

Hydrocarbons

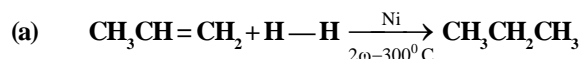
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C1 ALKANESMethods of Preparation of Alkanes and Cycloalkanes

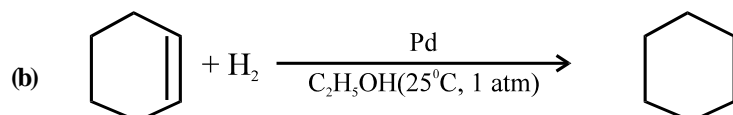
1. Hydrogenation of alkanes and alkynes :

(i) General Reactions :

Specified Examples :



[Any reduction that is carried out in this manner is called as Sabatier-Sanderen's reduction]

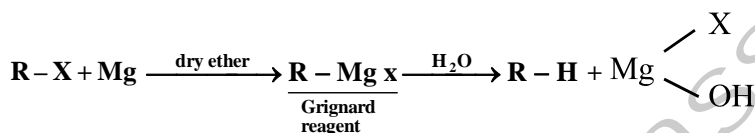


Limitation :

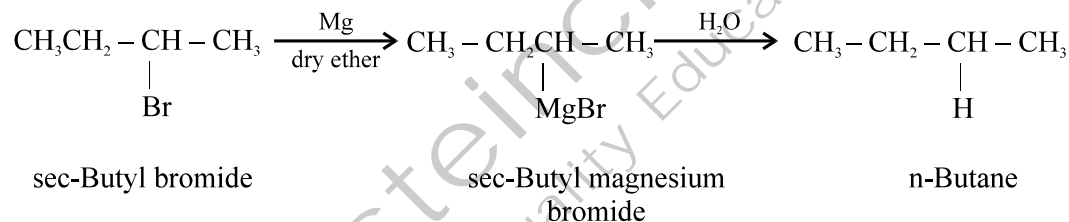
This method can not be used for the preparation of methane.

2. Reduction of Alkyl Halides :

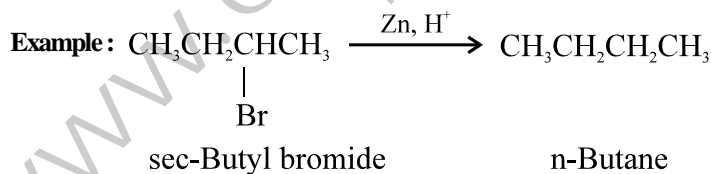
(a) Hydrolysis of Grignard reagent :



Examples :



(b) Reduction by metal and acid

(c) $4\text{R}-\text{X} + \text{LiAlH}_4 \rightarrow 4\text{R}-\text{H} + \text{LiX} + \text{AlX}_3$ [X ≠ F]LiAlH₄ can reduce 1^o and 2^o alkylhalide(d) $\text{R}-\text{X} + \text{n}(-\text{C}_4\text{H}_9)_3\text{SnH} \rightarrow \text{RH} + (\text{n}-\text{C}_4\text{H}_9)_3\text{SnX}$

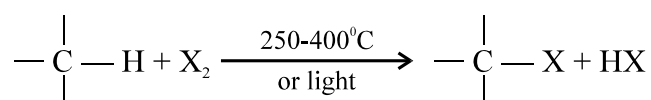
Tributyl tin hydride

[It can reduce 1^o, 2^o and 3^o alkyl halide].

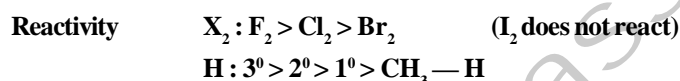
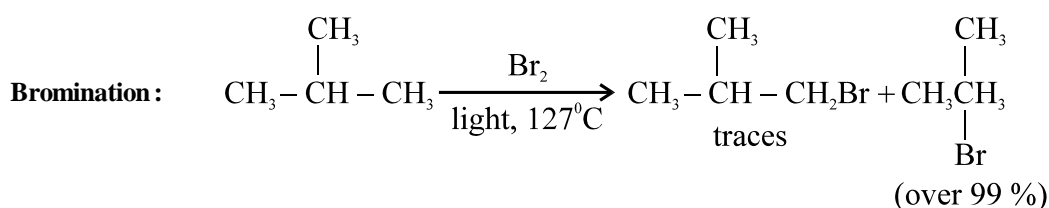
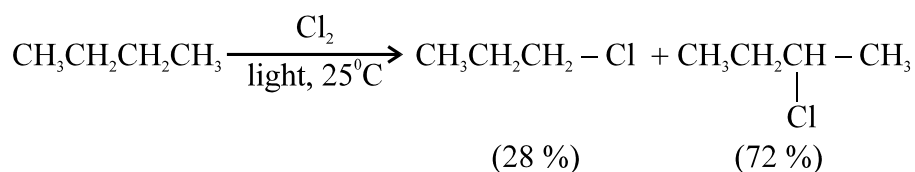
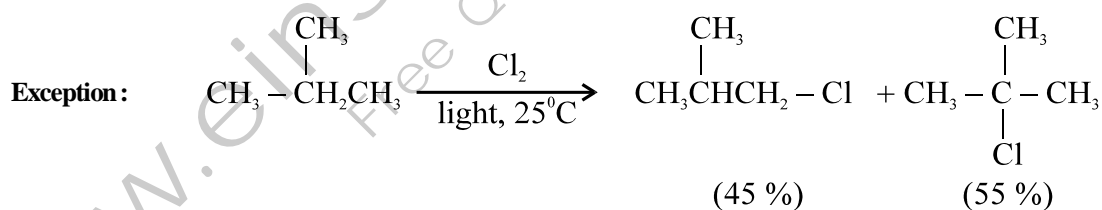
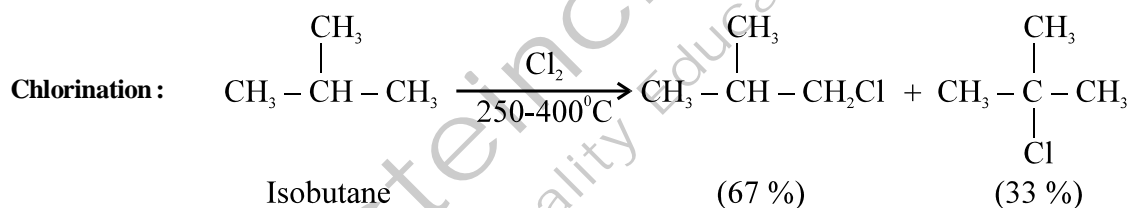
Practice Problems :

- By Wurtz reaction, a mixture of methyl iodide and ethyl iodide gives
 - propane
 - ethane
 - butane
 - a mixture of the above three
- Kolbe's synthesis of sodium salt of butanoic acid gives
 - n-hexane
 - isobutane
 - n-butane
 - propanone
- $(\text{CH}_3)_3\text{C}-\text{MgCl}$ on reaction with D_2O produces
 - $(\text{CH}_3)_3\text{CD}$
 - $(\text{CH}_3)_3\text{OD}$
 - $(\text{CD}_3)_3\text{CD}$
 - $(\text{CD}_3)_3\text{OD}$
- Aq. solution of potassium acetate is electrolysed. Possible organic products are :
 - CH_3-CH_3
 - $\text{CH}_3\text{COOCH}_3$
 - $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
 - both (a) and (b) are correct

[Answers : (1) d (2) a (3) a (4) d]

C2 General Chemical properties of alkanes :**1. Halogenation :**

Usually a mixture

**Example :**

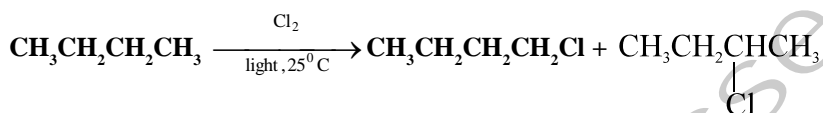
Conclusion :

1. Although both chlorination and bromination yield a mixture of isomers, the results given above shows that relative amounts of isomer differ markedly depending upon the halogen used.
2. Chlorination gives a mixture of isomers in which no one predominates. In bromination on contrast one isomer predominates to such an extent that as to be only product produced.

The factors determines the relative yields of isomeric products :

1. **Probability Factor :** This factor is based on the number of each kind of H-atom in the molecule. For example, In $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$ there are six equivalent 1°H 's and four equivalent 2°H 's. The ratio of abstraction of 1°H are thus 6 to 4 or 3 to 2.
 2. **Reactivity of H^\bullet :** The order of reactivity of H is $3^\circ > 2^\circ > 1^\circ$.
 3. **Reactivity of X^\bullet :** The more reactive Cl is less selective and more influenced by the probability factor. The less reactive Br is more selective and less influenced by the probability factor, as summarised by the reactivity-selectivity principle. If the attacking species is more reactive then it will be less selective, and yields will be closer to those expected from the probability factor.
- The rate of abstraction of hydrogen atoms is always found to follow the sequence $3^\circ > 2^\circ > 1^\circ$.
- At room temperature are 5 : 3.8 : 1 using these values we can predict the ratio of isomeric chlorine products from a given alkane.

Example :



$$\frac{\text{n-Butyl Chloride}}{\text{sec-Butyl Chloride}} = \frac{\text{no. of } 1^\circ\text{H}}{\text{no. of } 2^\circ\text{H}} \times \frac{\text{reactivity of } 1^\circ\text{H}}{\text{reactivity of } 2^\circ\text{H}}$$

$$= \frac{6}{4} \times \frac{1}{3.8} = \frac{6}{15.2} = \frac{28\%}{72\%}$$

- The same sequence of reactivity, $3^\circ > 2^\circ > 1^\circ$ is found in Bromination, but with enormously larger reactivity ratios. At 127°C the relative rate per hydrogen atom are 1600 : 82 : 1. Here, difference in reactivity are so marked so as to outweigh probability factor. Hence bromination is selective product.

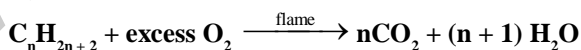
In bromination of isobutane at 127°C

$$\frac{\text{Isobutyl bromide}}{\text{tert-butyl bromide}} = \frac{\text{no. of } 1^\circ\text{H}}{\text{no. of } 3^\circ\text{H}} \times \frac{\text{reactivity of } 1^\circ\text{H}}{\text{reactivity of } 3^\circ\text{H}}$$

$$= \frac{9}{1} \times \frac{1}{1600} = \frac{9}{1600}$$

Hence, tert-butyl bromide happens to be the exclusive product (over 99%)

2. Combustion :

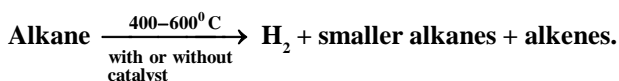


ΔH = enthalpy of combustion

Pyrolysis : (Cracking)

3. Decomposition of a compound by heat alone is known as Pyrolysis

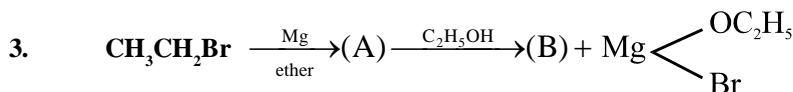
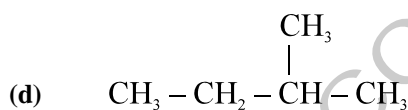
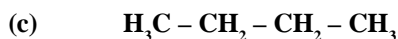
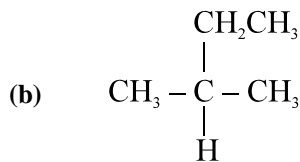
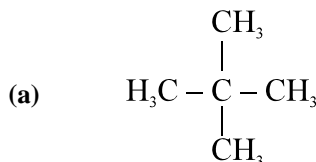
Pyrolysis of alkanes particularly when petroleum is concerned is known as cracking.



In thermal cracking alkanes are simply passed into a chamber to a high temperature. Large alkanes are converted into smaller alkanes, alkenes and some hydrogen.

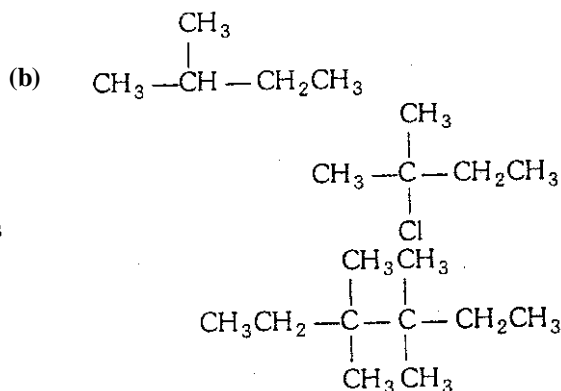
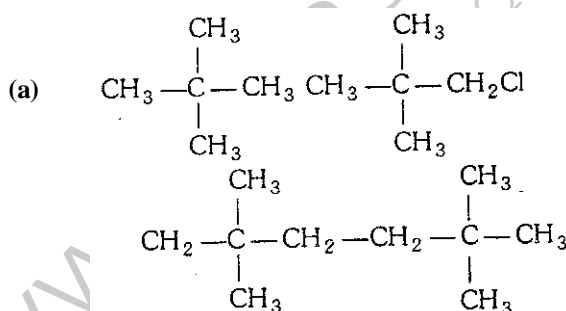
Practice Problems :

- The number of possible enantiomeric pairs that can be produced during mono chlorination of 2-methyl butane is
(a) 2 (b) 3 (c) 4 (d) 1
- An alkane with molecular mass 72 formed only one substitution product. Suggest a structure for the alkane.



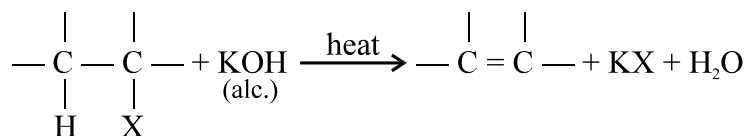
Thus A and B in the above reaction sequence are :

- (a) (A) $\text{CH}_3\text{CH}_2\text{MgBr}$ (b) (A) $\text{CH}_3\text{CH}_2\text{MgBr}$
(B) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
(c) (A) CH_3CH_3 (d) (A) CH_3COOH
(B) CH_3MgBr
(B) CH_3COCH_3
4.
$$\text{C}_5\text{H}_{12} + \text{Cl}_2 \xrightarrow{\text{light}} \text{C}_5\text{H}_{11}\text{Cl} \xrightarrow{\text{Na/ether}} (\text{C})$$
. Only one structure of B is possible (A), (B) and (C) are :

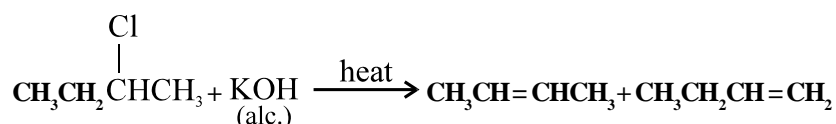
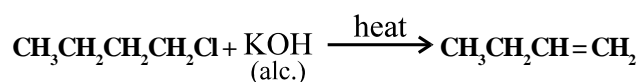


- (c) both correct (d) none is correct

[Answers : (1) a (2) a (3) b (4) a]

C3 ALKENESMethods of Preparation of Alkenes :1. Dehydrohalogenation of Alkyl-Halide : 1,2 - Elimination

Examples :

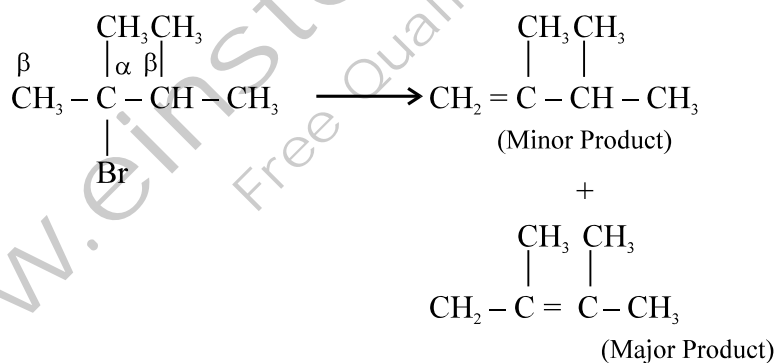
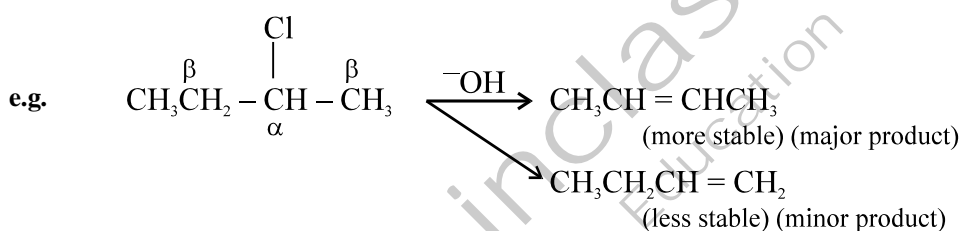


(cis or trans)

Discussion : Dehydrohalogenation means that there is an elimination of one hydrogen atom and one halogen atom. The reagent required is a base, whose function is to remove the hydrogen as a proton.

Now if alkyl halide has more than one β , hydrogen atom then that hydrogen is removed which result in more substituted alkene, this is according to saytzeff's rule.

More substituted alkene means that more no. of Alkyl groups are present around the double bond.

E₂ elimination reactions are characterised by the following :

1. Substrate contains a leaving group; an atom or group that leaves along with electron pair.
2. In position β to the leaving group the substrate contain H-atom that can be abstracted by base.
3. Reaction is brought about by a base.

Typically strong bases like OH^- , RO^- (alkoxide ion) derived from alcohol, $C_2H_5O^-$ ethoxide ion, tert-butoxide ion $(CH_3)_3CO^-$ etc.

Heterolytic bond dissociation energy : $RF > RCl > RBr > RI$

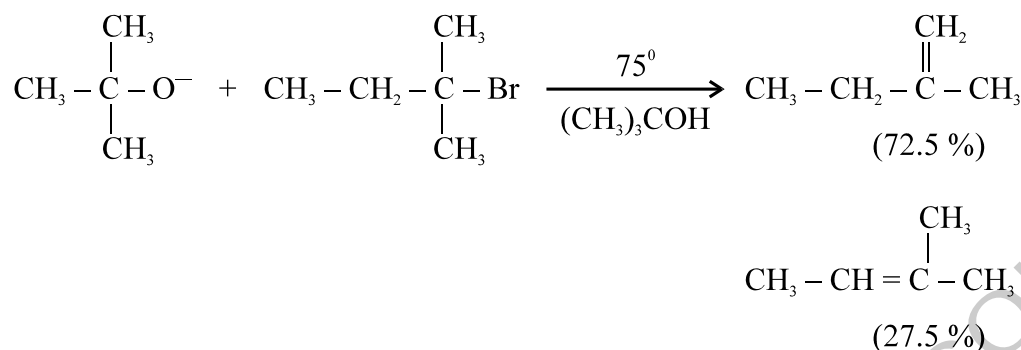
\therefore Reactivity towards E_2 : $RI > RBr > RCl > RF$

similarly reactivity order of R - X is $3^{\circ} > 2^{\circ} > 1^{\circ}$

as more substituted alkene will form as the branching will increase.

Kinetics of E_2 : Bimolecular. Rate of the reaction $r = k [\text{RX}] [:\text{Z}]$
Substrate Base

An exception to saytzeff's rule :

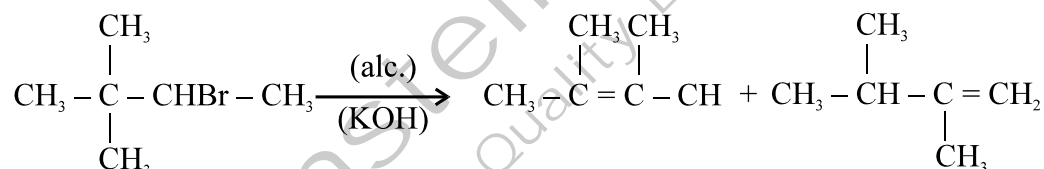


E_1 Mechanism : E_1 involves two steps for same process as it takes place in E_2 .

- The substrate undergo heterolysis slowly to form halide ion and a carbocation.
- In step (2) the carbocation readily loses a proton to the base and forms the alkene.
- Thus a carbocation may
 - combine with a nucleophile
 - can undergo rearrangement
 - eliminate a proton to form the alkene.
- Kinetics of E_1 reaction : $r = k [\text{RX}]$ [Unimolecular reaction]

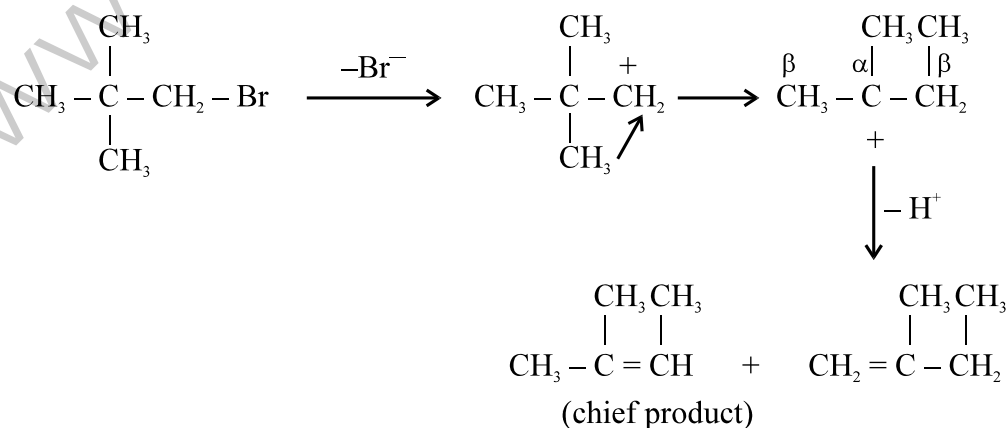
Order of reactivity of R - X for E_1 : $3^{\circ} > 2^{\circ} > 1^{\circ}$

Thus because of rearrangement skeleton of carbon chain changes :



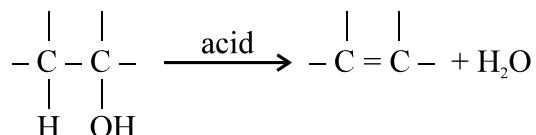
Alkene that doesnot contain α -hydrogen in the presence of base can undergo E_1 elimination as follows :

Explanation :

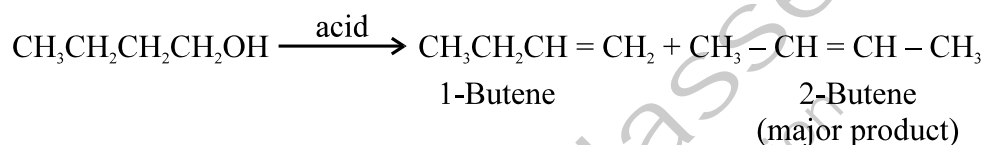
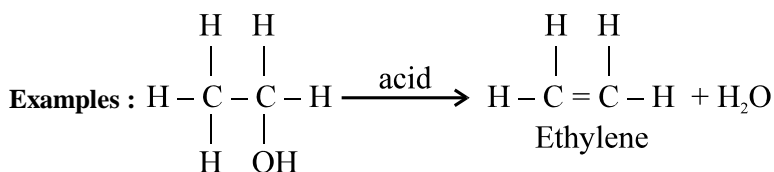


E₂ Vs E₁

- Reactivity of both mechanism increases with as we move from 1^o, 2^o to 3^o substrate.
- But E₂ mechanism depends on concentration of base whereas E₁ mechanism is independent of the concentration of base.
- Stronger the base more E₂ is favoured
- 1^o alkyl halide do not favour to form carbocation so they prefer E₂

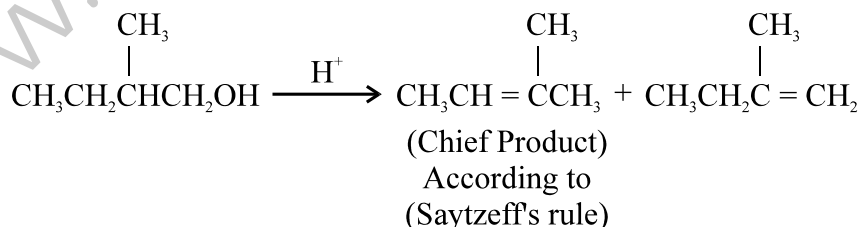
2. Dehydration of Alcohols :

Ease of dehydration of alcohol 3^o > 2^o > 1^o, as the intermediate formed is carbocation.



Dehydration is acid-catalyzed :- Acid transforms the poor leaving group (-OH) into the very good leaving group, -OH₂⁺

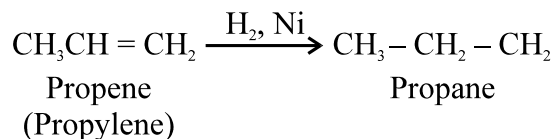
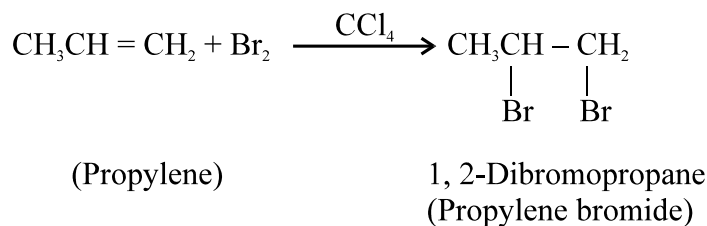
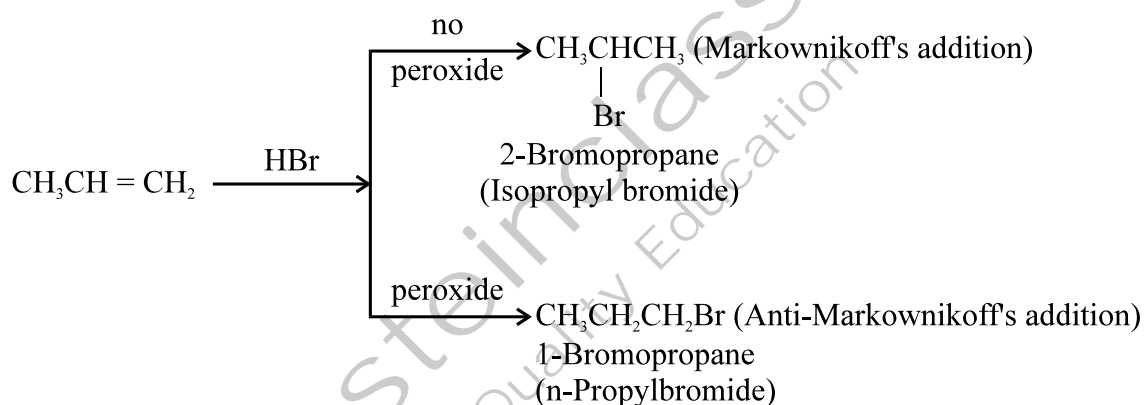
- As dehydration is acid catalysed as acid is not consumed in the reaction. Acid used in step (1) is regenerated in step (3).
- Dehydration is reversible :- Unlike base promoted 1, 2-elimination, this elimination is reversible.
- As we shall study later that acid catalysed the hydration of alkenes to give alcohol.
- Thus each step is reversible.
- Under the condition of dehydration, the alkene being quite volatile is generally driven from the reaction mixture and thus equilibrium (3) is shifted in the right side.
- As a consequence the entire reaction is forced toward elimination.
- Where the structure of alkyl group permits the rearrangement of carbocation takes place.

Practice Problems :

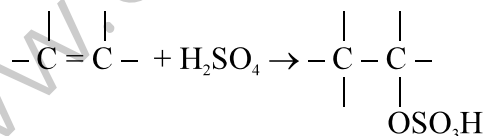
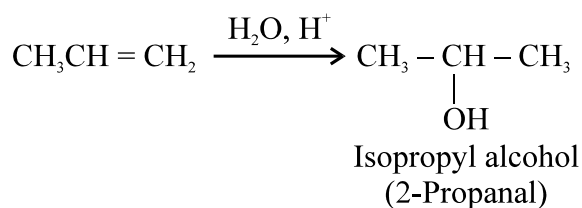
1. Identify the possible number of products in the following reaction : $C_6H_5CH_2CH(Cl)C_6H_5 \xrightarrow[\text{heat}]{\text{Alc.KOH}}$

- (a) 1 (b) 2 (c) 3 (d) 4

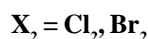
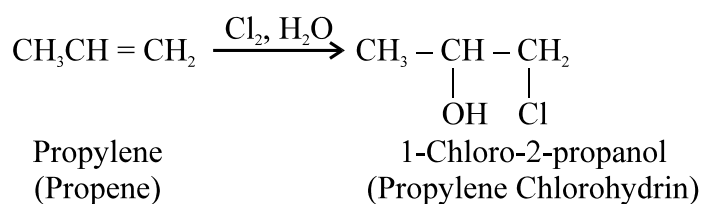
[Answers : (1) b]

C4 Chemical Properties of Alkene :**(Addition Reactions)****1. Addition of Hydrogen : Catalytic hydrogenation****2. Addition of halogens :****3. Addition of hydrogen halide :**

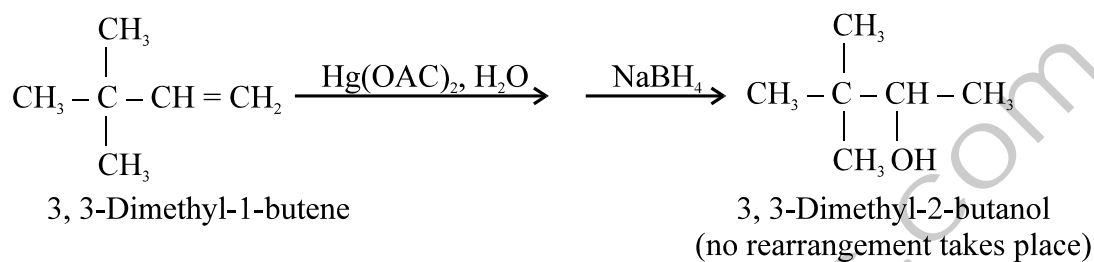
Peroxide has no effect on HF, HCl and HI

4. Addition of sulfuric acid :**5. Addition of dil-sulfuric acid :**

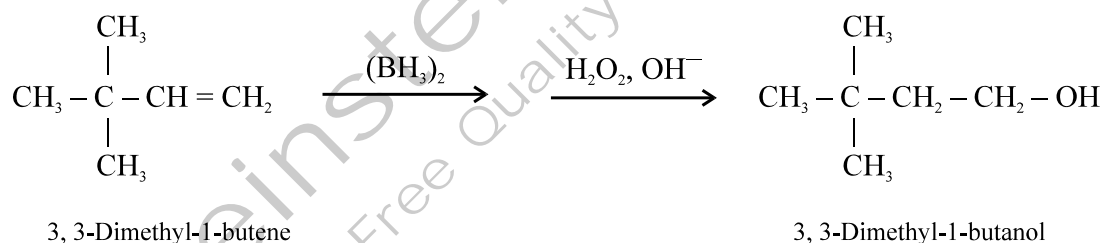
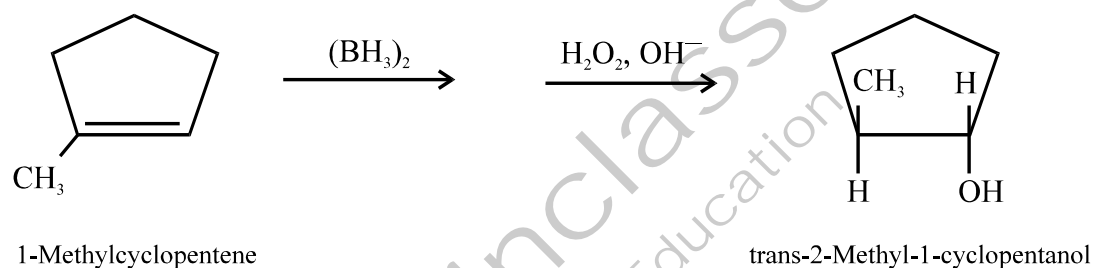
6. Halohydrin Formation :



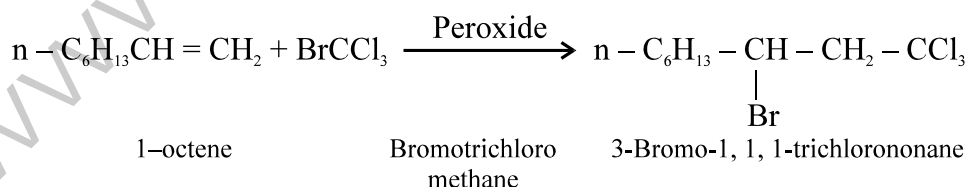
7. Oxymercuration-demercuration :

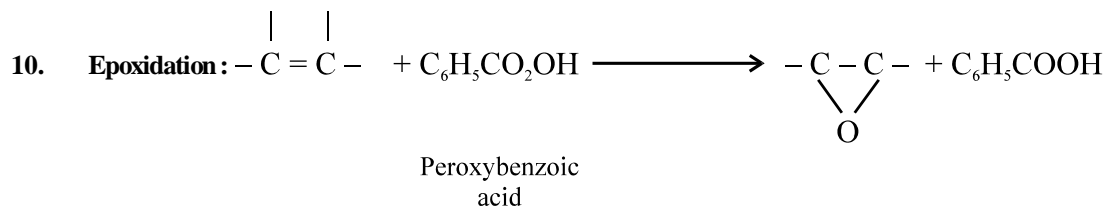


8. Hydroboration-Oxidation

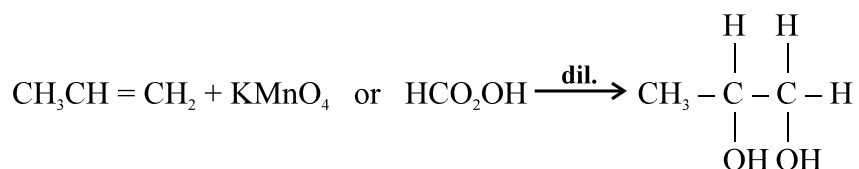


9. Addition of free radicals



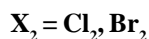
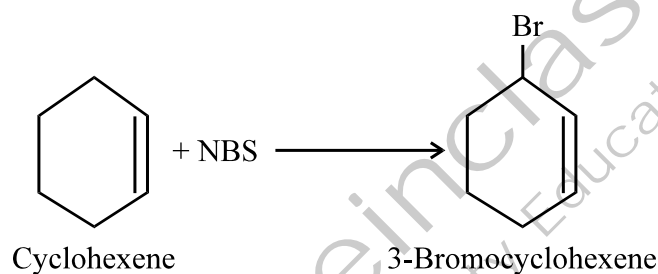
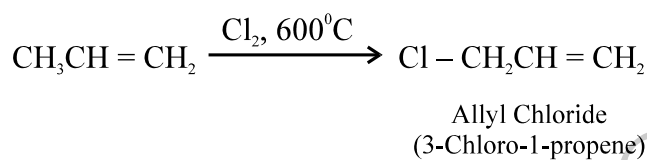


11. **Hydroxylation : Glycol formation**



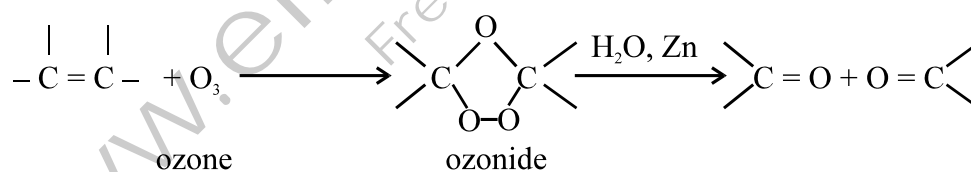
Substitution Reaction :

12. **Halogenation : Allylic Substitution**

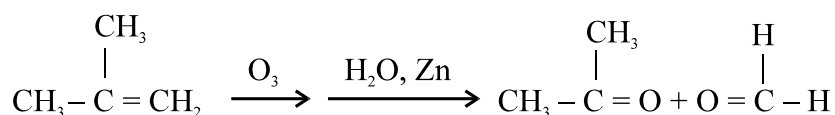
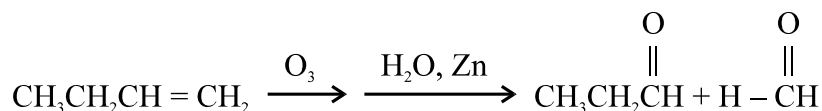


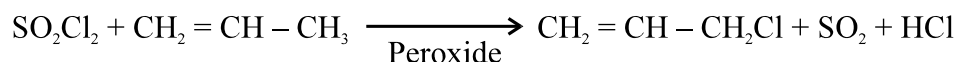
13. **Cleavage Reactions (very important) used to determine structure.**

Ozonolysis :

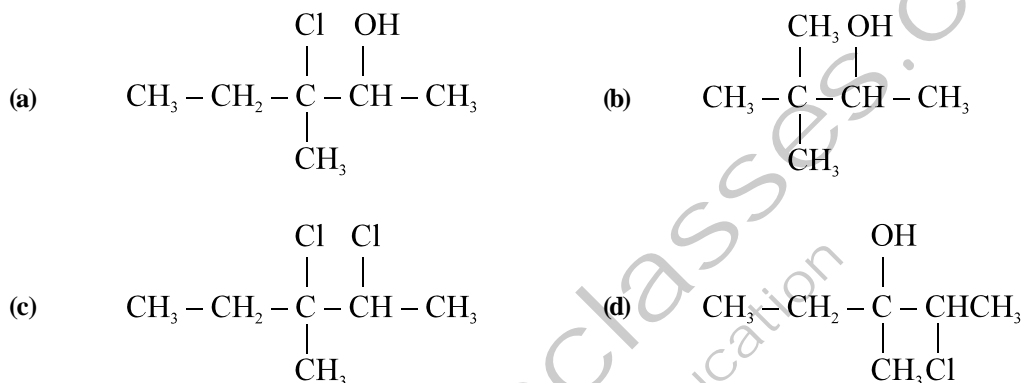


Example :

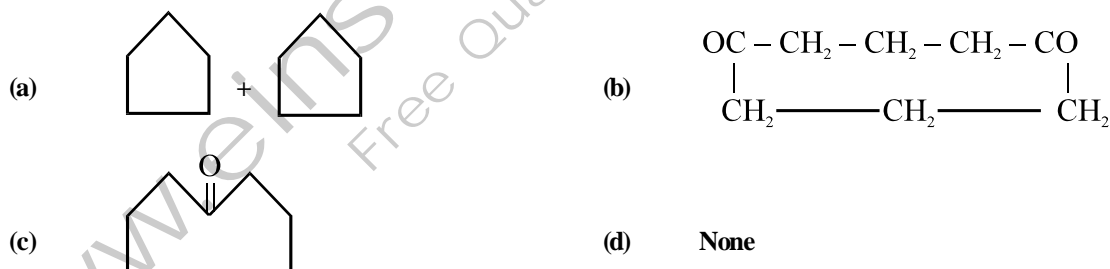


Substitution reactions at allylic positions :Practice Problems :

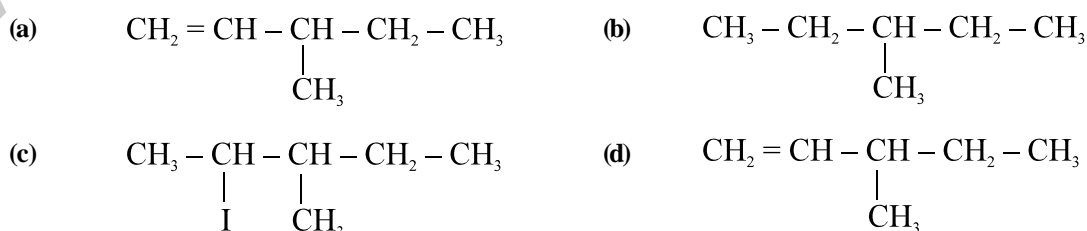
- A hydrocarbon containing 2 carbon atoms give Sabatier and Senderen's reaction but does not give precipitate with ammonical silver nitrate solution. The hydrocarbon in question is
 (a) Ethane (b) Acetylene (c) Ethylene (d) none of these
- Which of the following is not correct about the reaction $\text{CH}_2 = \text{CH}_2 + \text{Br}_2 \xrightarrow{\text{NaI(aq)}} :$
 (a) The products formed are $\text{CH}_2\text{BrCH}_2\text{Br}$ and $\text{CH}_2\text{BrCH}_2\text{I}$
 (b) The reaction follows polar mechanism
 (c) The reaction occurs readily in solution and is catalysed by inorganic halides
 (d) $\text{CH}_2\text{ICH}_2\text{I}$ is formed only
- 3-methyl-2-pentene on reaction with HOCl gives :



- Ozonolysis of  will give



- Sample of 2, 3-dibromo-3-methyl pentane is heated with zinc dust. The resulting product is isolated and heated with HI in the presence of phosphorus. Indicate which is the structure that represents the final organic product in the reaction



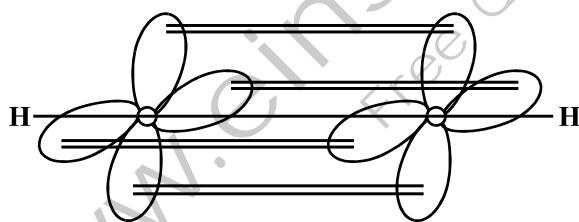
6. $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2 \xrightarrow[\text{1equiv.}]{\text{H}_2/\text{Pt}} \text{A} \xrightarrow{\text{O}_3/\text{H}_2\text{O}} \text{A and B are}$
- (a) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2, (\text{CH}_3\text{COOH} + \text{CO}_2)$
 (b) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3, \text{CH}_3\text{COOH} (2 \text{ mol})$
 (c) $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3, \text{CH}_3\text{CHO} (2 \text{ mol})$
 (d) $\text{CH}_3 - \text{CH}_2 - \text{CH} = \text{CH}_2, (\text{CH}_3\text{CH}_2\text{CHO} + \text{HCHO})$
7. Identify the set of reagents / reaction conditions 'X' and 'Y' in the following set of transformations
- $\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{Br} \xrightarrow{\text{X}} \text{Product}$
- $\text{Product} \xrightarrow{\text{Y}} \text{CH}_3 - \underset{\text{Br}}{\text{C}}\text{H} - \text{CH}_3$
- (a) X = dilute aqueous NaOH, 20°C;
Y = HBr/acetic acid, 20°C
 (b) X = concentrated alcoholic NaOH, 80°C,
Y = HBr / acetic acid, 20°C
 (c) X = dilute aqueous NaOH, 20°C,
Y = Br₂ / CHCl₃ / 0°C
 (d) X = concentrated alcoholic NaOH, 80°C ;
Y = Br₂ / CHCl₃ . 0°C

[Answers : (1) c (2) d (3) d (4) b (5) b (6) b (7) b]

C5 ALKYNES:

Electronic Structure of Triple Bond :

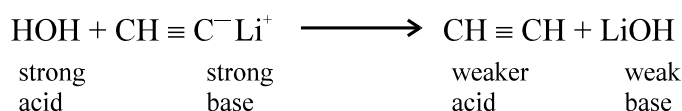
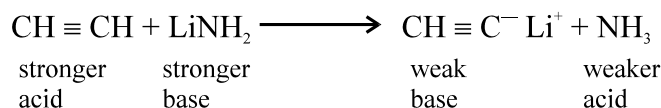
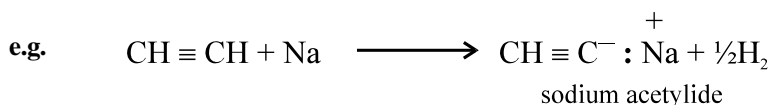
- Acetylene is known to have a linear structure.
- The carbon-hydrogen bond length of 1.06 Å is shorter than that in ethylene or in ethane. Thus it is stronger than either.
- The sp² – s σ-bonds are shorter than sp³ – s σ-bonds. The trend also holds for the sp – s bonds in acetylene.
- Superimposed on the σ-electrons are two orthogonal π-electron system.



Overlap of the p-orbitals on one carbon with the p-orbitals on the other carbon permits pairing of electrons. Two s-bonds are formed, which together make a single cylindrical sheath about the line joining the nuclei.

- Thus carbon-carbon "triple bond" is thus made up of one strong σ-bond and two weaker π-bonds. It has total strength of 198 kCal. It is stronger than the carbon-carbon double bond of ethylene and carbon-carbon single bond of ethane and is shorter than either.
2. Acidity of Alkynes : Very weak acids :
- In our earlier consideration of acids we took acidity to be a measure of the tendency of a compound to lose the hydrogen ion.
 - Appreciable acidity is shown by those compounds in which hydrogen is attached to rather electronegative atom like (F > O > N > C). The bond holding the hydrogen is polar, thus relatively positive hydrogen can separate as positive ion, and more electronegative atom can hold the negative charge effectively. In organic chemistry we are frequently concerned with the acidities of compounds do not turn litmus red or neutralize aqueous bases. Yet they have tendency to lose proton H⁺ to small

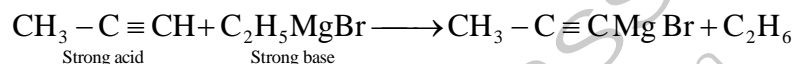
extent. A triply bonded carbon behaved as it is more electronegative than carbon which is singly or double bonded. As a result the hydrogen bonded to terminal alkyne shows the hydrogen bonded to terminal alkyne shows appreciable acidity.



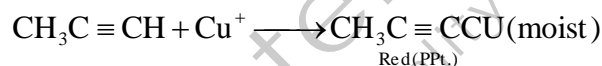
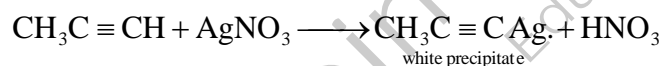
Relative Acidities : $\text{H}_2\text{O} > \text{ROH} > \text{HC} \equiv \text{CH} > \text{NH}_3 > \text{RH}$

Relative Basicities : $\text{OH}^- < \text{OR}^- < \text{CH} \equiv \overset{-}{\text{C}} < \text{NH}_2^- < \text{R}^-$

If a terminal alkyne is treated with an alkyl magnesium halide or an alkyl lithium the alkane is displaced from its salt and the metal acetylide is obtained.



only terminal alkynes give these reaction :



C6. Method of Preparation of Alkynes :

Industrial method of preparation :

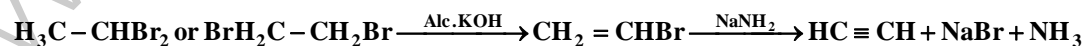
1. Acetylene is formed from the reaction of inorganic compound calcium carbide with water



2. $2\text{CH}_4 \xrightarrow{1500^\circ\text{C}} \text{CH} \equiv \text{CH} + 3\text{H}_2$

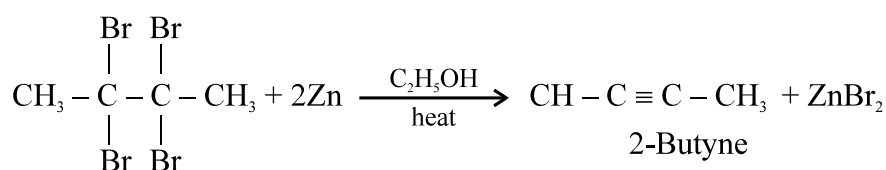
3. Laboratory methods of preparation :

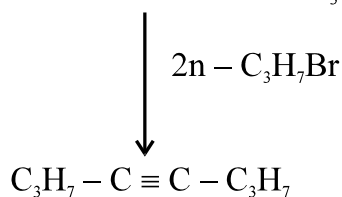
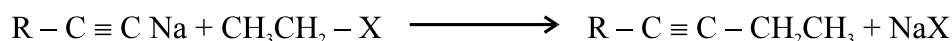
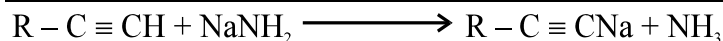
Dehydrohalogenation of gem or vicinal dihalite :



vinyl halide requires the stronger base sodamide NaNH_2 .

4. Dehalogenation of vic-tetrahalogen compounds :

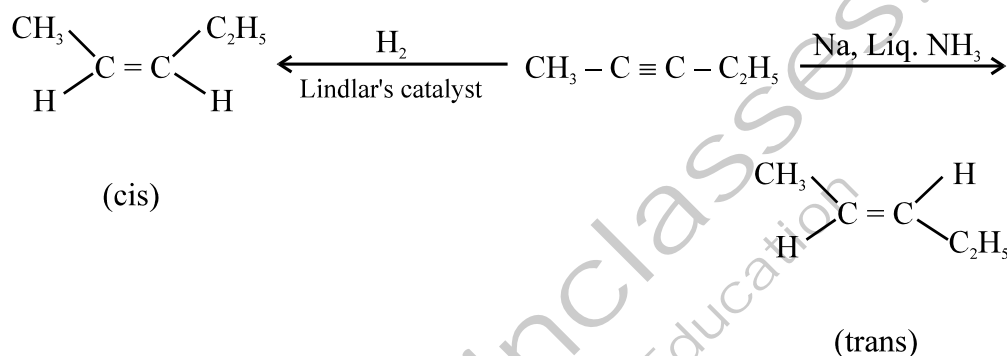
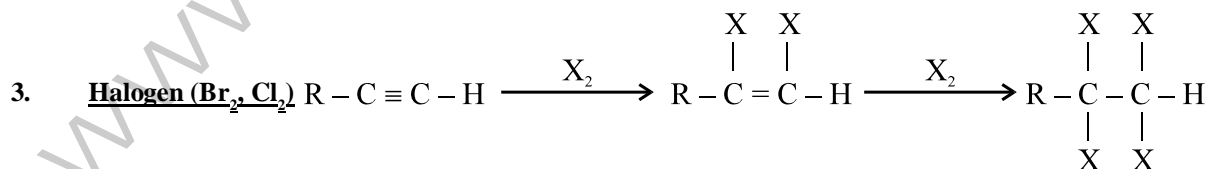
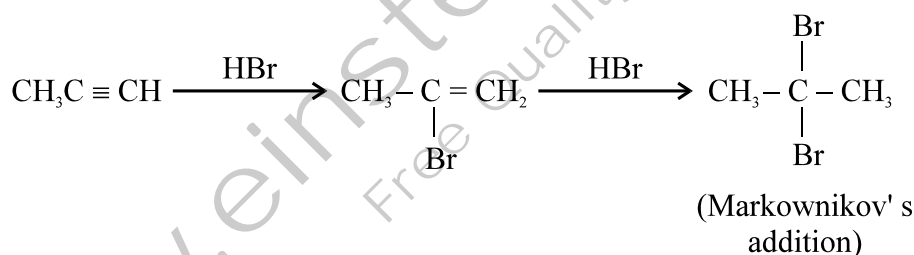


5. Alkyl substitution in acetylene (Method of preparation of higher alkynes):

This method is good for synthesis of alkynes when applied to primary halides that do not have branches close to reaction centre. With secondary halide and even with primary halides that have branches closer to the reaction centre, elimination is usually the major reaction.

C7 Chemical Properties of Acetylene :

Addition reaction at the triple bond : π -electrons of alkyne add electrophiles in reactions similar to additions to alkenes. Alkynes can add two moles of reagent but are less reactive than alkenes.

1. Hydrogenation $CH_3 - C \equiv C - CH_2CH_3 + 2H_2 \xrightarrow{Pt} CH_3CH_2CH_2CH_3$ 2. HX (HCl, HBr, HI)4. Addition of water