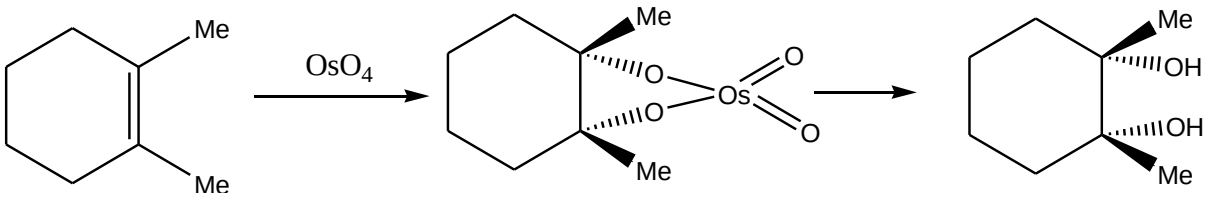
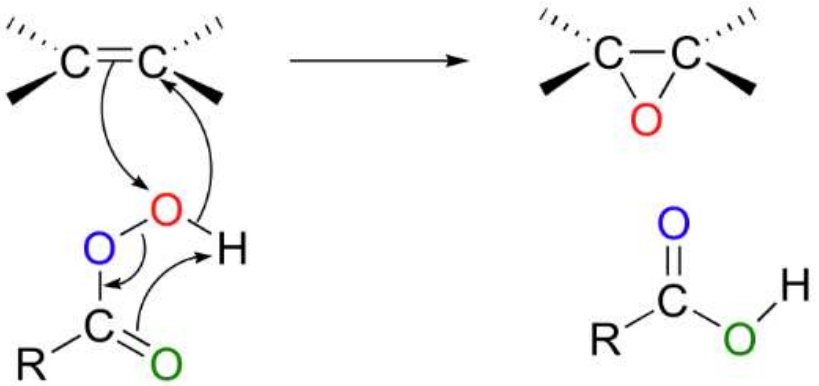
Module 5
Stereochemical aspects of Prevost and Woodward Hydroxylation, Hydroxylation by OsO_4 followed by reductive cleavage

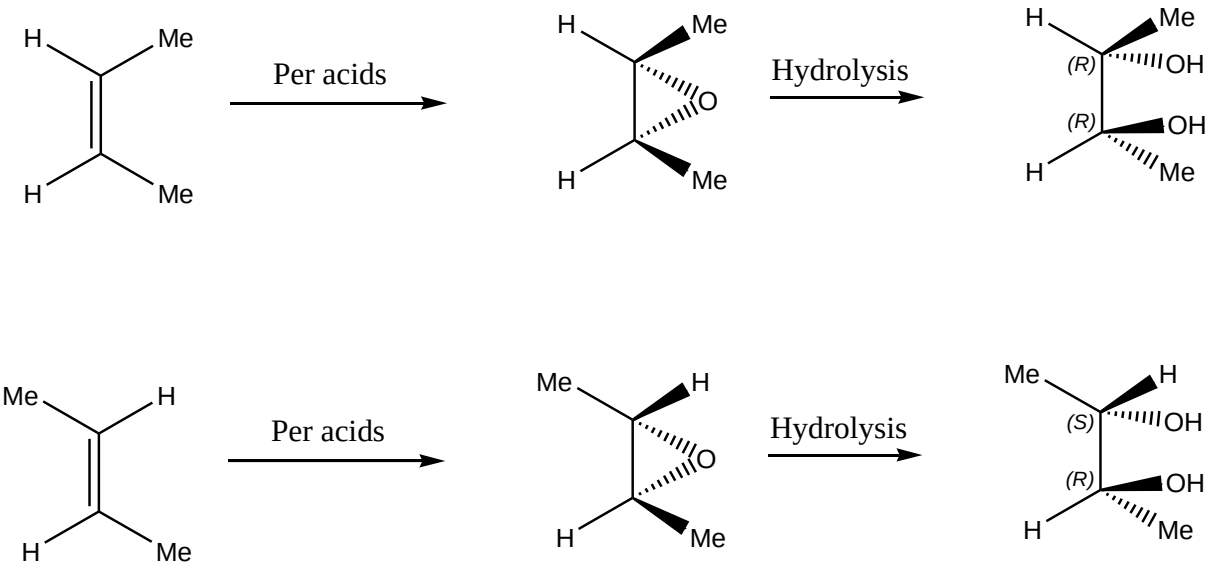
Hydroxylation of olefins give 1,2-glycols. There are different methods of hydroxylation of olefins. If we carry out the selective oxidation of a cyclic olefin, it gives rise to cis-1,2-glycol with osmium tetroxide. With aqueous alkaline potassium permanganate, cis addition takes place.



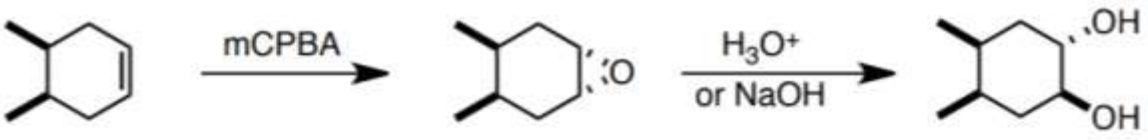
So, oxidation with osmium tetroxide, also known as osmylation and potassium with permanganate gives rise to syn glycol.

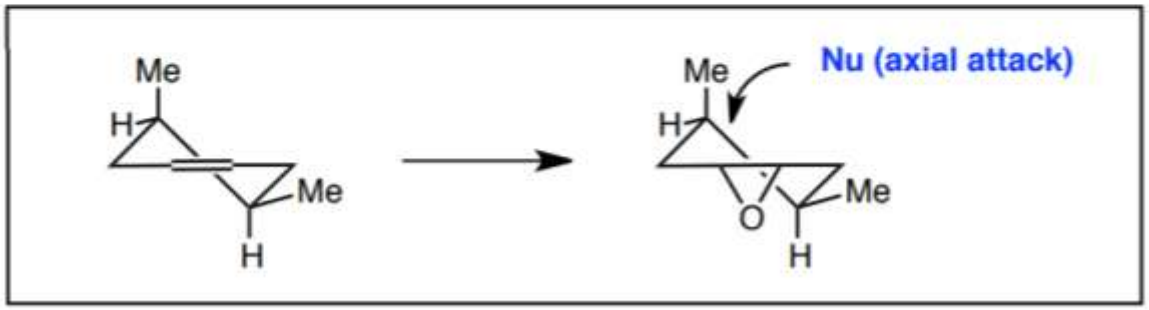
When you carry out oxidation with peroxy acids, then it goes through a epoxide intermediate, also known as the oxiran intermediate. In that case, you will get anti addition.





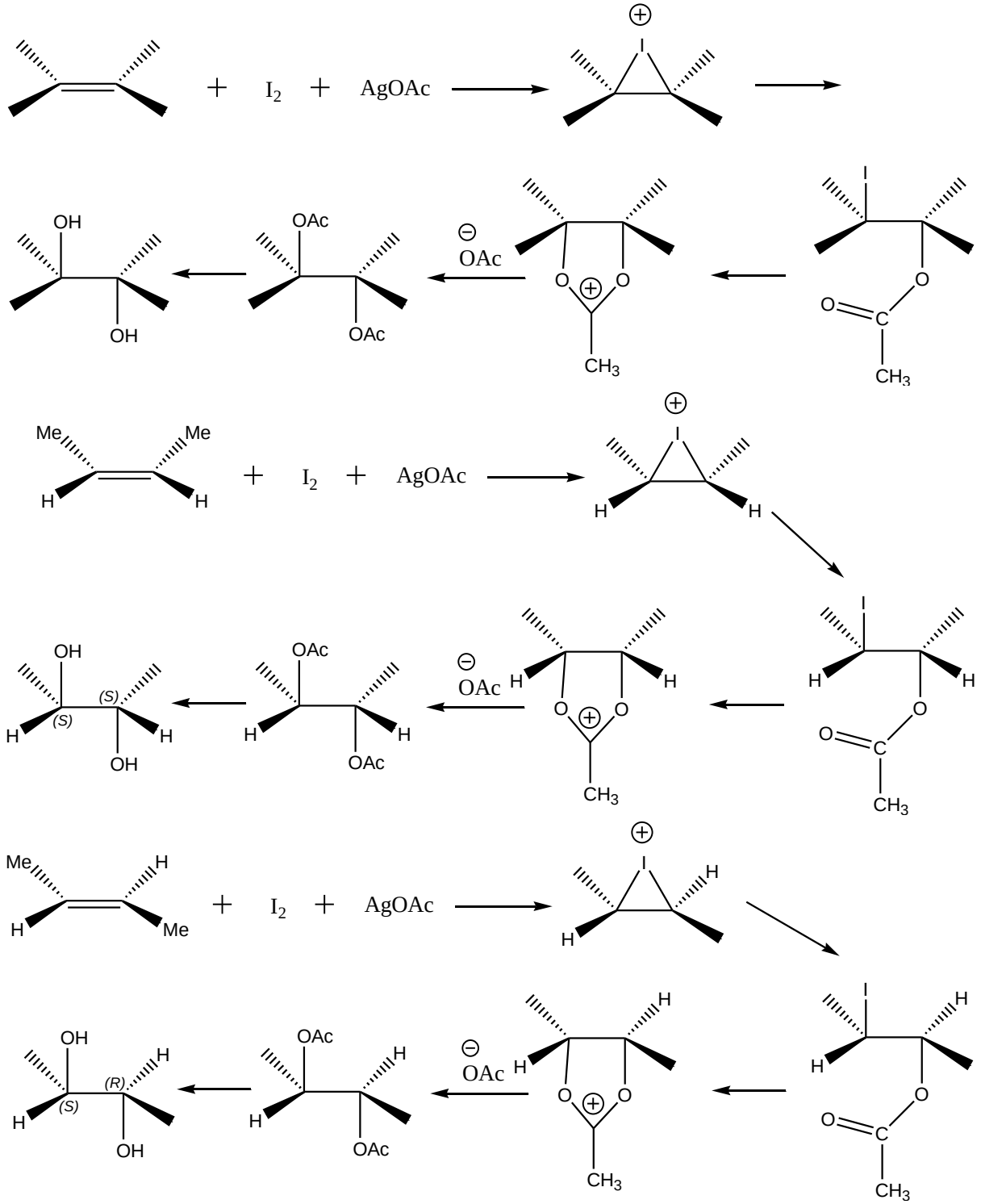
In case of the cyclic reaction, you will find the following product of hydroxylation using per acids and subsequently, the hydrolysis of the epoxide.





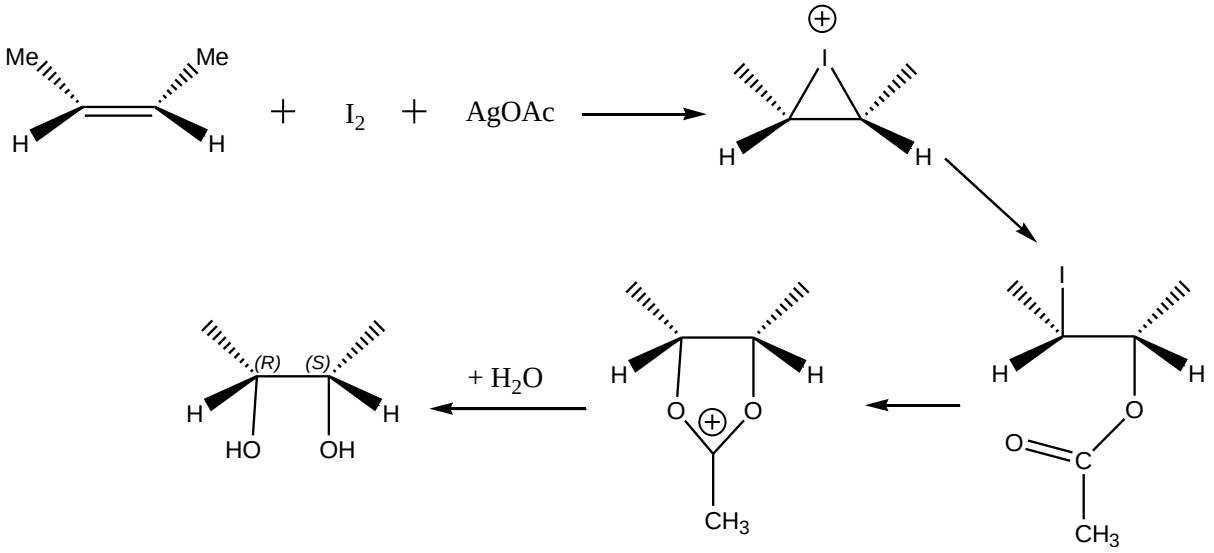
Prevost hydroxylation reaction

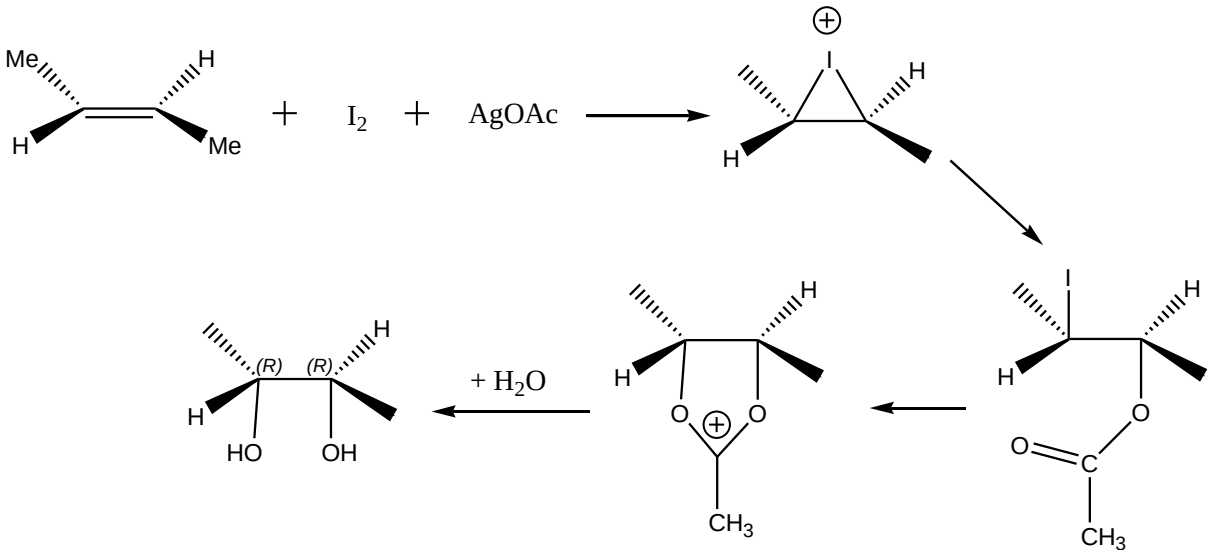
Hydroxylation can be carried out by using iodine and a silver salt. This is called Prevost reaction. This reaction goes through a cyclic iodonium ion followed by neighbouring group participation to give an anti glycol.



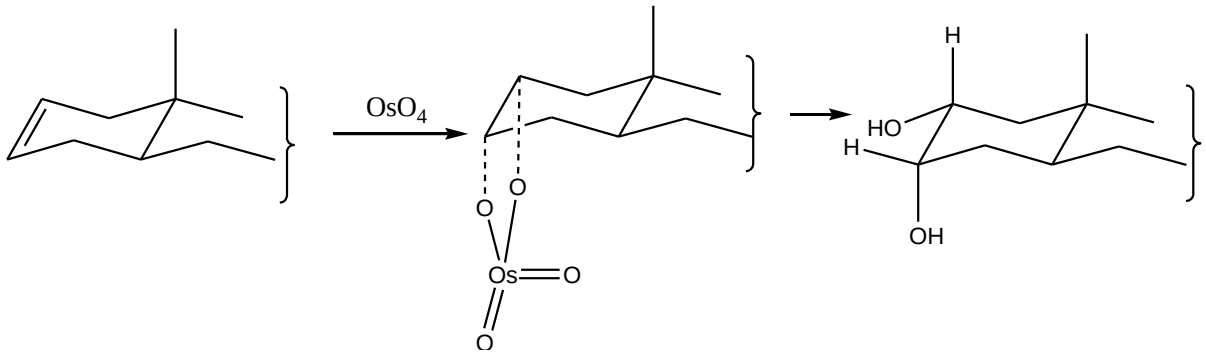
Woodward Hydroxylation reaction

If hydroxylation is carried out by using iodine and a silver salt in presence of moisture, then the intermediate acylium ion is directly hydrolysed and it gives rise to the syn glycol. This is called woodward hydroxylation reaction.

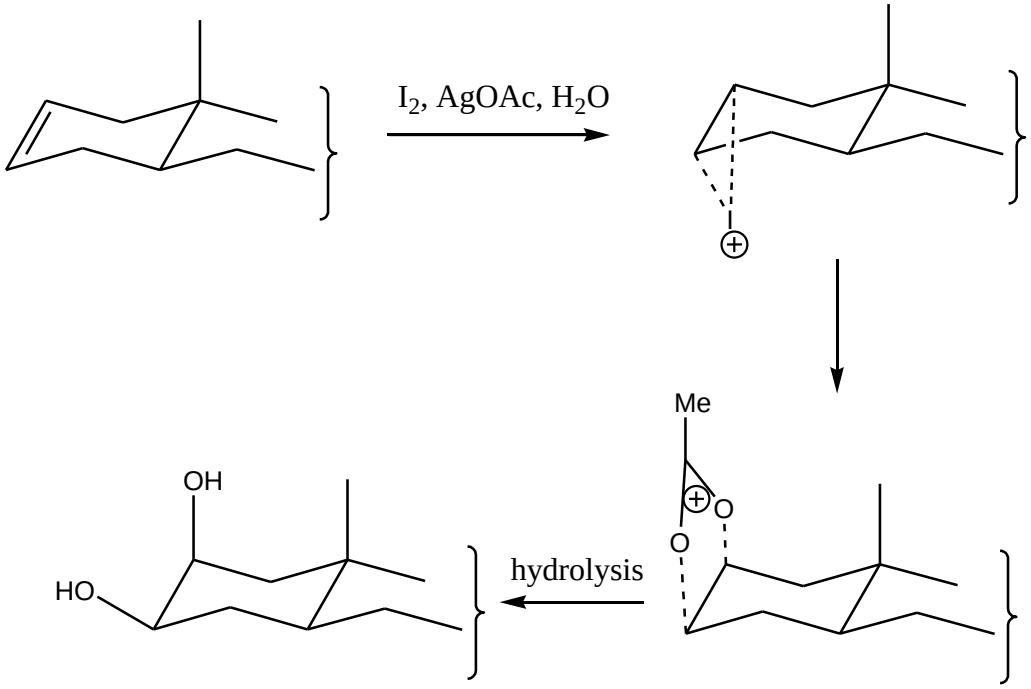




Osmium tetroxide oxidation and Woodward's modification of the Prevost reaction are complimentary to each other. This means that when we carry out these two reactions, we get diastereoselectively opposite products from these reactions. For example, this is the hydroxylation of 2,3-cholestane. Here, when we carry out osmium tetroxide oxidation, it gives the sterically less hindered syn glycol since it passes through only one ring intermediate.



Now, when we carry out the Woodward's hydroxylation, the reaction passes through two intermediates and the sterically more hindered syn glycol is formed. The stereochemistry is ultimately reversed from the previous reaction.



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