ADVANCED CHEMISTRY BLOC

(RE-READING ORGANIC CHEMISTRY)

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In a span of six episodes, we would be covering the indispensable points of organic chemistry, exactly what you need to understand or memorise in this column. Things are really simple in organic chemistry. You just take one step, means one concept or one reaction at a time. Rehearse and progress daily, without fail, even though for 30 minutes. Soon you will realise the things come to your mind effortlessly.

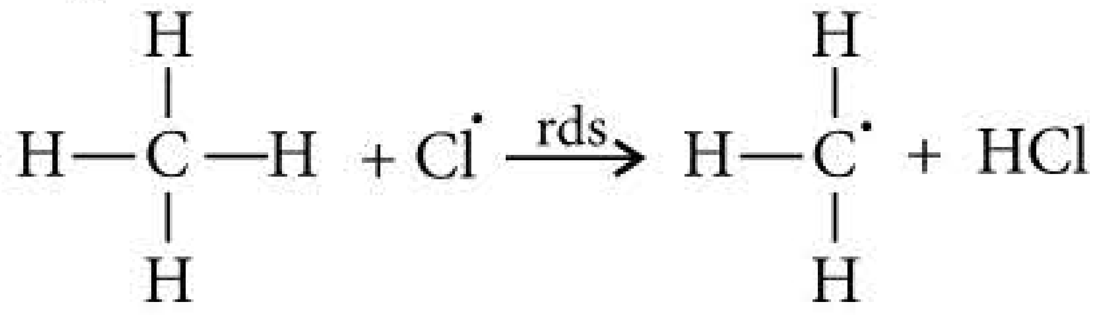
ALIPHATIC HYDROCARBONS

1. Halogenation of alkanes

Chlorination of methane

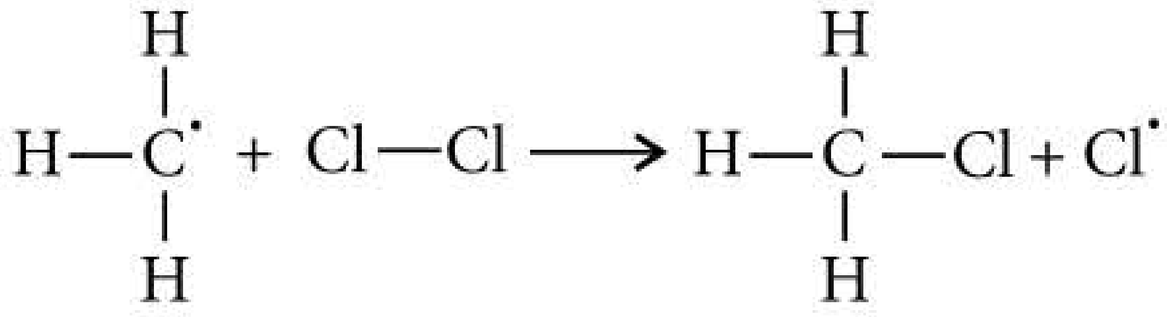
Step-1 : $Cl_2 \xrightarrow{h\nu} 2\dot{Cl}$

Step-2 :



$$H-\underset{H}{\overset{H}{C}}-H + \dot{Cl} \xrightarrow{rds} H-\underset{H}{\overset{H}{\dot{C}}} + HCl$$

Step-3 :

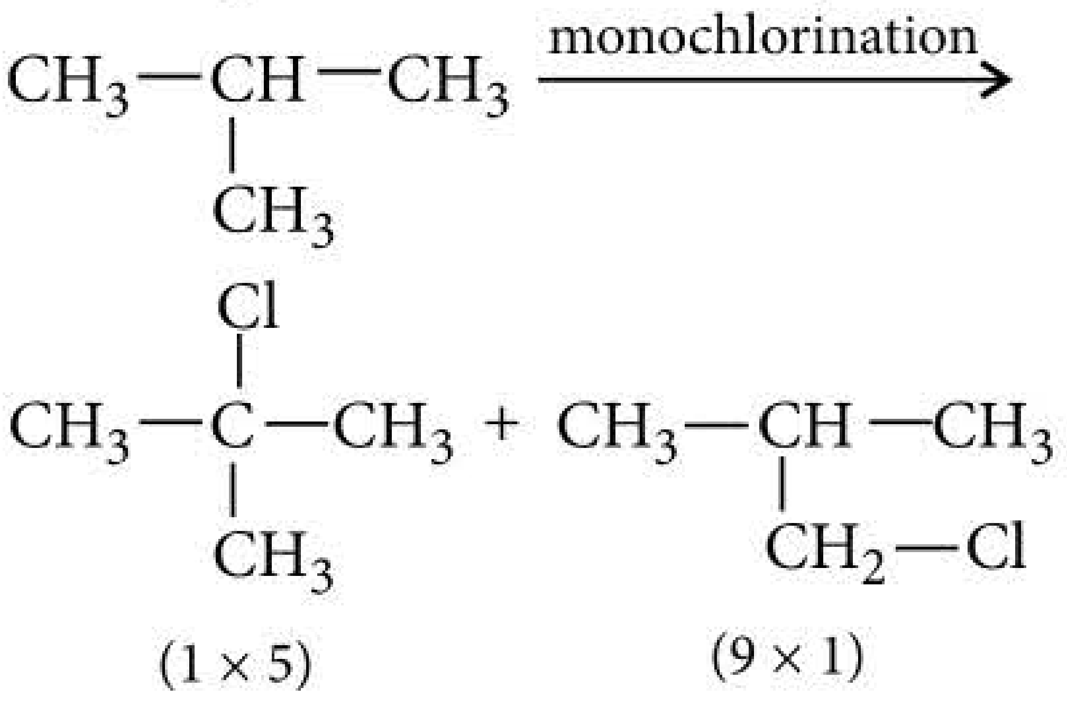


$$H-\underset{H}{\overset{H}{\dot{C}}} + Cl-Cl \longrightarrow H-\underset{H}{\overset{H}{C}}-Cl + \dot{Cl}$$

Step-2 is endothermic but step-3 is exothermic, thus overall process is exothermic. For all other alkanes, both steps are exothermic.

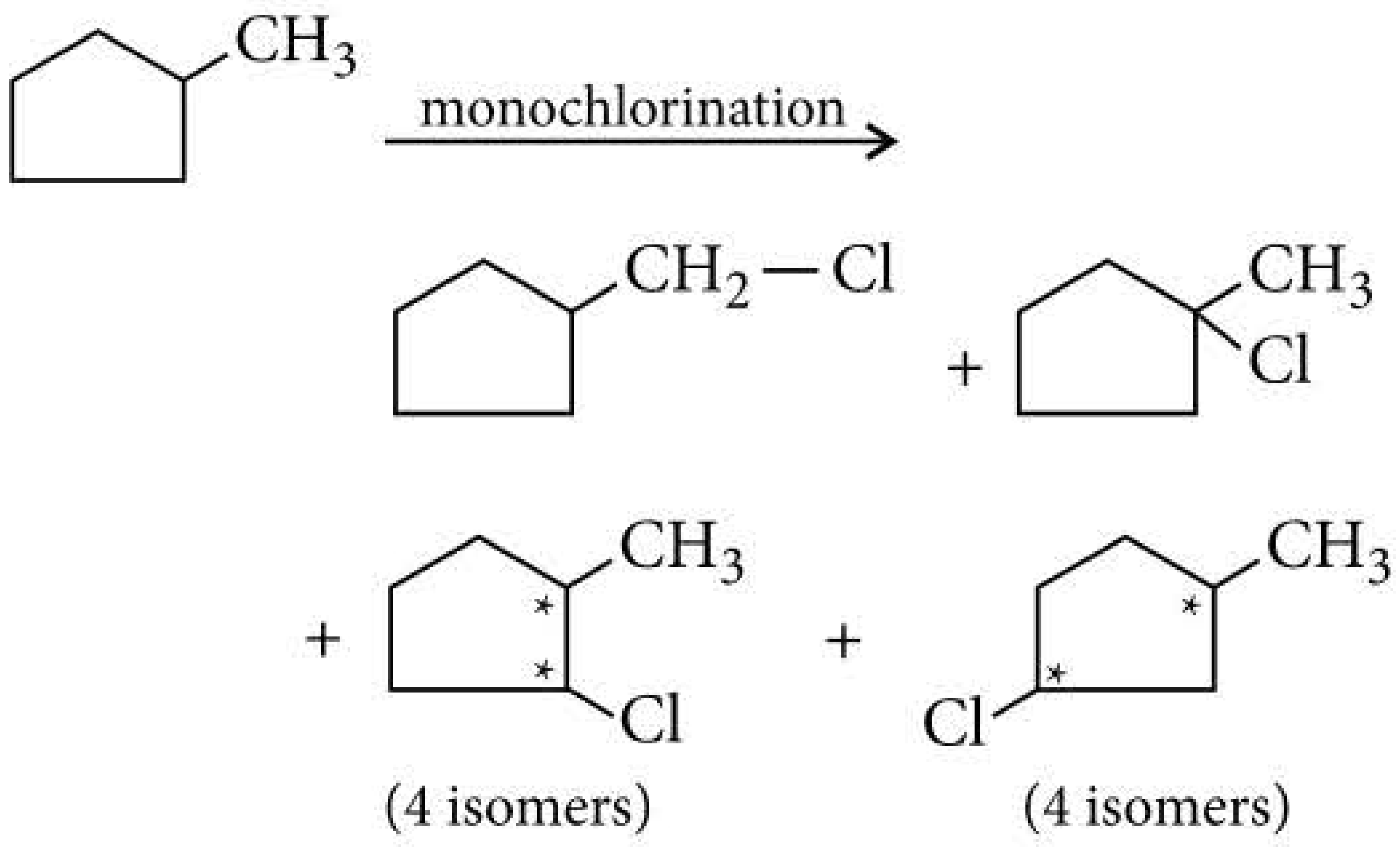
In chlorination, the selectivity of $\dot{Cl}$ towards primary, secondary and tertiary hydrogen is in the ratio of 1 : 3.8 : 5.

This helps us to calculate the product distribution.



$$CH_3-\underset{CH_3}{CH}-CH_3 \xrightarrow{monochlorination} \underset{(1\times5)}{CH_3-\underset{CH_3}{\overset{Cl}{C}}-CH_3} + \underset{(9\times1)}{CH_3-\underset{CH_2-Cl}{CH}-CH_3}$$

Relative amount of *t*-butyl chloride is 5 while for 2-methyl-1-chloropropane it is 9. No doubt, the later one is the major product.



Together there will be 10 isomers of product possible from the above reaction.

For bromination of methane, step-2 is endothermic but step-3 is exothermic. The overall process is weakly exothermic.

The selectivity ratio of $\dot{Br}$ towards 1°, 2° and 3° is 1 : 82 : 1600. So no need to calculate, you just go for tertiary product as the major product always.

2. Nitration of alkanes

Nitration involves C—C bond cleavage along with C—H bond.

$$CH_3-CH_3 \xrightarrow[\Delta]{HNO_3} CH_3-CH_2-NO_2 + CH_3-NO_2$$

3. Physical properties of alkanes

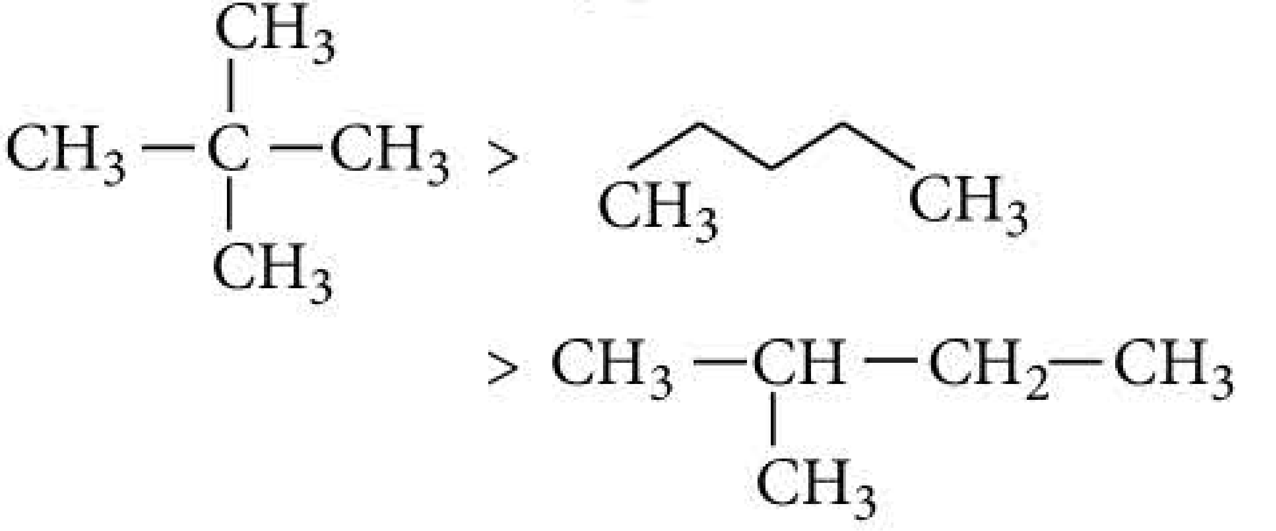
Melting point : $C_2H_6 > CH_4 > C_3H_8$

From propane onwards, melting point gradually increases though not regularly. The difference is less between odd and even as compared to that while moving from even to odd in case of *n*-alkanes. This is the "oscillation" or "alteration rule."

Check the data (No need to remember) :

Alkane	C_3H_8	n-C_4H_{10}	n-C_5H_{12}	n-C_6H_{14}
M.P.	−189.9 °C	−135 °C	−131.5 °C	−94.3°C

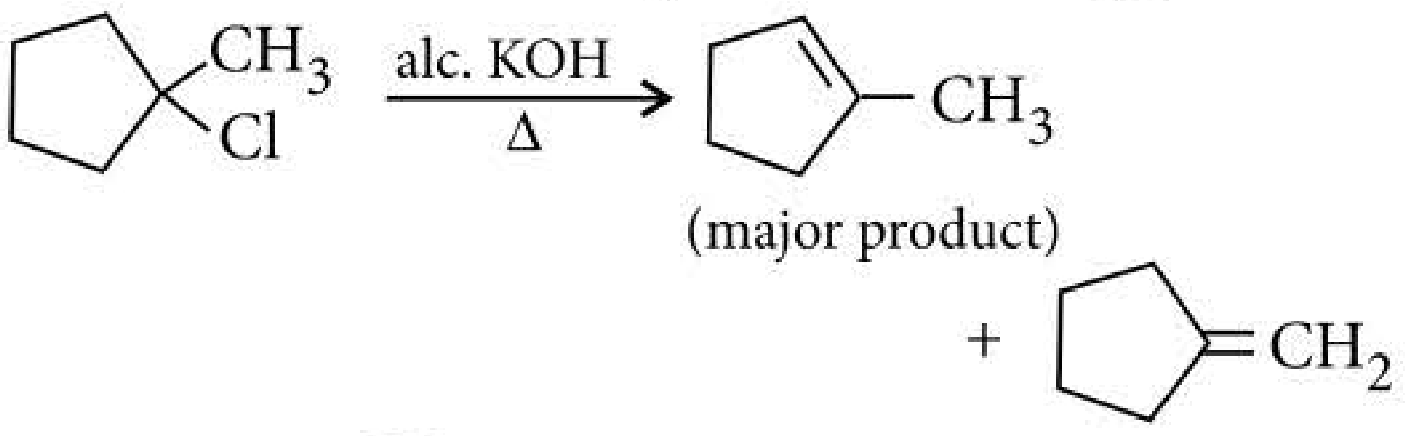
And order of melting point :

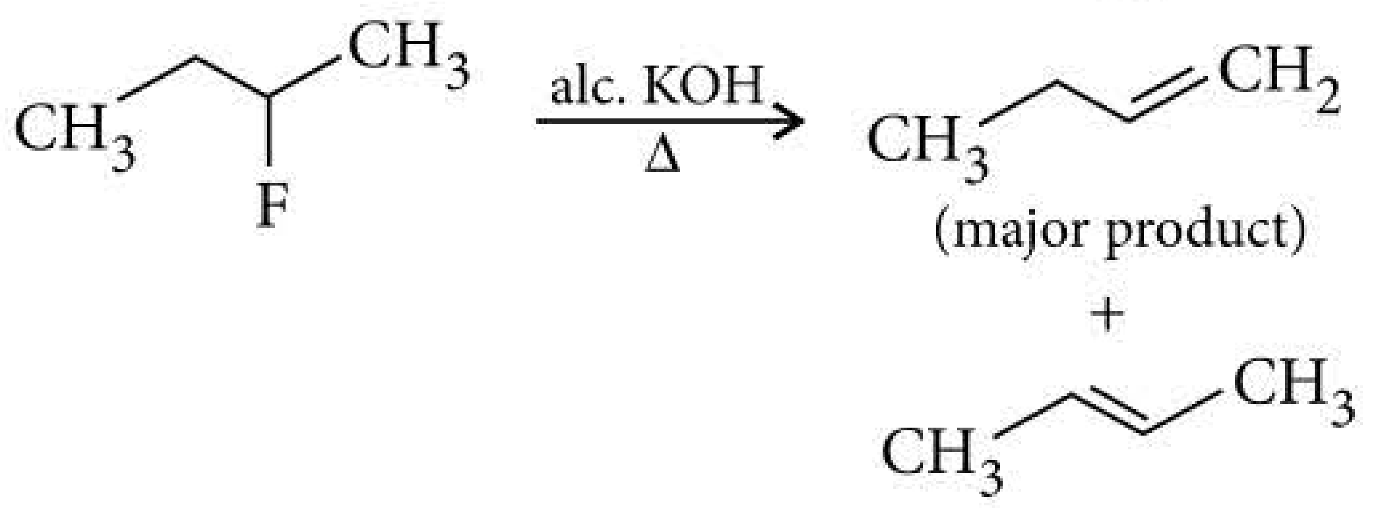


Boiling points for *n*-alkanes show a smooth increase along the series. For identical number of carbon containing compounds boiling point decreases with increase in branching.

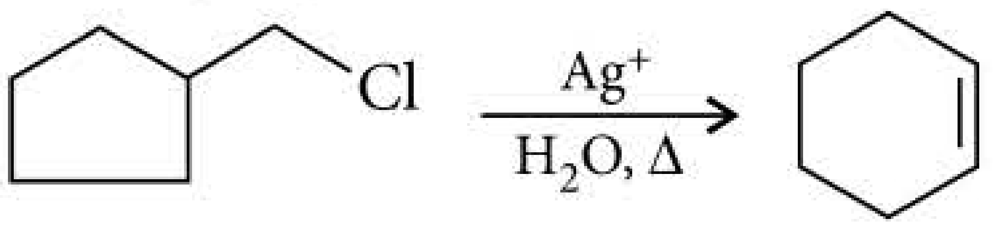
4. Preparation of alkenes

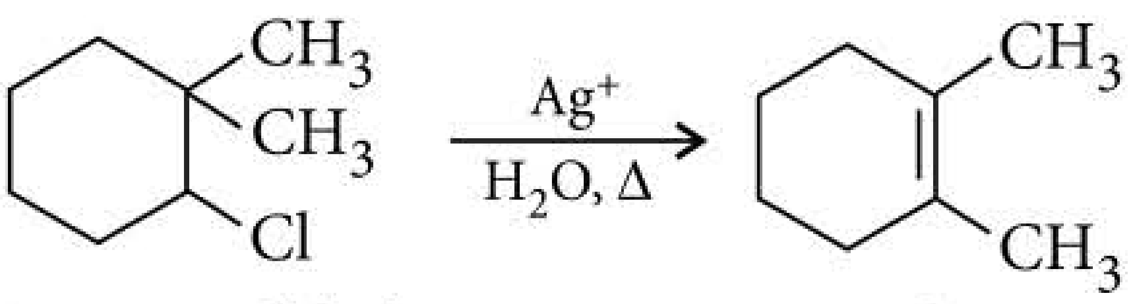
Strong base and heating condition on alkyl halides mostly certifies E_2 mechanism. Generally, it gives Saytzeff product except when –F or $-\overset{+}{N}H_3$ is the leaving group or bulky base is present where Hofmann elimination gives dominating product.





Branched alkyl halides, Ag^+ catalyst, weaker base like H_2O or CH_3OH and heating condition confirms E_1 mechanism. Saytzeff product is always the major product.

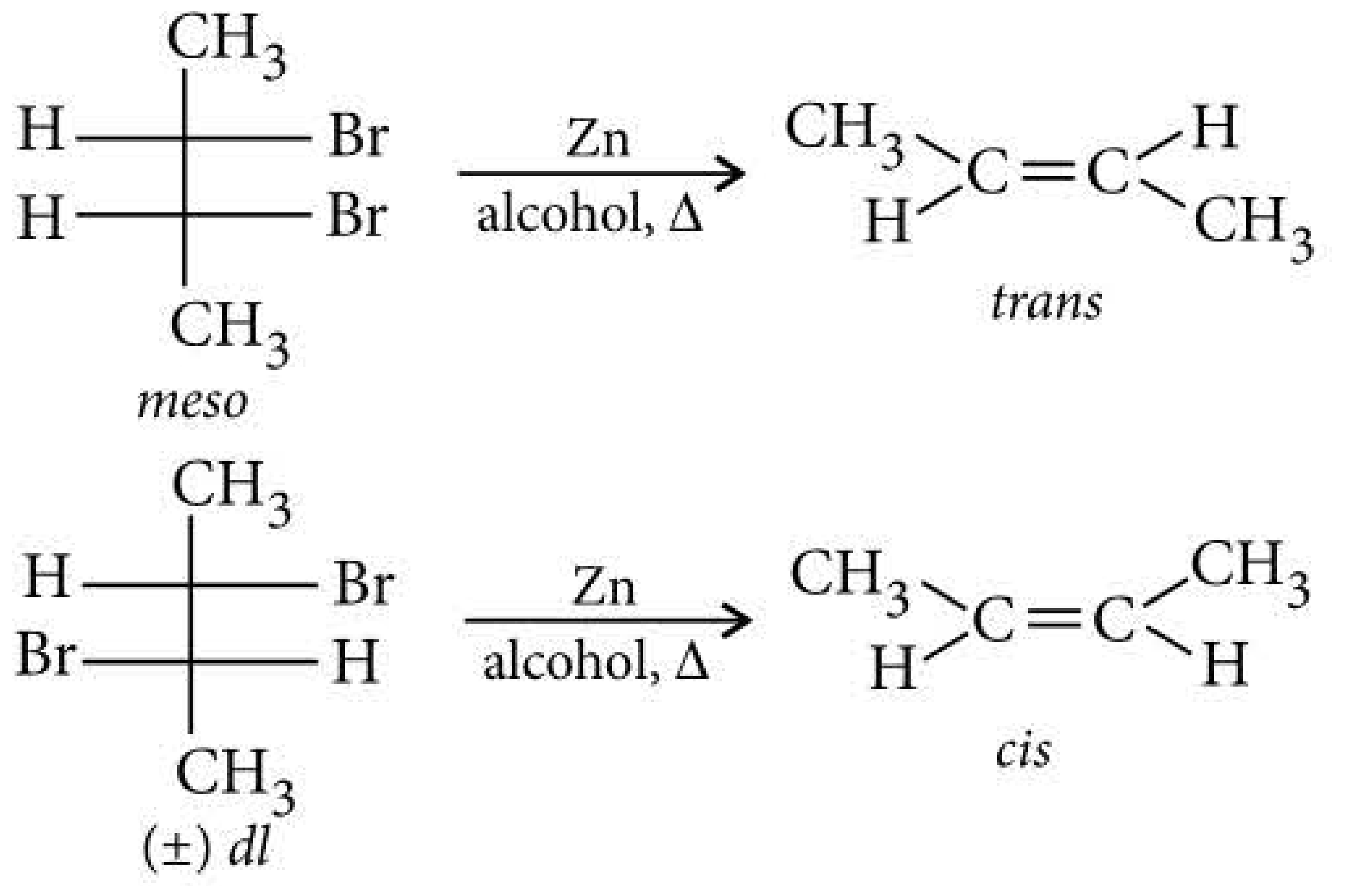




Zn is a dehalogenating agent that causes anti-elimination.

Remember the following table. Carefully check there is a symmetry.

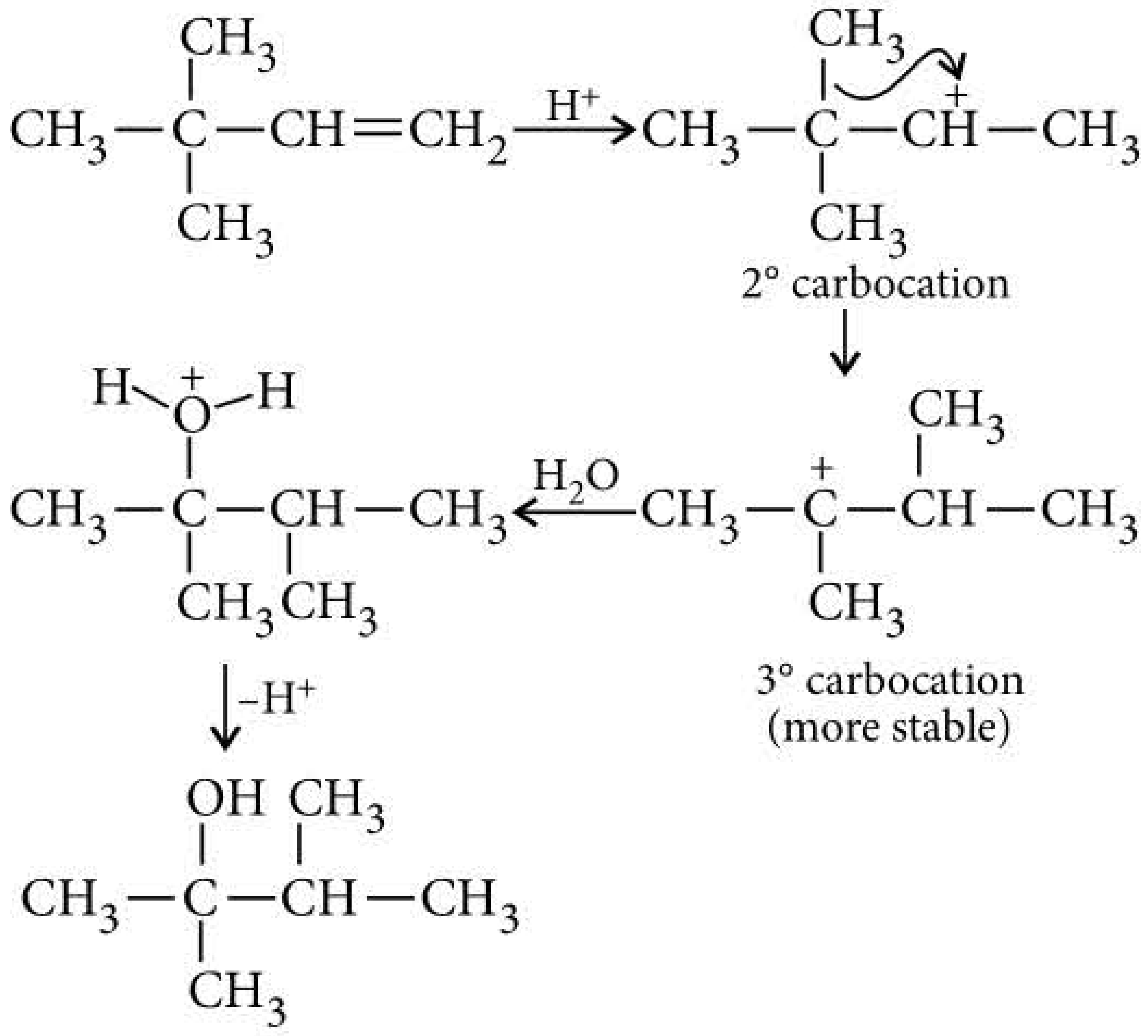
Alkene	Addition	Product
cis	*Syn*	*Meso*
cis	*Anti*	*dl* (±)
trans	*Anti*	*Meso*
trans	*Syn*	*dl* (±)



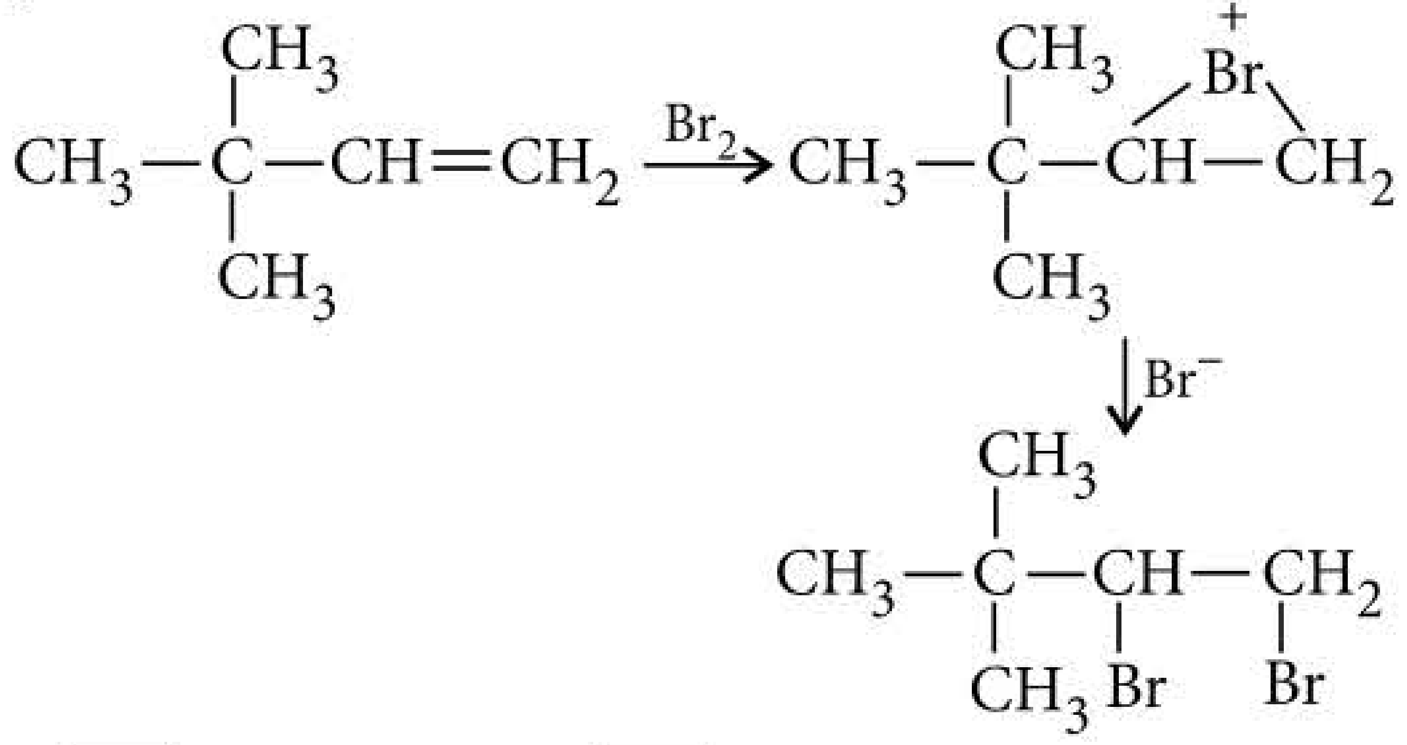
5. Addition reactions on alkenes

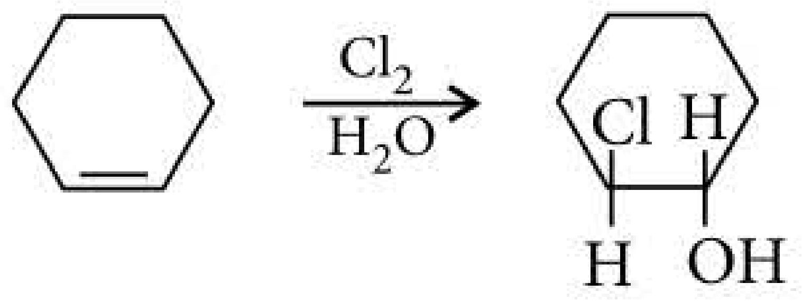
Alkenes generally follow addition electrophilic (AdE) mechanism.

Addition of HX and H_3O^+ : Alkene adds H^+ ion across double bond to give a carbocation, which rearranges and then pick the nucleophile.



But addition of Br_2, Cl_2/H_2O involve a cyclic halonium ion. Hence, no rearrangement takes place. The net result is anti-addition.





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