

**M.Sc. Semester-IV**  
**Core Course-9 (CC-9)**  
**Synthetic Organic Chemistry**



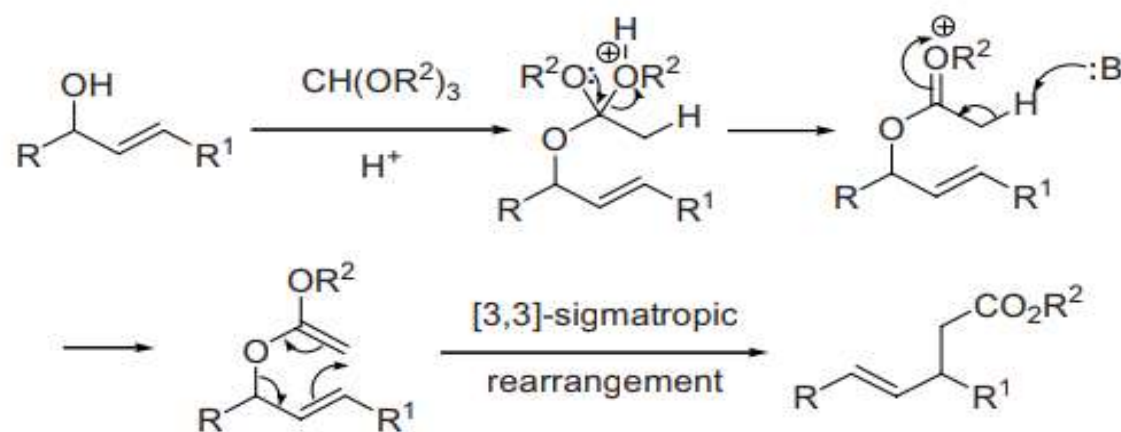
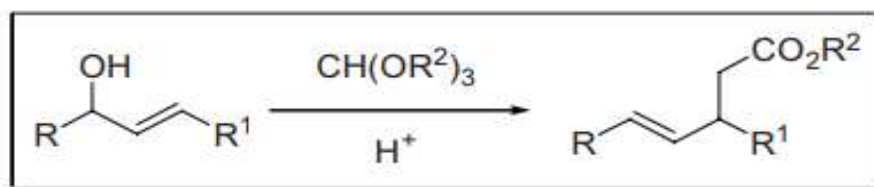
**II. Pericyclic Reactions**  
**7. Johnson-Claisen Rearrangement**



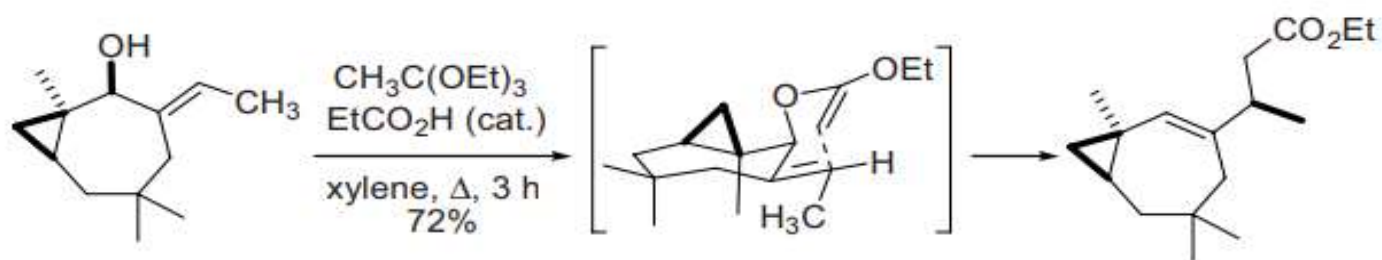
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## Johnson–Claisen orthoester rearrangement

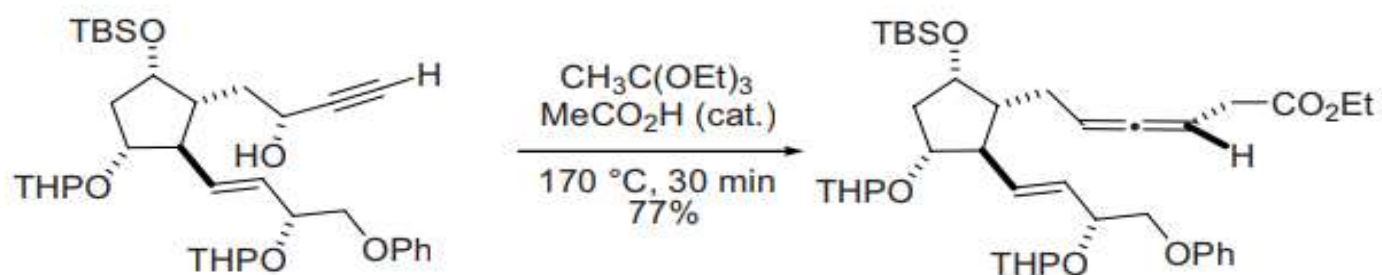
Heating of an allylic alcohol with an excess of trialkyl orthoacetate in the presence of trace amounts of a weak acid gives a mixed orthoester. Mechanistically, the orthoester loses alcohol to generate the ketene acetal, which undergoes [3,3]-sigmatropic rearrangement to give a  $\gamma,\delta$ -unsaturated ester.



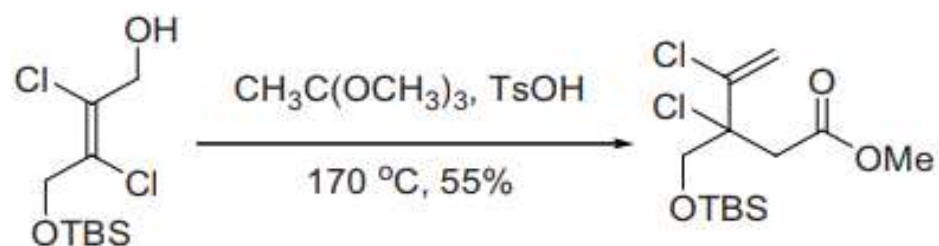
### Example 1<sup>2</sup>



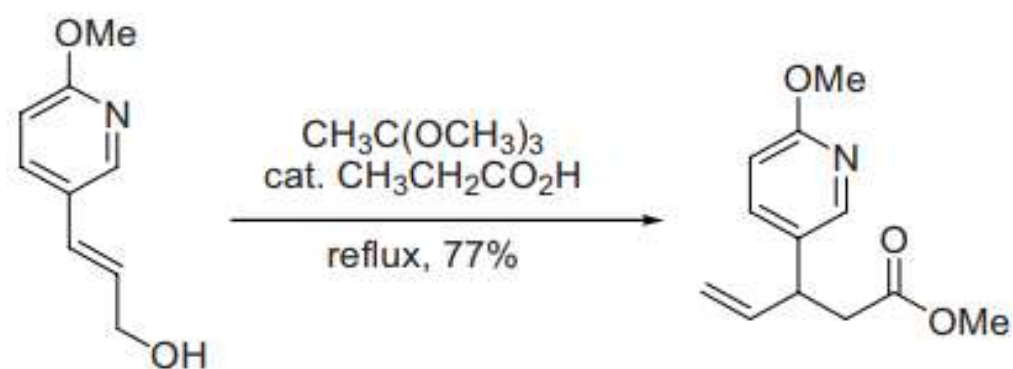
### Example 2<sup>3</sup>



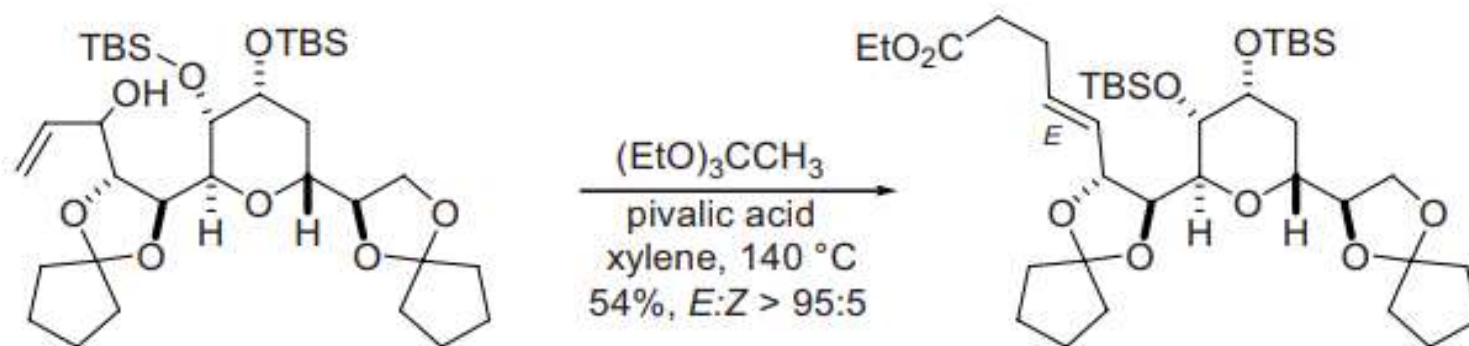
### Example 3<sup>4</sup>



### Example 4<sup>9</sup>



### Example 5<sup>10</sup>





## References

1. Johnson, W. S.; Werthemann, L.; Bartlett, W. R.; Brocksom, T. J.; Li, T.-t.; Faulkner, D. J.; Peterson, M. R. *J. Am. Chem. Soc.* **1970**, *92*, 741–743. William S. Johnson (1913–1995) was born in New Rochelle, New York. He earned his Ph.D. in only two years at Harvard under Louis Fieser. He was a professor at the University of Wisconsin for 20 years before moving to Stanford University, where he was credited with building the modern-day Stanford Chemistry Department.
2. Paquette, L.; Ham, W. H. *J. Am. Chem. Soc.* **1987**, *109*, 3025–3036.
3. Cooper, G. F.; Wren, D. L.; Jackson, D. Y.; Beard, C. C.; Galeazzi, E.; Van Horn, A. R.; Li, T. T. *J. Org. Chem.* **1993**, *58*, 4280–4286.
4. Schlama, T.; Baati, R.; Gouverneur, V.; Valleix, A.; Falck, J. R.; Mioskowski, C. *Angew. Chem., Int. Ed.* **1998**, *37*, 2085–2087.
5. Giardiná, A.; Marcantoni, E.; Mecozzi, T.; Petrini, M. *Eur. J. Org. Chem.* **2001**, 713–718.
6. Funabiki, K.; Hara, N.; Nagamori, M.; Shibata, K.; Matsui, M. *J. Fluorine Chem.* **2003**, *122*, 237–242.
7. Montero, A.; Mann, E.; Herradón, B. *Eur. J. Org. Chem.* **2004**, 3063–3073.
8. Scaglione, J. B.; Rath, N. P.; Covey, D. F. *J. Org. Chem.* **2005**, *70*, 1089–1092.
9. Zartman, A. E.; Duong, L. T.; Fernandez-Metzler, C.; Hartman, G. D.; Leu, C.-T.; Prueksaritanont, T.; Rodan, G. A.; Rodan, S. B.; Duggan, M. E.; Meissner, R. S. *Bioorg. Med. Chem. Lett.* **2005**, *15*, 1647–1650.
10. Hicks, J. D.; Roush, W. R. *Org. Lett.* **2008**, *10*, 681–684.
11. Williams, D. R.; Nag, P. P. *Claisen and Related Rearrangements*. In *Name Reactions for Homologations-Part II*; Li, J. J., Corey, E. J., Eds.; Wiley & Sons: Hoboken, NJ, **2009**, pp 68–72. (Review).

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