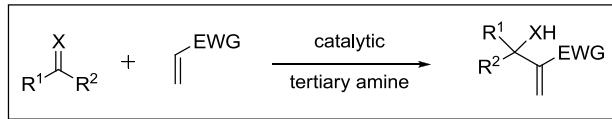


Baylis–Hillman reaction

Also known as the Morita–Baylis–Hillman reaction. It is a carbon–carbon bond-forming transformation of an electron-poor alkene with a carbon electrophile. Electron-poor alkenes include acrylic esters, acrylonitriles, vinyl ketones, vinyl sulfones, and acroleins. On the other hand, carbon electrophiles may be aldehydes, α -alkoxycarbonyl ketones, aldimines, and Michael acceptors.

General scheme:



$X = O, NR_2, EWG = CO_2R, COR, CHO, CN, SO_2R, SO_3R, PO(OEt)_2, CONR_2, CH_2=CHCO_2Me$

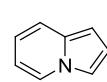
Catalytic tertiary amines:



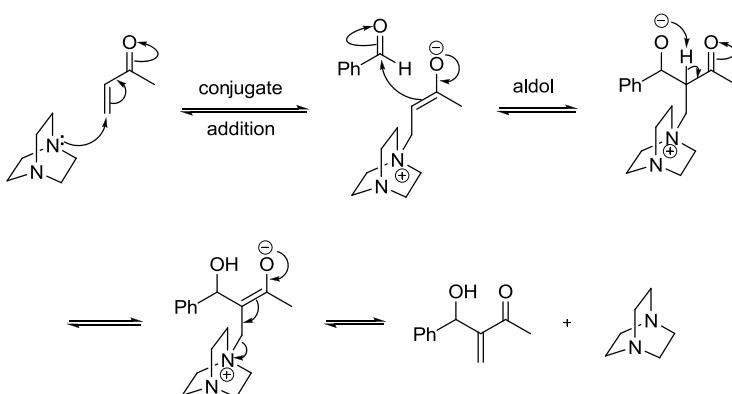
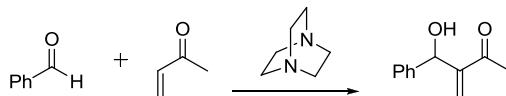
DABCO



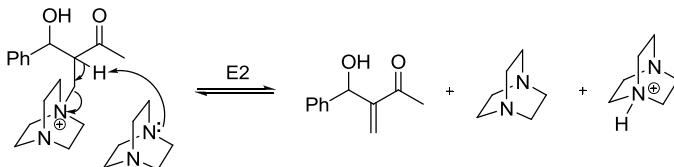
quinuclidine



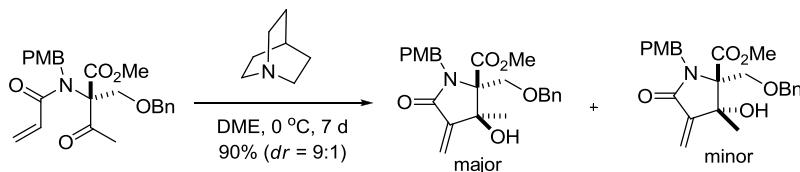
Indolizine



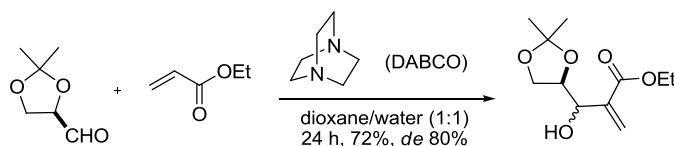
E2 (bimolecular elimination) mechanism is also operative here:



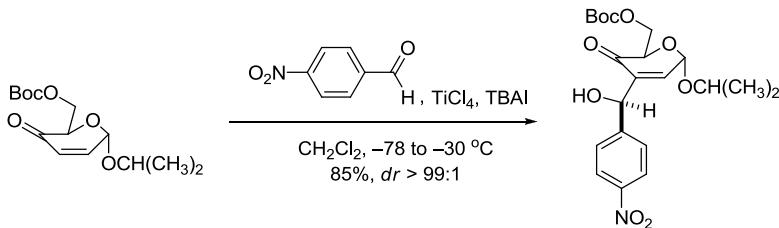
Example 1, Intramolecular Baylis–Hillman reaction⁶



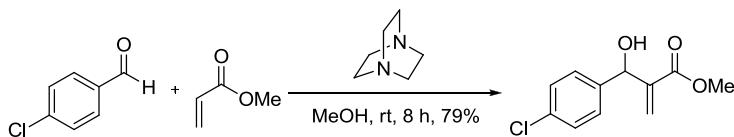
Example 2⁷



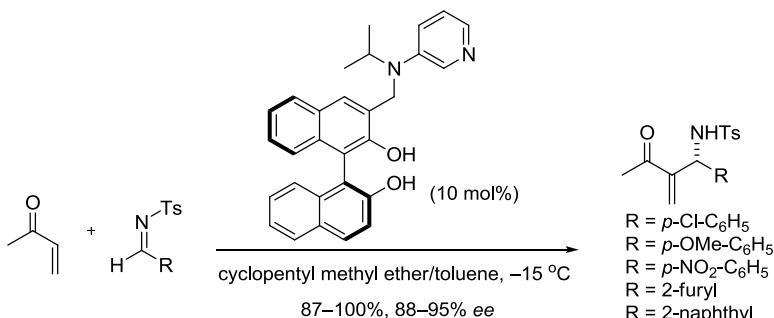
Example 3⁸



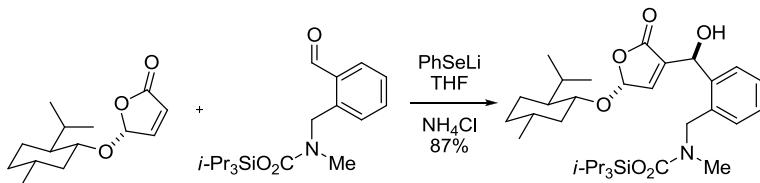
Example 4⁹



Example 5¹⁰



Example 6¹³



References

1. Baylis, A. B.; Hillman, M. E. D. Ger. Pat. 2,155,113, (1972). Both Anthony B. Baylis and Melville E. D. Hillman were chemists at Celanese Corp. USA.
2. Basavaiah, D.; Rao, P. D.; Hyma, R. S. *Tetrahedron* **1996**, *52*, 8001–8062. (Review).
3. Ciganek, E. *Org. React.* **1997**, *51*, 201–350. (Review).
4. Wang, L.-C.; Luis, A. L.; Agapiou, K.; Jang, H.-Y.; Krische, M. J. *J. Am. Chem. Soc.* **2002**, *124*, 2402–2403.
5. Frank, S. A.; Mergott, D. J.; Roush, W. R. *J. Am. Chem. Soc.* **2002**, *124*, 2404–2405.
6. Reddy, L. R.; Saravanan, P.; Corey, E. J. *J. Am. Chem. Soc.* **2004**, *126*, 6230–6231.
7. Krishna, P. R.; Narsingam, M.; Kannan, V. *Tetrahedron Lett.* **2004**, *45*, 4773–4775.
8. Sagar, R.; Pant, C. S.; Pathak, R.; Shaw, A. K. *Tetrahedron* **2004**, *60*, 11399–11406.
9. Mi, X.; Luo, S.; Cheng, J.-P. *J. Org. Chem.* **2005**, *70*, 2338–2341.
10. Matsui, K.; Takizawa, S.; Sasai, H. *J. Am. Chem. Soc.* **2005**, *127*, 3680–3681.
11. Price, K. E.; Broadwater, S. J.; Jung, H. M.; McQuade, D. T. *Org. Lett.* **2005**, *7*, 147–150. A novel mechanism involving a hemiacetal intermediate is proposed.
12. Limberakis, C. *Morita–Baylis–Hillman Reaction*. In *Name Reactions for Homologations-Part I*; Li, J. J., Ed.; Wiley: Hoboken, NJ, **2009**, pp 350–380. (Review).
13. Cheng, P.; Clive, D. L. *J. Org. Chem.* **2012**, *77*, 3348–3364.
14. Chandrasoma, N.; Brown, N.; Brassfield, A.; Nerurkar, A.; Suarez, S.; Buszek, K. R. *Tetrahedron Lett.* **2013**, *54*, 913–917.