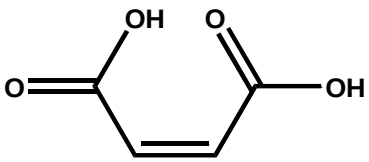
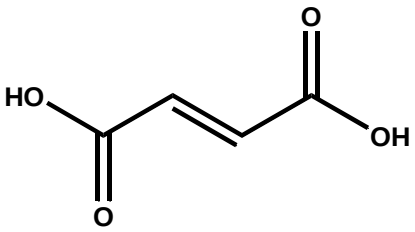
Module 4
Stereochemical aspects of polar addition reactions to alkene

Let us initially study two examples of addition reactions of alkenes: Bromination and bis-hydroxylation.

- Bromination: We will take two examples in this case: Maleic acid and Fumaric acid.

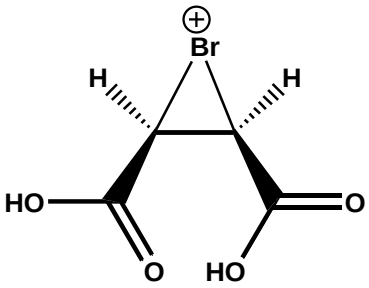


maleic acid

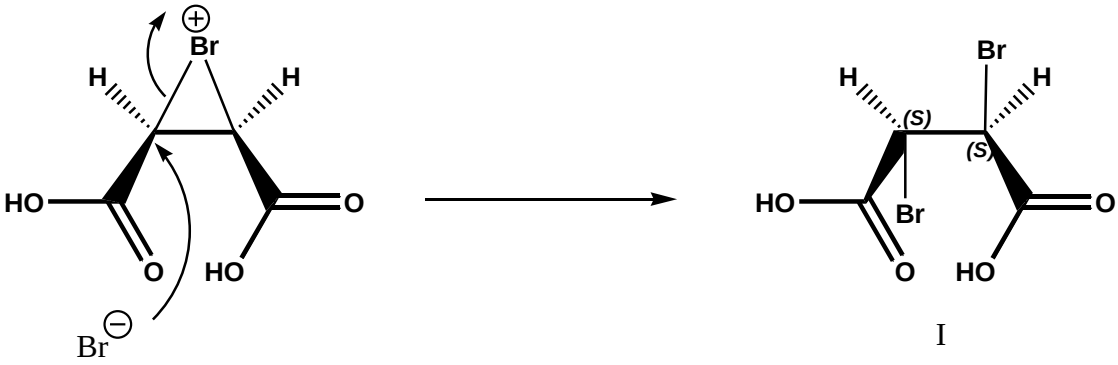


Fumaric acid

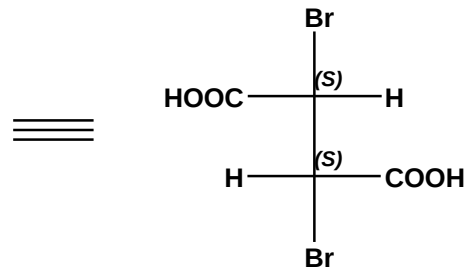
Bromination of maleic acid can take place along the two faces. The two faces are homotopic. Hence, when bromine attacks to maleic acid, we will get a single achiral bromonium ion intermediate.

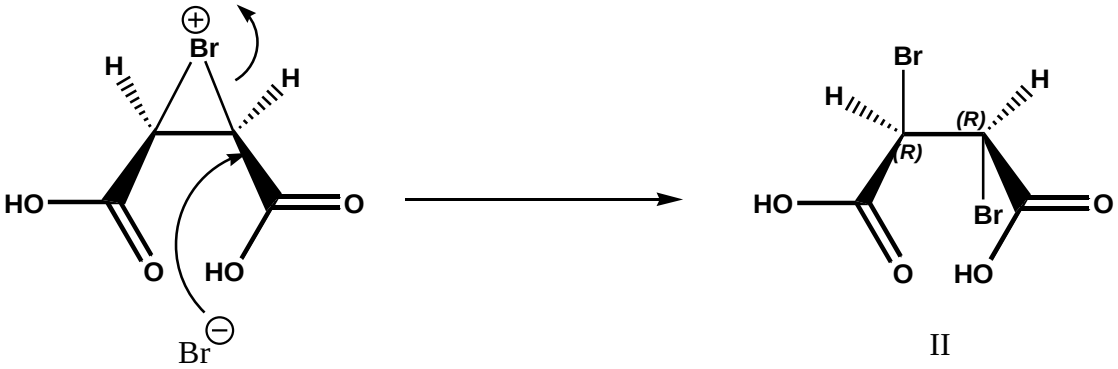


Now, bromine adds anti to this bromonium ion intermediate and gives rise to two enantiomers I and II.

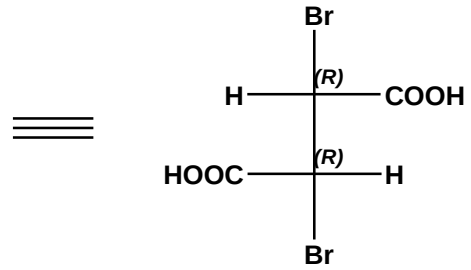


I





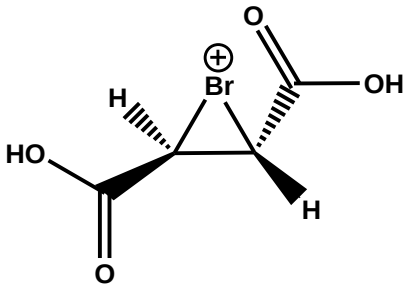
II

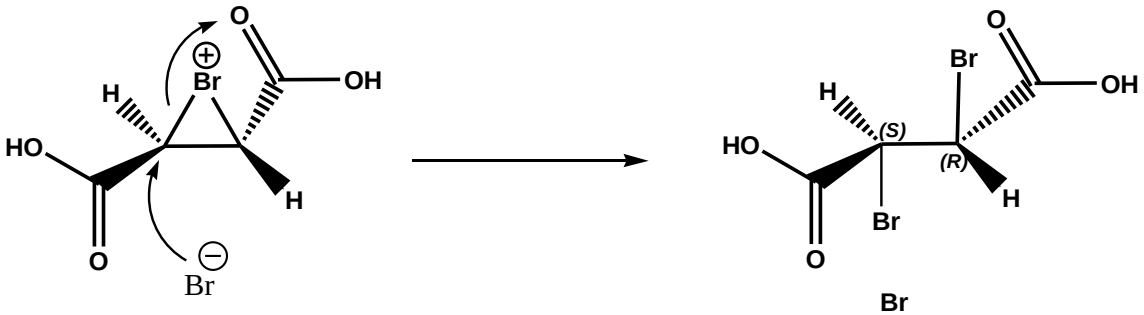


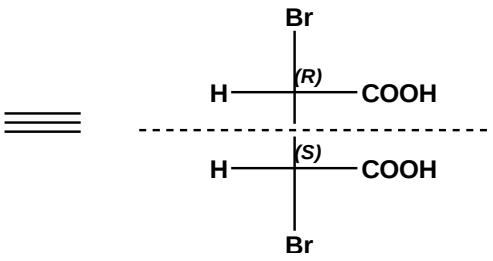
I and II are enantiomers and are equally probable to be formed. Hence, bromination of maleic acid gives (*d,l*) dibromosuccinic acid.

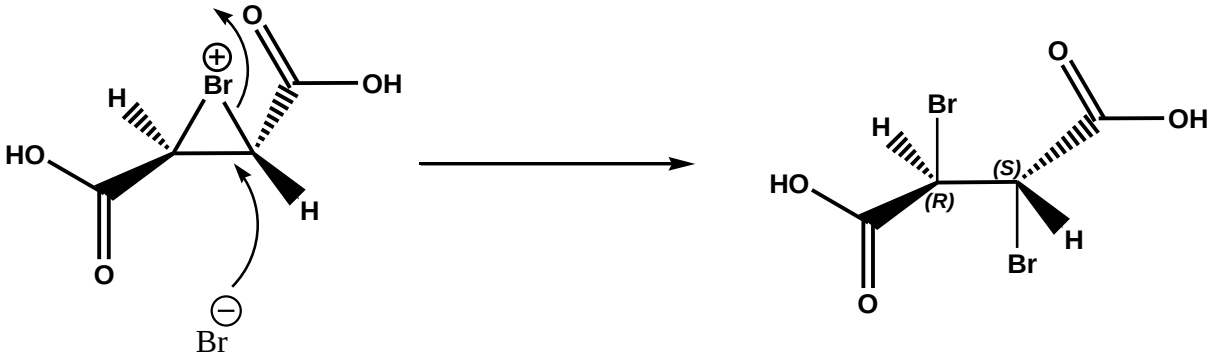
Now, let us study the case of fumaric acid. Bromination of maleic acid can take place along the two faces. The two faces are enantiotopic.

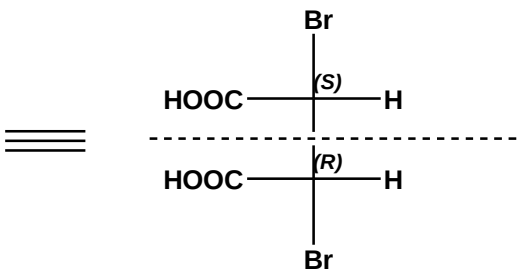
Hence, when bromine attacks to fumaric acid, we will get a chiral bromonium ion intermediate. So, we obtain a meso product from fumaric acid.





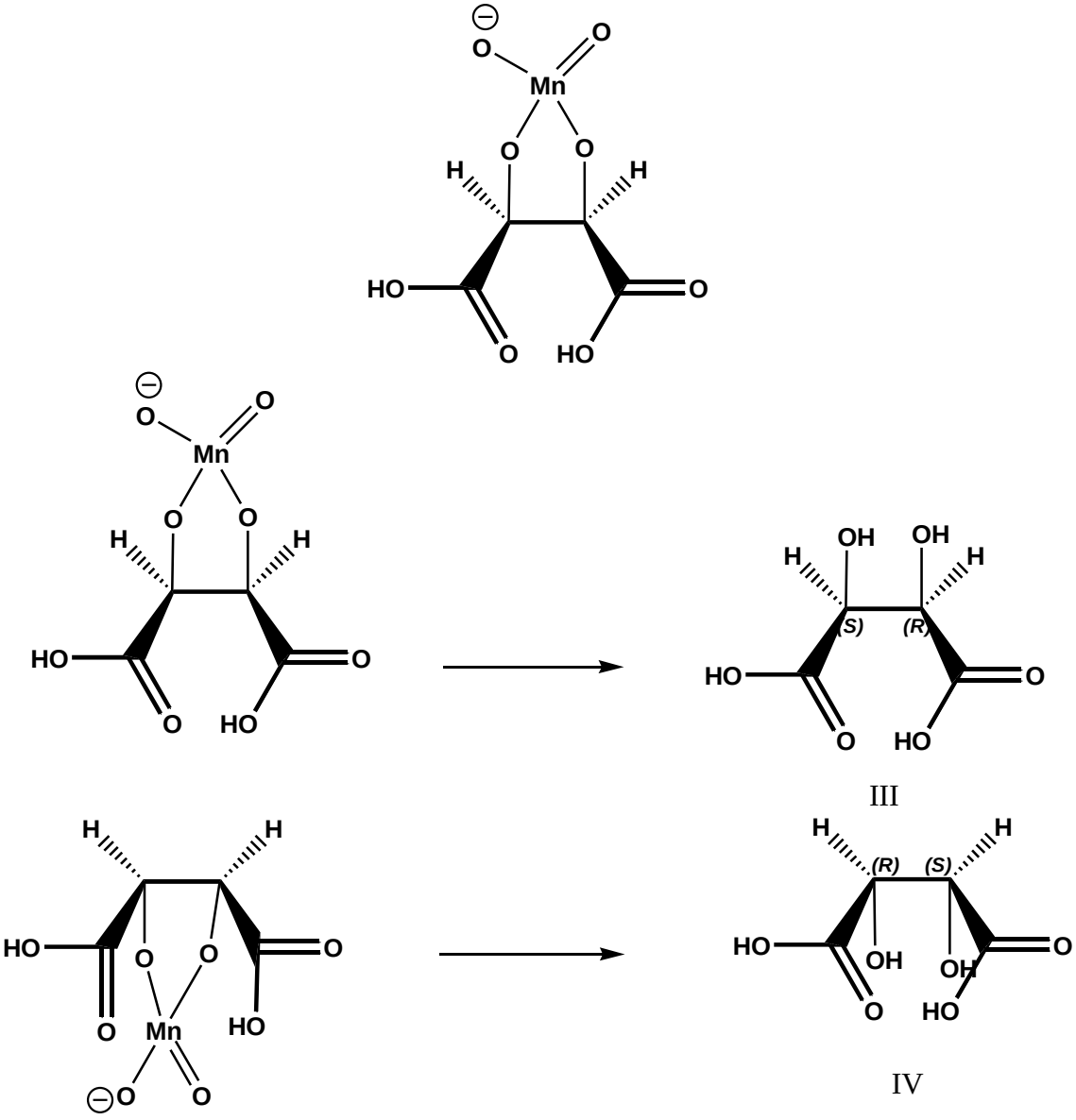






- Bis hydroxylation:

We will take the same two examples in this case: Maleic acid and Fumaric acid to study bis hydroxylation by potassium permanganate. The reaction proceeds through a cyclic intermediate and directly leads to the product by *syn* addition.

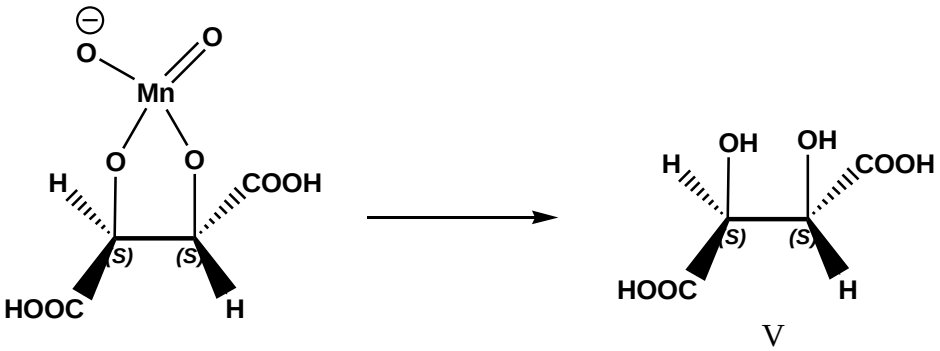


III

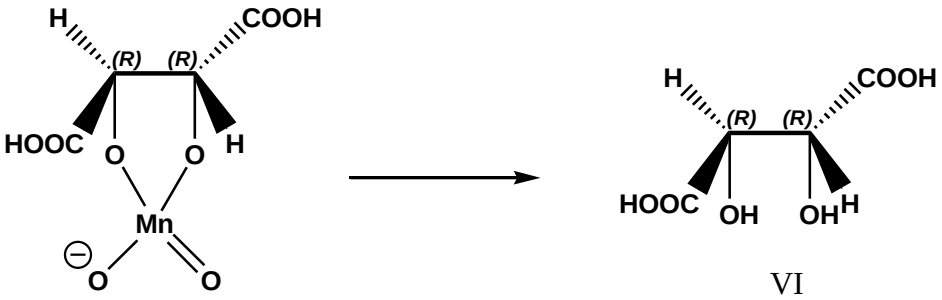
IV

III and IV are *meso* compounds. Tartaric acid is obtained from the reaction, which is achiral and named as *meso*-tartaric acid.

Now, let us study the bis hydroxylation in case of fumaric acid. In case of fumaric acid, the two transition states are enantiomeric and hence, the product obtained is a racemic mixture of two optically active forms. The tartaric acid obtained is (*d,l*) pair, resulting into a racemic mixture.

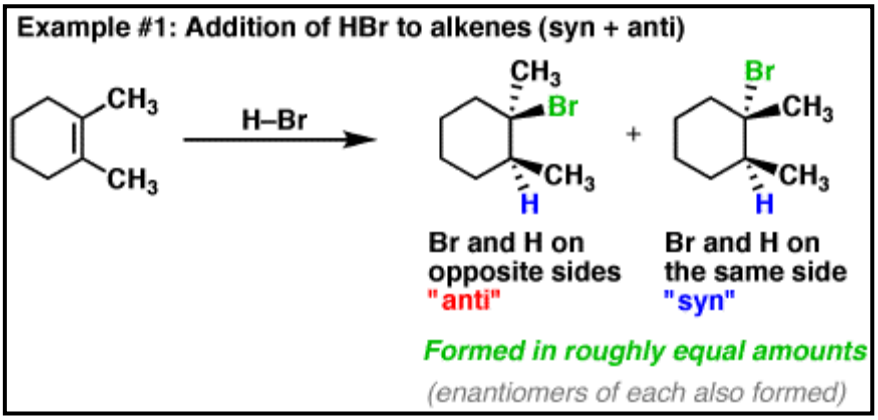


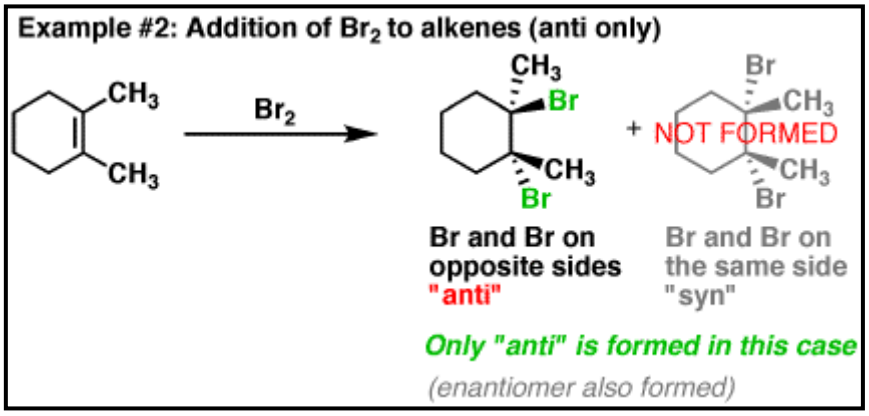
V

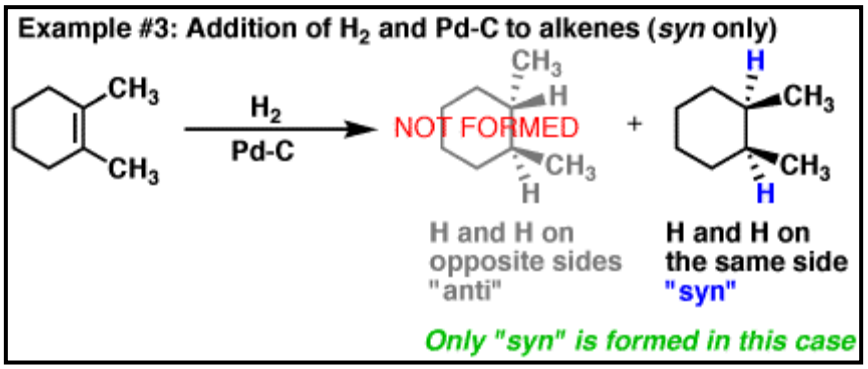


VI

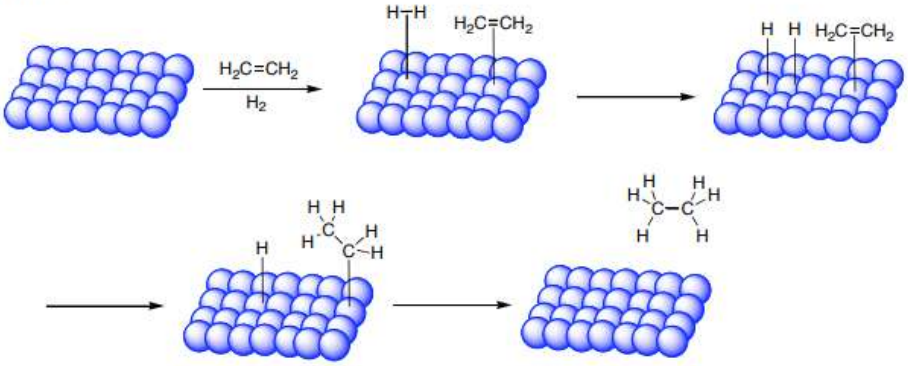
Now, study the following reactions:



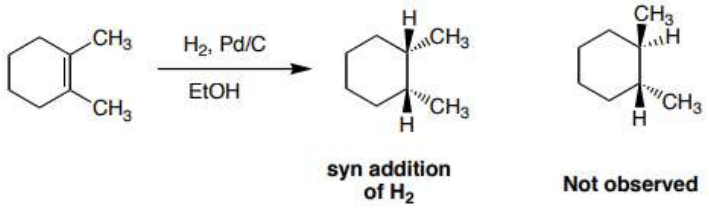




Mechanism:

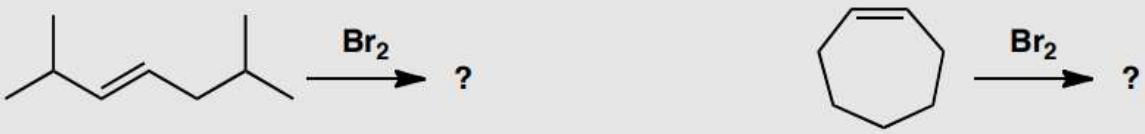


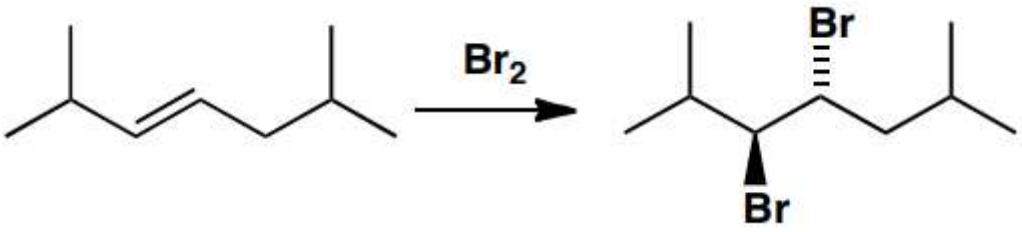
The addition of H_2 across the π-bond is *syn, i.e.*, from the same face of the double bond

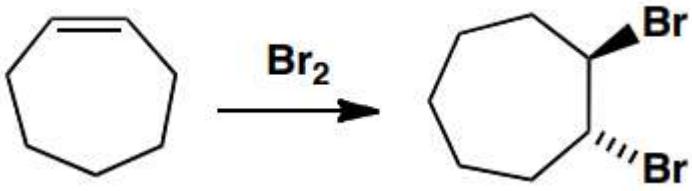


Thus, depending on the reagents, the stereochemistry of the products obtained from addition reactions of alkene always changes.

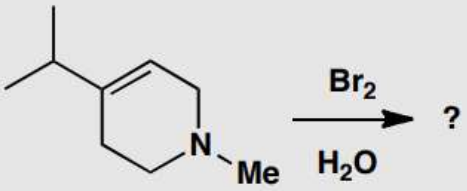
Suggest mechanism and products for these reactions.

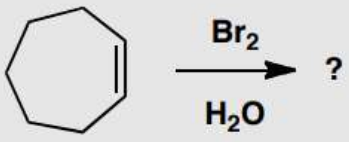


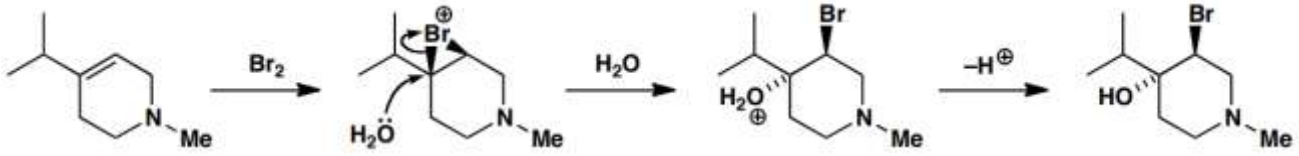


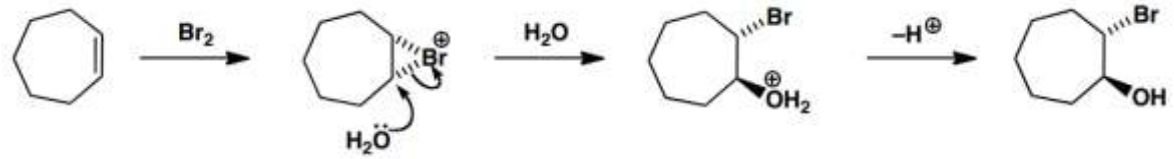


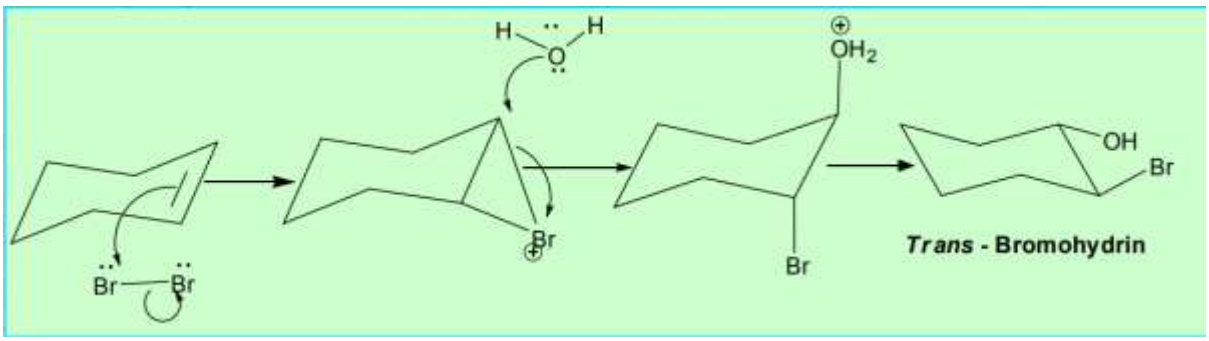
What will be the products of the addition of bromine water to these alkenes?







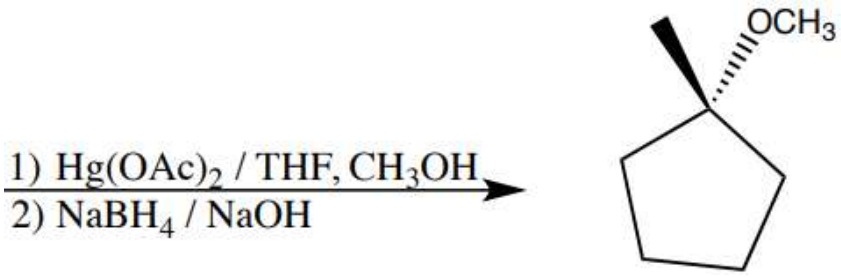




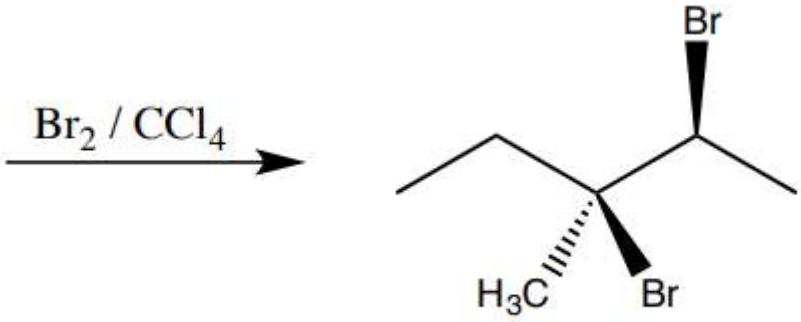
Module 4
Stereochemical aspects of polar addition reactions to alkene
Assignments

1. In each of the following reactions with alkenes, the starting reagent(s) are missing. Draw all structures that will produce the desired product in high yield.

A

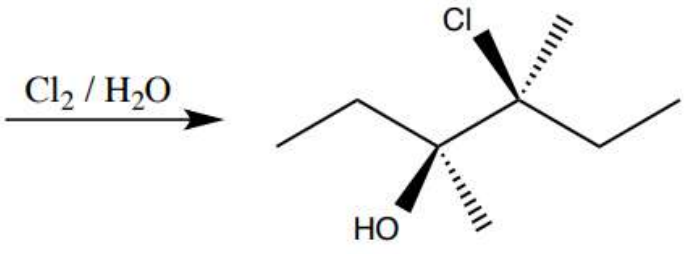


B



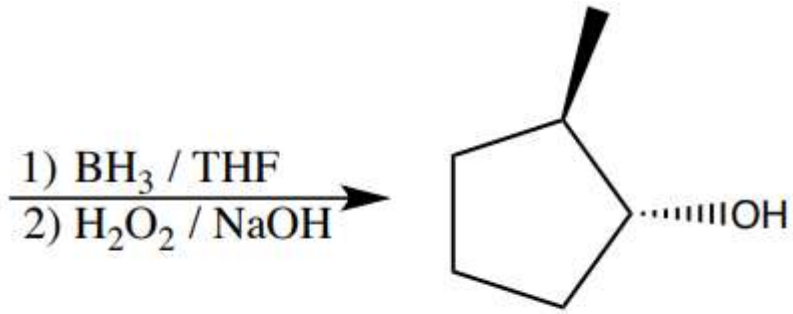
+ enantiomer

C



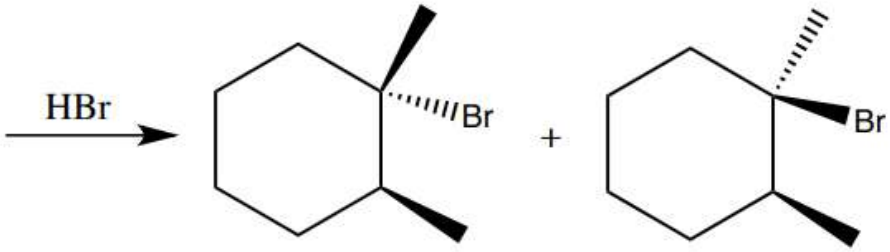
+ enantiomer

D



+ enantiomer

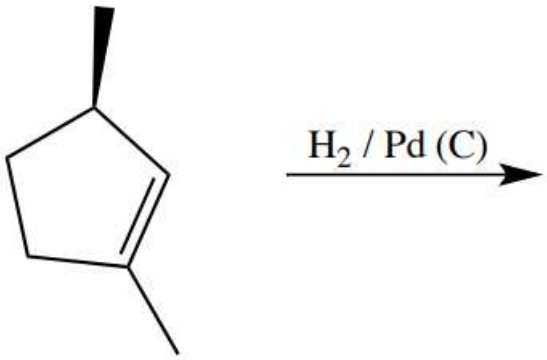
E



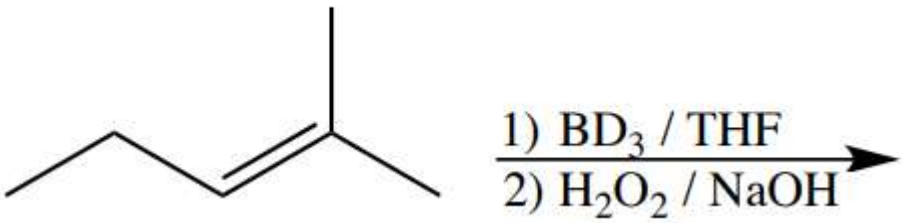
+ enantiomer + enantiomer

2. Provide products of the following reactions:

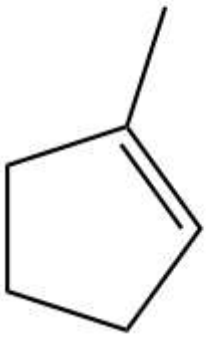
a)



b)

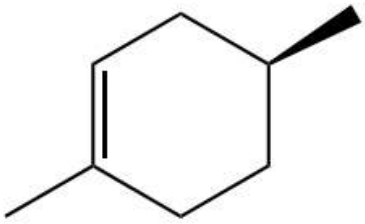


c)



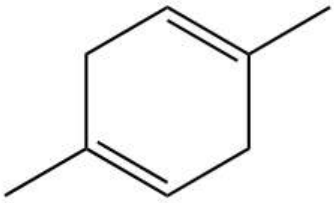
HBr / H-O-O-H

d)



1) $Hg(OAc)_2$ / THF, H_2O
2) $NaBH_4$ / NaOH

e)



HBr (excess)

3.

An unknown alkene with molecular formula C_8H_{16} is submitted for analysis to determine its structure. Ozonolysis under reducing conditions produce a ketone (shown below) as the only product. Hydrogenation of the unknown alkene with platinum affords a *meso* alkane. Determine the structure of the unknown alkene.

References used for preparing E-content and for further reading

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