirement. In fact, such selectivity simplifies the process of assembling a carbon framework, which involves creativity, originality and intellectual input and thus represents a forefront of research in the science of synthesis. For example, let us take methyl vinyl ketone (MVK) where there are possibilities for five different ways of constructing carbon–carbon bonds (Fig. 1). Functional groups play a key role in organic chemistry and the success of organic synthesis depends on functional group transformations.

The Baylis–Hillman reaction is one such interesting reaction, which involves the selective atom-economical

Raju Jannapu Reddy

Raju Jannapu Reddy was born in 1977 in Kantayapalem, Warangal, Andhra Pradesh, India. He obtained BSc (1999) and MSc (2001) degrees from the Kakatiya University, Warangal, India. After working for one year in Dr Reddy's laboratories as a chemist, he joined the PhD program in the University of Hyderabad in August, 2002 under the supervision of Professor Basavaiah, working on the development of the Baylis–Hillman reaction as a useful synthetic tool in organic synthesis.

Deevi Basavaiah

Deevi Basavaiah was born in Valiveru, a village near Tenali, India. After obtaining PhD (1979) under the supervision of Professor Gurbakhsh Singh from the Banaras Hindu University, India, he worked as a post-doctoral fellow in the research group of Professor H. C. Brown, Purdue University, USA, for three years. In 1984 he joined as a faculty member in the School of Chemistry, University of Hyderabad, where he is currently a professor. The development of the Baylis–Hillman reaction is the main aim of his research work. His current research interests also include asymmetric catalysis.

Kalapala Venkateswara Rao

Kalapala Venkateswara Rao was born in 1978 in Penumudi, a village near Repalle, Andhra Pradesh, India. After completion of graduation from the Nagarjuna University, Guntur, he joined as a post-graduate student in 1999 in the Department of Chemistry, Sri Venkateswara University, Tirupati and obtained his MSc (organic chemistry) degree in 2001. Presently, he is working towards a PhD degree in the University of Hyderabad under the supervision of Professor Basavaiah on the "Development of New Catalysts/Catalytic Systems for the Borane-Mediated Asymmetric Reduction of Prochiral Ketones".

School of Chemistry, University of Hyderabad, Hyderabad-500 046, India. E-mail: dbsc@uohyd.ernet.in; Fax: (+)91-40-23012460

† Since there is a limit on number of references, only essential references have been selected and several leading references could not be cited. The references that appeared in earlier reviews[1,2] (except the initial reports) are also not cited.

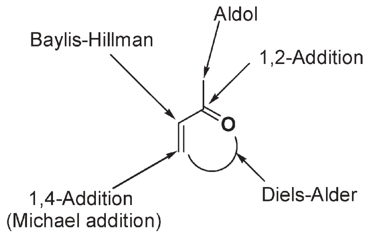


Fig. 1 Five possible ways of constructing C–C bonds with ***MVK***.

construction of a carbon–carbon bond at the α-position of an activated alkene, providing densely functionalized molecules. This reaction has earned overwhelming synthetic popularity in recent years as evidenced by the publication of four major reviews[1,2] and a large number of research papers. We have been working for the last twenty-two years on various aspects of this reaction and have also written two major reviews: one in *Tetrahedron* (1996)[2a] and the second in *Chemical Reviews* (2003).[2b] As regular practitioners of this interesting reaction, we strongly feel that it is desirable to highlight its present status in an overview in terms of its ***attractions***, ***opportunities***, and ***challenges*** in order to provide a better understanding of this reaction. Another important purpose of writing this *tutorial review* is to provide an appropriate emphasis on the need for discovering and developing more and more such *novel efficient synthetic reactions* for the benefit of the chemical community, and thereby to society at large.

2. Origin,[3] growth, and present status

The origin of this reaction dates back to a German patent filed in the year 1972 by A. B. Baylis and M. E. D. Hillman. They reported that the reaction of activated alkenes, such as α,β-unsaturated esters, amides, nitriles and ketones, with a variety of aldehydes, under the catalytic influence of a tertiary bicyclic amine such as 1,4-diazabicyclo[2.2.2]octane (DABCO), pyrrocoline (indolizine) or quinuclidine, produces multifunctional molecules (Fig. 2).[3a]

Despite the atom-economical nature of this reaction and its possibility of possessing high synthetic potential, this reaction did not receive proper attention from organic chemists for more than a decade. In 1982, Drewes and Emslie reported, for the first time, the reaction of ethyl acrylate with acetaldehyde under the influence of DABCO and successfully employed this adduct in the synthesis of integerrinecic acid.[4a] In 1983, Hoffmann and Rabe reported an interesting reaction between methyl/*tert*-butyl acrylates and various aldehydes under the catalytic influence of DABCO to provide the corresponding α-hydroxyalkyl acrylate adducts and elegantly applied one of these adducts for synthesis of racemic mikanecic acid.[4b] Subsequent initial reports, from Perlmutter,[5a] Basavaiah,[5b] Villieras,[5c] Isaacs,[5d] Knochel[5e] and others,[1,2] have indeed changed the fate of this reaction and transformed it into a very useful and promising tool for the construction of carbon–carbon bonds in synthetic chemistry.

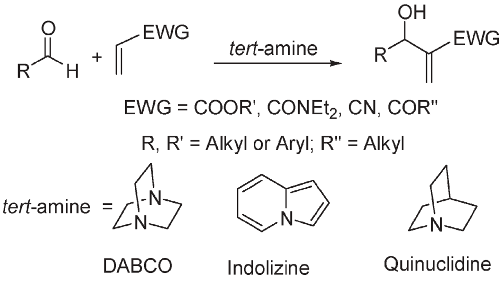
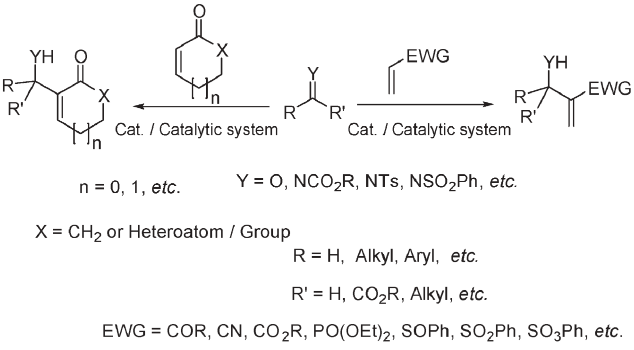


Fig. 2 The Baylis–Hillman reaction: Original patent information.



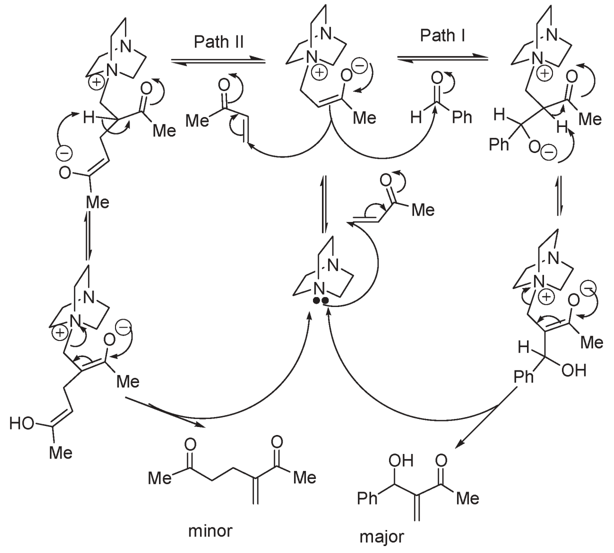
Scheme 1 The Baylis–Hillman reaction.

During the past twenty years this reaction has earned a respectable place in the list of efficient carbon–carbon bond forming reactions. This reaction may be now defined as a one-pot combination of successive Michael, aldol (Michael or alkylation) and elimination reactions. Thus, this is a three component reaction involving construction of a carbon–carbon bond between the α-position of an activated alkene and an electrophile under the influence of a catalyst/catalytic system providing a densely functionalized molecule (Scheme 1). Certain activated alkynes and allenes have also been employed for Baylis–Hillman coupling with electrophiles.[1b,2,6,8] In case the electrophile is prochiral this reaction generates a stereogenic center, thus offering challenges for developing its asymmetric version. Also non-carbon electrophiles have been employed in this fascinating reaction, thus alkyl azodicarboxylates rapidly couple with activated alkenes under the influence of a catalyst, leading to the construction of a C–N bond, providing an interesting class of functionalized molecules.[2b]

3. Mechanism[1,2]

The most widely accepted mechanism of this fascinating reaction is presented in Scheme 2 by taking the model reaction between methyl vinyl ketone as the activated alkene, and benzaldehyde as the electrophile in the presence of DABCO as the catalyst.

The present status of the reaction may be attributed to (i) its operational simplicity in the one-pot atom-economical construction of carbon–carbon bonds providing densely functionalized molecules; (ii) its interesting mechanistic aspects; (iii) the challenges and opportunities it offers in developing its asymmetric and intramolecular versions; and also (iv) the enormous applications of the Baylis–Hillman adducts, due to the proximity of the three chemospecific functional groups, in a number of organic transformation methodologies and stereoselective processes, often leading to the synthesis of very useful molecules of medicinal importance.[1,2]



Scheme 2 A plausible mechanistic pathway.

4. Three essential components[1,2]

During the past twenty years there has been an explosive growth of this reaction with respect to all the three essential components. A variety of acyclic activated alkenes, alkynes and allenes (Fig. 3), cyclic activated alkenes (Fig. 4), electrophiles (Fig. 5), amine catalysts (Fig. 6) and non-amine catalysts (Fig. 7) have been successfully employed in the Baylis–Hillman coupling reaction.

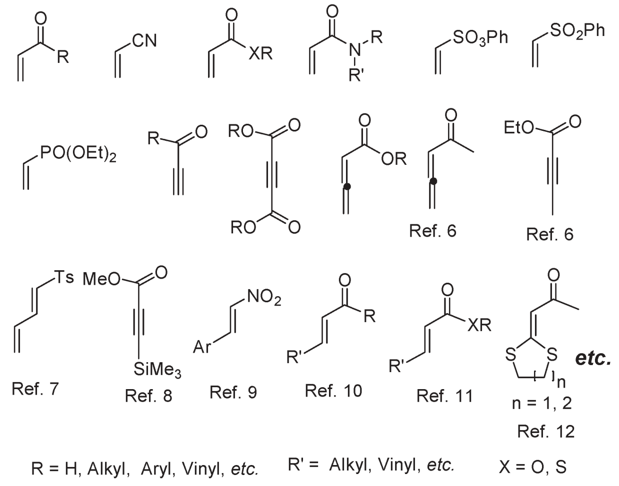


Fig. 3 Acyclic activated alkenes, alkynes and allenes.[1,2,6–12]

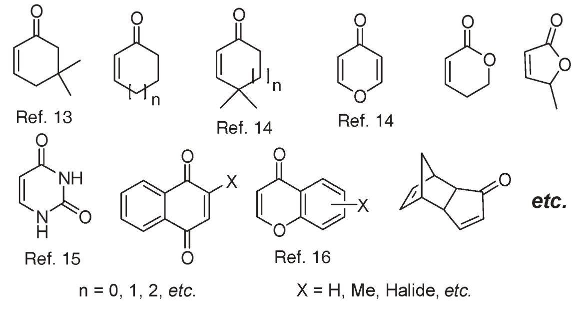


Fig. 4 Cyclic activated alkenes.[1,2,13–16]

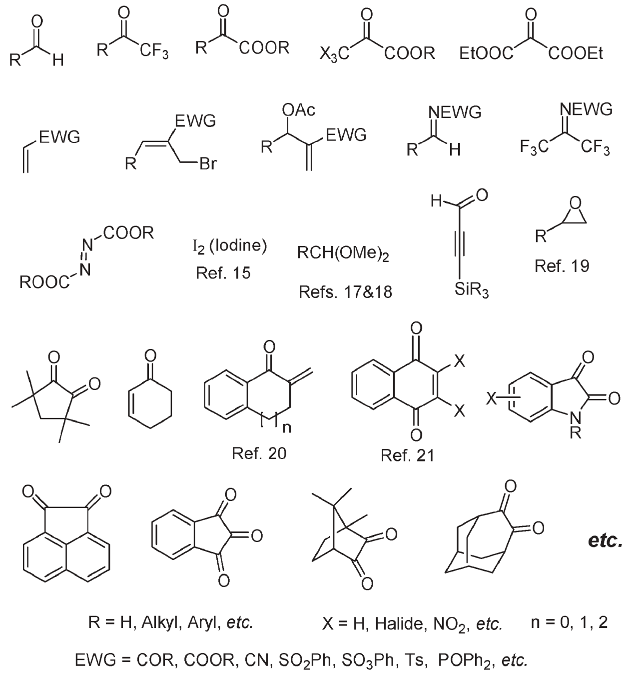


Fig. 5 Electrophiles.[1,2,15,17–21]

4.1 Challenges ahead

4.1.1 Activated alkenes. Although a large variety of activated alkenes (alkynes/allenes) were successfully employed in this interesting reaction, still, applications of several β-substituted activated alkenes, such as β-substituted acrylic esters, vinyl aldehydes, ketones, nitriles, and sulfones (Fig. 8), have not been well studied (very few reports are known under high

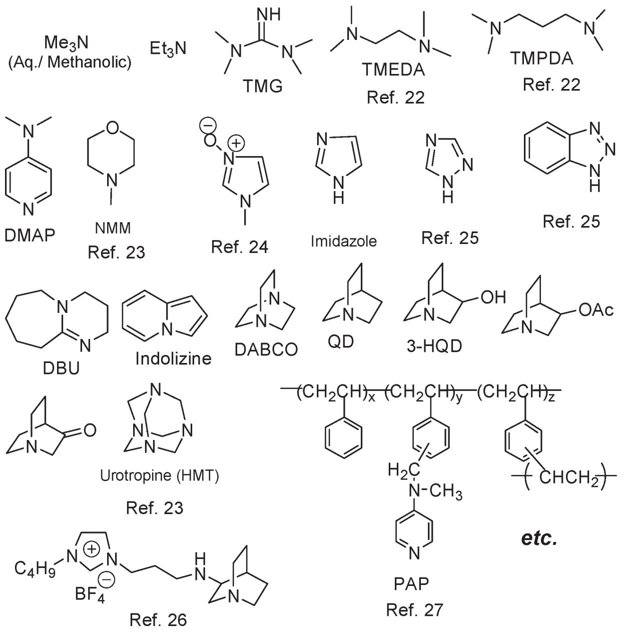


Fig. 6 Amine catalysts.[1,2,22–27]

$TiCl_4$/Chalcogenides; $TiCl_4$; $BF_3.OEt_2$ / Tetrahydrothiophene derivatives; BBr_3/Me_2S; R_3P (Refs. 28&29); R_2AlI, NaOMe (Ref. 14); K_2CO_3 / MeOH (Ref. 14);

MgI_2 (Ref. 19); $MgBr_2$ (Ref. 30);

R = Alkyl, Aryl

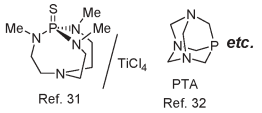


Fig. 7 Non-amine catalysts/reagents.[1,2,14,19,28–32]

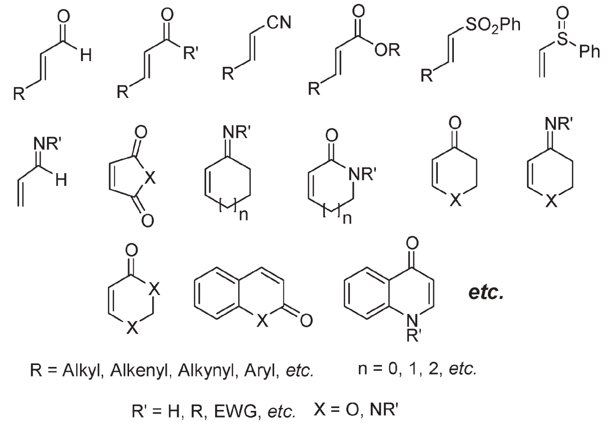


Fig. 8 Activated alkenes which need more attention/to be accommodated.

pressure conditions or with certain electrophiles).[1b,2,9–12] Vinyl sulfoxides need high pressure[1b,2] and therefore methods have to be developed to bring them into the scope of the reaction under normal conditions. Also several classes of activated alkenes (some representative examples are listed in Fig. 8) have not yet entered the territory of this reaction.

4.1.2 Electrophiles. Despite the use of a variety of electrophiles, some common electrophiles, such as simple ketones (usually need high pressure),[2b] simple alkyl/allyl halides, tosylates, mesylates, triflates, aziridines, epoxides (only two reports[19,33]available), imines, and even more reactive electrophiles, such as acid chlorides, did not find their appropriate place in the scale of this reaction (Fig. 9). Also, it will be fascinating to develop a general methodology for the hitherto unknown oxa-Baylis–Hillman reaction using appropriate oxygen electrophiles (Fig. 10).

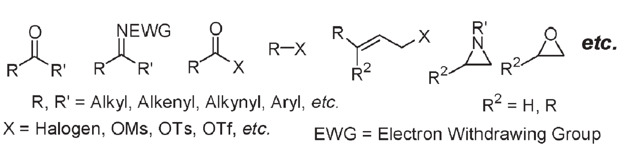


Fig. 9 Electrophiles which need more attention/to be accommodated.

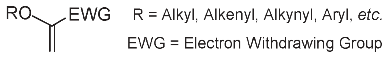


Fig. 10 Oxa-Baylis–Hillman adducts:Future challenge.

4.1.3 Catalysts. A large number of tertiary amines and polymer-bound tertiary amine catalysts have been successfully employed in various Baylis–Hillman reactions. It is worth mentioning here that phosphine-catalyzed dimerization of activated alkenes was reported as early as 1963, in a patent, by Rauhut and Currier.[28] More interestingly, in 1968, Morita and co-workers described an elegant reaction between aldehydes and activated alkenes under the influence of tricyclohexylphosphine, leading to the formation of multifunctional molecules.[29] Now it is well established that various phosphines catalyze a variety of Baylis–Hillman reactions.[1b,2,31,32] Also chalcogenides in combination with Lewis acids, various Lewis acids (without chalcogenides) and other non-amine reagents, mediate the Baylis–Hillman reaction (Fig. 7). However, DABCO is the only catalyst that is applicable for most of the reactions involving different activated alkenes and various electrophiles. Therefore, it is necessary to design and develop new catalysts for accommodating more and more activated alkenes and electrophiles. Interestingly, electrophile-induced (electrophile-containing nucleophilic species) and activated alkene-induced (activated-alkene-containing nucleophilic species) Baylis–Hillman reactions are also known.[17,34] It is, in fact, the present day challenge to develop more such electrophile- and activated-alkene-induced Baylis–Hillman reactions due to the difficulties involved in and attractions of such endeavors.

5. Rate acceleration

Rate acceleration is one of the important aspects, as Baylis–Hillman reactions are usually slow and the reaction may take days to weeks for completion depending on the reactivity of all the three essential components (activated alkene, electrophile and catalyst). Although some systematic studies have been carried out to improve the rate of the reaction on the basis of microwave irradiation, ultrasound, temperature, high pressure conditions, silica gel solid phase medium, increased amounts of catalyst, hydroxy solvents/polar solvents, ionic liquids, and additives *etc.*, the Baylis–Hillman reaction still offers challenges in terms of rate acceleration with respect to operational simplicity.[1,2]

6. Asymmetric version

This reaction has the provision to generate a stereogenic center in the case of a prochiral electrophile. An asymmetric version can, in principle, be achieved in four different possible ways *i.e.* (i) using an enantiopure (enriched) activated alkene system; (ii) using an enantiopure (enriched) electrophile component; (iii) using a chiral catalyst; and (iv) using a chiral solvent or any other chiral medium/additives. In fact, efforts were made in all these directions and reasonable success was accomplished in certain aspects.[1,2]

6.1 Enantiopure activated alkenes[2b]

Enantiopure activated alkenes, mostly acrylates derived from various chiral auxiliaries, have been examined to achieve high diastereoselectivities. Some representative enantiopure

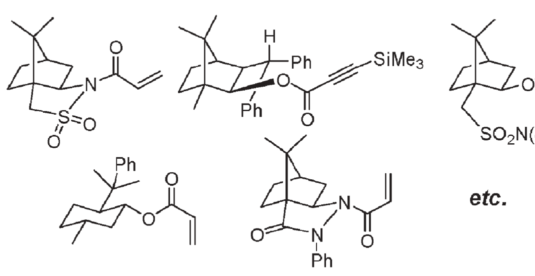


Fig. 11 List of representative enantiopure activated alkenes.[2b]

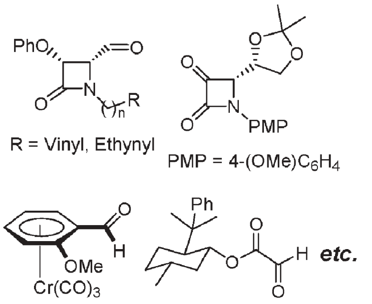


Fig. 12 List of representative enantiopure electrophiles.[2b]

activated alkenes, which provide high diastereoselectivities, are shown in Fig. 11.

6.2 Enantiopure electrophiles[2b]

Various enantiopure electrophiles have also been employed as substrates in the asymmetric Baylis–Hillman reaction and some of the effective enantiopure electrophiles, which exhibit high selectivity, are shown in Fig. 12.

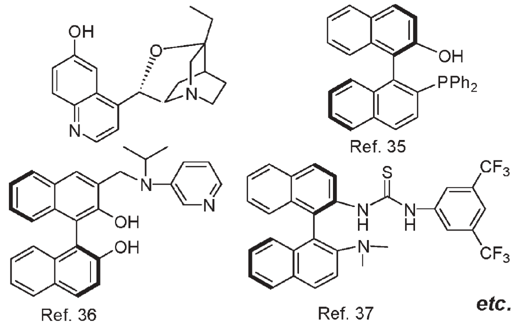
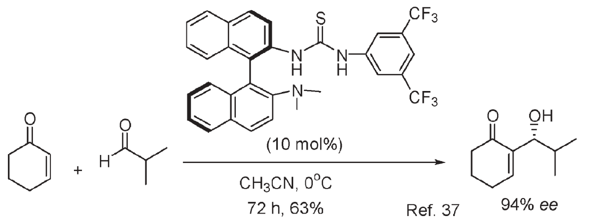


Fig. 13 List of representative chiral catalysts.[2b,35–37]



Scheme 4

6.3 Chiral catalysts: major challenge[2b]

The real attraction and challenge lie in the domain of asymmetric catalysts. Although several attempts have been made in this direction, there are only a few catalysts known to provide high enantioselectivities for specific substrates (representative catalysts that provided high selectivities are presented in Fig. 13 and also some representative examples are shown in Schemes 3 and 4).[35–37] Development of highly appropriate asymmetric catalysts that can be applied to most classes of activated alkenes and electrophiles is indeed the present-day challenge and demand.

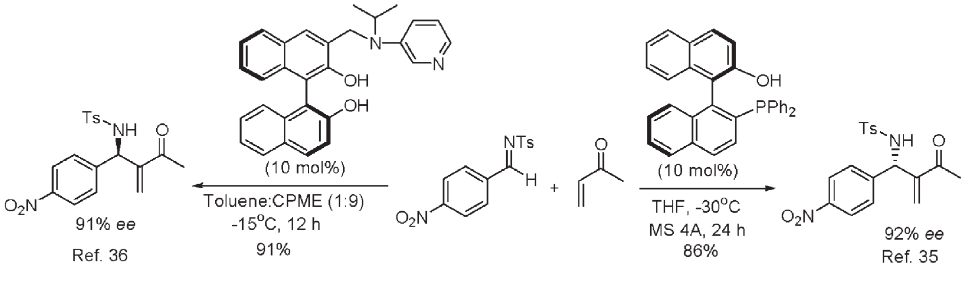
6.4 Enantiopure catalytic sources[2b]

Several enantiopure catalytic sources (also called additives), which can interact with the activated alkene/electrophile either by hydrogen bonding or by coordination, thereby differentiating the diastereomeric transition states formed by the reaction of the activated alkene with the electrophile in the presence of the phosphine or tertiary amine catalyst, to induce high enantioselectivity, have been developed. Some of the successful and promising enantiopure catalytic sources are shown in Fig. 14[17,38–40] (one representative example is shown in Scheme 5[39]).

6.5 Mechanistic challenges and stereoselectivity

Although all the investigations suggest a similar mechanistic pathway (Michael, aldol and elimination as shown in Scheme 2), many aspects of the rate limiting step (RLS) are not yet understood.[1,2,41–44] Most of these mechanistic studies have been concentrated on acrylates (as activated alkenes) and aldehydes (as electrophiles), although several types of activated alkenes and electrophiles have been used in the Baylis–Hillman reaction. Therefore, the Baylis–Hillman reaction still offers challenges in terms of its mechanistic aspects.

Some of the recent reports on the mechanistic investigation offer some possible explanation for the low success rate of the asymmetric version of the Baylis–Hillman reaction. Aggarwal



Scheme 3

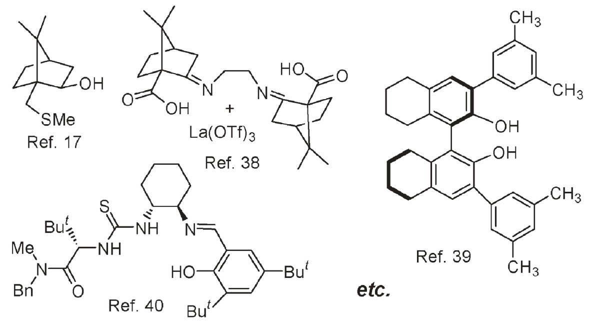
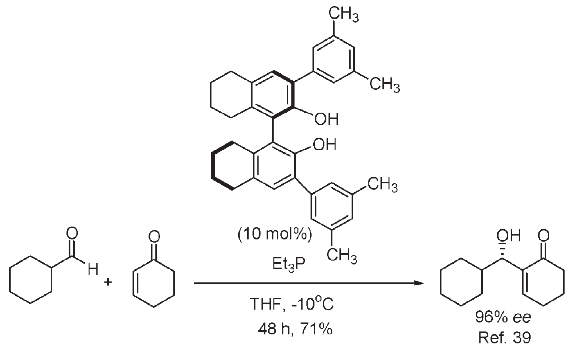
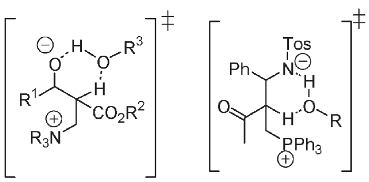


Fig. 14 List of representative enantiopure catalytic sources.[2b,17,38–40]



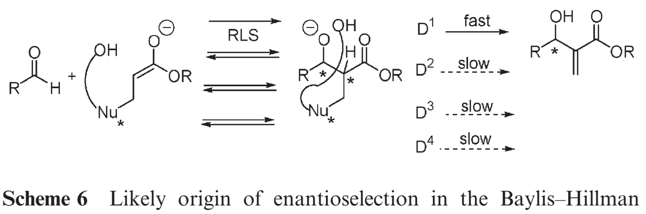
Scheme 5

and co-workers[42] have proposed the transition state (**I**) (Fig. 15) for the proton migration, in the presence of protic species [a similar transition state (**II**) was proposed by Leitner and co-workers for the phosphine-catalyzed Baylis–Hillman reaction between aldimines and MVK (Fig. 15)[43]]. In the case of the asymmetric Baylis–Hillman reaction with chiral catalysts having a protic source, proton migration will be faster in one of the diastereomers generated by the aldol reaction of the enolate (from the activated alkene) onto the electrophile, and the other diastereomer reverts back to starting materials, thus providing the Baylis–Hillman adducts with high enantioselectivity (Scheme 6).[42]

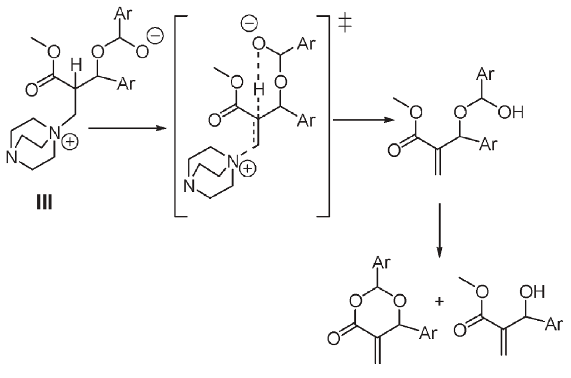


I **II**

Fig. 15 Possible transition states for the proton migration.



Scheme 6 Likely origin of enantioselection in the Baylis–Hillman reaction. D$^{1-4}$ are diastereomers of the alkoxide adduct. (Reprinted with permission from ref. 42. Wiley-VCH, STM-Copyright & Licences).



Scheme 7 Possible hemiacetal transition state.

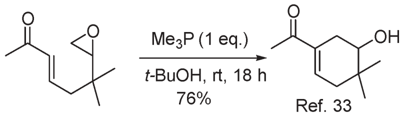
McQuade and co-workers[44] have proposed a hemiacetal intermediate (**III**) for the proton migration *via* a six-membered transition state (Scheme 7). 1,3-Interaction in the transition state of the hemiacetal formation might allow a specific diastereomer to react faster compared to other diastereomers, leading to the formation of the product with high selectivity.

6.6 Developing a promising chiral catalyst: real challenge

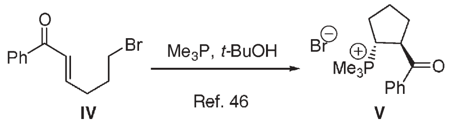
Since two new stereogenic centers are generated *via* the reaction of the enolate, obtained by Michael addition of the chiral catalyst to the activated alkene, with the prochiral electrophile, in principle there is possibility of formation of four diastereomeric transition states. Therefore, development of the most appropriate chiral catalyst(s), which selectively favor(s) only one of these four possible transition states thereby providing high enantioselectivity (either by thermodynamic control or by kinetic control), or permit(s) the selective transformation of one of the diastereomers into the product (while allowing others to revert back to the starting materials) resulting in high enantioselectivity (as proposed by Aggarwal[42] and McQuade[44]), continues to be a challenging and exciting endeavor in the Baylis–Hillman chemistry.

7. Intramolecular Baylis–Hillman reaction and challenges

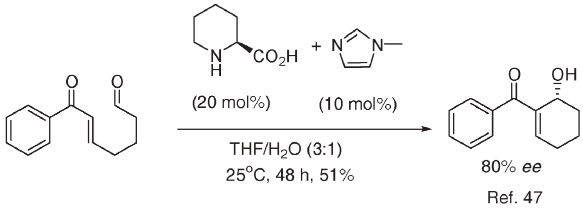
Although some examples of intramolecular Baylis–Hillman reactions are reported in the literature,[2b,33,45–48] this aspect is still in its infancy. Most of the known reports are based on the cyclizations of combinations of enone–enone, enone–acrylate, enone–aldehyde, unsaturated thioester–aldehyde, enone–allylic carbonate frameworks *etc.* Recently Krafft and Wright have reported an interesting intramolecular Baylis–Hillman reaction of an enone–epoxide system (one representative example is shown in Scheme 8).[33] During their work on the intramolecular Baylis–Hillman reaction of **IV**,[46] Krafft and co-workers have also isolated ketophosphonium salt (**V**)



Scheme 8



Scheme 9



Scheme 10

(Scheme 9) which, in fact, supports the proposed mechanistic pathway (as shown in Scheme 2) for the Baylis–Hillman reaction.

Intramolecular Baylis–Hillman ring closing reactions offer opportunities and provide challenges in designing various other classes of substrates containing different combinations of acrylate–allyl halide, acrylate–keto ester, enone (acrylate)–aldimine and so many others, which will lead to the development of all types of ring closing reactions, thereby providing many cyclic structural frameworks which will be of biological interest.

Another most challenging aspect will be the development of asymmetric versions of the intramolecular Baylis–Hillman reaction (only a few reports are known so far;[47,48] one representative example is shown in Scheme 10[47]). Also, development of multi-Baylis–Hillman reactions (Fig. 16) and their asymmetric versions will be future challenges and attractions in this fascinating reaction.

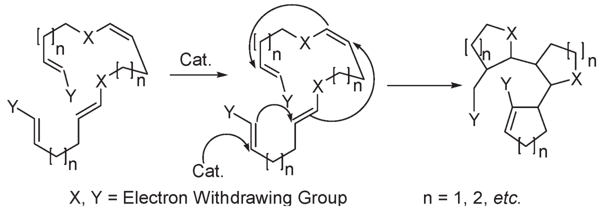


Fig. 16 Multi-Baylis–Hillman reaction strategy: Future challenge.

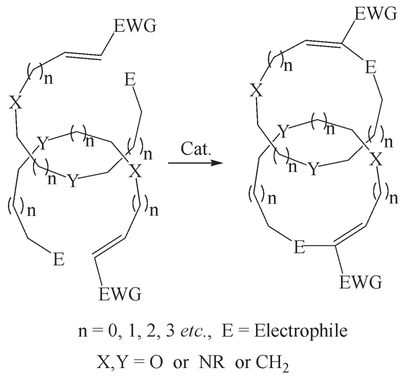


Fig. 17 Two intramolecular Baylis–Hillman reactions: catenane formation: Future challenge.

The most interesting and intellectually exciting aspect will be the design of appropriate substrates that would undergo, simultaneously, two specific intramolecular Baylis–Hillman ring closing reactions leading to an interesting formation of a catenane framework, possibly stabilized by stereochemically-/structurally-favorable interactions such as hydrogen bonding, hydrophobic/electrostatic interactions *etc.* (Fig. 17). Its asymmetric version will be another challenge for organic chemists.

8. Future directions

The Baylis–Hillman reaction has tremendous scope for multi-dimensional growth in terms of its three essential components, an asymmetric version through the design of appropriate chiral catalyst(s), an intramolecular (and its asymmetric) version and mechanistic aspects and, thus, has become a novel source of attraction, opportunities and challenges with respect to originality, novelty and intellectual capabilities in

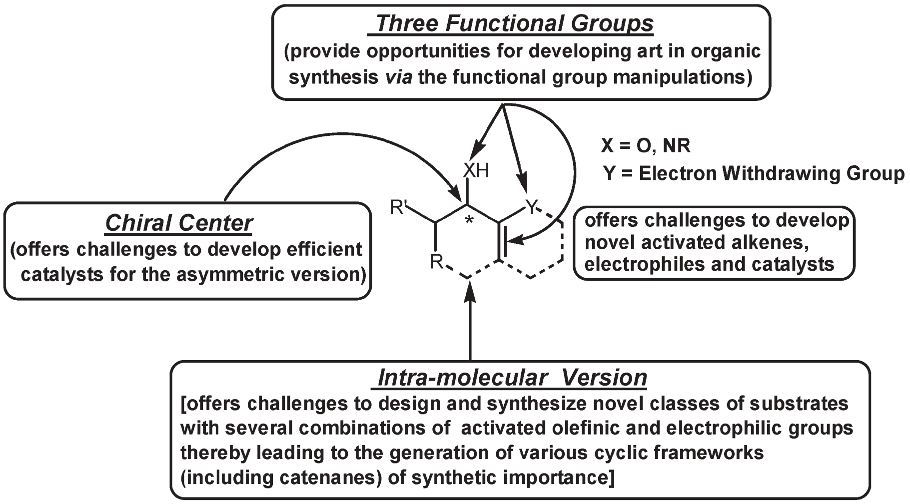


Chart 1

understanding the above-mentioned aspects and in developing the most appropriate strategies/procedures. Since the Baylis–Hillman adducts contain a minimum three functional groups in close-proximity, they provide opportunities to the synthetic chemists to properly tune and appropriately use them for the synthesis of various molecules of biological importance (Chart 1).

Abbreviations

CPME	Cyclopentyl methyl ether
DABCO	1,4-Diazabicyclo[2.2.2]octane
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DMAP	4-(Dimethylamino)pyridine
EWG	Electron withdrawing group
HMT	Hexamethylenetetramine
3-HQD	3-Hydroxyquinuclidine
MVK	Methyl vinyl ketone
NMM	*N*-Methylmorpholine
PAP	Polymer-bound 4-(*N*-benzyl-*N*-methylamino)-pyridine
PMP	*p*-Methoxyphenyl
PTA	1,3,5-Triaza-7-phosphaadamantane
QD	Quinuclidine
TMEDA	*N*,*N*,*N*′,*N*′-Tetramethylethylenediamine
TMG	Tetramethylguanidine
TMPDA	*N*,*N*,*N*′,*N*′-Tetramethyl-1,3-propanediamine

Acknowledgements

We thank DST (New Delhi) and CSIR (New Delhi) for financial support. We thank UGC (New Delhi) for recognizing our University of Hyderabad as a "*University with Potential for Excellence (**UPE**)*" and also for recognizing the School of Chemistry as a "*Center for Advanced Studies in Chemistry*" and providing some instrumental facilities. KVR and RJR thank CSIR (New Delhi) for their research fellowships.

References

1 (*a*) S. E. Drewes and G. H. P. Roos, *Tetrahedron*, 1988, **44**, 4653; (*b*) E. Ciganek, *Organic Reactions*, ed. L. A. Paquette, Wiley, New York, vol. 51, 1997, p. 201.

2 (*a*) D. Basavaiah, P. Dharma Rao and R. Suguna Hyma, *Tetrahedron*, 1996, **52**, 8001; (*b*) D. Basavaiah, A. Jaganmohan Rao and T. Satyanarayana, *Chem. Rev.*, 2003, **103**, 811.

3 (*a*) A. B. Baylis and M. E. D. Hillman, *Chem. Abstr.*, 1972, **77**, 34174q (*German patent* 2155113, 1972); (*b*) M. E. D. Hillman and A. B. Baylis, *US patent* 3743669, 1973.

4 (*a*) S. E. Drewes and N. D. Emslie, *J. Chem. Soc., Perkin Trans. 1*, 1982, 2079; (*b*) H. M. R. Hoffmann and J. Rabe, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 795.

5 (*a*) P. Perlmutter and C. C. Teo, *Tetrahedron Lett.*, 1984, **25**, 5951; (*b*) D. Basavaiah and V. V. L. Gowriswari, *Tetrahedron Lett.*, 1986, **27**, 2031; (*c*) H. Amri and J. Villieras, *Tetrahedron Lett.*, 1986, **27**, 4307; (*d*) J. S. Hill and N. S. Isaacs, *Tetrahedron Lett.*, 1986, **27**, 5007; (*e*) P. Auvray, P. Knochel and J. F. Normant, *Tetrahedron Lett.*, 1986, **27**, 5095.

6 Y.-L. Shi and M. Shi, *Org. Lett.*, 2005, **7**, 3057.

7 T. G. Back, D. A. Rankic, J. M. Sorbetti and J. E. Wulff, *Org. Lett.*, 2005, **7**, 2377.

8 Y. Matsuya, K. Hayashi and H. Nemoto, *J. Am. Chem. Soc.*, 2003, **125**, 646.

9 N. Rastogi, I. N. N. Namboothiri and M. Cojocaru, *Tetrahedron Lett.*, 2004, **45**, 4745.

10 Y.-L. Shi, Y.-M. Xu and M. Shi, *Adv. Synth. Catal.*, 2004, **346**, 1220.

11 Y.-L. Shi and M. Shi, *Tetrahedron*, 2006, **62**, 461.

12 Y.-B. Yin, M. Wang, Q. Liu, J.-L. Hu, S.-G. Sun and J. Kang, *Tetrahedron Lett.*, 2005, **46**, 4399.

13 D. Basavaiah, B. Sreenivasulu and A. Jaganmohan Rao, *J. Org. Chem.*, 2003, **68**, 5983.

14 S. Luo, X. Mi, H. Xu, P. G. Wang and J.-P. Cheng, *J. Org. Chem.*, 2004, **69**, 8413.

15 M. E. Krafft and J. W. Cran, *Synlett*, 2005, 1263.

16 D. Basavaiah and A. Jaganmohan Rao, *Tetrahedron Lett.*, 2003, **44**, 4365.

17 T. Kataoka and H. Kinoshita, *Eur. J. Org. Chem.*, 2005, 45.

18 J. S. Rao, J.-F. Briere, P. Metzner and D. Basavaiah, *Tetrahedron Lett.*, 2006, **47**, 3553.

19 A. Kattuboina, P. Kaur, C. Timmons and G. Li, *Org. Lett.*, 2006, **8**, 2771.

20 C. A. Evans and S. J. Miller, *J. Am. Chem. Soc.*, 2003, **125**, 12394.

21 C. H. Lee and K.-J. Lee, *Synthesis*, 2004, 1941.

22 K. Y. Lee, S. GowriSankar and J. N. Kim, *Tetrahedron Lett.*, 2004, **45**, 5485.

23 P. R. Krishna, E. R. Sekhar and V. Kannan, *Synthesis*, 2004, 857.

24 Y.-S. Lin, C.-W. Liu and T. Y. R. Tsai, *Tetrahedron Lett.*, 2005, **46**, 1859.

25 S. Luo, X. Mi, P. G. Wang and J.-P. Cheng, *Tetrahedron Lett.*, 2004, **45**, 5171.

26 X. Mi, S. Luo and J.-P. Cheng, *J. Org. Chem.*, 2005, **70**, 2338.

27 A. Corma, H. Garcia and A. Leyva, *Chem. Commun.*, 2003, 2806.

28 M. M. Rauhut and H. Currier, *Chem. Abstr.*, 1963, **58**, 11224a [(American Cyanamid Co.), *US patent* 3074999, 1963].

29 K. Morita, Z. Suzuki and H. Hirose, *Bull. Chem. Soc. Jpn.*, 1968, **41**, 2815.

30 H.-X. Wei, R. L. Jasoni, J. Hu, G. Li and P. W. Pare, *Tetrahedron*, 2004, **60**, 10233.

31 J. You, J. Xu and J. G. Verkade, *Angew. Chem., Int. Ed.*, 2003, **42**, 5054.

32 Z. He, X. Tang, Y. Chen and Z. He, *Adv. Synth. Catal.*, 2006, **348**, 413.

33 M. E. Krafft and J. A. Wright, *Chem. Commun.*, 2006, 2977.

34 D. Basavaiah and A. Jaganmohan Rao, *Chem. Commun.*, 2003, 604.

35 M. Shi and L.-H. Chen, *Chem. Commun.*, 2003, 1310.

36 K. Matsui, S. Takizawa and H. Sasai, *J. Am. Chem. Soc.*, 2005, **127**, 3680.

37 J. Wang, H. Li, X. Yu, L. Zu and W. Wang, *Org. Lett.*, 2005, **7**, 4293.

38 K.-S. Yang, W.-D. Lee, J.-F. Pan and K. Chen, *J. Org. Chem.*, 2003, **68**, 915.

39 N. T. McDougal and S. E. Schaus, *J. Am. Chem. Soc.*, 2003, **125**, 12094.

40 I. T. Raheem and E. N. Jacobsen, *Adv. Synth. Catal.*, 2005, **347**, 1701.

41 L. S. Santos, C. H. Pavam, W. P. Almeida, F. Coelho and M. N. Eberlin, *Angew. Chem., Int. Ed.*, 2004, **43**, 4330.

42 V. K. Aggarwal, S. Y. Fulford and G. C. Lloyd-Jones, *Angew. Chem., Int. Ed.*, 2005, **44**, 2.

43 P. Buskens, J. Klankermayer and W. Leitner, *J. Am. Chem. Soc.*, 2005, **127**, 16762.

44 K. E. Price, S. J. Broadwater, B. J. Walker and D. T. McQuade, *J. Org. Chem.*, 2005, **70**, 3980.

45 (*a*) R. R. Huddleston and M. J. Krische, *Synlett*, 2003, 12; (*b*) J. L. Methot and W. R. Roush, *Adv. Synth. Catal.*, 2004, **346**, 1035.

46 M. E. Krafft, T. F. N. Haxell, K. A. Seibert and K. A. Abboud, *J. Am. Chem. Soc.*, 2006, **128**, 4174.

47 C. E. Aroyan, M. M. Vasbinder and S. J. Miller, *Org. Lett.*, 2005, **7**, 3849.

48 S.-H. Chen, B.-C. Hong, C.-F. Su and S. Sarshar, *Tetrahedron Lett.*, 2005, **46**, 8899.