STEREOCHEMISTRY OF ADDITION OF BROMINE TO ALKENES

Addition of Bromine to alkenes is stereospecifically trans.

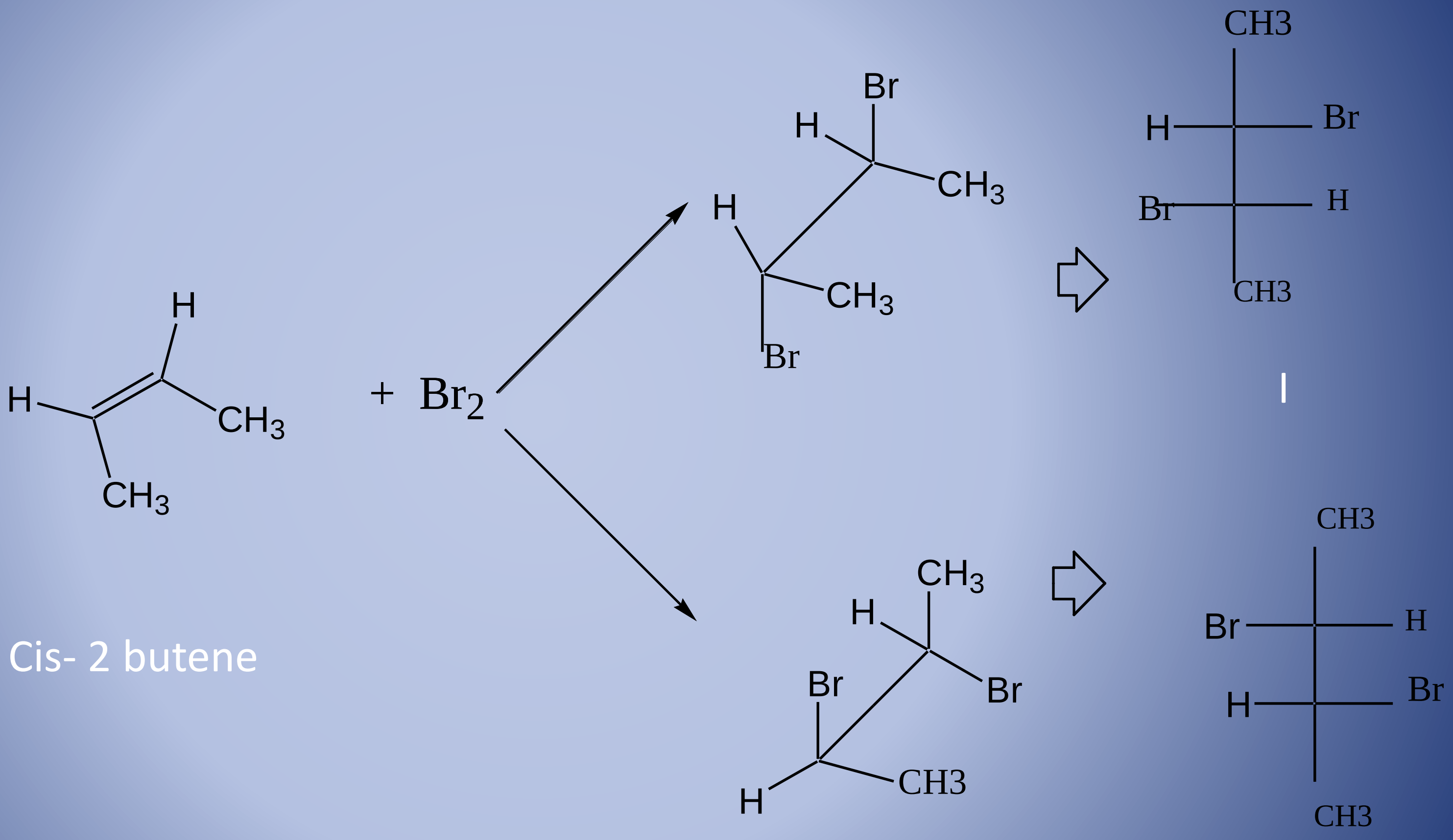
There are two ways of bromine addition to alkenes :

1: Addition to the same face of the alkene i.e syn-addition

2: Addition to the opposite face of the alkene i.e trans or anti-addition .

The stereospecificity of bromine addition can be explained by considering the anti-addition or trans-addition.

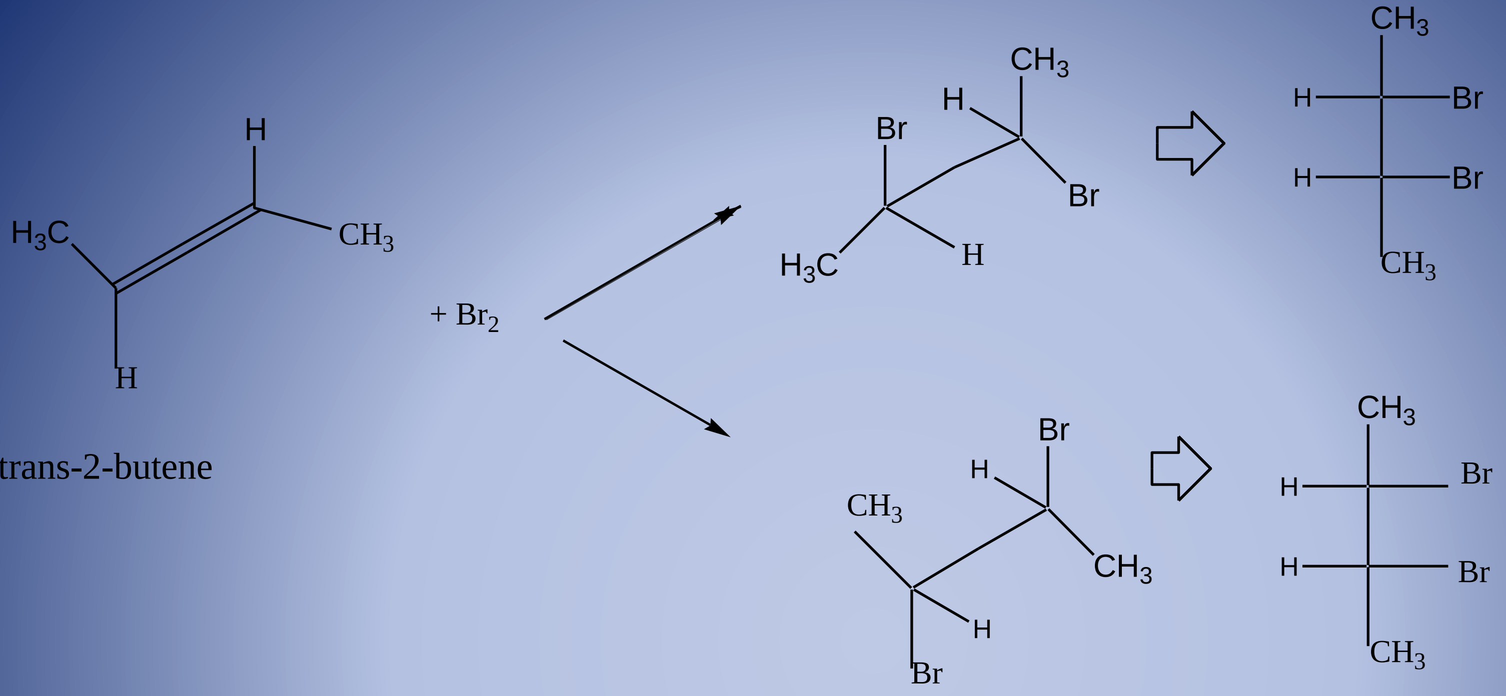
OPEN CARBOCATION MECHANISM :



Cis- 2 butene

I

I and II are Enantiomers

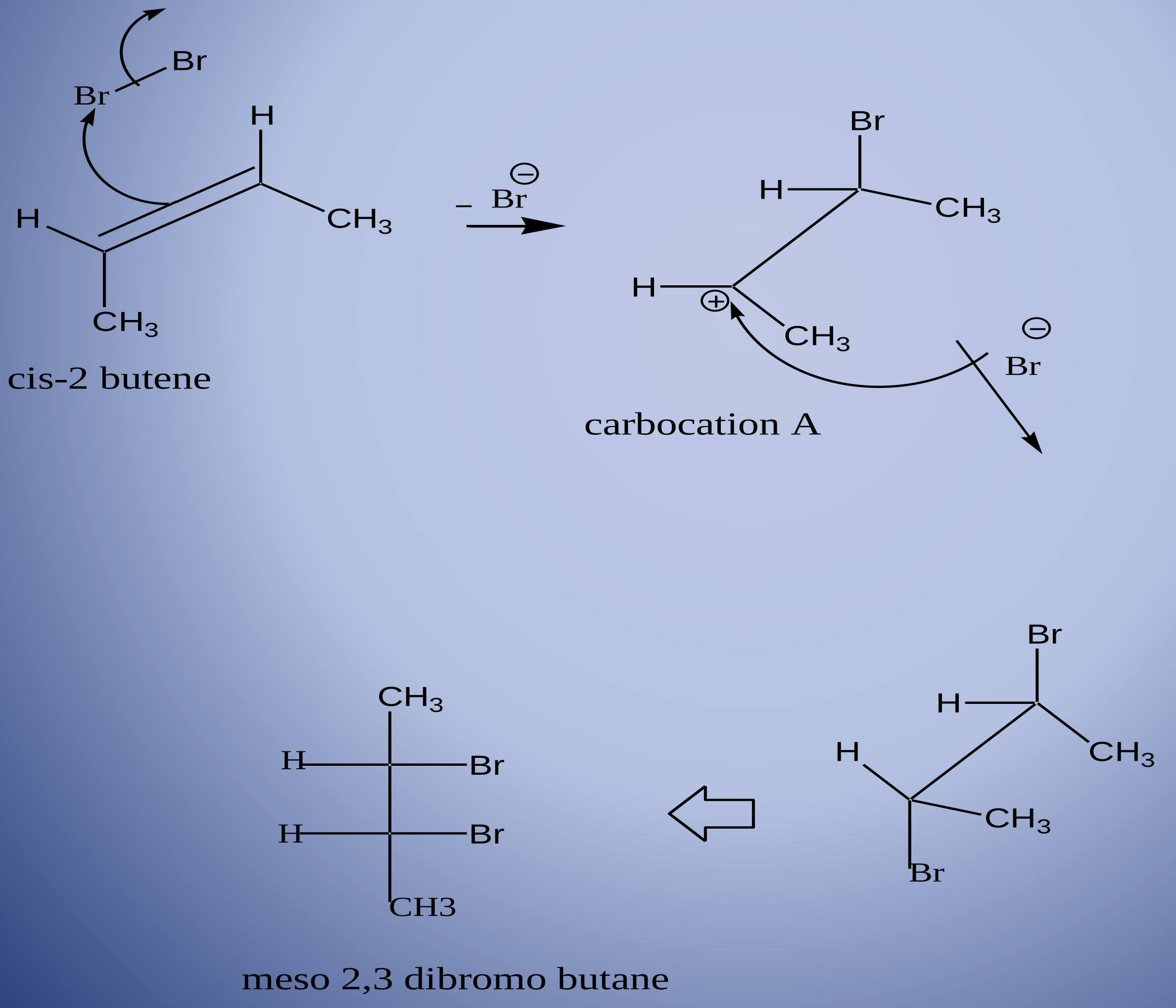


trans-2-butene

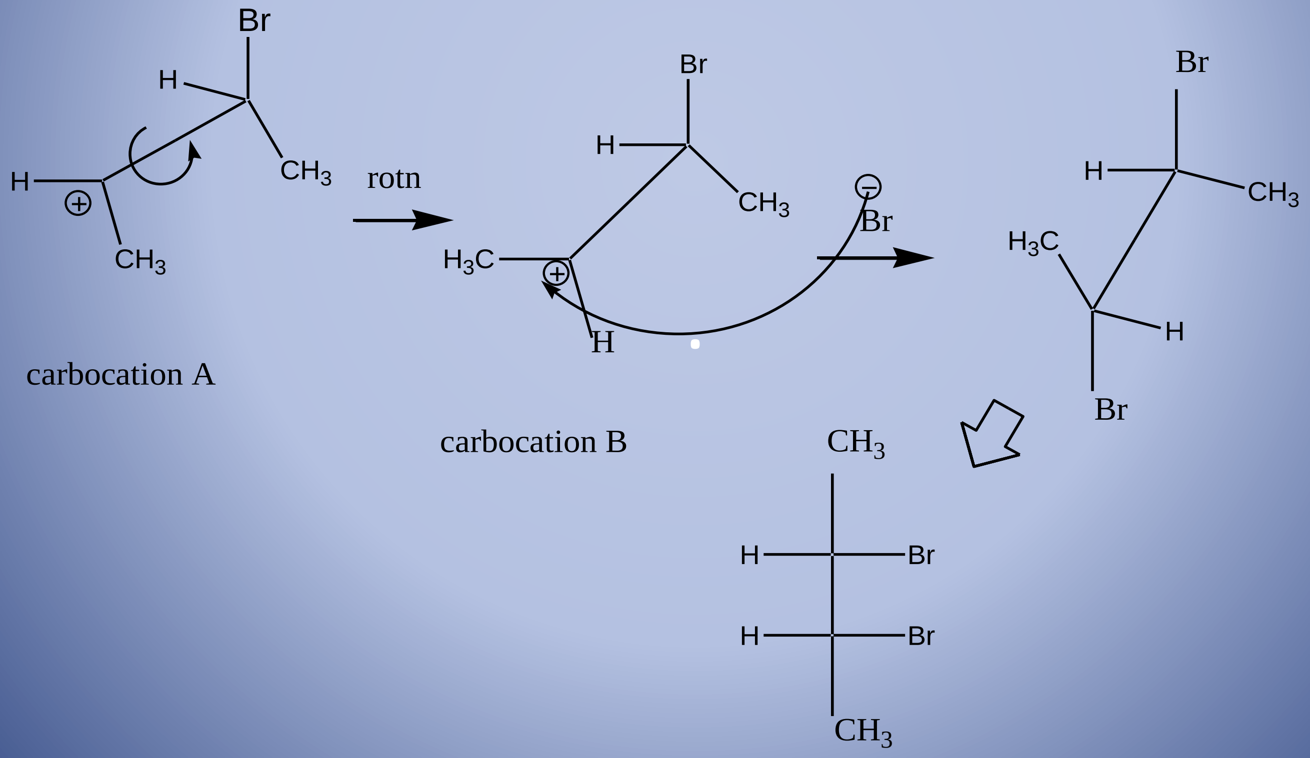
Meso 2,3 di bromo butane

Limitations of the open carbocation mechanism

- In the addition of bromine to cis 2- butene, the bromonium ion would attack one face of the alkene to form a flat carbocation. Then the bromide ion would attack the bottom face of the alkene. Thus anti-addition to cis-2 butene leads to the formation of an enantiomer.



The attack of the bromide ion to the carbocation from the bottom is not very likely on account of the flat struture of the carbocation. *If we rotate the carbocation A around the carbon-carbon bond,* a new carbocation B will be formed and the bottom side attack on the new carbocation will produce a meso 2,3-dibromo butane and not the enantiomers. This *is contrary to the known facts as this amounts to the syn-addition of bromine to cis-2 butene*.



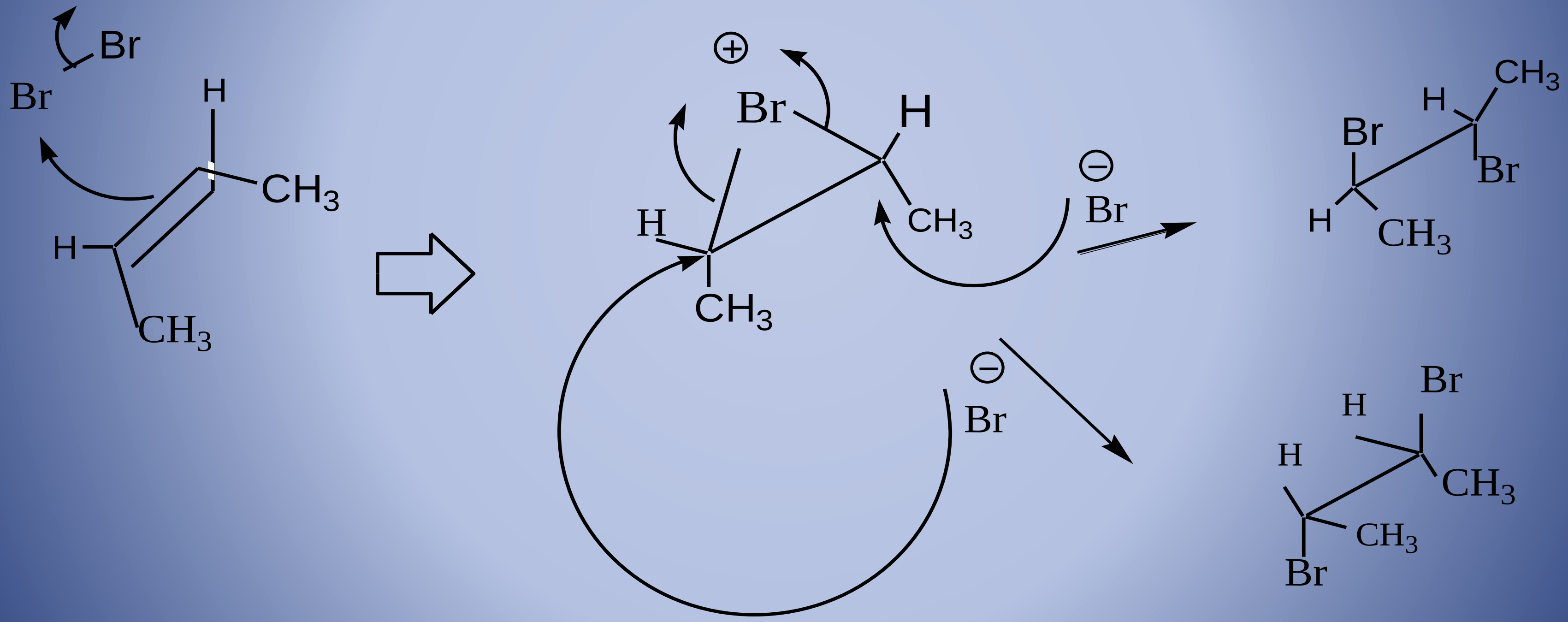
carbocation A

carbocation B

meso 2,3 dibromo butane

Bromnonium ion mechanism

- To account for the stereochemistry of bromine addition to alkenes, a cyclic bromonium ion mechanism has been proposed. Consider the anti – addition of bromine to cis- 2 butene as follows :



∓ 2;3 dibromo butane

- It also explain satisfactorily the formation of only the racemic mixture of 2,3 di bromo butane and not the meso compd if addition takes place at the cis- 2 butene.
- Similarly addition of bromine to trans 2- butene produce the meso compd by cyclic bromonium mechanism.
-

  Attack of the cyclic bromonium ion by bromide ion from opposite sides is equally likely and the enantiomers are formed in equal amount.
  The cyclic structure of bromonium ion prevents rotation about the carbon carbon bond. It also limits the attack of bromide ion exclusively to the opposite sides of the cyclic bromonium ion.
  The bromonium ion mechanism overcomes both the limitations of the open carbocation mechanism.

B. Sc V Semester

D. F. Diengdoh

Department of Chemistry