

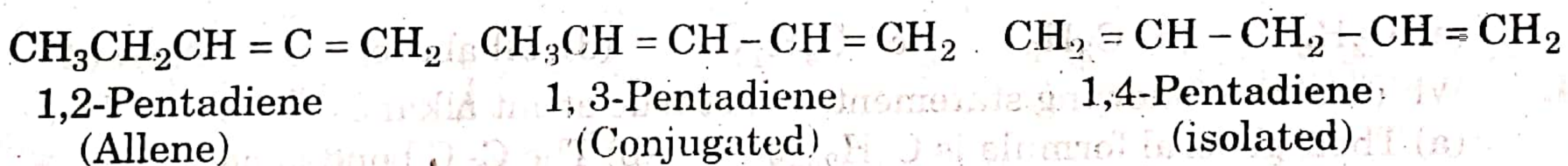
# 5.

## UNSATURATED HYDROCARBONS ALKENES AND ALKYNES

### 5.1 Introduction

Hydrocarbons in which all the four valencies of carbon are not fully satisfied, contain less than maximum number of hydrogen atoms, and have carbon-carbon multiple bonds, are called *unsaturated hydrocarbons*. Unsaturated hydrocarbons can be divided into two main classes, alkenes and alkynes. The unsaturated hydrocarbons which contain at least one carbon-carbon double bond are called **alkenes**. They have the general formula  $C_nH_{2n}$  ( $n$  = number of C atoms). As a class alkenes are commonly known as **olifines** (Latin; oleum = oil ; ficare = to make) because the lower members form oily products on treatment with chlorine or bromine.

Many alkenes contain more than one carbon-carbon double bond. They are called **alkadienes**, if the number of double bonds is two, **alkatrienes** for three double bonds etc. If two double bonds are adjacent, they are called **conjugated double bonds** and the alkenes with conjugated double bonds are called **allenes**. The allenes are highly reactive compounds and are therefore difficult to prepare, thus only few allenes are known. If the two double bonds are separated by a single bond, they are called **conjugated double bonds** and the diene is called **conjugated diene**. If the two double bonds are separated by two or more single bonds, they are called **isolated double bonds** and the diene is called **isolated diene**.



The term alkene is specifically used for those unsaturated hydrocarbons which have isolated carbon-carbon double bonds. The carbon-carbon double bond is called **olifinic bond**.

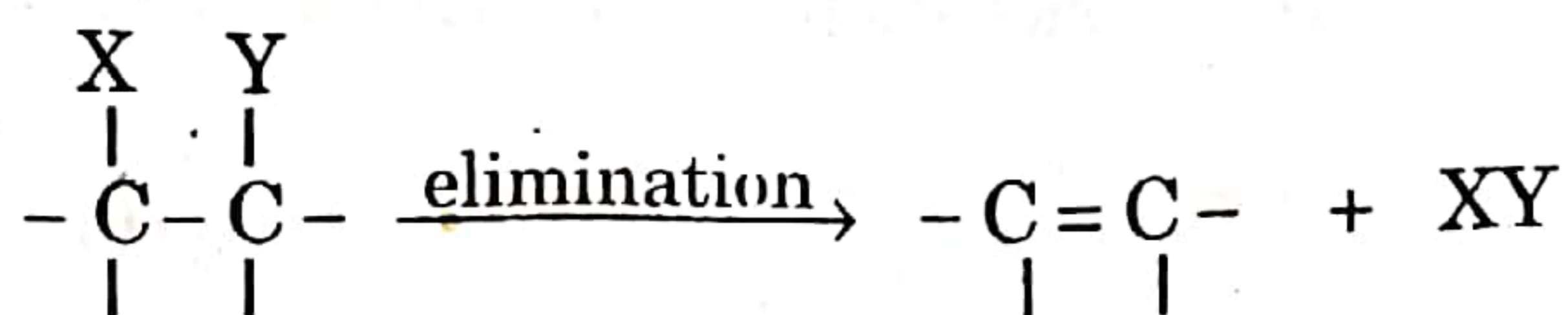
The unsaturated hydrocarbons that contain a triple bond ( $-\text{C} \equiv \text{C}-$ ) in their molecules are called **alkynes** and are isomeric with **alkadienes**. A triple bond is comprised of one strong  $\sigma$  bond and two weaker  $\pi$  bonds. The general formula for alkyne is  $C_nH_{2n-2}$ . The first and the most important member of the alkyne series is acetylene,  $\text{HC} \equiv \text{CH}$ , and hence they are also called **Acetylenes**, and the triple bond is often referred to as the **acetylenic linkage**.

### 5.2 ALKENES

#### Methods of preparation of Alkenes

Alkenes may be prepared from saturated compounds by the elimination of atoms or groups from two adjacent (vicinal) carbon atoms. Such reactions are called **elimination reactions**. "Reactions in which two atoms or groups are eliminated from two adjacent carbon atoms of the substrate molecule to form a multiple bond are

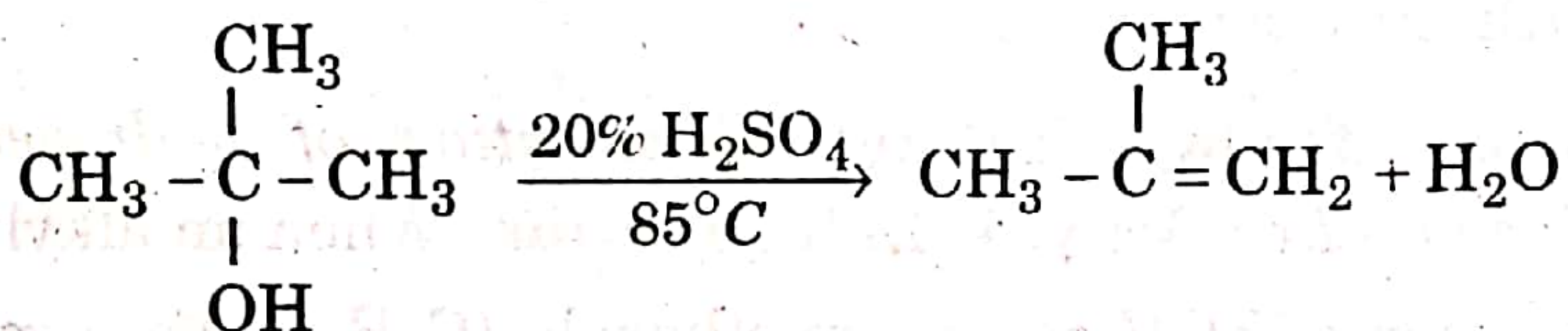
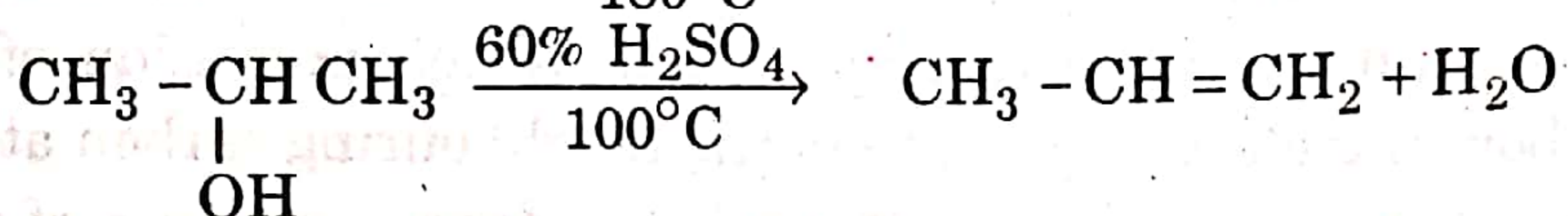
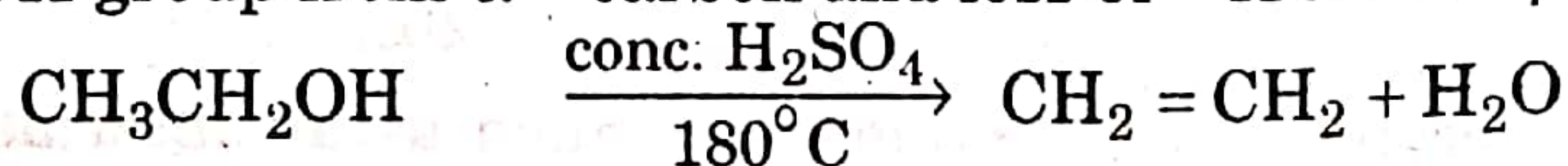
called **elimination reactions**"



There are three common types of elimination reactions.

1. Dehydration of alcohols
2. Dehydrohalogenation of alkyl halides
3. Dehalogenation of vicinal dihalides.

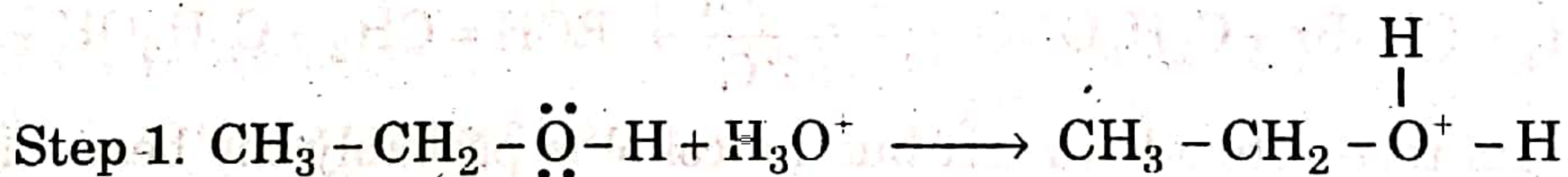
**1. Dehydration of Alcohols.** Alcohols on heating in the presence of a Bronsted acid such as sulphuric acid, phosphoric acid or a Lewis acid such as alumina ( $\text{Al}_2\text{O}_3$ ) lose a molecule of water to form an alkene. The dehydration of an alcohol involves loss of the  $-\text{OH}$  group from  $\alpha$ -carbon and loss of  $-\text{H}$  from a  $\beta$ -carbon.



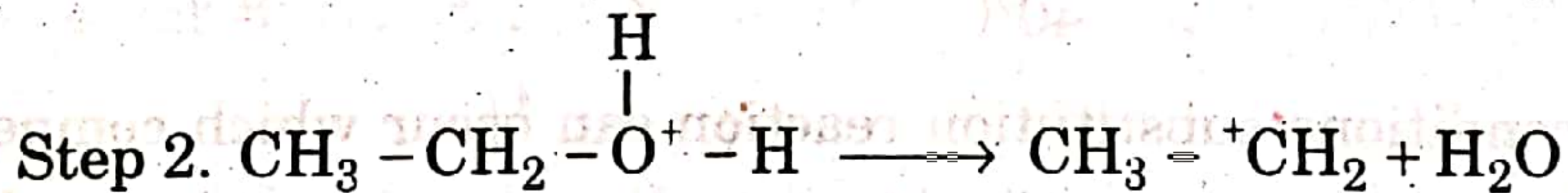
The ease of dehydration of alcohols is: tert > sec > primary.

**Mechanism.** The most accepted mechanism for the acid catalysed dehydration of alcohols involves the following three steps.

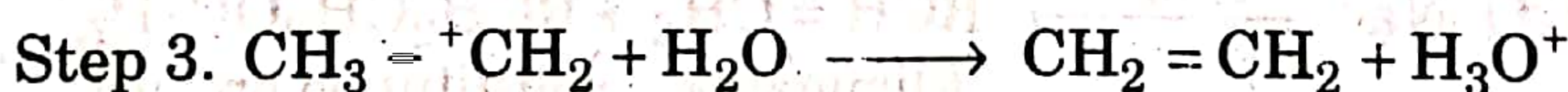
1. In the first step, a proton is rapidly transferred from the acid to one of the unshared electron pair of the oxygen atom of alcohols to form protonated alcohol.



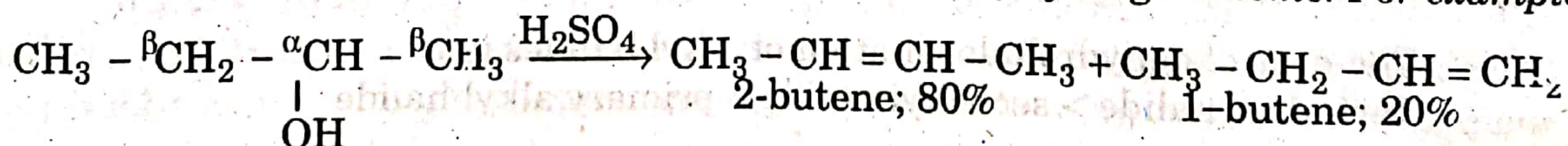
2. The positive charge on the oxygen of the protonated alcohol weakens the  $\text{C}-\text{O}$  bond. Thus the  $\text{C}-\text{O}$  bond breaks to form carbonium ion, leaving a water molecule.



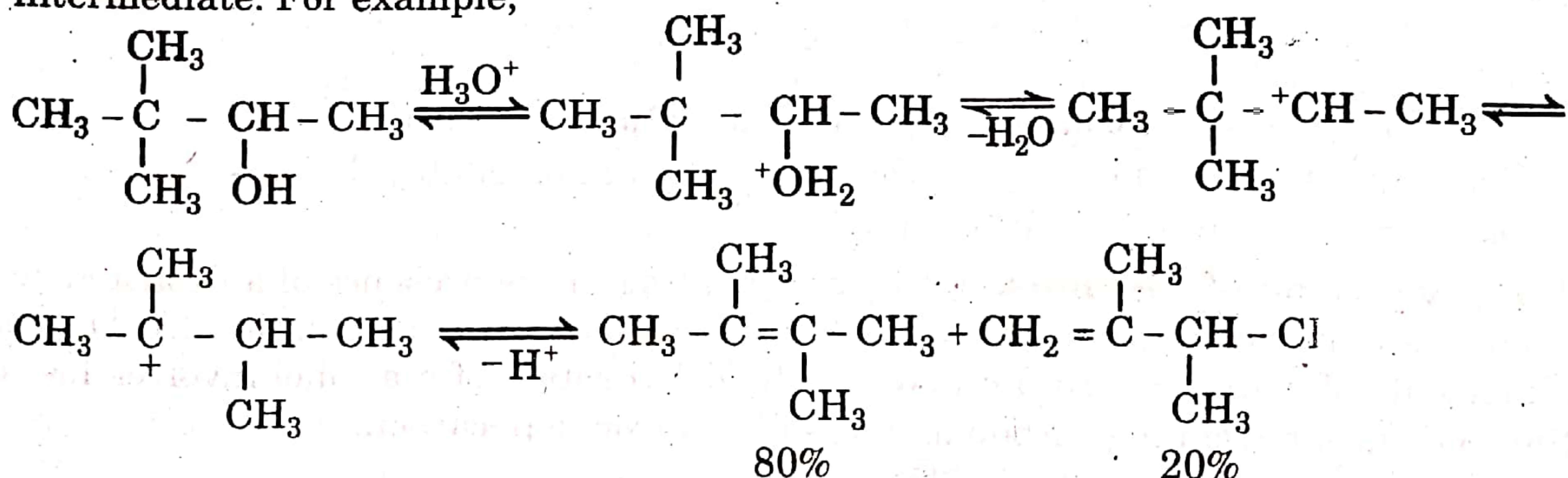
3. The carbonium ion stabilizes itself by transferring a proton to a water molecule, resulting in the formation of alkene.



**Orientation in Elimination.** Alcohols containing more than one  $\beta$ -carbon bearing hydrogen atoms, on dehydration gives mixture of alkenes in accordance with Saytzeff rule. The rule states that when alternative exist, hydrogen is preferentially eliminated from the carbon atom with fewer number of hydrogen atoms. For example,

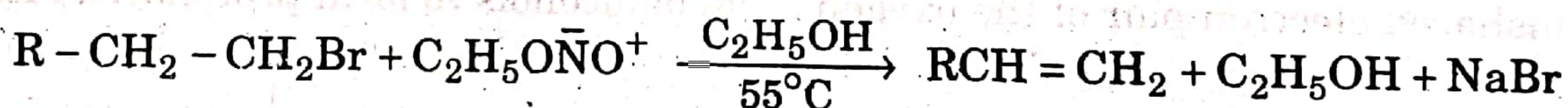
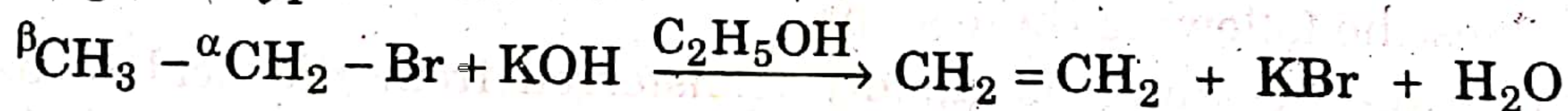


**Carbonium Ion Rearrangement.** Some primary and secondary alcohols also under go rearrangement of their carbon skeleton, involving carbonium ion as an intermediate. For example,

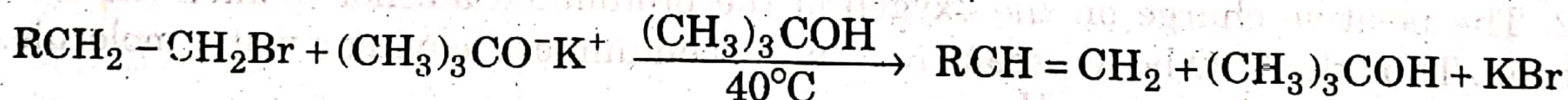


In this reaction, the secondary carbonium ion formed as an intermediate is converted into a more stable tertiary carbonium ion by the migration of methyl group, along with its bonding electron pair, from the neighbouring carbon atom. The tertiary carbonium ion then undergoes deprotonation to form a mixture of isomeric alkenes in accordance with the Saytzeff rule.

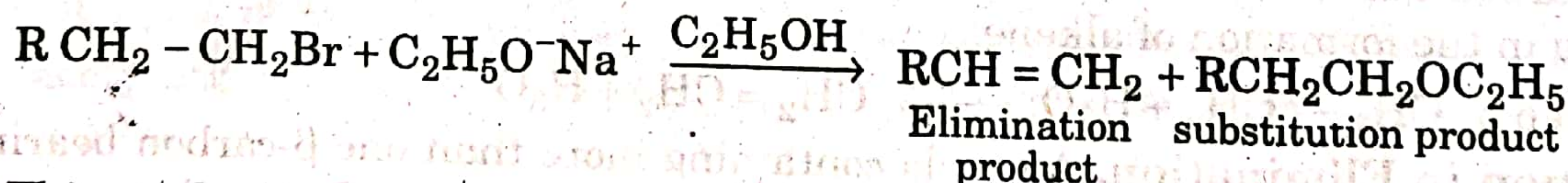
**2. Dehydrohalogenation of alkyl halides.** *Elimination of hydrogen halide molecule from alkyl halide is called dehydrohalogenation.* When an alkyl halide is heated with ethanolic solution of KOH or sodium ethoxide ( $\text{C}_2\text{H}_5\text{O}^- \text{Na}^+$ ) in ethanol, a molecule of hydrogen halide is eliminated and an alkene is formed. The reaction goes through E2 type elimination.



Potassium tert-butoxide in tert-butyl alcohol is probably the best reagent for an elimination reaction.



Under these conditions substitution reaction can occur which competes with the elimination reaction.

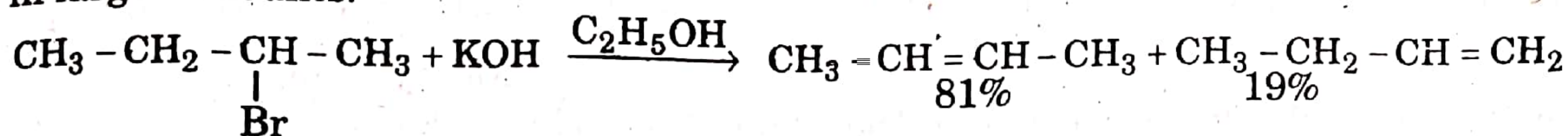


This method gives satisfactory results only with secondary and tertiary alkyl halides but not with primary alkyl halides because substitution reaction dominates and ether is the main product.

The ease of dehydrohalogenation of alkyl halides is:

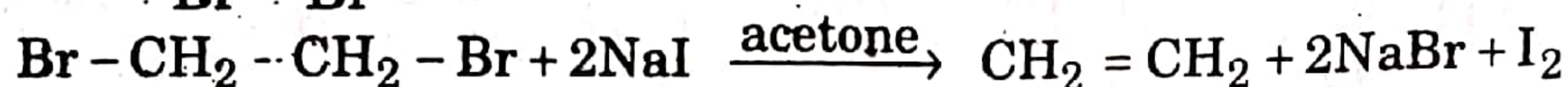
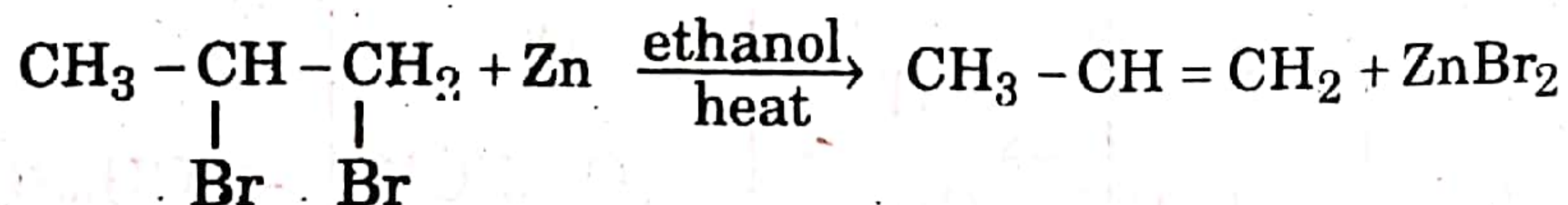
Tert alkyl halide > sec alkyl halide > primary alkyl halide.

If  $\beta$ -hydrogen is available at more than one position, a mixture of isomeric alkenes is formed, the more highly branched alkene being formed in larger amounts.

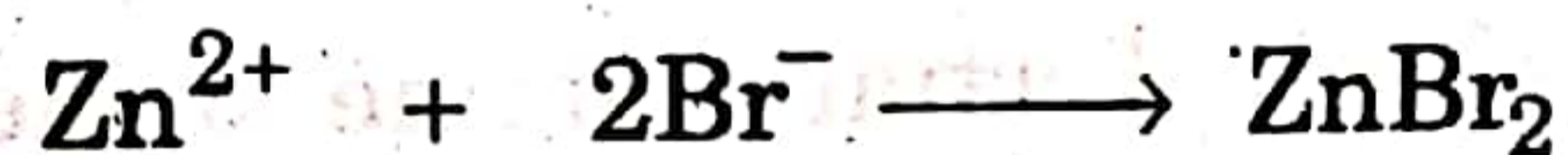
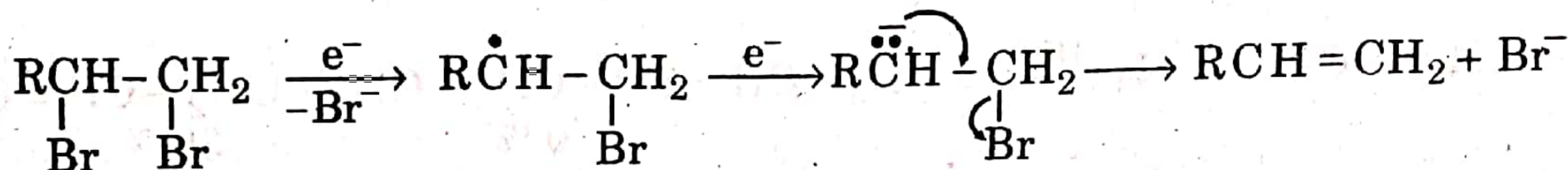


The mechanism of the elimination reaction is discussed in chapter Alkyl Halides.

**3. Dehalogenation of Vicinal dihalides.** A compound having two halogen atoms on adjacent carbon atoms is called Vicinal dihalide (or vic-dihalide). Vicinal dihalide on heating with Zn dust in ethanol or NaI in acetone gives alkenes.



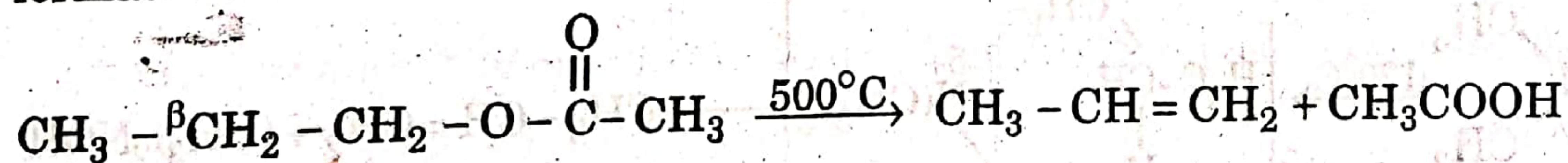
**Mechanism:** Dehalogenation takes place on the surface of the metal and a possible mechanism is as follows:



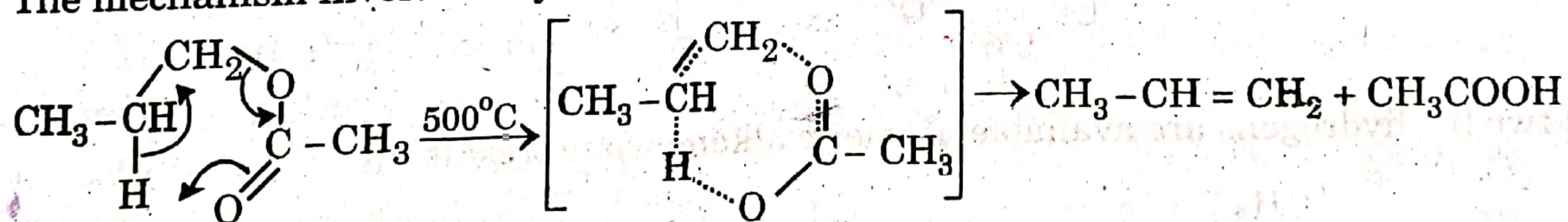
#### 4. Thermal Elimination (Or Pyrolytic elimination) Reactions

These reactions are brought about on heating a compound without the presence of other reagent. These reactions involve a cyclic transition state and needs the two eliminating groups to be cis - to each other, i.e, both the proton and the other leaving group are removed from the same side of the molecule. In these reactions no rearrangement of carbon skeleton occurs. Some important reactions involving cyclic transition states are given below:

**(i) Pyrolysis of esters.** When esters that have hydrogen on the  $\beta$  - carbon atom of the alkoxy group are heated to  $500^\circ\text{C}$ , elimination of carboxylic acid occurs with the formation of an alkene. n-Propyl acetate on heating to  $500^\circ\text{C}$  gives propene.

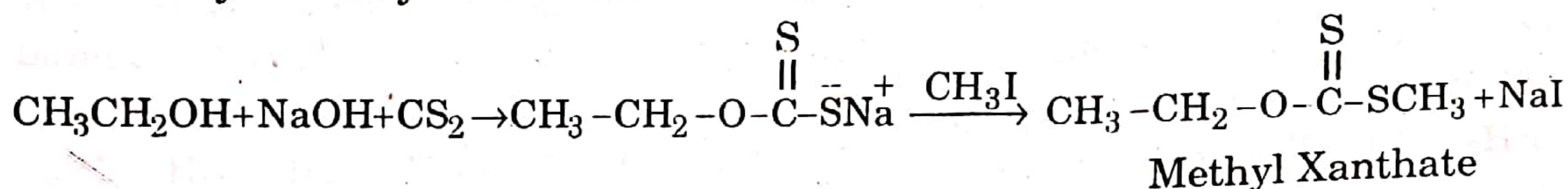


The mechanism involves a cyclic transition state is explained below:

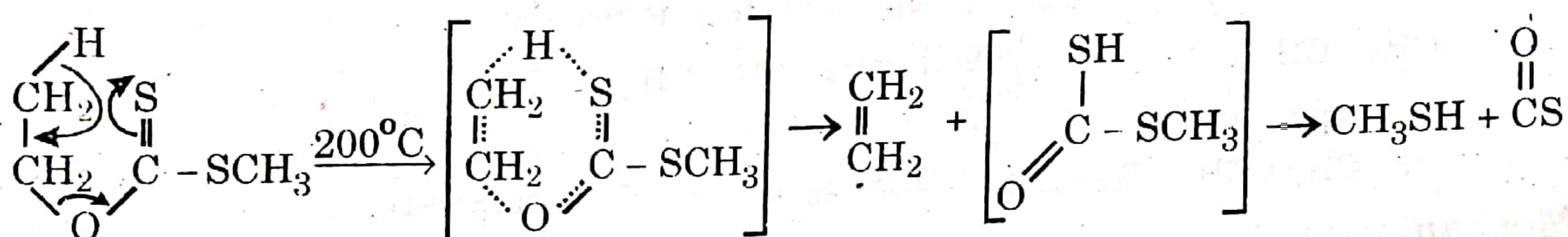
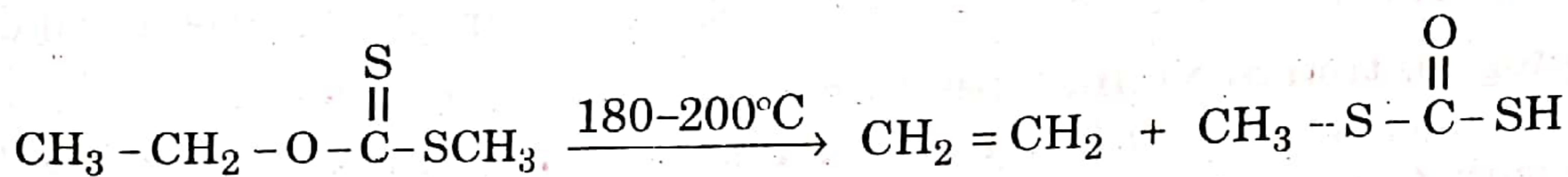


**(ii) Chugaev Reaction (Pyrolysis of Xanthate esters).** Xanthates are the dialkyl derivatives of dithiocarbamic acids and are prepared by treating an alcohol with NaOH and  $\text{CS}_2$  to give sodium xanthate ( $\text{RO} - \text{CS} - \text{SNa}$ ), which on treatment

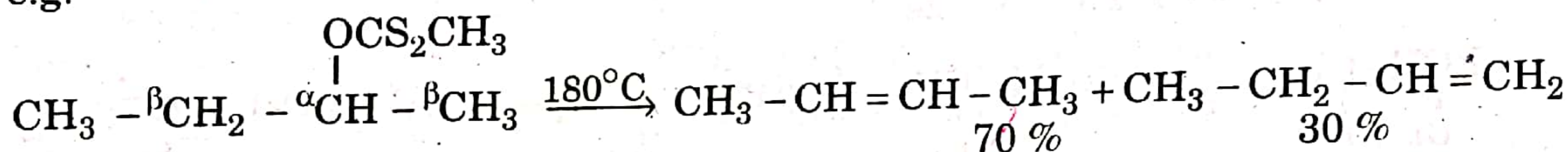
with methyl iodide yields xanthate ester.



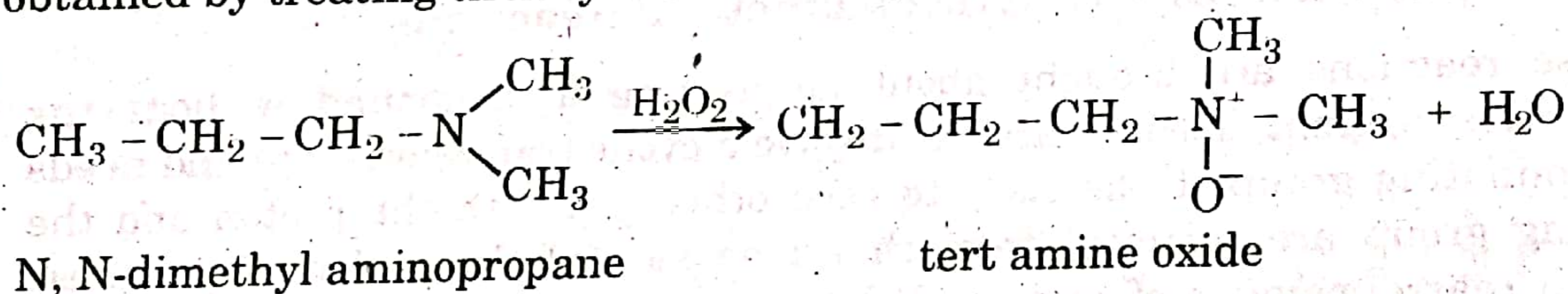
The xanthate ester is then heated to 180 – 200 C to produce alkene.



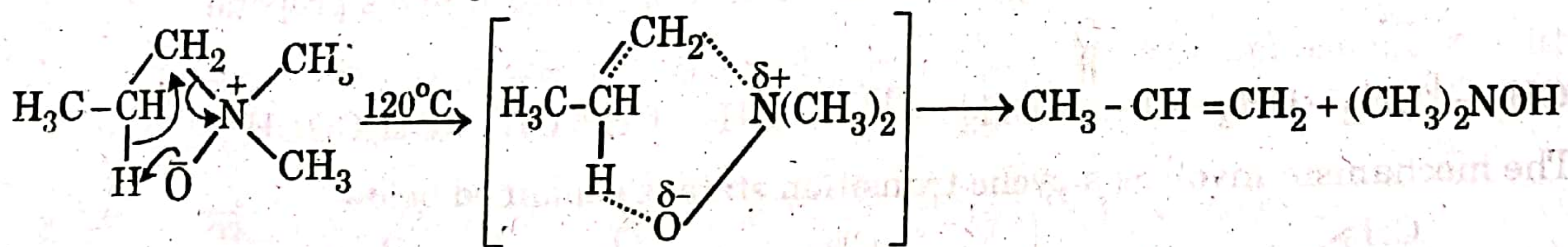
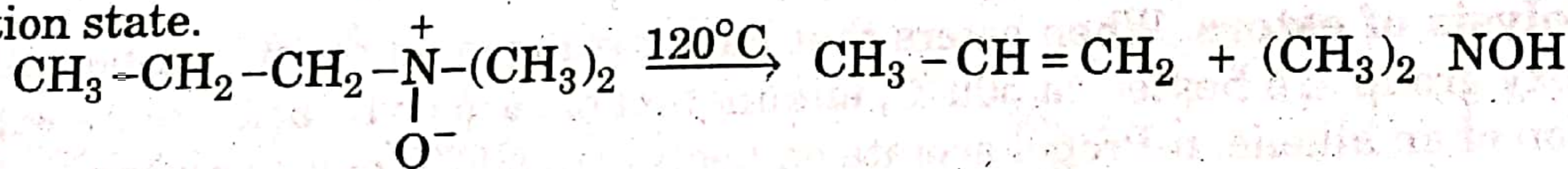
When more than one  $\beta$ -hydrogens are available, isomeric alkenes are obtained, e.g.



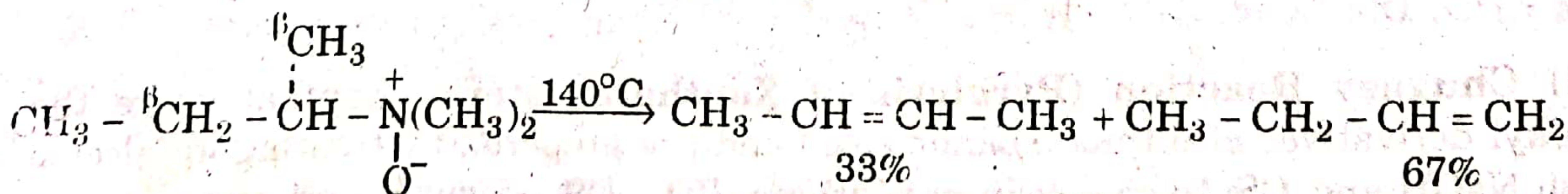
(iii) **Cope Reaction (Pyrolysis of amine oxide).** Tertiary amine oxides are obtained by treating tertiary amine with hydrogen peroxide,  $\text{H}_2\text{O}_2$ .



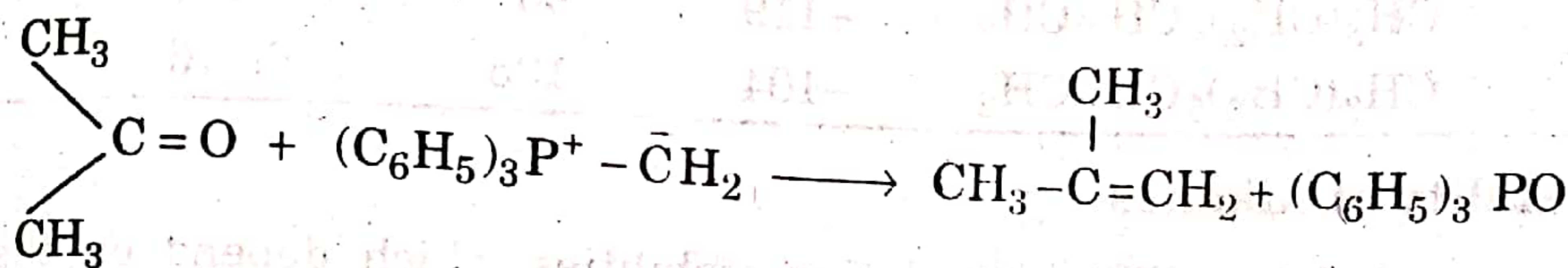
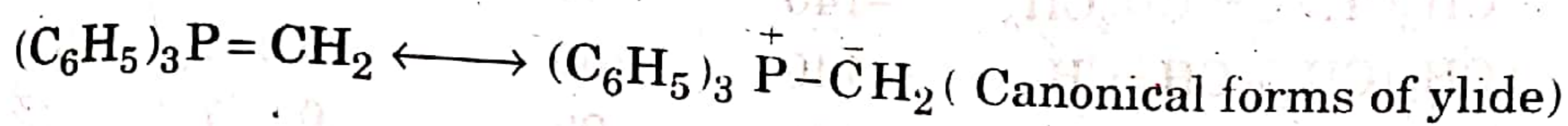
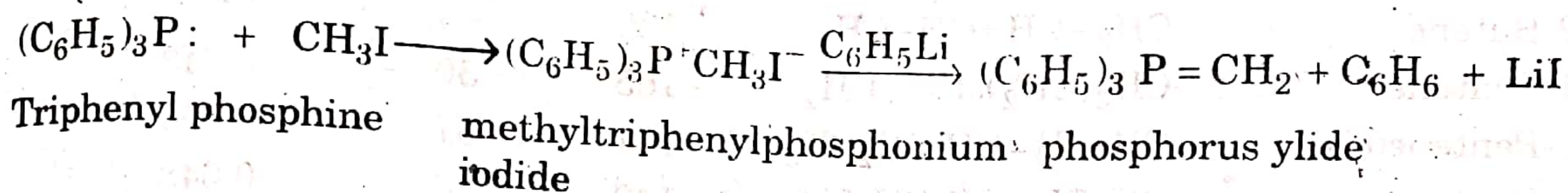
The amine oxide when heated to 120 – 150°C gives alkene via a cyclic transition state.



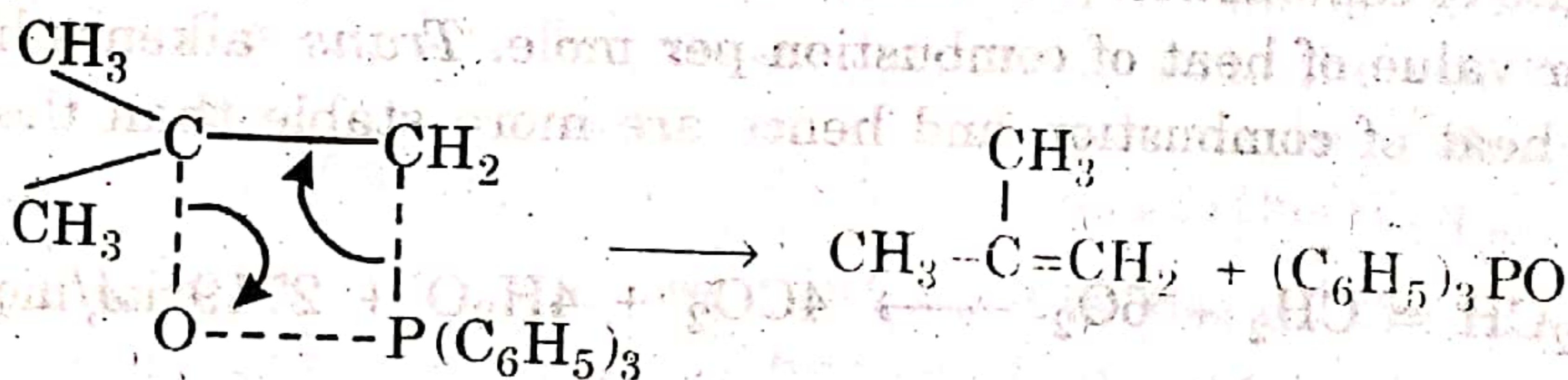
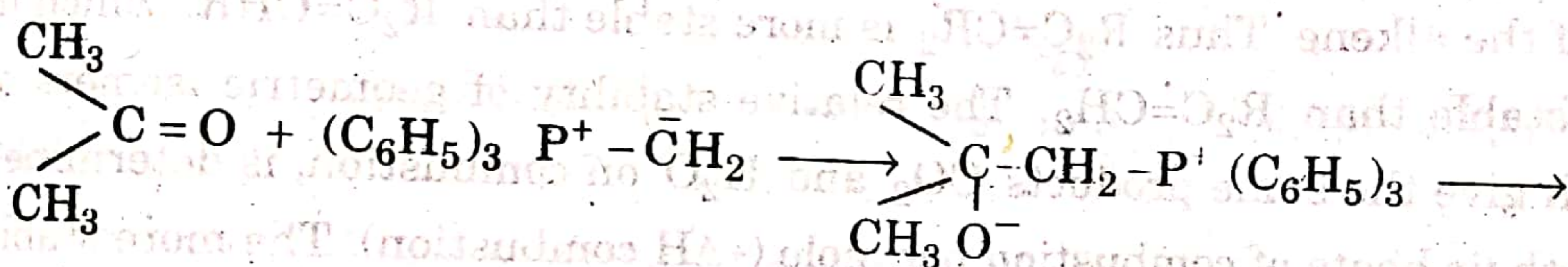
If two  $\beta$  - hydrogens are available, isomeric alkene would result.



(iv) **Wittig Reaction.** In the Wittig reaction an aldehyde or ketone is treated with a phosphorus ylide to give an alkene through a four centre transition state. Phosphorus ylides, which are hybrids of two canonical forms, are usually prepared from triphenylphosphine and alkyl halides which react together to form phosphonium salts which on treatment with a strong base as NaOH or *n*-butyllithium or phenyllithium in dry ether, gives a phosphorus ylide.



The reaction proceeds through a four centre transition state:



### 5.3 Physical properties of Alkenes

Like alkanes, the only forces that influence the physical properties of alkenes are the weak van der Waals attractive forces. Therefore, the physical properties of alkenes are essentially the same as those of the corresponding alkanes.

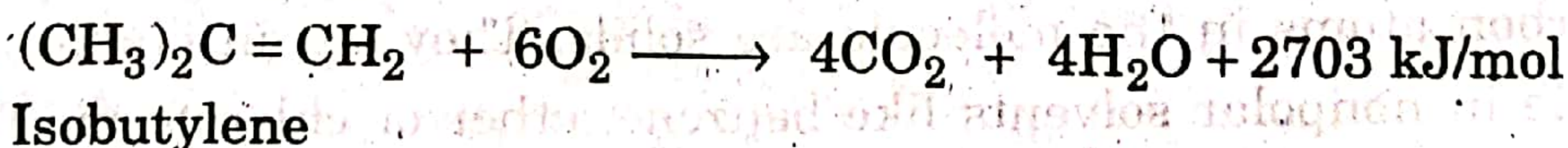
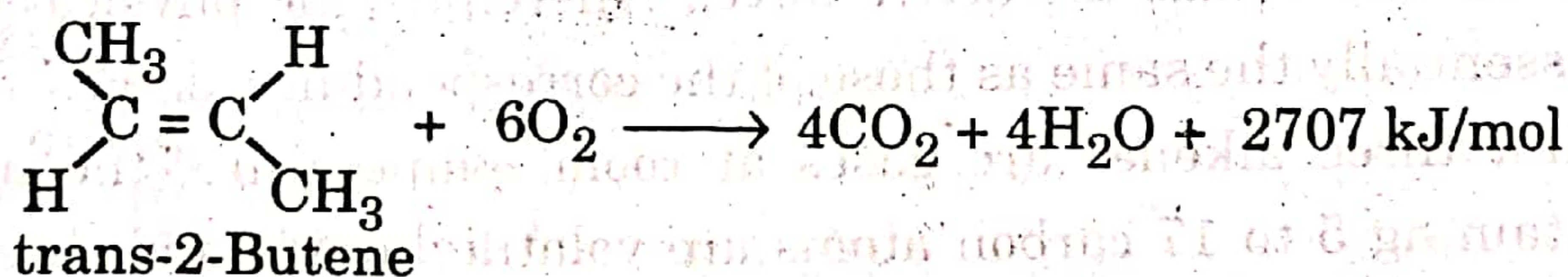
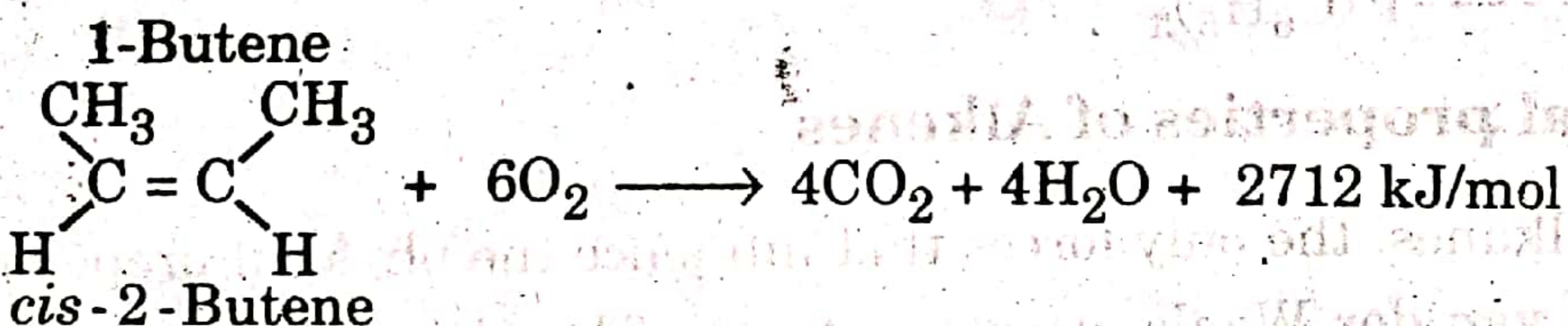
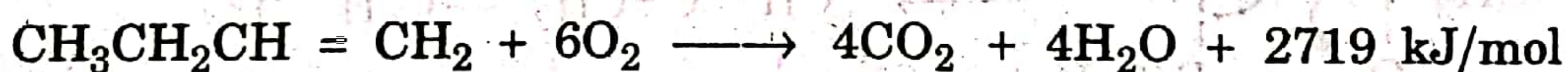
The first three alkenes are gases at room temperature, the next fourteen members containing 5 to 17 carbon atoms are volatile liquids and those with more than 18 carbon atoms in the molecule are solids. They are insoluble in water but quite soluble in nonpolar solvents like benzene, ether or chloroform. They are less dense than water. The boiling and melting points, in general, rise with increasing molecular mass. Branching, however, lowers the boiling point.

Table 5.1 Physical Constants of Alkenes

Name	Formula	M.p.(°C)	B.p.(°C)	Density (g/cm <sup>3</sup> )
Ethene	CH <sub>2</sub> =CH <sub>2</sub>	-169	-102	0.6100
Propene	CH <sub>3</sub> -CH=CH <sub>2</sub>	-185	-47	0.6104
1-Butene	CH <sub>3</sub> -CH <sub>2</sub> -CH=CH <sub>2</sub>	-185	-6.5	0.6255
2-Butene	CH <sub>3</sub> -CH=CH-CH <sub>3</sub>	-139	-3.7	--
1-Pentene	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> CH=CH <sub>2</sub>	-165	30	0.643
2-Pentene(cis)	CH <sub>3</sub> CH=CHCH <sub>2</sub> CH <sub>3</sub>	-151	37	0.656
2-Pentene(trans)	CH <sub>3</sub> CH=CHCH <sub>2</sub> CH <sub>3</sub>	-140	36	0.648
1-Hexene	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>3</sub> CH=CH <sub>2</sub>	-140	63	0.674
1-Heptene	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> CH=CH <sub>2</sub>	-119	93	0.697
1-Octene	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> CH=CH <sub>2</sub>	-104	123	0.716

#### 5.4 Relative stability of Alkenes

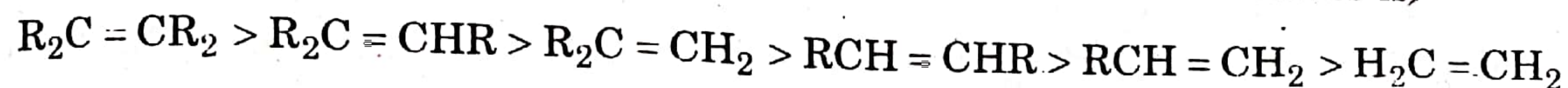
Different alkenes have different relative stabilities which depend on the position of the double bond in the molecule, and the number, nature and relative positions of the substituents on the double-bonded carbon atoms. The greater the number of alkyl groups attached to the double-bonded carbon atoms, the greater is the stability of the alkene. Thus R<sub>2</sub>C=CR<sub>2</sub> is more stable than R<sub>2</sub>C=CHR, which in turn is more stable than R<sub>2</sub>C=CH<sub>2</sub>. The relative stability of geometric isomers of alkenes, which give the same products CO<sub>2</sub> and H<sub>2</sub>O on combustion, is determined by comparing their heats of combustion per mole (-ΔH combustion). The more stable isomer has the smaller value of heat of combustion per mole. *Trans* alkenes have the smaller values of heat of combustion and hence are more stable than the *cis* isomers.



The *cis* isomer has higher energy because there is greater steric repulsion between its alkyl groups on the same side of the double bond than between an alkyl group and H in the *trans* isomer. These repulsions are greater with larger alkyl

groups, which produce larger energy differences between geometric isomers.

In 1-butene, there is virtually no steric strain. Therefore, 2-butene is more stable because of steric repulsion than 1-butene which is supported by the heat of combustion. Thus the generally order of relative stabilities of alkenes is;



### 5.5 General patterns of reactivity of Alkenes

The characteristic feature of the alkene structure is the carbon - carbon double bond, which consists of a strong  $\sigma$  bond and a weak  $\pi$  bond. The  $\sigma$  bond is formed by the overlap of  $sp^2$  hybrid orbitals end-to-end and is symmetrical about an axis linking the two carbon atoms. The  $\pi$  bond is formed by the sidewise overlap of two  $p$  orbitals and has a cloud of electrons above and below the plane of the  $\sigma$  frame work. Thus  $\pi$  electrons are loosely held and are, therefore, available to a reagent that is seeking electrons (i.e, electrophilic reagent). Thus double bond acts as a nucleophile. Therefore, electrophiles or acids would react with an alkene. The typical reaction of an alkene is thus electrophilic addition. Free radicals also seek an electron, so alkenes also undergo free-radical addition.

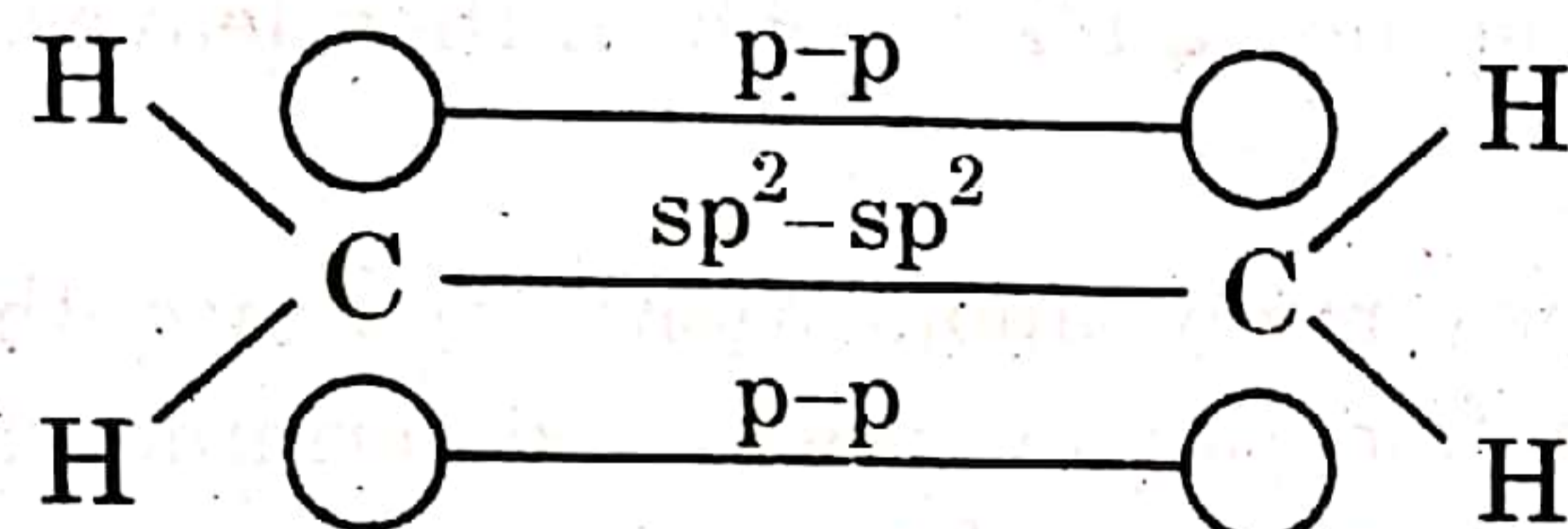
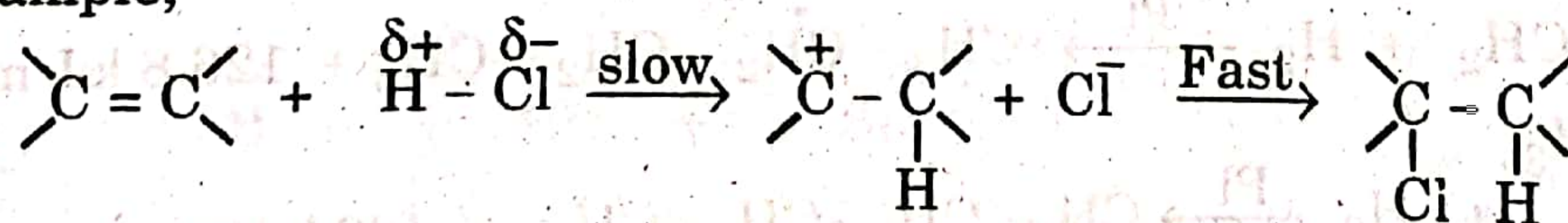


Fig.5.1 Carbon - carbon double bond and a  $\pi$  bond showing cloud of  $\pi$  electrons.

Most alkenes contain not only the C - C double bond but also alkyl groups, which have essentially the alkane structure. Thus the reactions of alkenes can be divided into two main categories. (i) Addition reactions due to the carbon-carbon double bond, and (ii) Substitution reactions due to the alkyl groups.

**Mechanism of Addition to C-C double bond.** The addition of electrophilic reagent to a double bond generally takes place in two steps. In the first step one of the double-bonded carbon forms a bond with an electrophilic part of the reagent to form an intermediate carbocation, which then rapidly combines with the other part of reagent which now acts as a nucleophile to give the addition product in the second step.

For example,



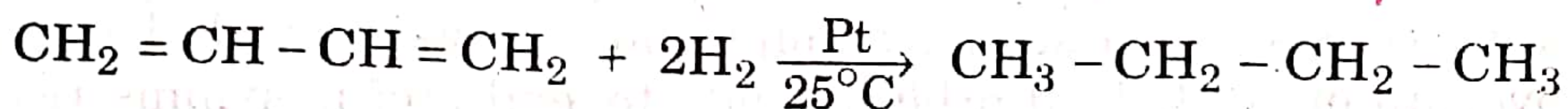
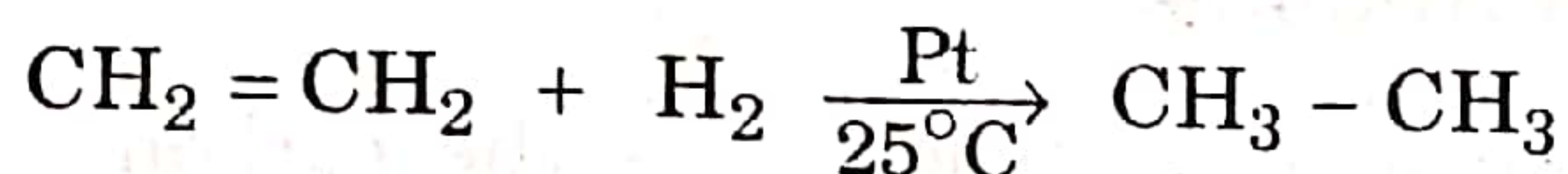
### 5.6 Chemical properties (Reactions) of Alkenes

**1. Hydrogenation (Addition of Hydrogen).** The reaction of an unsaturated compound with hydrogen in the presence of a finely divided metal catalyst to form a saturated compound is called **catalytic hydrogenation**.



The most commonly used catalysts are platinum, palladium and nickel. Pt is used as PtO, Pd is employed as a fine powder supported on charcoal, nickel is used as **Raney Nickel** which is obtained by dissolving Ni-Al alloy in NaOH which dissolves Al leaving Ni as a fine suspension, called **Raney Nickel**.

Alkenes react with hydrogen under pressure and in the presence of Ni, Pt or Pd catalyst to form alkanes.

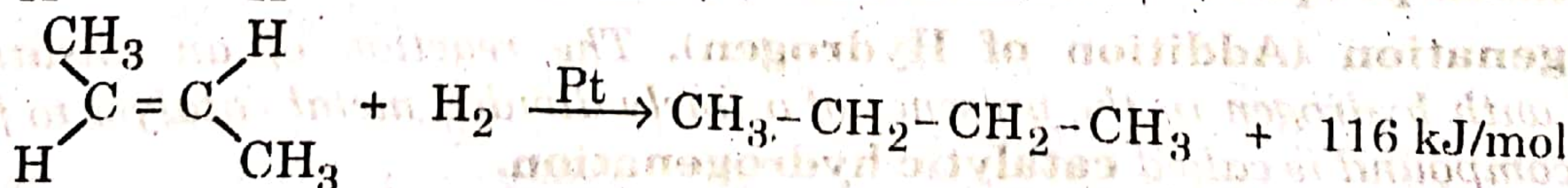
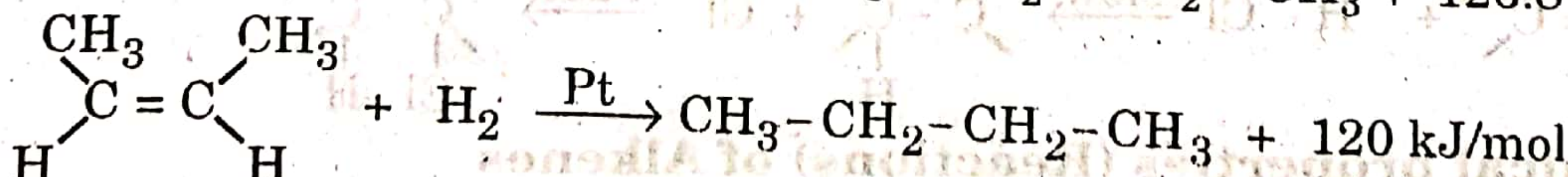
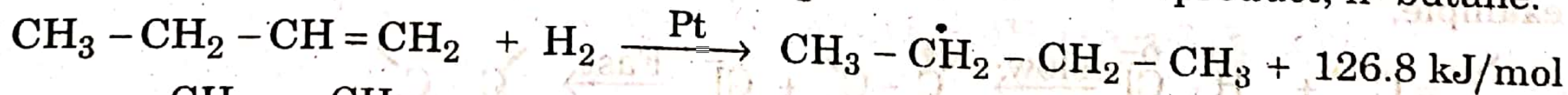


Hydrogenation is carried out in a solvent; alcohol, acetic acid and ethyl acetate are generally employed. The addition of hydrogen to an alkene is a cis addition. The hydrogenation of alkenes occurs at the surface of the metal catalyst. The metal adsorbs hydrogen by providing electrons to form the metal hydrogen bonds. At the same time, alkene is also adsorbed on the surface of the metal that breaks the  $\pi$  bond of the alkene and helps in a step-wise transfer of hydrogen atoms to the alkene to produce the corresponding alkane which then leaves the surface of the metal.

Catalytic hydrogenation has many applications (i) Since the reaction is quantitative, therefore, hydrogenation can be used to determine the number of double bonds in a polyalkene by measurement of volume of hydrogen used. Vitamin A requires five molecules of hydrogen for complete reduction and hence has five double bonds in its molecule.

(ii) An important industrial application of catalytic hydrogenation is the preparation of vegetable ghee from vegetable oil.

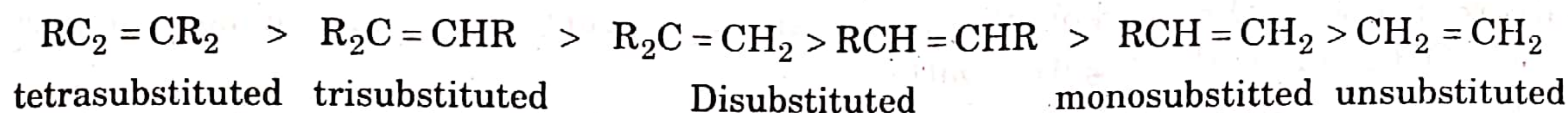
(iii) **Heats of Hydrogenation.** Hydrogenation of alkenes is an exothermic reaction. *The amount of heat evolved when one mole of an alkene is hydrogenated is called heat of hydrogenation.* The heat of hydrogenation of most alkenes is about 126 kJ for each double bond in a molecule. However, the heats of hydrogenation of individual alkenes may slightly differ from this value. These differences in heats of hydrogenation allow us to measure the relative stabilities of alkene isomers when hydrogenation convert them to the same product. Consider, for example, the hydrogenation of isomeric alkenes, 1-butene, cis-2-butene and trans-2-butene, each of which adds one molecule of hydrogen to produce the same product, n-butane.



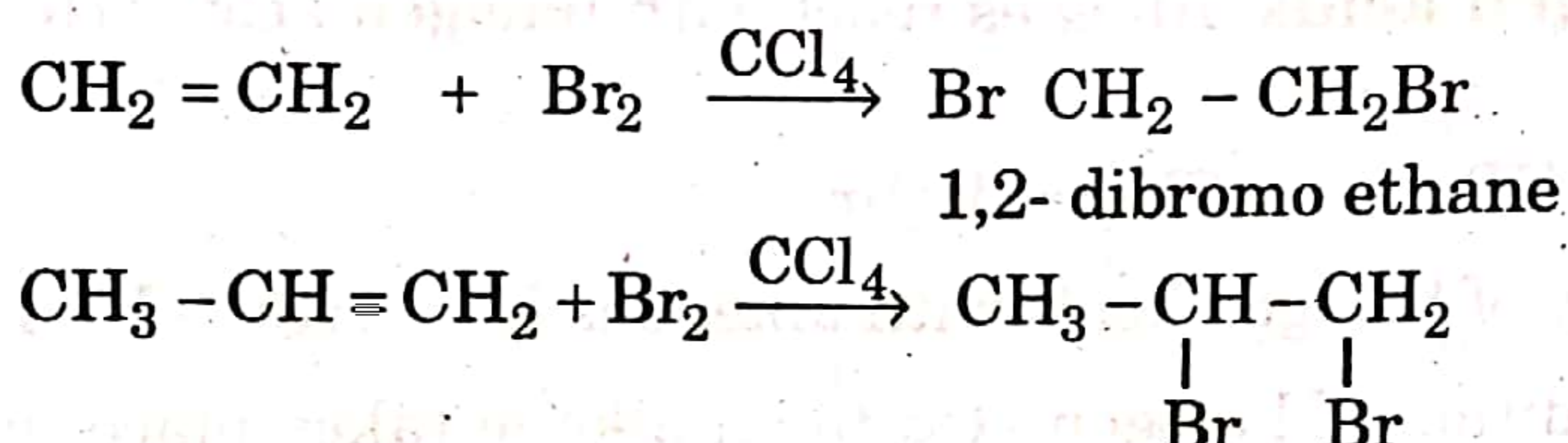
This can be seen that of the three isomeric alkenes, that 1-butene evolves the largest amount of heat of hydrogenation and trans-2-butene evolves the least. Thus trans-2-butene is the most stable and 1-butene is the least stable isomer and cis-2-butenes lies in between.

Comparing the heats of hydrogenation of 1-butene and 2-butene, we conclude that greater the number of alkyl groups attached to the doubly bonded carbon atoms, the greater is the stability of the alkene.

The **order of stabilities** of alkenes in general terms is as follows:

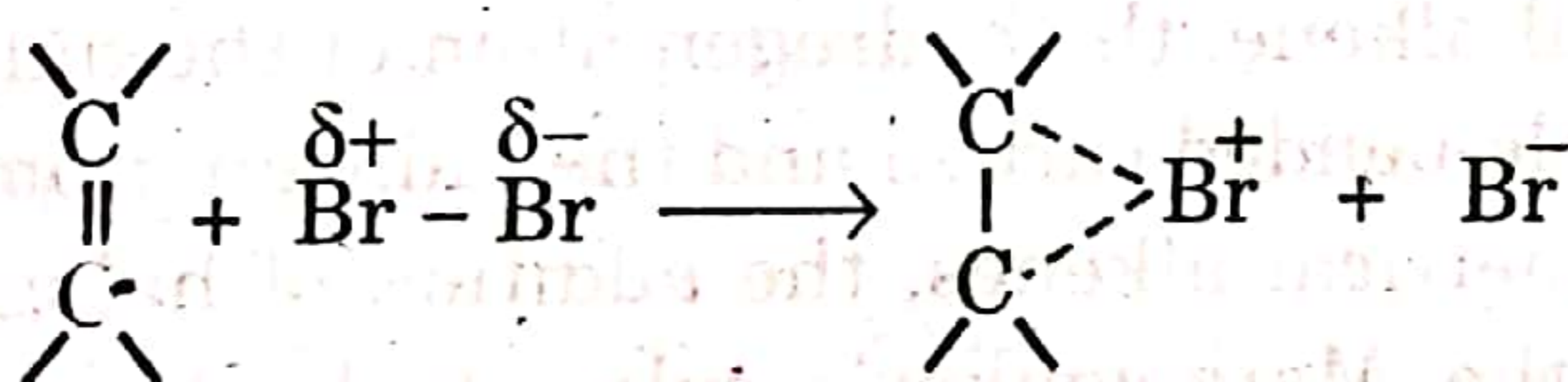


**2. Addition of Halogens.** Alkenes react with chlorine or bromine in an inert solvent like  $\text{CCl}_4$  at room temperature to form vicinal dichloride or vic-dibromide. Fluorine reacts too violently to be controllable and iodine does not give stable vic-diiodides.



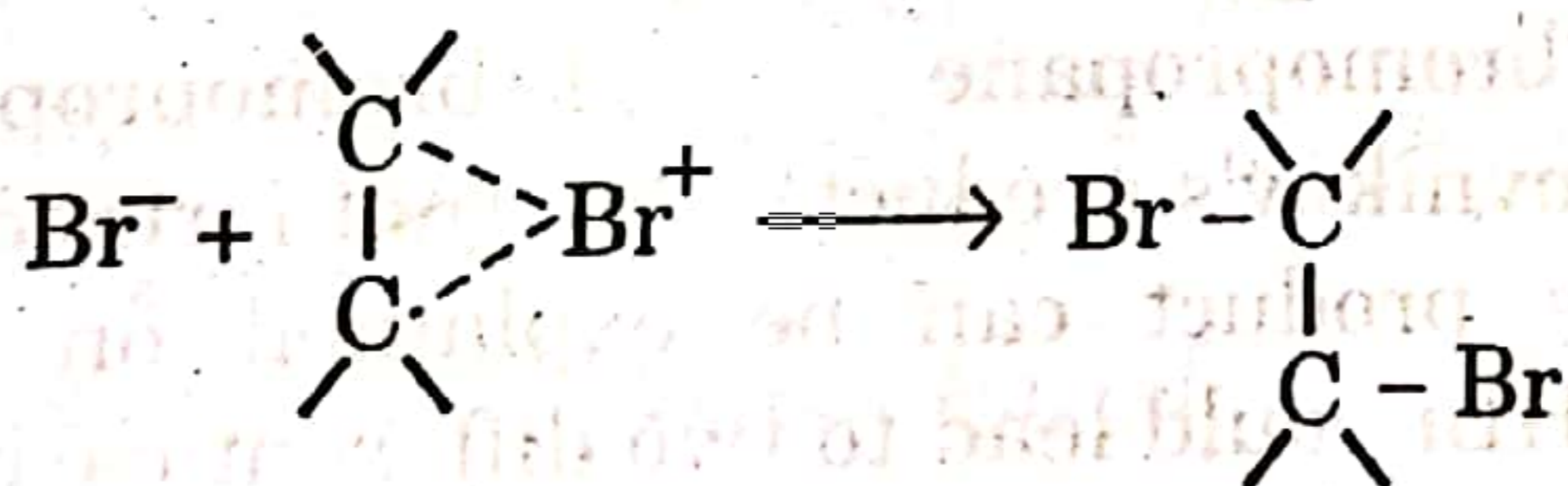
The addition of bromine to alkene is used as a simple qualitative test for unsaturation. The red colour of bromine solution is rapidly discharged when it adds to alkene to form colourless dibromo compound.

**Mechanism:** The  $\pi$  electrons of the double bond attack on one of the bromine atoms to form cyclic bromonium ion and bromide ion.

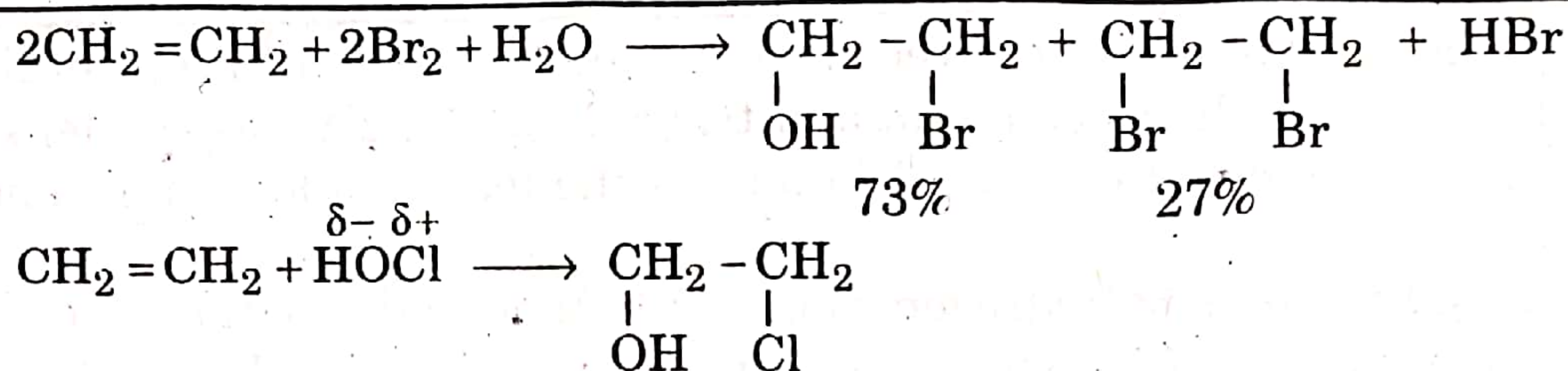


In fact, as the  $\pi$  electrons of the alkene approach the bromine molecule, the Br-Br bond is induced to be polarized and is thus weakened which is finally broken heterolytically.

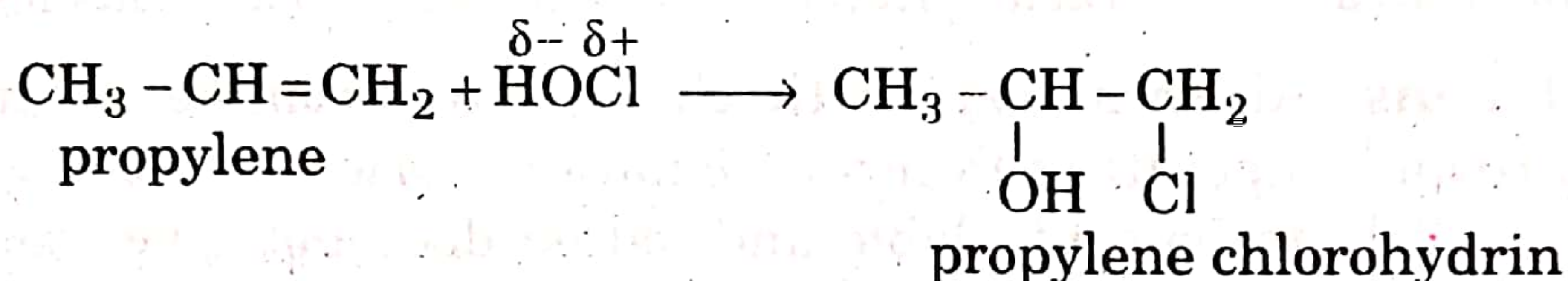
The bromide ion thus produced then attacks one of the carbon atoms of the bromonium ion from the backside to form the trans-addition product.



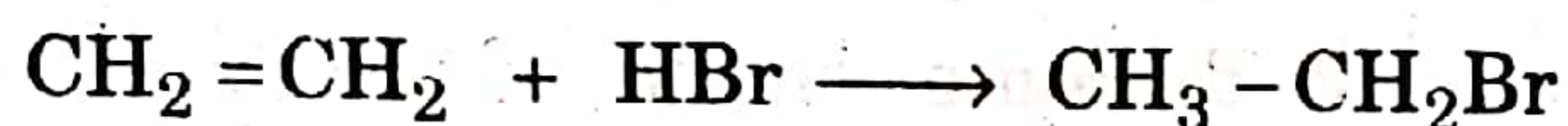
**3. Addition of hypohalous acid.** When halogenation of an alkene is conducted in aqueous solution, halohydrin is formed in addition to vic-dihalide, the major product is halohydrin which shows the addition of hypohalous acid (HOX) across the double bond.



In case of unsymmetrical alkenes the positive halogen of the hypohalous acid, is attached to the carbon atom having the greater number of hydrogens in accordance with the Markovnikov's rule. In these acids, halogen is the positive part and -OH group is the negative part.

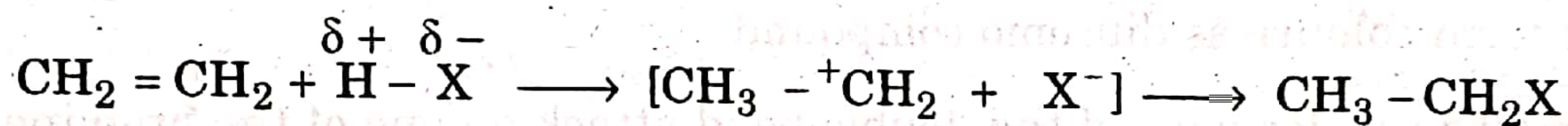


**4. Addition of halogen acids.** Alkenes react with halogen acids (HCl, HBr, or HI) to form alkyl halides.



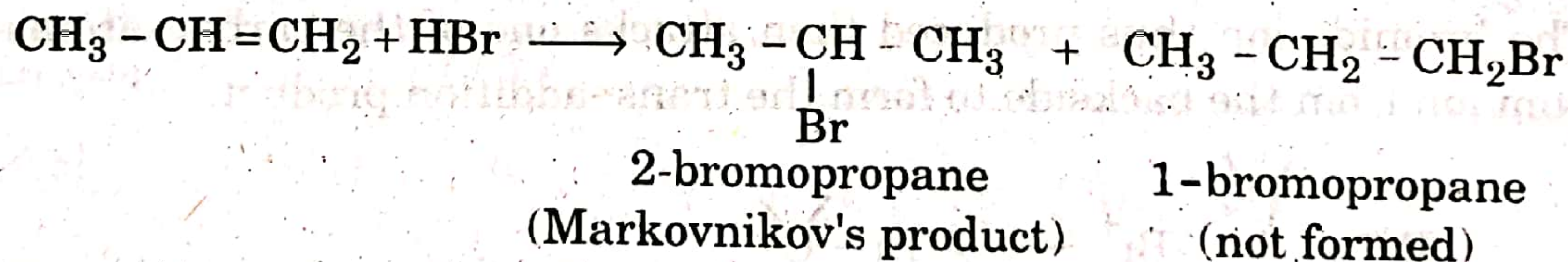
The order of reactivity of halogen acids with alkene is  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

**Mechanism.** The addition of halogen acid to an alkene takes place in two steps. In the first step the alkene accepts a proton of the halogen acid to form carbocation as intermediate that combines with halide ion to form an alkyl halide in the second step.

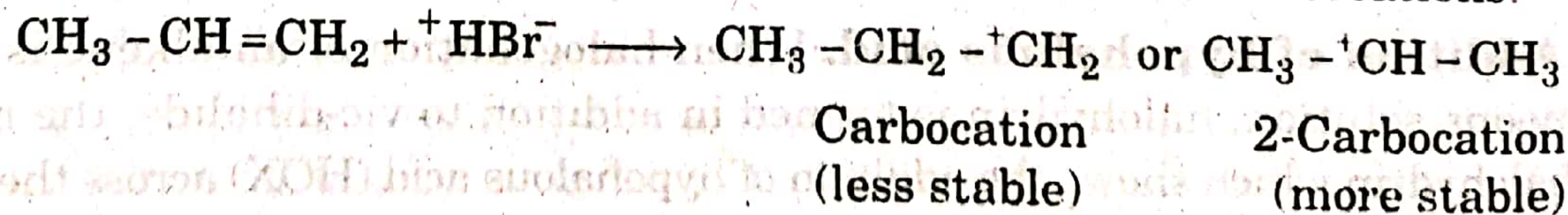


#### Orientation of addition: Markovnikov's Rule

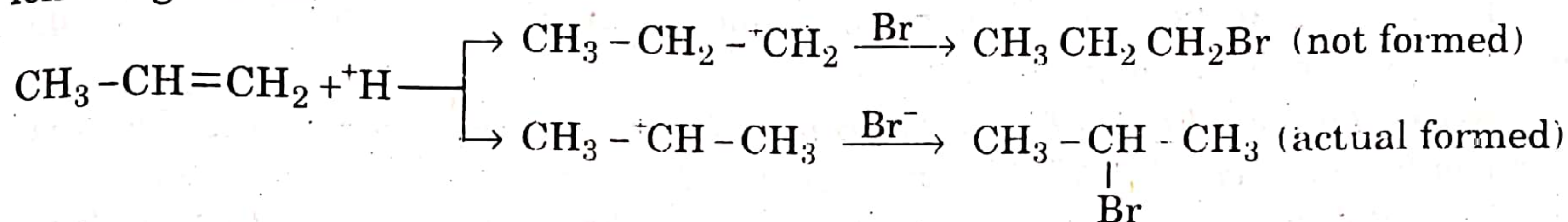
In the case of symmetrical alkene, the hydrogen atom of the halogen acid can attach itself to either of the double-bonded carbon and the halogen atom to the other. However, in the case of unsymmetrical alkenes, the addition of halogen acid to an unsymmetrical alkene follows the Markovnikov's rule which states that "in the addition of H - X to an unsymmetrical alkene, the hydrogen adds to the carbon of the double bond with greater number of hydrogens". Thus the addition of HBr to propene gives 2-bromopropane and not 1-bromopropane.



Formation of Markovnikov's product can be explained on the basis of carbocation formed. The addition of HBr could lead to two different carbocations.



These two carbocations are not of equal stability, however. The secondary carbocation is more stable than the primary carbonium ion. The greater stability of the secondary carbocation accounts for the correct prediction of the overall addition of Markovnikov's rule. Thus in the addition of HBr to propene, the reaction takes the following course.



The stability of carbocations decreases in the following order.



### Modern Statement of Markovnikov's Rule

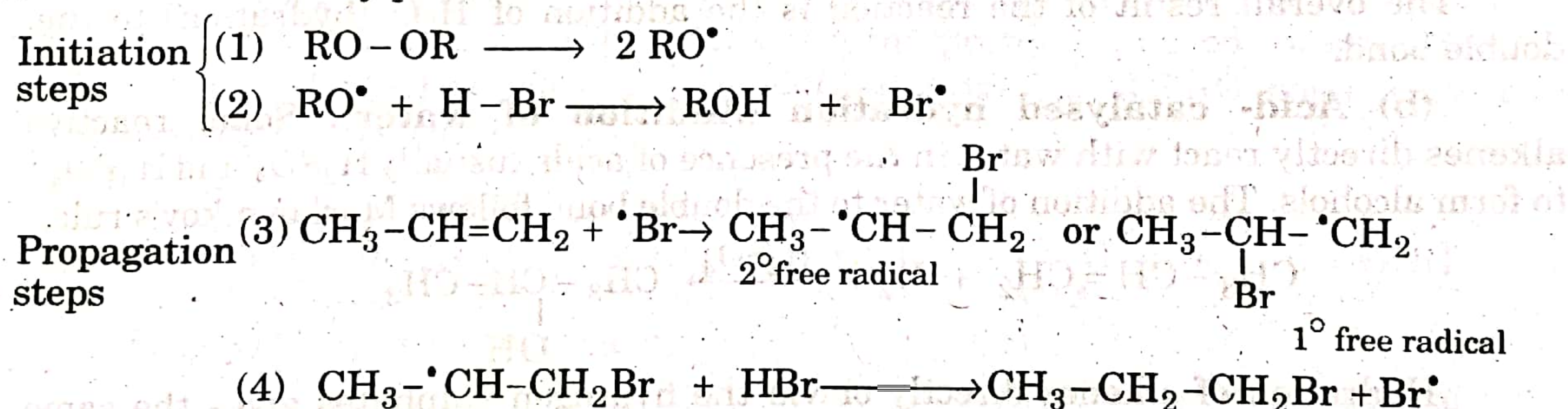
Since carbocation are formed in an ionic or polar reactions, therefore, the Markovnikov's rule can be stated as. "*In the ionic addition of an unsymmetrical reagent to a double bond, the positive portion of the adding reagent attaches itself to a carbon of the double bond so as to yield the more stable ion*". Markovnikov's rule is obeyed only under polar conditions.

### Anti-Markovnikov Addition. Free - Radical Addition to Alkenes

It has been observed that the addition of HBr (not HCl or HI) to an unsymmetrical alkenes in the presence of peroxides involves free radical mechanism and give the product contrary to Markovnikov's rule. Such additions are sometimes referred to as anti-Markovnikov's addition. For example, the addition of HBr to propene in presence of peroxides gives 1-bromopropane rather than 2-bromopropane.



The mechanism for anti-Markovnikov addition of HBr is a free radical chain reaction initiated by peroxides.



Step 1 is the simple homolytic cleavage of the peroxide molecule to produce two peroxy free radicals.

Step 2 shows the abstraction of a hydrogen atom for HBr by the peroxy radical generating bromine radical.

Step 3 determines the final orientation of bromine in the product. Secondary (2°) free radical is more stable than the primary (1°) free radical; therefore the product corresponds to the stable 2° free radical.

Step 4 is simply the abstraction of a hydrogen atom from HBr by the more stable radical produced in step 3. The Br<sup>•</sup> free radical is regenerated which continues the chain reaction.

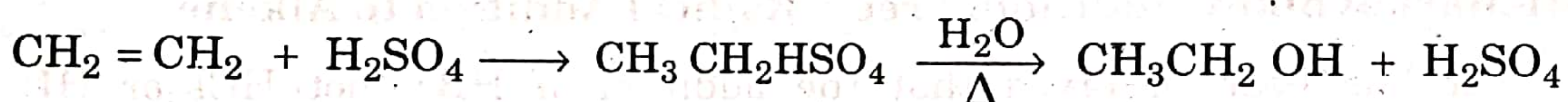
The order of stability of free radicals is: tert > sec > primary.

In addition to peroxides, such free radicals are also initiated by light, high temperature or even oxygen.

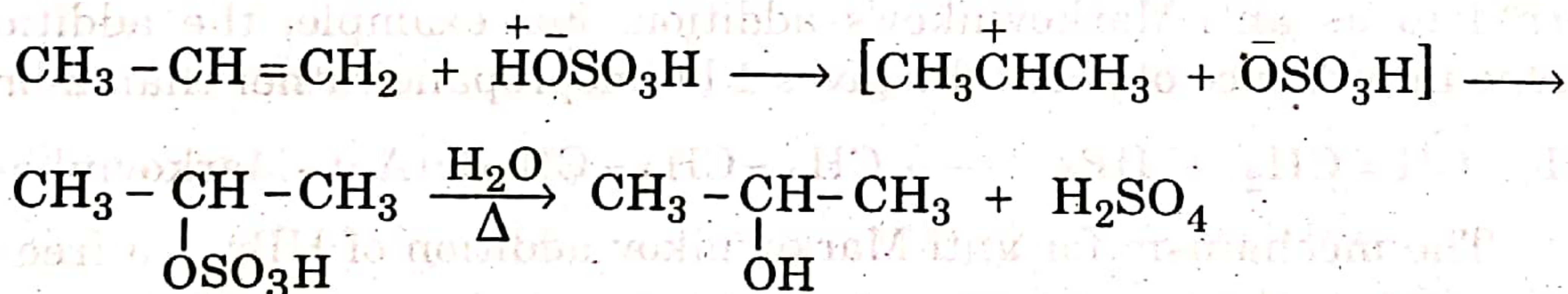
**Note.** That addition of HBr to propene in the presence of peroxide and non-polar conditions gives 1-bromopropane an anti-Markovnikov's product, whereas in the presence of polar conditions the reaction gives 2-bromopropane, a Markovnikov's product.

**5. Hydration.** The process of addition of water to alkenes across the double bond to form alcohols is called **hydration**. The hydration of alkenes can be brought about as follows:

(a) **Addition of sulphuric acid.** Alkenes react with cold concentrated sulphuric acid to form alkyl hydrogen sulphates. Markovnikov's rule is followed in case of unsymmetrical alkenes. Alkyl hydrogen sulphate solution on dilution with water followed by heating gives an alcohol.

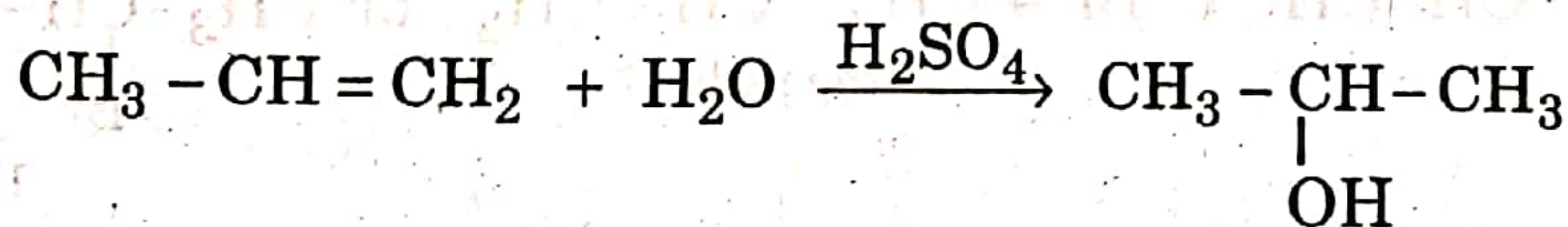


The addition of sulphuric acid to the double bond involves the same mechanism as does the addition of HX.

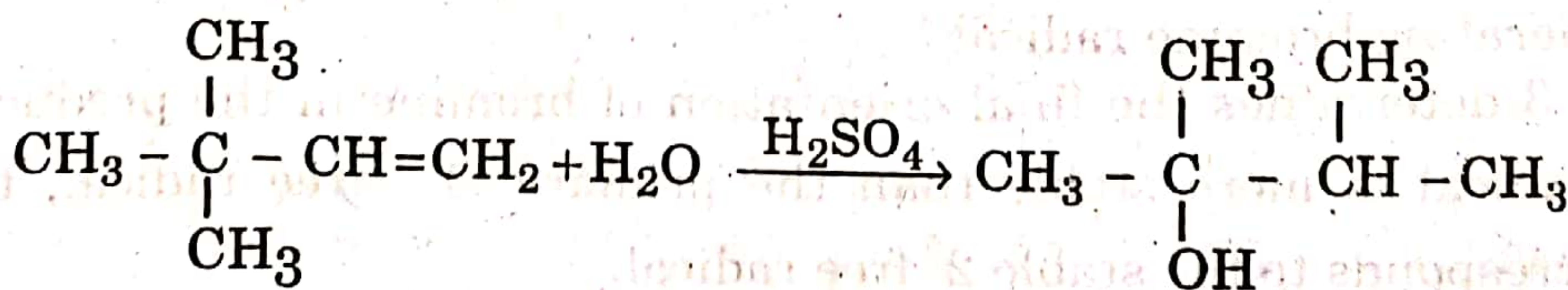


The overall result of the reaction is the addition of H<sub>2</sub>O (hydration) to the double bond.

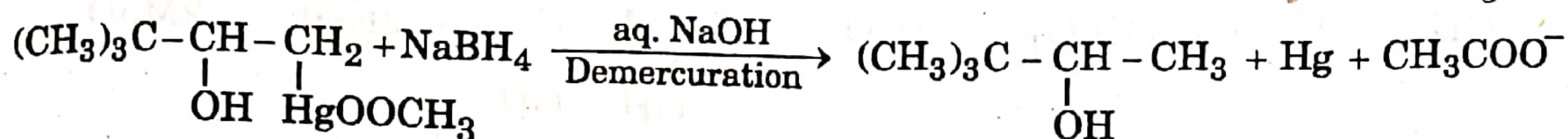
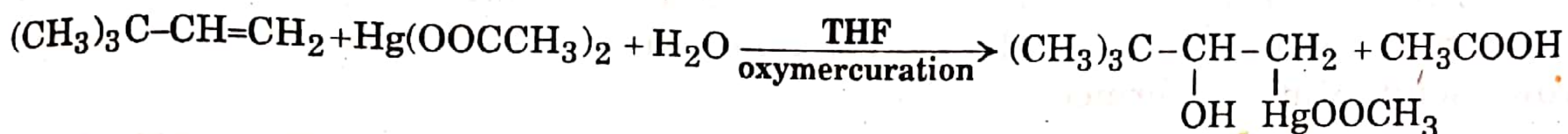
(b) **Acid-catalysed hydration (Addition of water).** Some reactive alkenes directly react with water in the presence of acids (usually H<sub>2</sub>SO<sub>4</sub> and H<sub>3</sub>PO<sub>4</sub>) to form alcohols. The addition of water to the double bond follows Markovnikov's rule.



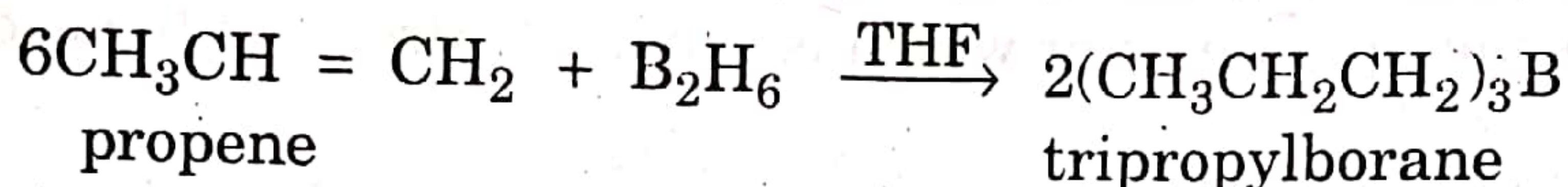
Hydration of alkenes directly or via the hydrogen sulphates gives the same **Markovnikov's** product because both proceed through the same intermediate carbocation and if these are capable of undergoing rearrangement, unexpected alcohols may be obtained from alkenes.



Rearrangement may be avoided if the alkene is treated with mercuric acetate in tetrahydrofuran (THF), followed by reduction in aqueous NaOH with sodium borohydride. This method is called **oxymercuration-demercuration**.

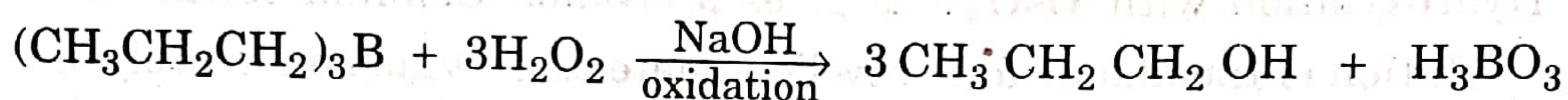


(c) **Hydroboration.** Hydration may also be achieved by hydroboration. Diborane ( $\text{B}_2\text{H}_6$ ) reacts with alkenes to form trialkylboranes. Diborane is a dimer of borane,  $\text{BH}_3$ . Diborane is commercially available in THF solution in the form of THF:  $\text{BH}_3$ .



With unsymmetrical alkenes, the addition of borane,  $\text{BH}_3$ , to a double bond, occurs in a manner such that the boron is attached to the less substituted carbon and hydrogen to the more substituted carbon of the double bond.

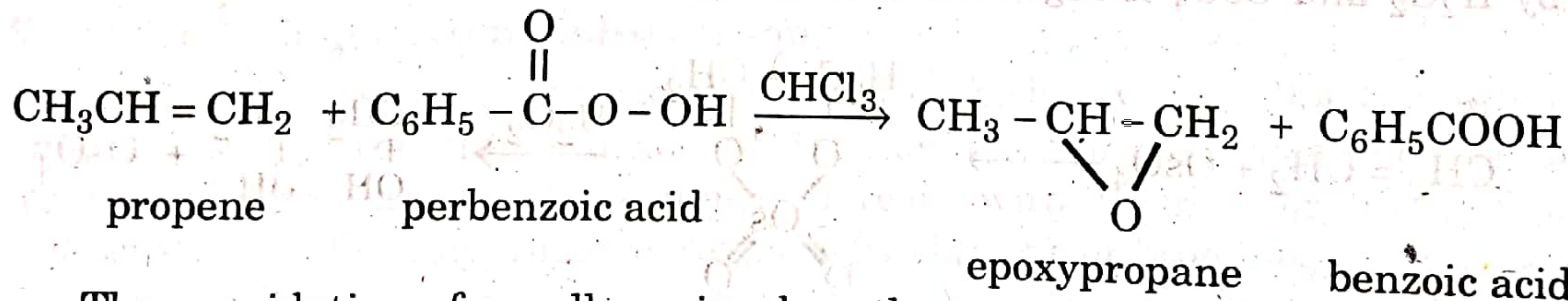
Trialkylboranes on oxidation with alkaline hydrogen peroxide yield corresponding alcohol.



The net result of the hydration-oxidation is the anti-Markovnikov's addition of water to a double bond.

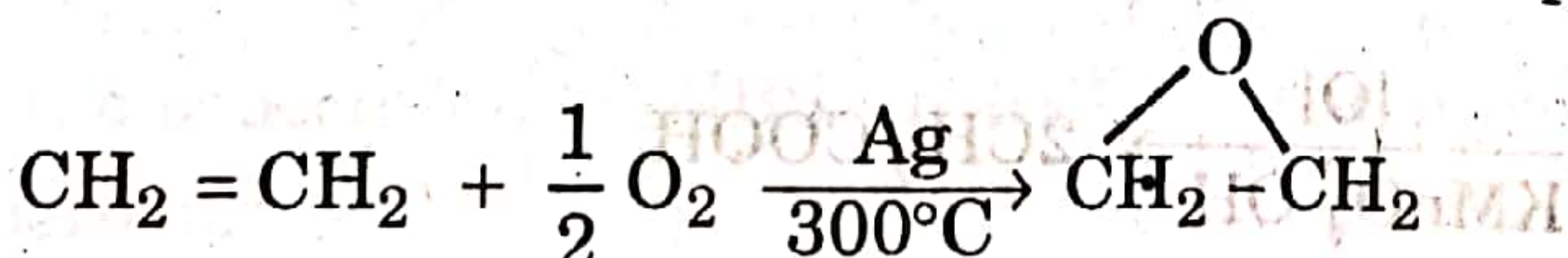
**6. Oxidation of alkenes.** Oxidizing agents are electron deficient species whereas the alkene double bond is rich in electrons. Hence alkenes react with various oxidizing agents to give different oxidation products depending on the nature of the oxidizing agent, the reaction conditions and extent of oxidation.

(i) **Epoxidation.** Peroxy acids (or simply peracids) like per acetic acid or per benzoic acid react with alkenes to form **epoxides** and the process is called **epoxidation**. Epoxides are cyclic ethers with three-membered rings. In IUPAC nomenclature epoxides are called **Oxiranes**.



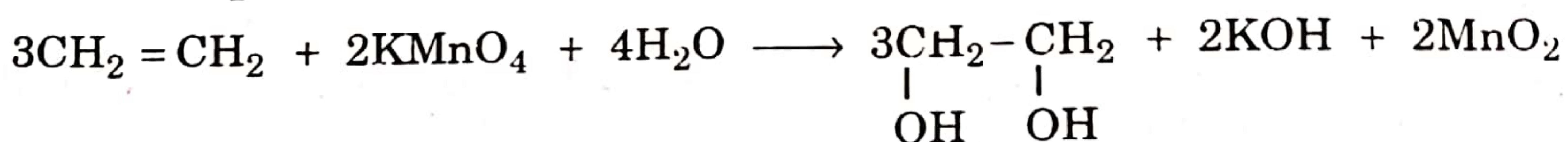
The epoxidation of an alkene involves the transfer of an oxygen atom from the peracid to the alkene. Epoxides are unstable compounds and are used as intermediates for the preparation of higher alcohols.

**Catalytic oxidation (epoxidation).** Alkenes react with oxygen in the presence of silver catalyst at  $250 - 400^\circ\text{C}$  to form epoxides.



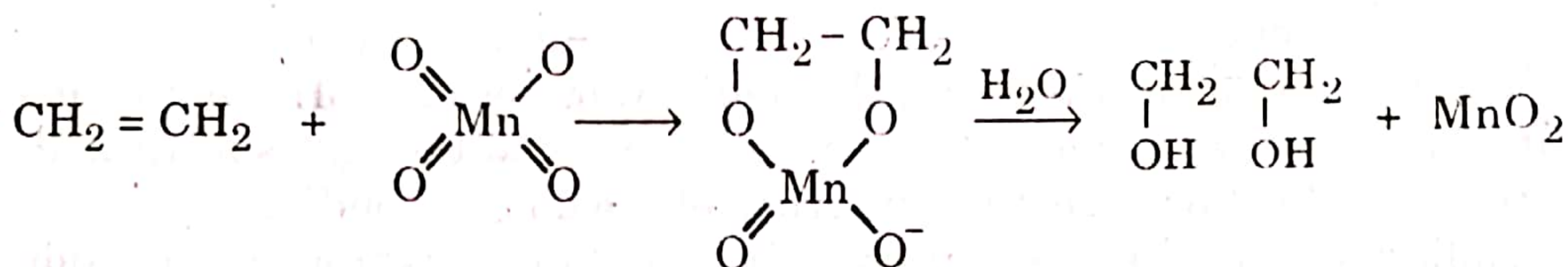
(ii) **Hydroxylation.** The hypothetical addition of hydrogen peroxide to the alkene double bond is called hydroxylation.

Alkenes react with cold dilute potassium permanganate solution to form vicinal diol (commonly called glycol). The pink colour of  $\text{KMnO}_4$  is discharged and a brown solid,  $\text{MnO}_2$  is formed.

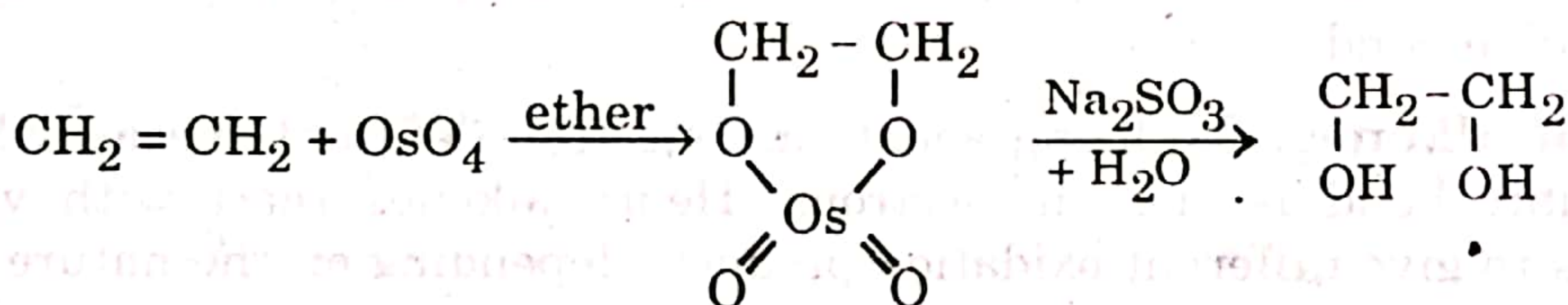


This reaction is used as a test for the presence of a double bond (unsaturation) in an organic molecule and is known as **Baeyer's test**.

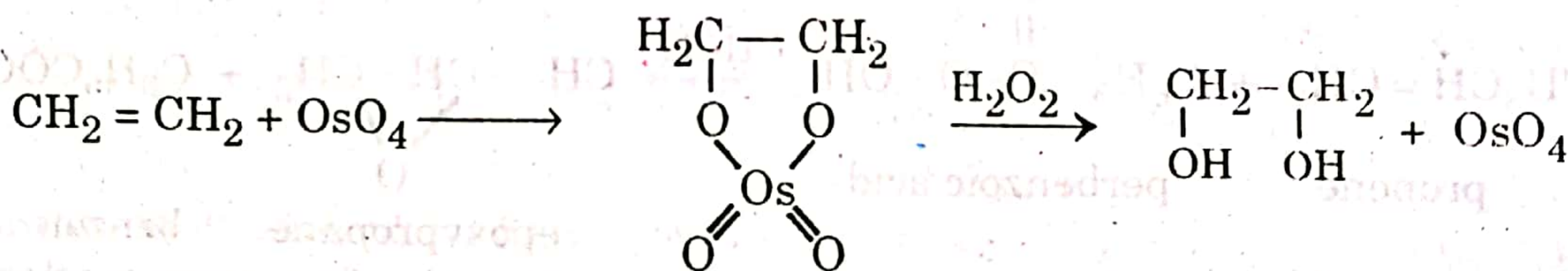
The reaction occurs with cis addition and involves the formation of an intermediate cyclic manganate ester which is rapidly hydrolysed to cis-diol.



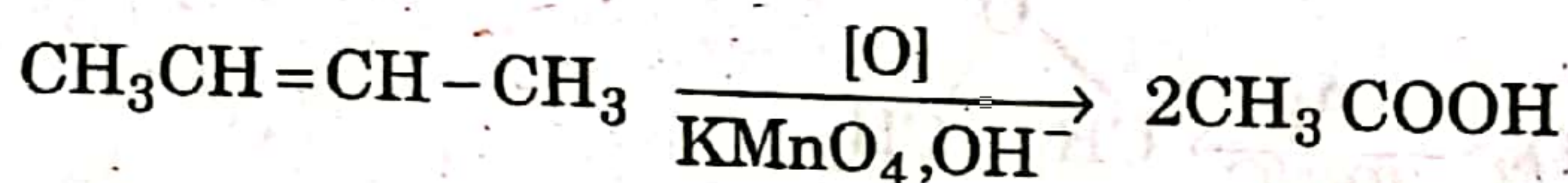
Hydroxylation with  $\text{OsO}_4$  also gives a cis-diol. Osmium tetroxide with an ethereal solution of the alkene forms cyclic osmate ester which on hydrolysis with an aqueous solution of sodium sulphite yields cis-diol.

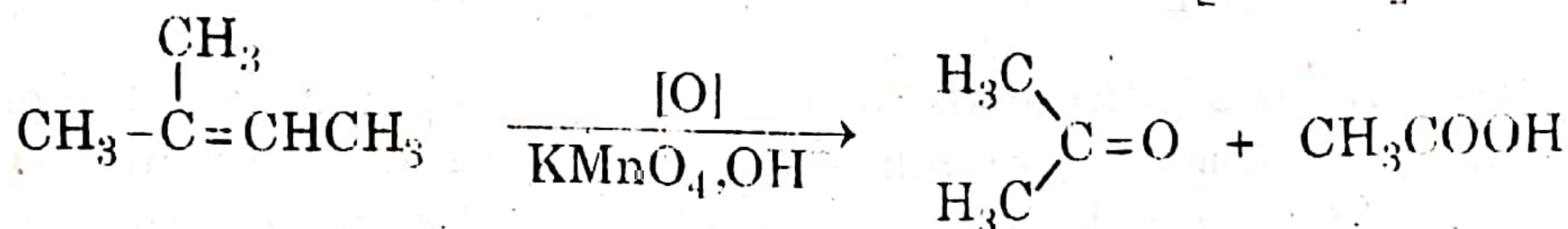
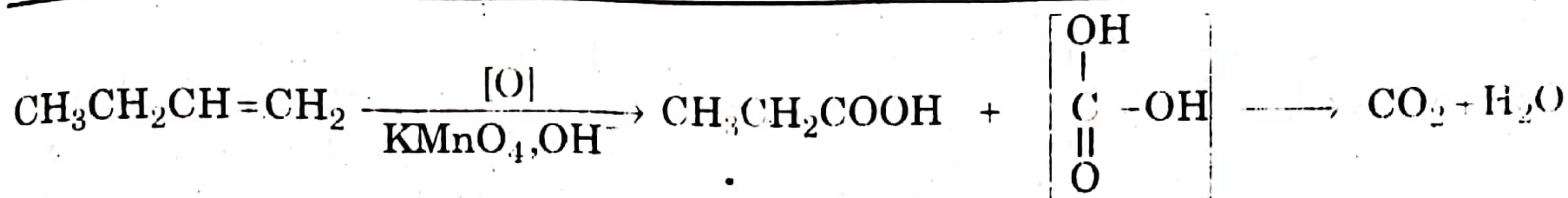


$\text{OsO}_4$  is very expensive and highly toxic, Use of hydrogen peroxide in tert-butyl alcohol with a catalytic amount of  $\text{OsO}_4$  provides a cheaper and convenient method for the hydroxylation. The osmate ester formed initially is converted to cis-diol by  $\text{H}_2\text{O}_2$  and  $\text{OsO}_4$  is regenerated for further use.



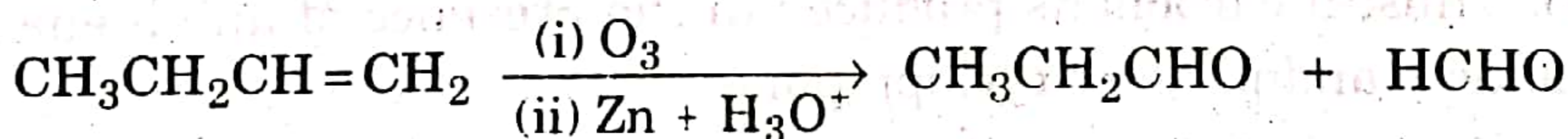
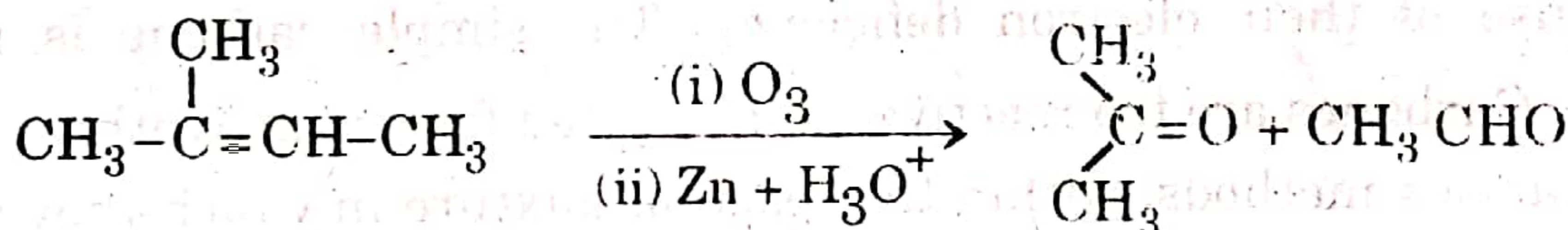
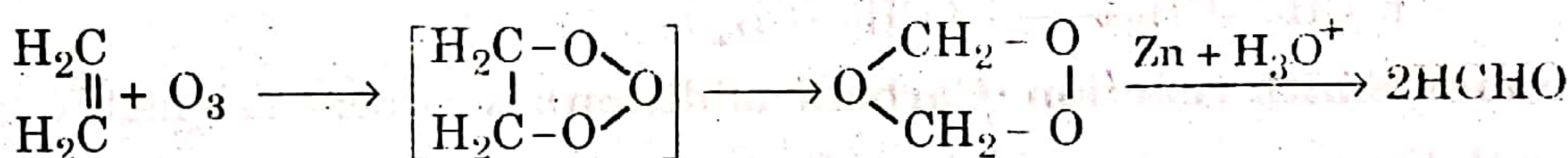
(iii) **Oxidative Cleavage of double bond.** The oxidation of alkenes with hot concentrated  $\text{KMnO}_4$  solution cleavages (split) the alkene at the double bond to form ketones and/or acids. Usually each doubly bonded carbon is oxidized to  $\text{C}=\text{O}$ , while any hydrogen attached to these carbons is oxidized to  $-\text{OH}$  group.





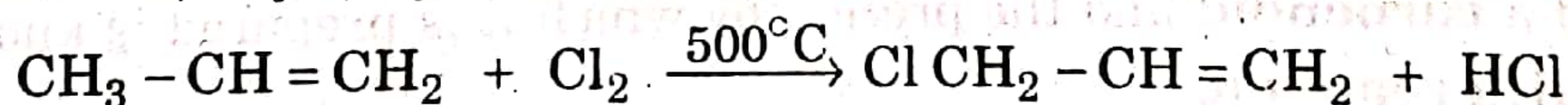
The oxidative cleavage of alkene may be used to locate the position of the double bond in the molecule. A better and more useful oxidative cleavage of the double bond can generally be accomplished by ozone.

**(iv) Ozonization (Ozonolysis).** Ozone ( $\text{O}_3$ ) reacts vigorously with alkenes to form ozonides. The process is called **ozonolysis** and is carried out by passing ozone containing air through a solution of an alkene in an inert solvent like chloroform. The ozone molecule adds to the double bond forming, initially an addition product, a **molozone**, which rearranges rapidly to form an **ozonide**. Ozonides are unstable and tend to decompose explosively. They are, therefore, not isolated, but are reduced directly by treatment with zinc dust in a dilute acid. The reduction produces carbonyl compounds (either aldehydes or ketones or an aldehyde and a ketone depending on the structure of the alkene). Identification of carbonyl products helps to locate the position of double bond in an alkene.



## 7. Allylic Halogenation (substitution).

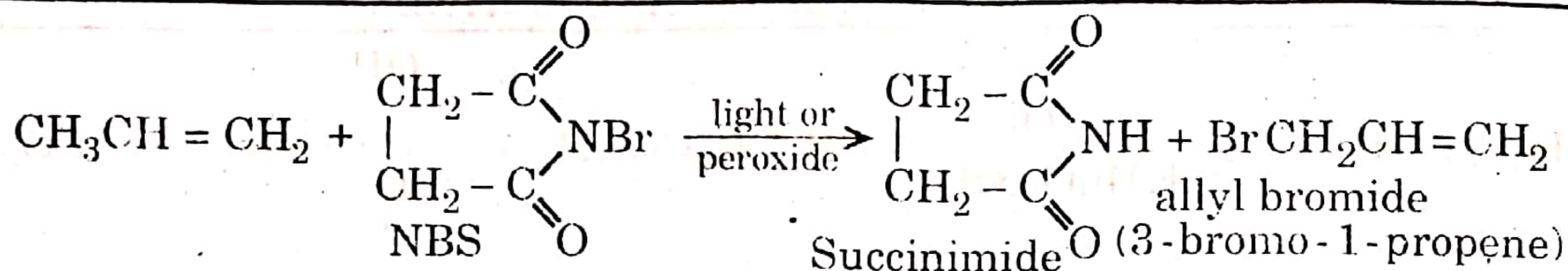
Since higher alkenes have alkyl groups which have the alkene structure, they should undergo the free radical substitution reactions characteristic of alkenes. Therefore, when an alkene is made to react with chlorine or bromine at high temperatures, allylic hydrogen is replaced by chlorine or bromine.



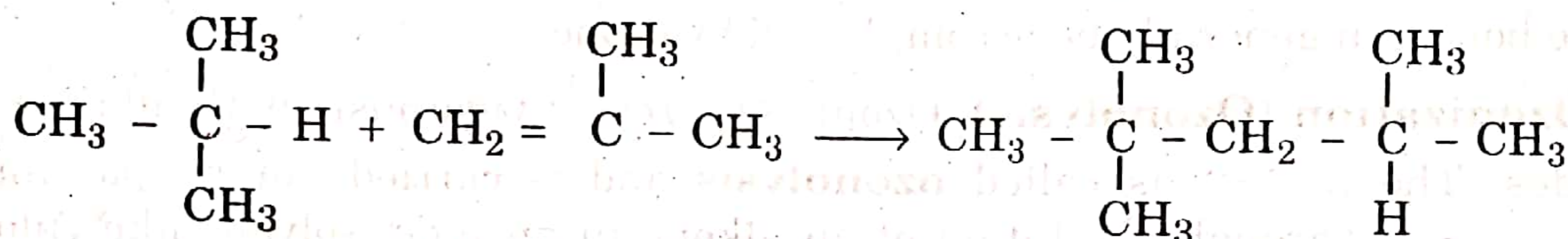
A hydrogen on a carbon atom which is directly attached to a double bonded carbon atom is called **allylic hydrogen** and the reaction in which allylic hydrogen is replaced by halogen is known as **substitution reaction**.

Allylic bromination can be brought about at lower temperatures by the use of N-bromosuccinimide (NBS) in  $\text{CCl}_4$  in the presence of free radical initiator i.e., light or peroxid.

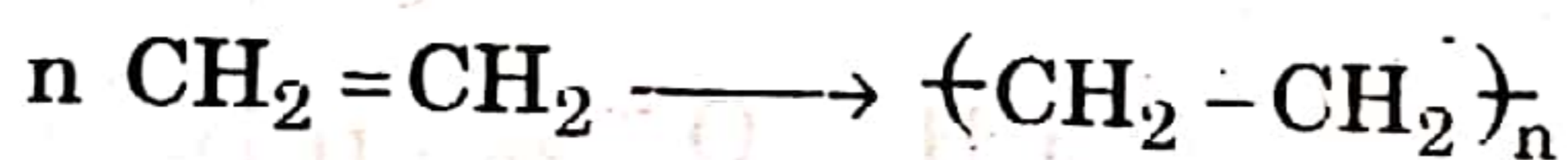




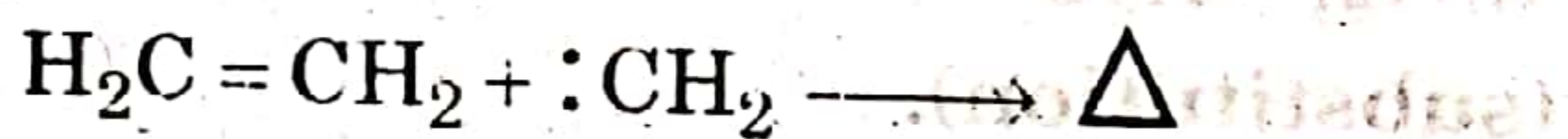
**8. Alkylation (Addition of alkanes).** Some alkanes add to alkenes in the presence of  $\text{H}_2\text{SO}_4$  or  $\text{HF}$  to produce higher alkanes. The process is called **alkylation of alkenes**. For example, 2-methyl propane adds to 2-methylpropene in the presence of  $\text{H}_2\text{SO}_4$  to form 2, 2, 4-trimethylpentane – the well known antiknock fuel used in petroleum industry.



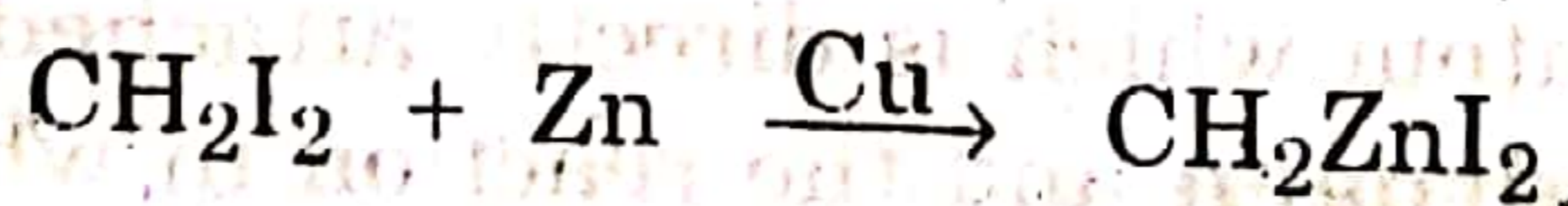
**9. Polymerization.** The process by which small molecules (monomers) join together to form large molecules (polymers) is known as **polymerization**. In fact, a polymer is a molecule with repeating structural units. Polymerization involves a large number of monomers and gives rise to a macromolecule, commonly known as polymer. Simple alkenes polymerize to form larger molecules. Polymerization of alkenes is essentially the conversion of  $\pi$  bonds into  $\sigma$  bonds which is thermodynamically favourable process. (For detail see Synthetic Polymers Chapter 14).



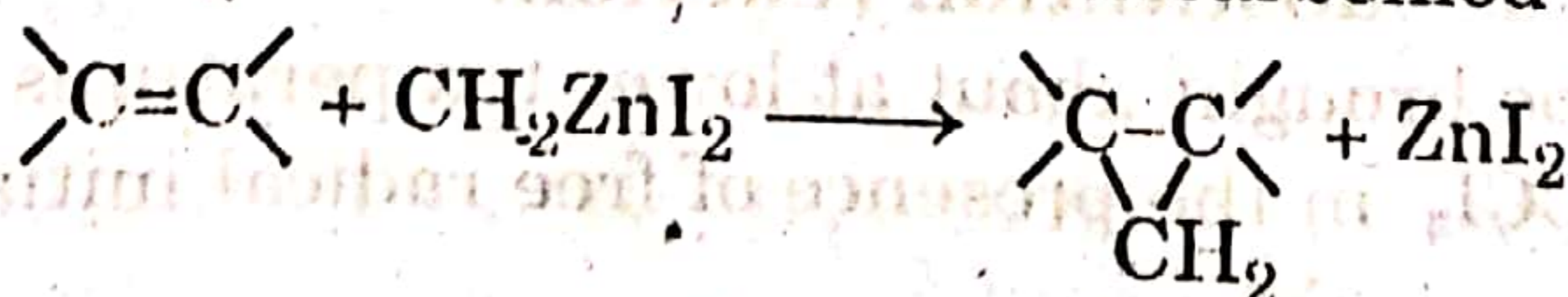
**10. Simmons-Smith reaction (Carbene addition):** A carbene is a highly reactive species with the general formula  $\text{R}_2\ddot{\text{C}}$ . Carbenes possess only six electrons and are electrophilic because of their electron deficiency. The simple carbene is named methylene ( $\text{H}\ddot{\text{C}}\text{H}$ ). Carbenes are too reactive to be isolated for use in synthesis. They are prepared, by various methods, within the reaction mixture in which they will be consumed (*in situ*). Thus, if carbene is produced in the presence of an alkene, it will readily add to an alkene and produce cyclopropane.



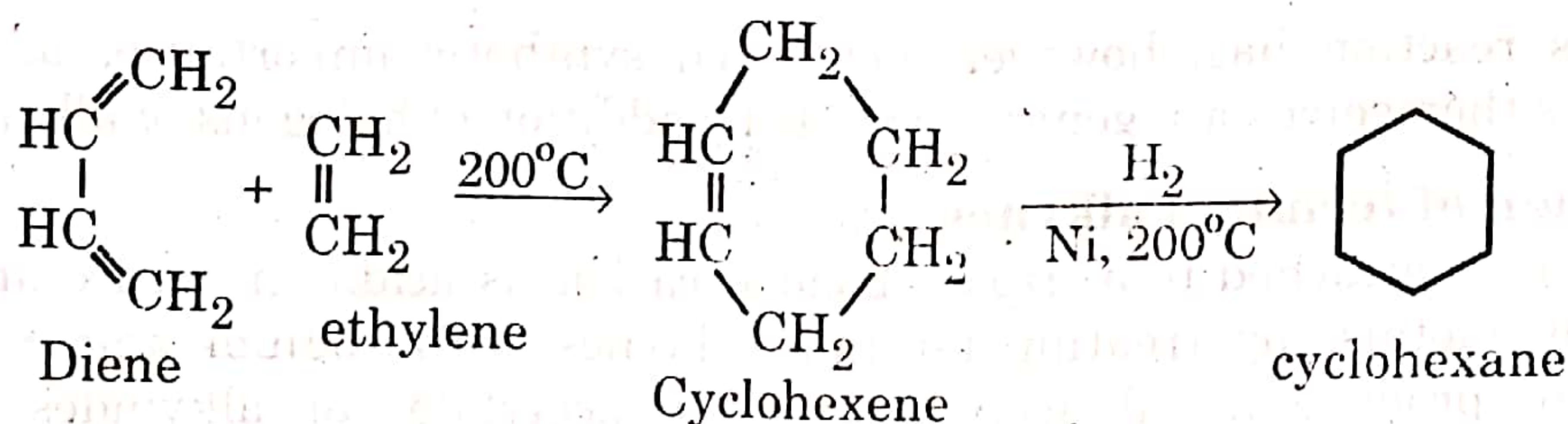
A useful approach of adding methylene to an alkene is by treating alkene with diiodomethane in the presence of Zn-Cu alloy, Zn-Cu couple alloy generates a carbene complex which reacts with alkenes to form cyclopropanes. The reagent is termed a **carbenoid** and the process by which it is prepared is known as the **Simmons-smith reaction**.



A carbenoid (carbene complex)



**11. Diels-Alder reaction.** A conjugated diene and an alkene form a cyclohexene which on catalytic, hydrogenation gives a cyclohexane. An alkene with  $2\pi$  electrons, called **dienophile**.



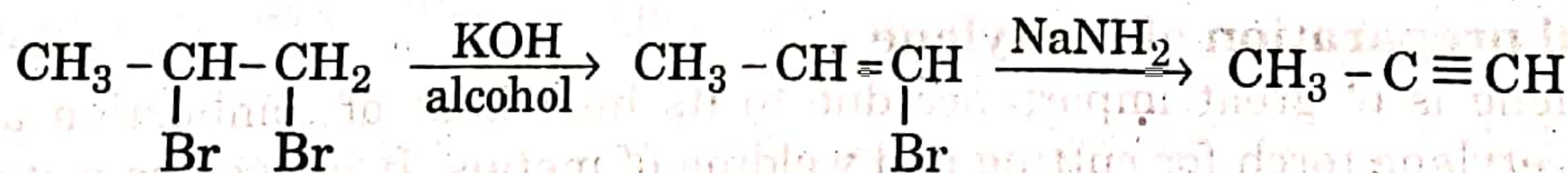
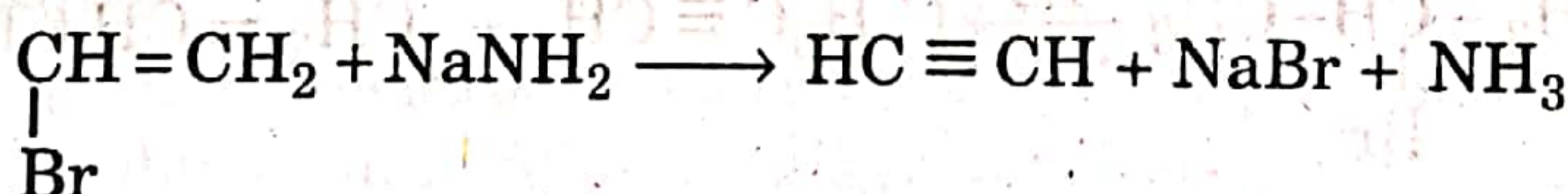
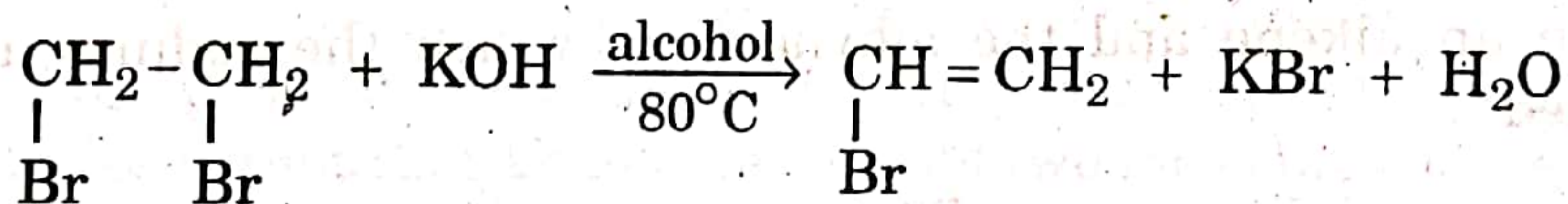
### Tests for Alkenes

1. Alkenes react rapidly with a dilute solution of bromine in  $\text{CCl}_4$ , and as a result the reddish brown colour of bromine is discharged.
2. Alkenes are oxidized by cold dilute aqueous solution of potassium permanganate and as a result the pink colour of  $\text{KMnO}_4$  solution disappears.
3. Alkenes dissolve in cold concentrated sulphuric acid and forms a single phase. An alkane does not dissolve in  $\text{H}_2\text{SO}_4$  and hence a two phase system results.
4. Alkenes form yellow  $\pi$ -complexes with tetranitromethane.

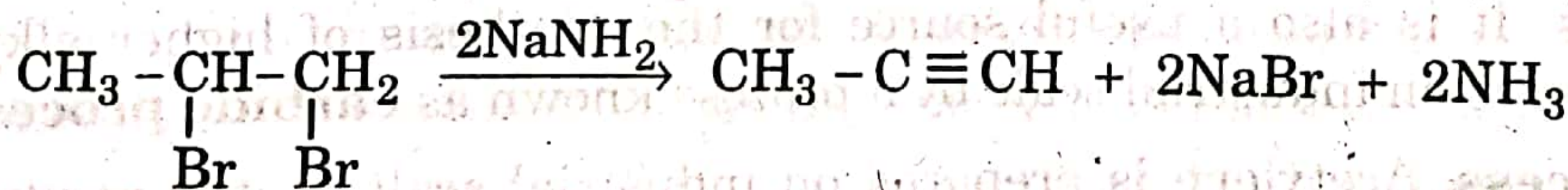
## ALKYNES

### 5.7 Preparation of Alkynes

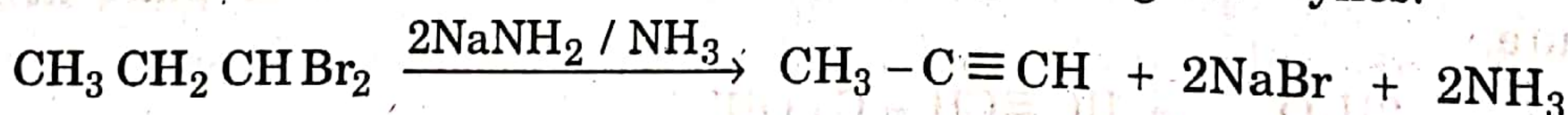
**1. Dehydrohalogenation of Vicinal Dihalides.** Vicinal-dihalides on treatment with alcoholic  $\text{KOH}$  followed by sodium amide ( $\text{NaNH}_2$ ) yield alkynes. The removal of second molecule of  $\text{HX}$  requires more drastic conditions, therefore, a stronger base  $\text{NaNH}_2$  is used to remove the second  $\text{HBr}$  molecule.



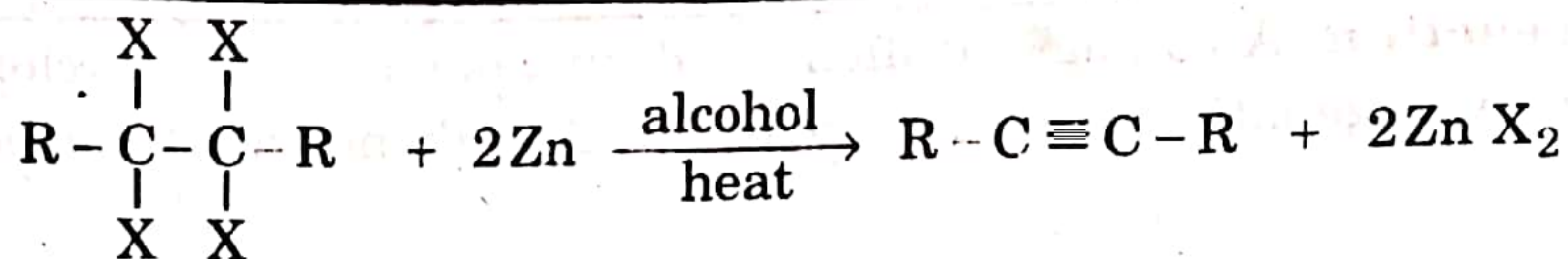
The vic-dihalides may be directly treated with  $\text{NaNH}_2$  to give alkynes.



Even geminal-dihalides on treatment with a strong base give alkynes.



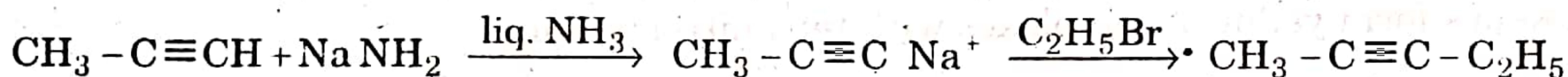
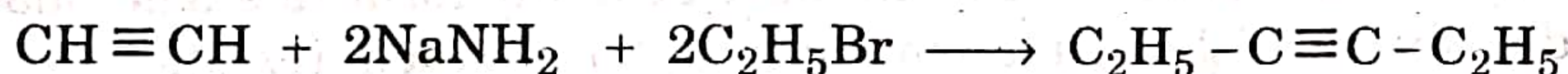
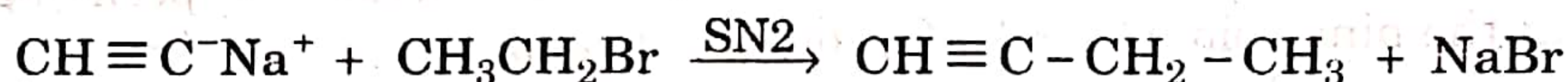
**2. Dehalogenation of tetrahalides.** When tetrahalides, having two halogen atoms on each of the two adjacent carbon atoms (halides containing a  $-\text{CX}_2-\text{CX}_2-$  system), are heated with zinc dust in alcohol, remove the halogen atoms to form alkynes.



This reaction has, however, not much synthetic importance, because the tetrahalides themselves are generally made by addition of halogens to alkynes.

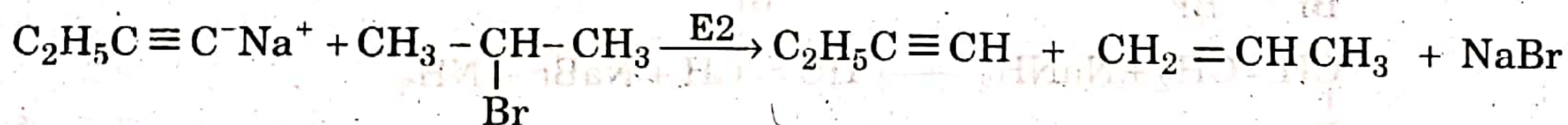
### 3. Alkylation of terminal alkynes

Hydrogen attached to a triple-bonded carbon is acidic in nature and can be replaced by metals, by treating terminal alkynes with sodium amide in liquid ammonia to produce metal acetylides. These acetylides or alkynides are good nucleophiles and react with primary alkyl halides to form higher alkynes through  $\text{S}_{\text{N}}2$  type reactions.



The main advantage of this method is that it can be used to **convert lower alkynes into higher alkynes**.

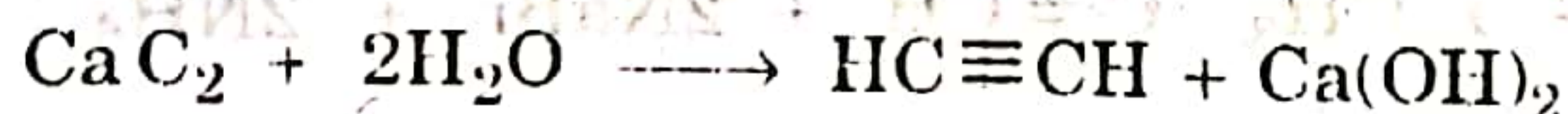
This method is only useful for primary alkyl bromides or iodides, since chloride ion is not a good leaving group. Further when secondary or tertiary alkyl halides are used, the alkynides (acetylides) ion acts as a base rather than as a nucleophile and the major result is an  $\text{E}2$  elimination. The products of the elimination are an alkene and the alkyne from which the sodium alkynide was originally formed.



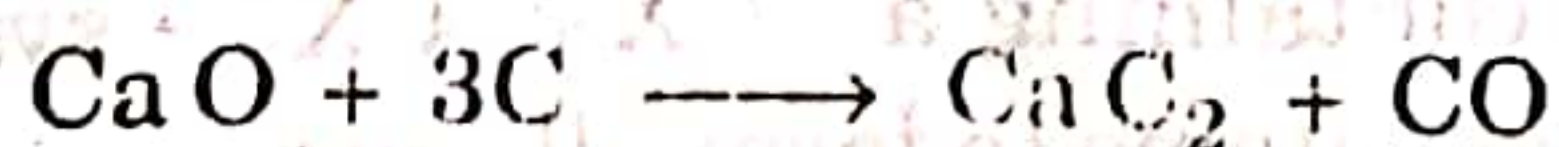
### 4. Industrial preparation of Acetylene

Acetylene is of great importance due to its high heat of combustion and is used in oxyacetylene torch for cutting and welding of metals. It is used as a starting material for the manufacture of large number of compounds which are used to prepare polymers. It is also a useful source for the synthesis of higher alkynes. Acetylene is prepared on industrial scale by a process known as **carbide process**.

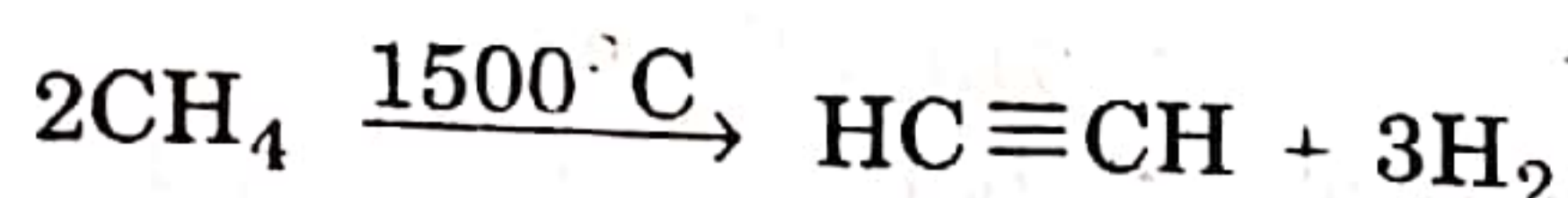
**(i) Carbide process.** Acetylene is prepared on industrial scale by the reaction of calcium carbide with water. The reaction is exothermic and takes place at room temperature.



Calcium carbide is obtained by heating lime with coke in an electric furnace.



(ii) **From natural gas.** Acetylene is also prepared on industrial scale by pyrolysis of natural gas at 1500°C.



### 5.8 Physical properties of Alkynes

The boiling points, melting points and densities of the simple alkynes are slightly higher than those of the corresponding alkenes and alkanes. Terminal alkynes have low boiling points than the isomeric alkynes.

Alkynes are insoluble in water but readily soluble in organic solvents such as benzene, acetone and ethanol.

**Table 5.2 Physical Constants of Alkynes**

Compound	b.p. (°C)	m.p. (°C)	Density
Ethyne	-84	-82	-
Propyne	-23	-102	-
1-Butyne	8	-123	0.65
2-Butyne	27	-32	0.691
1-Pentyne	40	-90	0.694
2-Pentyne	56	-109	0.711
1-Hexyne	71	-132	0.716

### 5.9 Comparison of reactivities of Alkenes and Alkynes

In alkynes, each triply bound carbon is *sp* hybridized, and contain one  $\sigma$  bond and two  $\pi$  bonds, while in alkenes doubly bound carbons contain one  $\sigma$  bond and one  $\pi$  bond. The alkynes are unsaturated compounds like alkenes. They therefore resemble alkenes in most of their reactions. For example addition of hydrogen, halogens and hydrogen halides to alkynes is very much like the addition of these reagents to alkenes except that an alkyne can add two molecules of these reagents in a stepwise manner.

Although the  $\pi$ -electron density on a C-C triple bond in alkynes is higher than that of a double bond in alkenes, alkynes are less reactive than alkenes toward electrophilic reagent. This is, because the electrons are more firmly held in acetylenic linkage and therefore, are not easily available to an electrophilic reagent. Further, they offer less resistance to a nucleophilic reagent, thus alkynes undergo nucleophilic addition, that are virtually unknown for simple alkenes.

The hydrogens of acetylene and terminal alkynes are much more acidic than those of ethene and ethane. This can be explained on the basis of hybridization state of carbon in each compound. Terminal alkynes, where the carbon is *sp* hybridized with 50% *s* character, is much more acidic than ethene (*sp*<sup>2</sup> hybridized, 33.3% *s* character) which in turn is more acidic than ethane (25% *s* character). Increased *s* character means that the electrons are closer to the nucleus and hence are firmly held by the carbon nuclei. Therefore, release of attached hydrogen as a proton is easier in terminal alkynes relative to alkenes and alkanes.

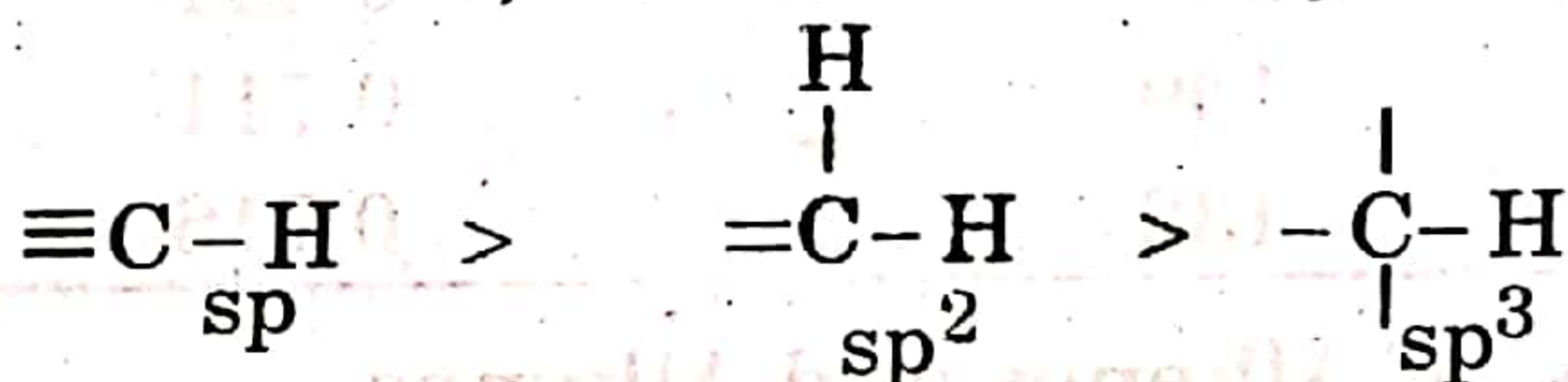
Generally, similar compounds differ in acidity because their conjugate bases differ in stability. Alkynes form a more stable anion than do alkenes and alkanes. We can conclude, then, that the conjugate base of the alkyne (acetylide anion,  $\text{RC}\equiv\text{C}^-$ ) is more stable than the conjugate bases of both alkenes and alkanes, alkynes are the most acidic of the three types of hydrocarbons.

The  $sp$  hybridized bonds are linear in alkynes, ruling out *cis* *trans* isomers in which substituents must be on different sides of the multiple bond, while geometric isomerism in alkenes is the result of restricted rotation about the double bond.

### 5.10 Chemical properties (Reactions) of alkynes

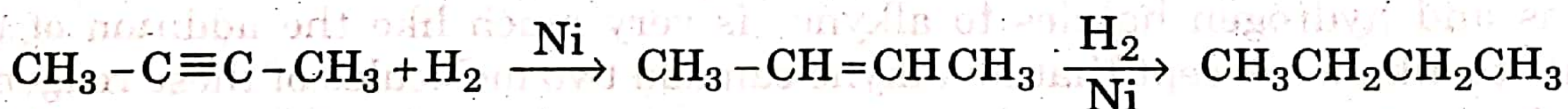
Alkynes give the same kind of addition reactions as do alkenes. These reactions are due to the availability of the loosely held  $\pi$  electrons. However, with alkynes the addition may take place in one step or two steps, depending upon conditions.

Alkynes, in general, are less reactive than alkenes toward electrophilic reagents but are more reactive toward nucleophilic reagents. The acetylenic hydrogen is acidic in nature, thus alkynes undergo certain reactions which are not commonly observed with alkenes. "The more  $s$  character in the  $\text{C}-\text{H}$  bond, the more acidic is the  $\text{H}$ ". Therefore, the order of acidity of hydrocarbons is

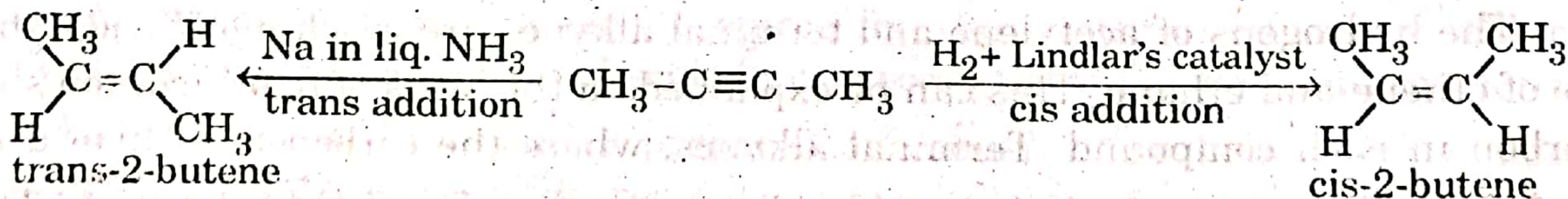


Some of the important reactions are described below:

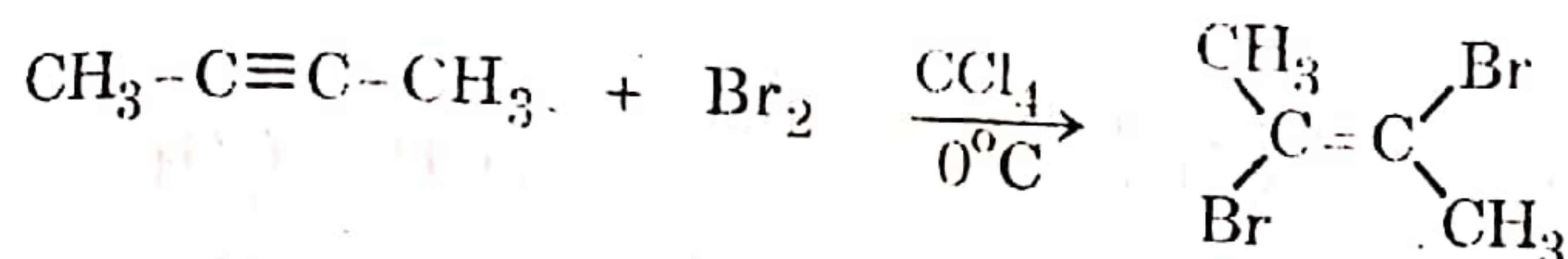
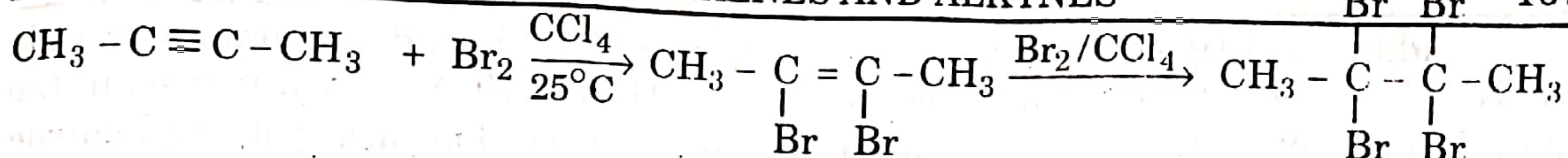
**1. Hydrogenation (Reduction).** In the presence of Pt, Pd or Raney-nickel catalyst, alkynes add up two moles of hydrogen in two steps, first forming the corresponding alkenes and finally alkanes.



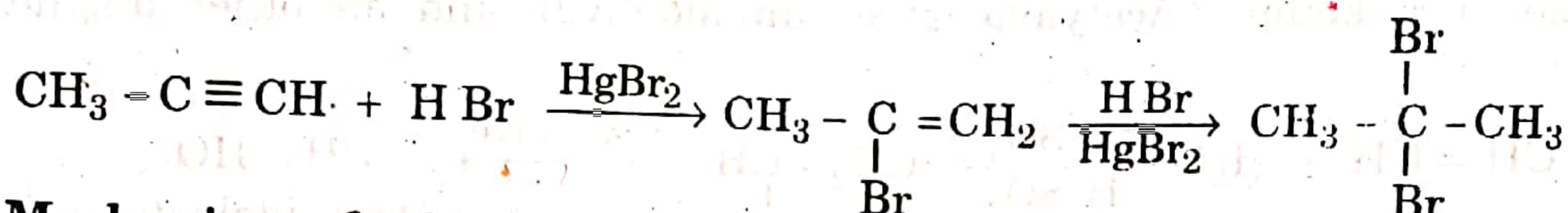
However, hydrogenation of alkynes can be stopped at the alkene stage by the use of special catalysts or reagents and calculated amount of hydrogen. The alkene formed may be *cis* or *trans* depending upon the choice of catalyst. Reduction of alkynes with Lindlar's catalyst (i.e., Pd supported over  $\text{BaSO}_4$  partially poisoned by quinoline) yields a *cis*-alkenes, whereas with sodium in liquid ammonia gives a **trans-alkene**.



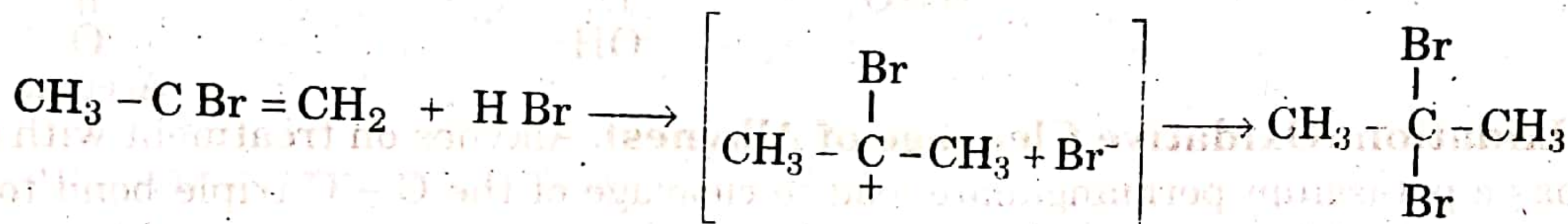
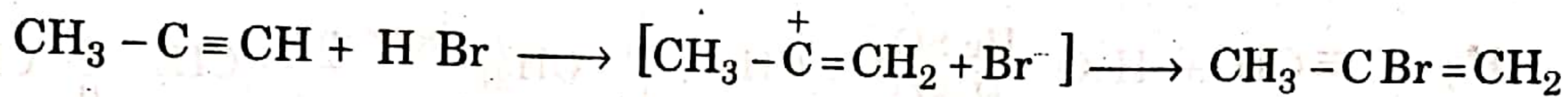
**2. Addition of Halogens ( $\text{Cl}_2$  or  $\text{Br}_2$ ).** Halogens add to alkynes in two steps forming a dihalide and then tetrahalides. The reaction can be stopped after the addition of 1 molecule of halogen by carrying out the reaction at lower temperature and the dihalide produced has the *trans*-structure.



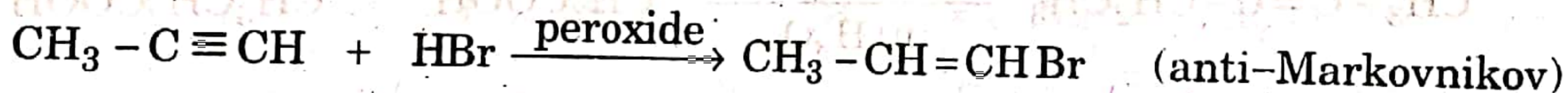
**3. Addition of hydrogen halides and other acids.** Alkynes react with hydrogen halides (usually HCl and HBr) to form either haloalkenes or geminal dihalides depending on whether one or two molecules of the hydrogen halide are used. Both addition follow Markovnikov's rule. The order of reactivity of halogen acids is  $\text{HI} > \text{HBr} > \text{HCl}$ . The reaction is generally catalyzed by corresponding metallic halides.



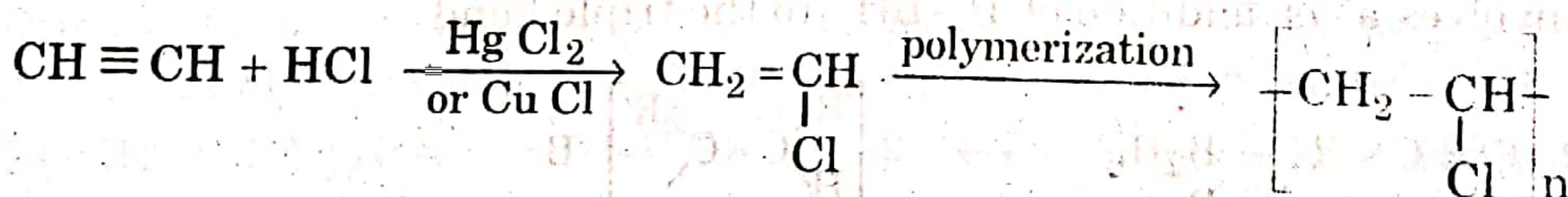
**Mechanism** of addition is similar to the mechanism proposed for polar addition of halogen acids.



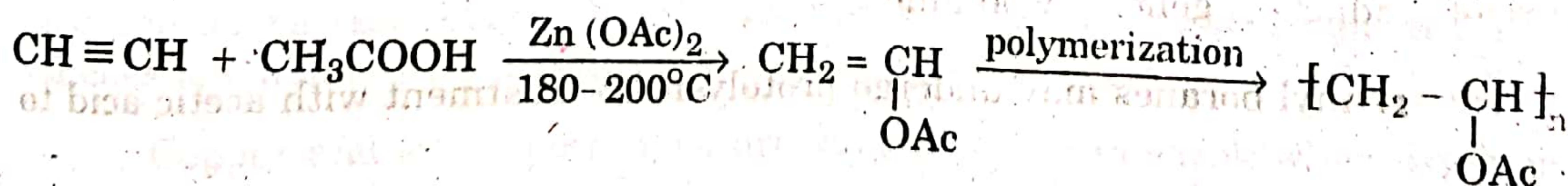
In the presence of peroxides, the addition of HBr to alkynes follows the anti-Markovnikov's rule as in the case of alkenes. The addition occurs through a free radical mechanism.



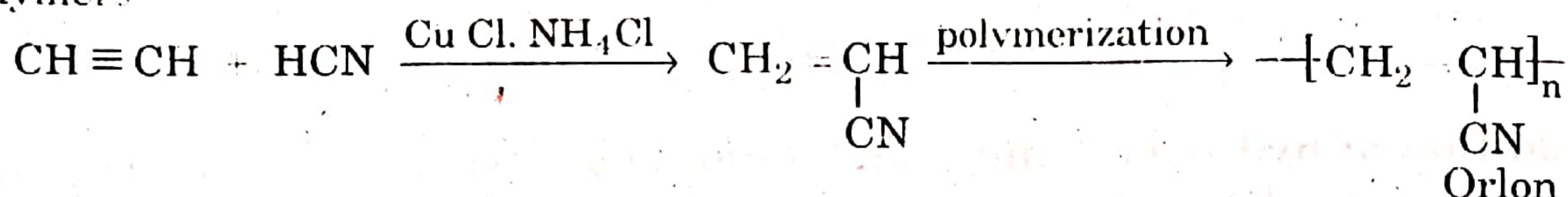
Addition of hydrogen chloride to acetylene in the presence of mercuric chloride or cuprous chloride process produces vinyl chloride ( $\text{CH}_2 = \text{CHCl}$ ) which polymerizes to polyvinyl chloride (PVC) which is used for the manufacture of gramophone records, transparent wrapping and pipes.



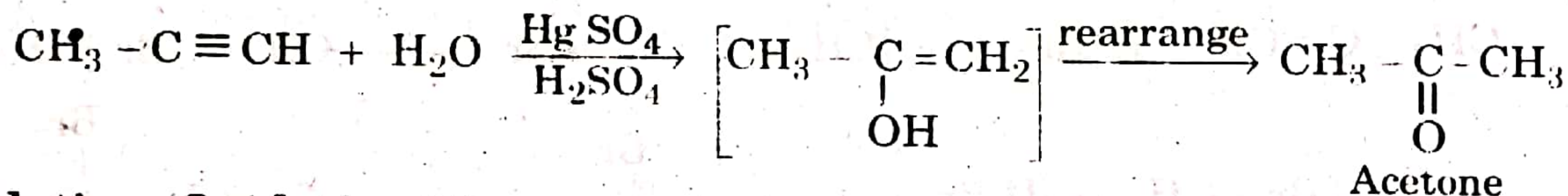
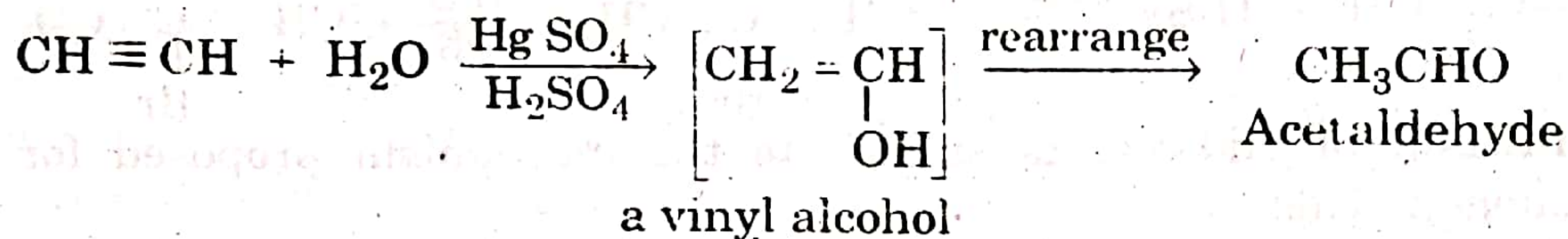
Similarly, addition of acetic acid in the presence of zinc acetate or mercuric acetate to acetylene produces vinyl acetate ( $\text{CH}_2 = \text{CHOCOCH}_3$ ) which polymerizes readily to give polyvinyl acetate which is used in water-base paints.



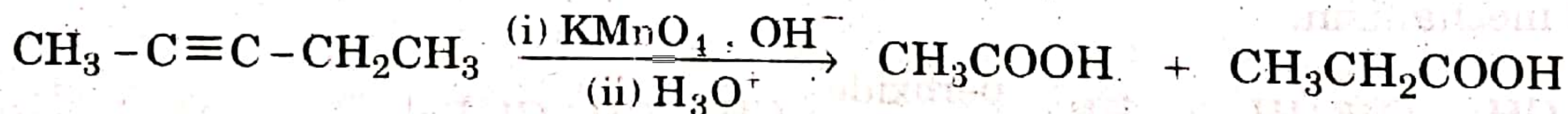
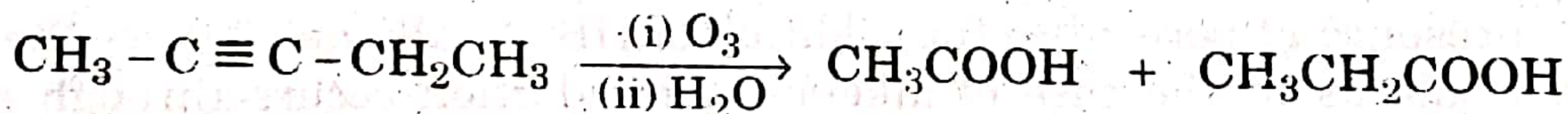
Addition of HCN in the presence of cuprous chloride and ammonium chloride to acetylene gives vinyl cyanide (acrylonitrile,  $\text{CH}_2 = \text{CHCN}$ ) which is used in the manufacture of polymers. The fabrics orlon and acrilon are polyacrylonitrile polymers



**4. Addition of water (Hydration).** Alkynes react with water in the presence of mercuric sulphate and sulphuric acid to form an aldehyde or a ketone. The addition follows Markovnikov's rule. The initially formed vinylic alcohol is unstable and rapidly undergoes tautomerization under the reaction conditions to form an aldehyde or a ketone. Acetylene gives an aldehyde and all other alkynes give ketones.

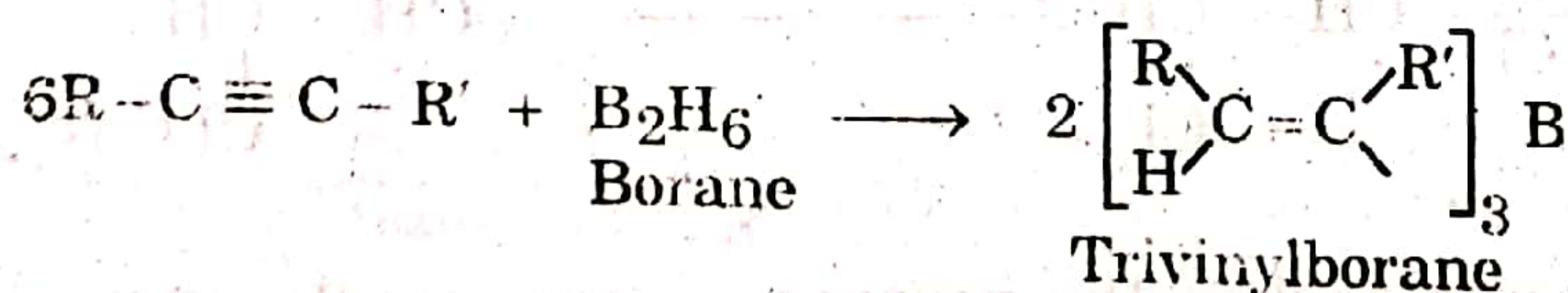


**5. Oxidation (Oxidative Cleavage of Alkynes).** Alkynes on treatment with ozone or basic potassium permanganate lead to cleavage of the C - C triple bond to form carboxylic acids.



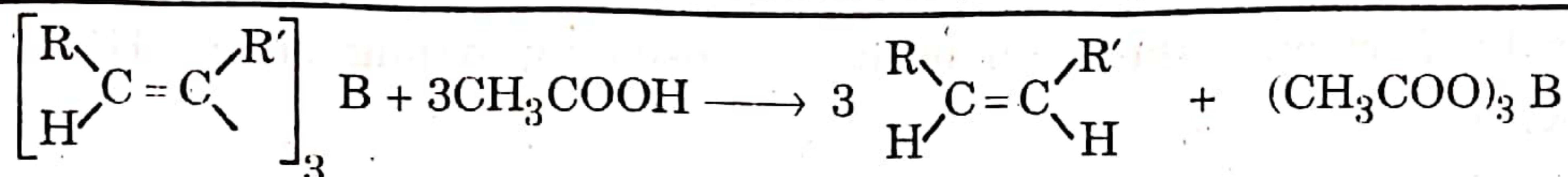
The oxidative cleavage can be used to locate the position of a triple bond in a molecule.

**6. Hydroboration.** Alkynes, like alkene, react with diborane to form trivinylboranes which, like trialkylboranes, enter into several useful reactions. The reaction involves a *cis* addition of H - BH<sub>2</sub> to the triple bond.

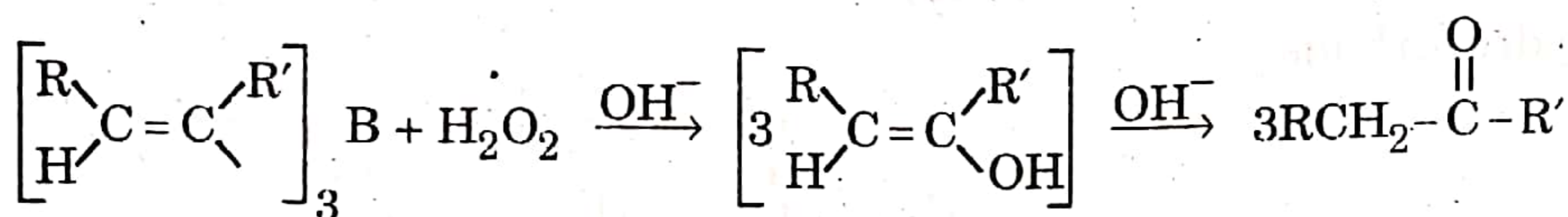


The reaction is useful for the terminal alkynes and for symmetrical disubstituted acetylenes. However, with unsymmetrical disubstituted acetylenes a mixture of products is generally obtained.

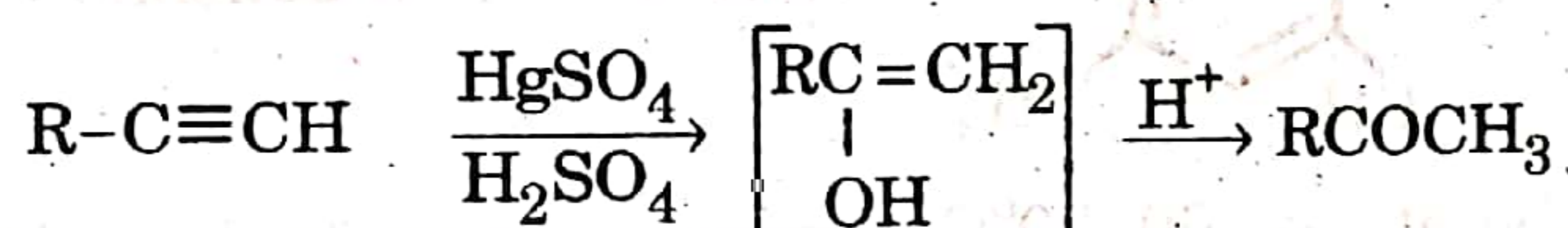
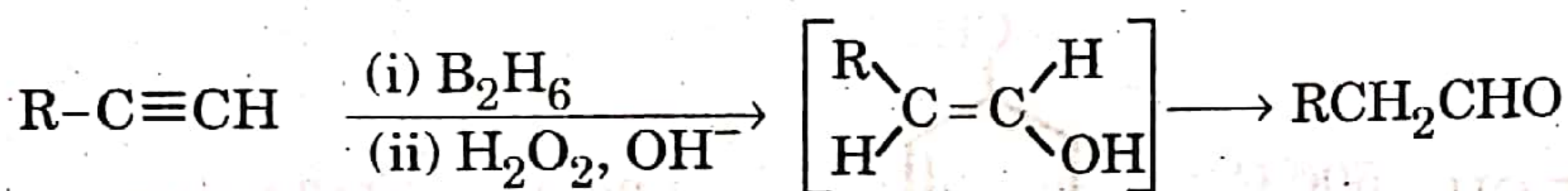
The trivinyl boranes may undergo protolysis on treatment with acetic acid to give alkenes



Thus the overall result of the hydroboration-protolysis is the hydrogenation of an alkyne to form a *cis* alkene. The trivinylboranes on oxidation with alkaline  $\text{H}_2\text{O}_2$  give vinyl alcohols which tautomerize quantitatively to the corresponding aldehydes or ketones.

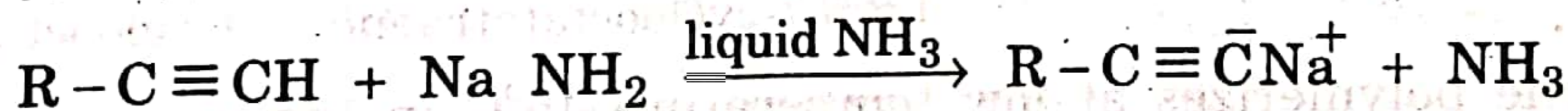


The overall result of the hydroboration-oxidation is the hydration of the triple bond in accordance with the anti-Markovnikov's rule. Thus a terminal alkyne in this case gives an aldehyde, whereas the direct hydration of a terminal alkyne by means of  $\text{HgSO}_4 - \text{H}_2\text{SO}_4$  gives a ketone.



## 7. Acidity and formation of metal acetylides

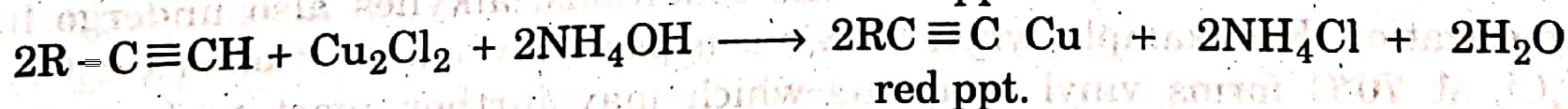
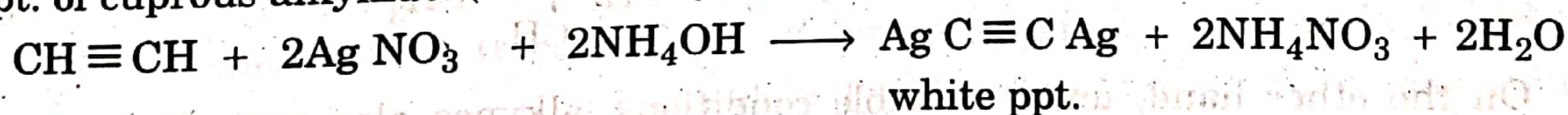
Hydrogens in acetylene ( $\text{H} - \text{C} \equiv \text{C} - \text{H}$ ) or 1-alkynes ( $\equiv \text{C} - \text{H}$ ) are weakly acidic in nature. They can be replaced by metals to form metal acetylides. Thus acetylene or 1-alkynes (terminal alkynes) react with heated sodium or sodium amide in liquid ammonia to form sodium alkynides.



Sodium acetylides react with primary alkyl halides to form **higher alkynes**.



Acetylene and 1-alkynes react with ammonical solution of silver nitrate or ammonical solution of cuprous chloride to form white ppt. of silver alkynide or red ppt. of cuprous alkynide. (sodium alkynides are hydrolysed by water).

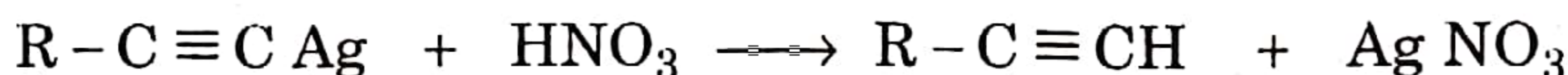


Since 2-alkynes (or other nonterminal alkynes), alkenes and alkanes fail to give the above test, hence these reactions may be used to distinguish 2-alkynes, alkenes and alkanes from 1-alkynes.

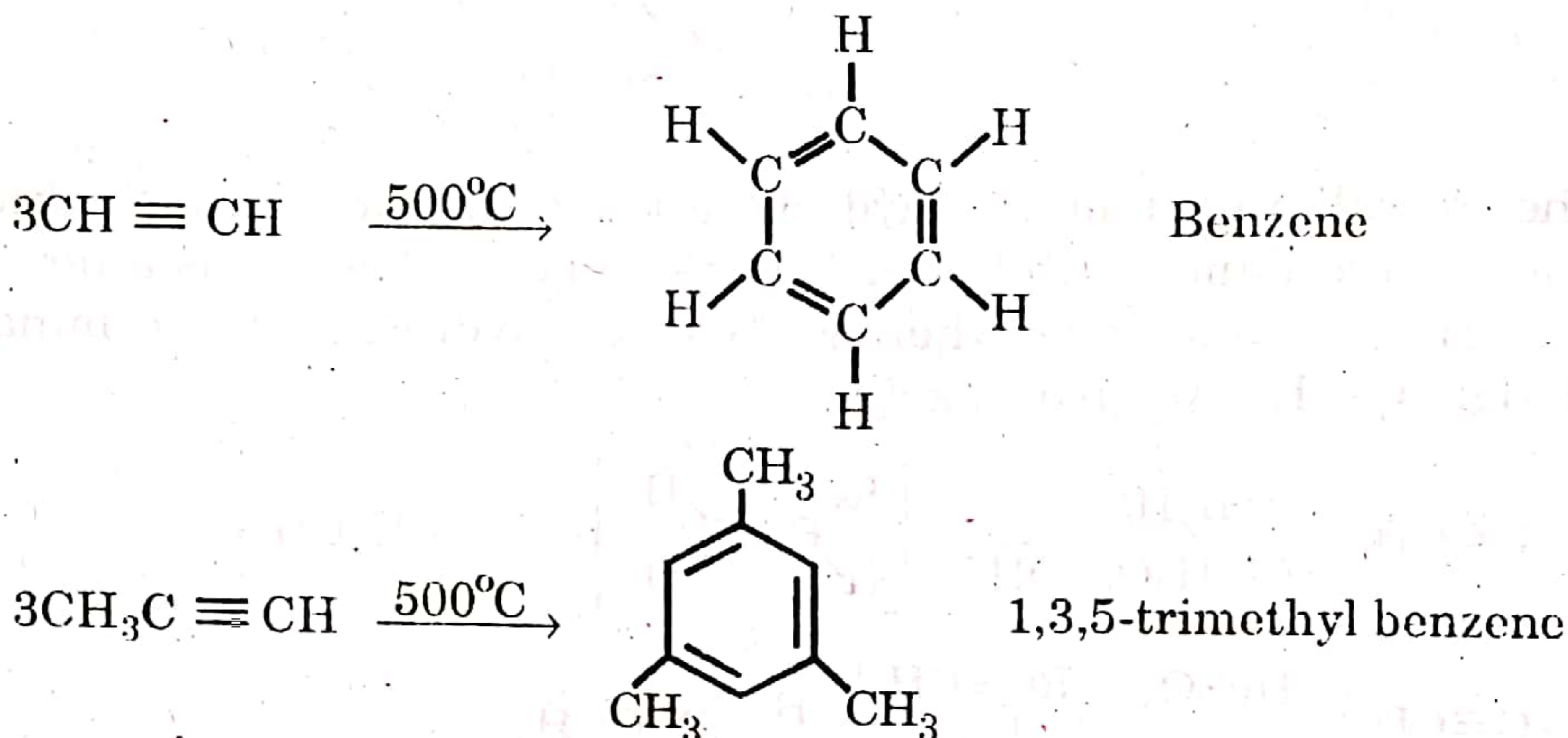
Copper and silver acetylides are very sensitive to shock when dry and may



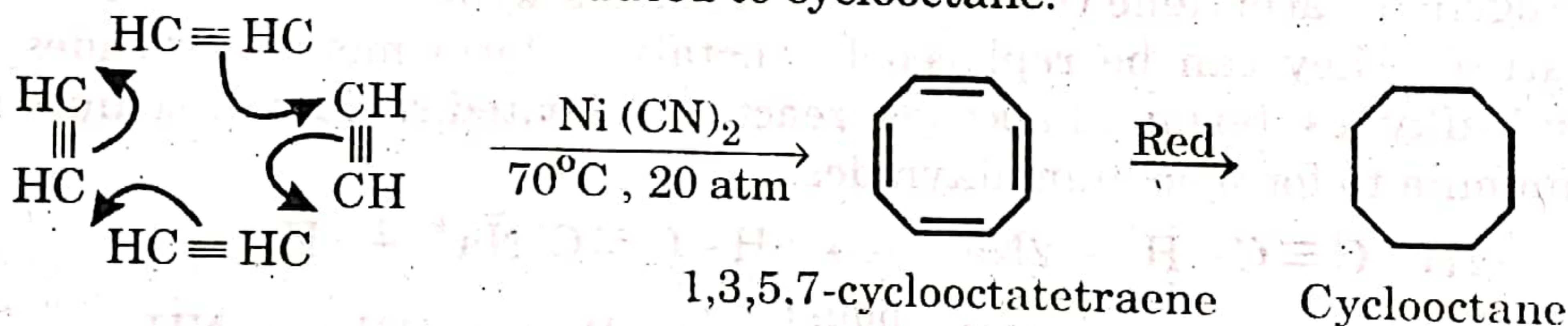
explode violently. However, they can be decomposed by strong acids ( $\text{HNO}_3$ ) to regenerate alkynes.



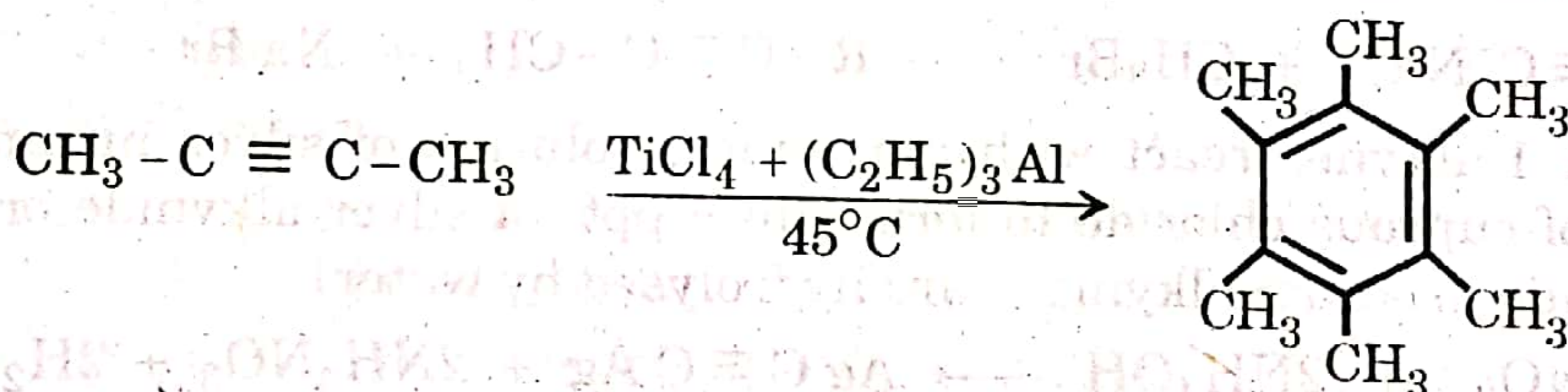
**8. Polymerization** Alkynes undergo polymerization in two different ways depending upon the reaction conditions. At high temperature they undergo cyclic polymerization. Alkynes when passed through a red hot iron tube, they polymerize to form aromatic hydrocarbons.



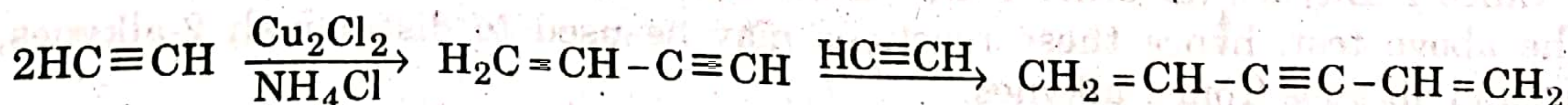
Acetylene, in an inert solvent at  $60-70^\circ\text{C}$  under a pressure of 10-20 atmosphere in the presence of a suitable catalyst like  $\text{Ni}(\text{CN})_2$ , tetramerizes to form cyclooctatetraene which can be reduced to cyclooctane.



2-butyne polymerizes at low temperature  $45^\circ\text{C}$  in the presence of suitable catalyst to form hexamethyl benzene.

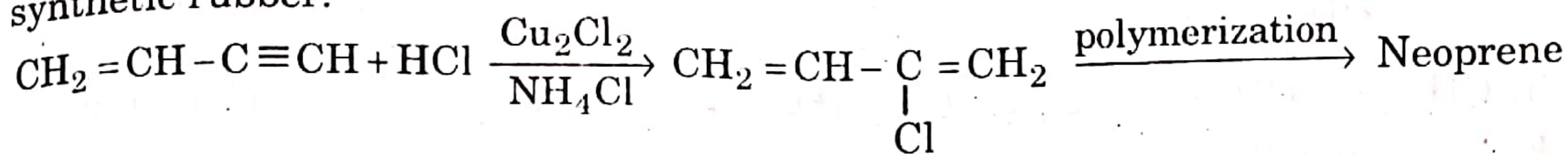


On the other hand, under suitable conditions, alkynes also undergo linear polymerization. For example, when acetylene is passed into a solution of  $\text{Cu}_2\text{Cl}_2$  and  $\text{NH}_4\text{Cl}$  at  $70^\circ\text{C}$  forms vinyl acetylene which may further react to form divinyl acetylene.

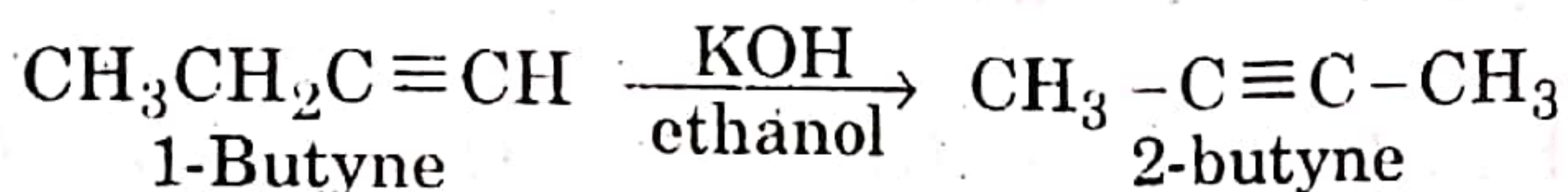


Vinyl acetylene on treatment with  $\text{HCl}$  gives 2-chloro-1,3-butadiene

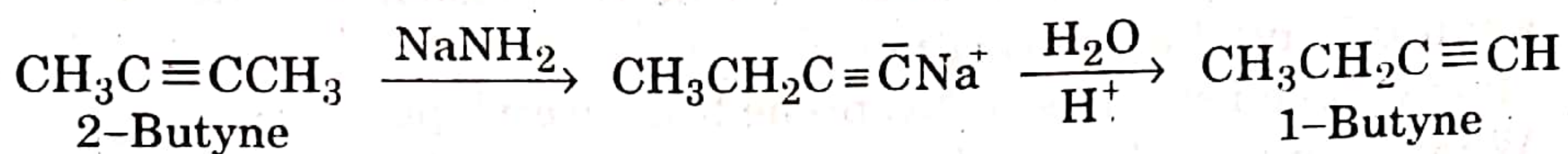
(chloroprene) which readily polymerizes to form neoprene, which is used as a synthetic rubber.



**9. Isomerization.** Alkynes isomerize under the influence of either an acidic or a basic catalyst. When 1-alkynes are treated with sodium amide in ethanol, 2-alkynes are obtained.



On the other hand, when 2-alkynes are treated with sodium amide in an inert solvent, sodium derivative of 1-alkyne is produced, which on treatment with dilute acid gives 1-alkyne.



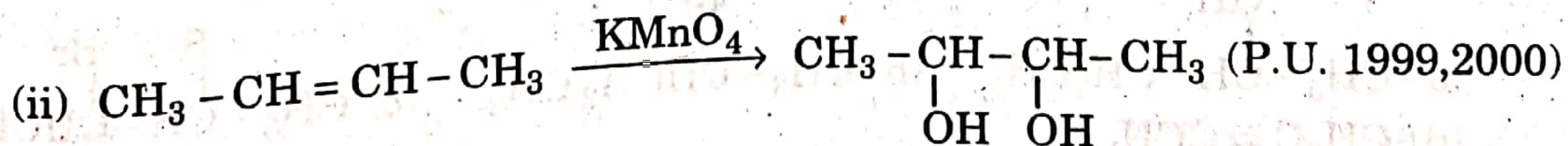
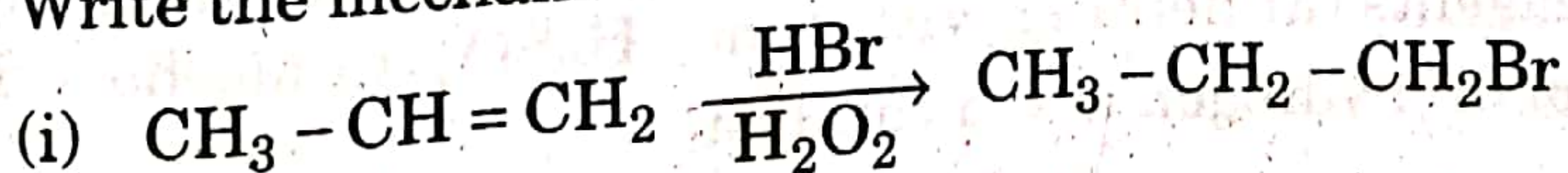
### Spectroscopic identification of alkenes and alkynes

The UV absorption spectra of alkenes show  $\lambda_{\text{max}}$  at 171 nm. The IR spectra of alkenes show C-H stretching absorptions at 3000-3100  $\text{cm}^{-1}$ . Carbon-carbon double bonds give stretching absorption peaks at 1620-1680  $\text{cm}^{-1}$ . Absorptions arising from C-H bending vibrations are at 600-1000  $\text{cm}^{-1}$ .

The UV absorption spectra of alkynes show  $\lambda_{\text{max}}$  at 173 nm. The IR spectra of alkynes show stretching absorptions at ~3300  $\text{cm}^{-1}$ . Carbon-carbon triple bond gives stretching absorption peaks at 2100-2260  $\text{cm}^{-1}$ . These absorptions are weak and will be absent if the triple bond is symmetrically substituted.

## Questions

- 1.(a) How alkenes are prepared from alcohols and pyrolytic eliminations? Give in detail the various steps and reactions involved.
- (b) Discuss the following reactions with reference to alkenes: (i) Hydration (ii) Oxidation (iii) Ozonolysis (iv) Polymerization. (P.U. 1988,1994)
2. Define and explain: (i) Anti-Markovnikov addition (ii) Allylic bromination
3. Write the mechanism of the following reactions:

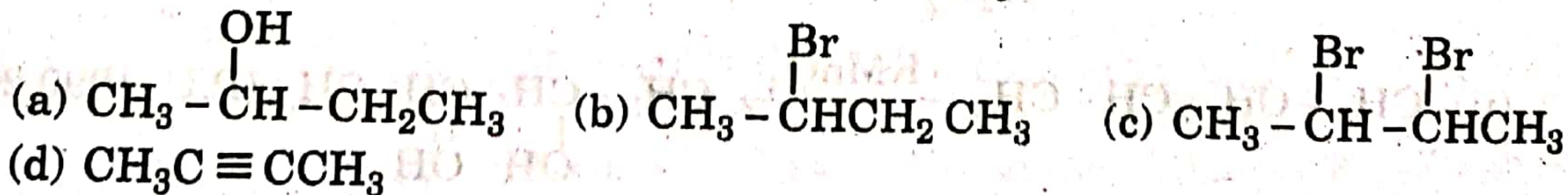


4. How will you synthesize the following alkenes by using Wittig Reaction?  

$$\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} = \text{CH}_2 \end{array}$$
 (i)  $\text{C}_6\text{H}_5\text{CH} = \text{CHC}_6\text{H}_5$  (P.U. 1999)
5. Explain the following reactions with suitable examples: (i) Wittig reaction (P.U. 2000, 2001)  
 (ii) Pyrolytic Elimination
6. Give two methods each to prepare: (i) 1-Butene (ii) 1-Butyne (P.U. 2003)
7. How is acetylene prepared in the laboratory? How does it react with the following reagent?  
 (i)  $\text{H}_2 / \text{Pd}$  (ii)  $\text{H}_2 / \text{Pd} / \text{BaSO}_4$  (iii)  $\text{HBr}$  (iv)  $\text{H}_2\text{O} / \text{H}_2\text{SO}_4 / \text{HgSO}_4$   
 (v)  $\text{AgNO}_3 + \text{NH}_4\text{OH}$  (vi)  $\text{Cu}_2\text{Cl}_2 + \text{NH}_4\text{OH}$
8. How would you establish the position of the double bond in an alkene? Give two examples to prove your method.
9. Write notes on: (i) Markovnikov rule (ii) Ozonolysis (iii) Anti-Markovnikov addition (iv) Polymerization
10. How will you synthesise Neoprene from acetylene?
11. What happens when acetylene is passed through.  
 (i) red hot tube (ii) ammonical silver nitrate solution (iii) ammonical cuprous chloride solution (iv) dilute  $\text{H}_2\text{SO}_4$  in the presence of  $\text{HgSO}_4$ .
12. Describe the relative stability of alkenes. Arrange the following alkenes in order of increasing stability, give reason for your answer.  
 (i)  $\text{CH}_2 = \text{CH}_2$  (ii)  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 - \text{C} = \text{CH} - \text{CH}_3 \end{array}$  (iii)  $\begin{array}{c} \text{CH}_3 \\ \diagup \\ \text{CH}_2 = \text{C} \\ \diagdown \\ \text{CH}_3 \end{array}$   
 (iv)  $\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{C} = \text{C} \\ \diagup \quad \diagdown \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$  (v)  $\text{CH}_3 - \text{CH} = \text{CH}_2$  (vi)  $\text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3$
13. Describe the general patterns of reactivity of alkenes.
14. How will you distinguish between 1-butyne and 2-butyne.

### SHORT QUESTIONS

1. What happens when propene is subjected to ozonolysis?  
**Ans:** A mixture of ethanal and methanal is formed.
- $$\text{CH}_3 - \text{CH} = \text{CH}_2 \xrightarrow[\text{(ii) Zn} + \text{H}_3\text{O}^+]{\text{(i) O}_3} \text{CH}_3\text{CHO} + \text{HCHO}$$
2. Give structural formulas for the reactants that form 2-butene when treated with the following reagents: (a) heating with conc.  $\text{H}_2\text{SO}_4$  (b) alcoholic  $\text{KOH}$  (c)  $\text{Zn}$  dust and alcohol (d) hydrogen and a catalyst.



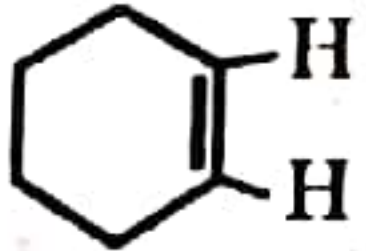
3. Why are dry gaseous hydrohalogen acids and not their aqueous solution used to prepare alkyl halide from alkenes?

**Ans.** Dry hydrogen halides are stronger acids and better electrophiles than the  $\text{H}_3\text{O}^+$  formed in their water solutions. Furthermore,  $\text{H}_2\text{O}$  is a nucleophile that can react with  $\text{R}^+$  to give an alcohol.

4. Arrange the following alkenes in order of increasing reactivity on addition of hydrohalogen acids. (a)  $\text{H}_2\text{C} = \text{CH}_2$  (b)  $(\text{CH}_3)_2\text{C} = \text{CH}_2$  (c)  $\text{CH}_3\text{CH} = \text{CHCH}_3$ .

**Ans.** The relative reactivities are directly related to the stabilities of the intermediate carbocation ( $\text{R}^+$ ). 2-methyl propene, (b) is more reactive because it forms the tertiary  $(\text{CH}_3)_2\overset{+}{\text{C}}\text{CH}_3$ . The next most reactive is 2-butene, (c) which forms the sec.  $\text{CH}_3\overset{+}{\text{C}}\text{HCH}_2\text{CH}_3$ . Ethylene forms the  $1^\circ \text{CH}_3\overset{+}{\text{C}}\text{H}_2$  and is least reactive. The order of increasing reactivity is:  $\text{H}_2\text{C} = \text{CH}_2 > \text{CH}_3\text{CH} = \text{CHCH}_3 > (\text{CH}_3)_2\text{C} = \text{CH}_2$ .

5. Give the products formed on hot permanganate cleavage of the following compounds:

(a)  $\text{H}_2\text{C} = \text{CH}_2$  (b)  $\text{CH}_3\text{CH} = \text{CHCH}(\text{CH}_3)_2$  (c)  $(\text{CH}_3)_2\text{C} = \text{C}(\text{C}_2\text{H}_5)_2$  (d) 

**Ans.** A terminal double carbon with 2 hydrogens forms  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ; a carbon with 1H of the double bond gives a carboxylic acid,  $\text{RCOOH}$ ; a carbon with no hydrogen of the double bond gives a ketone,  $\text{R}_2\text{C} = \text{O}$ .

(a)  $\text{H}_2\text{C} = \text{CH}_2$  gives  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

(b)  $\text{CH}_3\text{CH} = \text{CHCH}(\text{CH}_3)_2$  gives  $\text{CH}_3\text{COOH} + \text{HOOCCH}(\text{CH}_3)_2$

(c)  $(\text{CH}_3)_2\text{C} = \text{C}(\text{C}_2\text{H}_5)_2$  gives  $(\text{CH}_3)_2\text{C} = \text{O} + \text{O} = \text{C}(\text{C}_2\text{H}_5)_2$

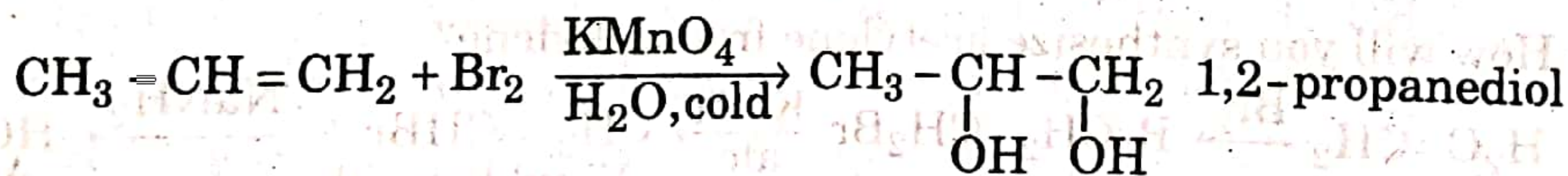
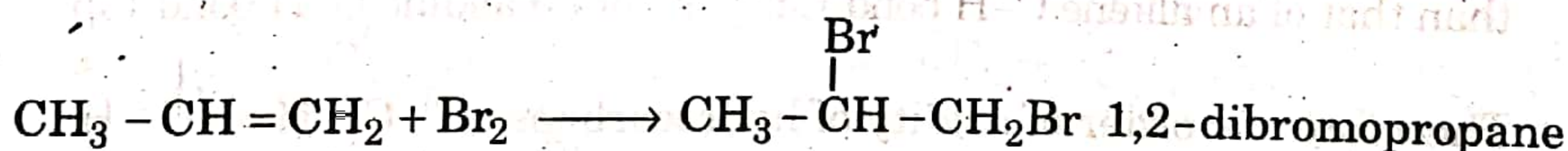
(d)  $\text{HOOC}(\text{CH}_2)_4\text{COOH}$

6. What happens when propene is treated with  $\text{HBr}$  in the presence of peroxide?

**Ans.** n-propyl bromide is formed:  $\text{CH}_3 - \text{CH} = \text{CH}_2 + \text{HBr} \xrightarrow{\text{H}_2\text{O}_2} \text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$

7. How will you distinguish between propene and propane?

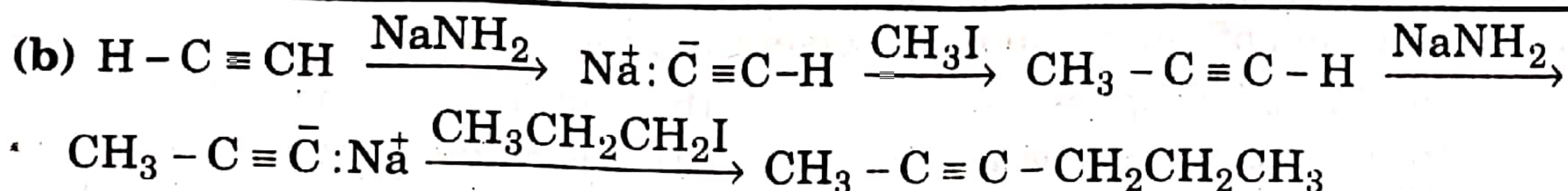
**Ans.** Both propene and propane are gases. Pass them through dilute cold  $\text{KMnO}_4$  solution (purple) or  $\text{Br}_2$  in  $\text{CCl}_4$  solution (red). Propene will decolourise both the solution; Propane does not react.



8. How will you synthesize 1-butyne from acetylene?

**Ans.**  $\text{HC} \equiv \text{CH} \xrightarrow{\text{NaNH}_2} \text{HC} \equiv \text{C}^- \text{Na}^+ \xrightarrow{\text{CH}_3\text{CH}_2\text{Br}} \text{HC} \equiv \text{CCH}_2\text{CH}_3$  1-butyne





### Multiple Choice Questions

- Which of the following is the major product of the reaction:  
 $\text{C}_6\text{H}_5\text{CH}=\text{CH}_2 \xrightarrow[\text{Br}_2/\text{CH}_3\text{OH}]{\text{dilute solution}} ?$ 

<p>(a) <math>\text{C}_6\text{H}_5-\overset{\text{OCH}_3}{\underset{ }{\text{C}}}\text{Br}-\text{CH}_2\text{Br}</math></p> <p>(c) <math>\text{C}_6\text{H}_5\text{CHBr}-\text{CH}_2\text{Br}</math></p>	<p>(b) <math>\text{C}_6\text{H}_5-\overset{\text{OCH}_3}{\underset{ }{\text{C}}}\text{H}-\text{CH}_2\text{Br}</math></p> <p>(d) <math>\text{C}_6\text{H}_5\text{CH}_2-\text{CHBr}_2</math>     <b>Ans: (b)</b></p>
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- Which of the addition reactions below will not proceed under ordinary conditions?
 

(a) $\text{CH}_2=\text{CH}_2 + \text{HCl} \longrightarrow$	(b) $\text{CH}_2=\text{CH}_2 + \text{HOSO}_3\text{H} \longrightarrow$
(c) $\text{CH}_2=\text{CH}_2 + \text{NaOH} \longrightarrow$	(d) $\text{CH}_2=\text{CH}_2 + \text{Br}_2 \longrightarrow$ <b>Ans: (c)</b>
- If an alkene gives 2-butanone and propanal when treated with  $\text{O}_3$  followed by Pd and  $\text{H}_2$ . What is the structure of alkene.
 

<p>(a) <math>\text{CH}_3\text{CH}_2-\overset{\text{CH}_3}{\underset{ }{\text{C}}}=\text{CHCH}_2\text{CH}_3</math></p> <p>(c) <math>\text{CH}_3-\text{CH}_2-\overset{\text{CH}_2}{\underset{  }{\text{C}}}-\text{CH}_2\text{CH}_3</math></p>	<p>(b) <math>\text{CH}_3\text{CH}_2\text{CH}=\overset{\text{CH}_3}{\underset{ }{\text{C}}}-\text{CH}-\text{CH}_3</math></p> <p>(d) <math>\text{CH}_3-\overset{\text{CH}_3}{\underset{ }{\text{C}}}=\text{CH}-\text{CH}_2\text{CH}_2\text{CH}_3</math>     <b>Ans: (a)</b></p>
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- Which of the following reacts with  $\text{H}_2$  and Ni to form propane?
 

(a) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	(b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$
(c) $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_3$	(d) $\text{CH}_3\text{CH}=\text{CH}_2$ <b>Ans: (d)</b>
- What is the major product when propene is treated with  $\text{KMnO}_4$ .
 

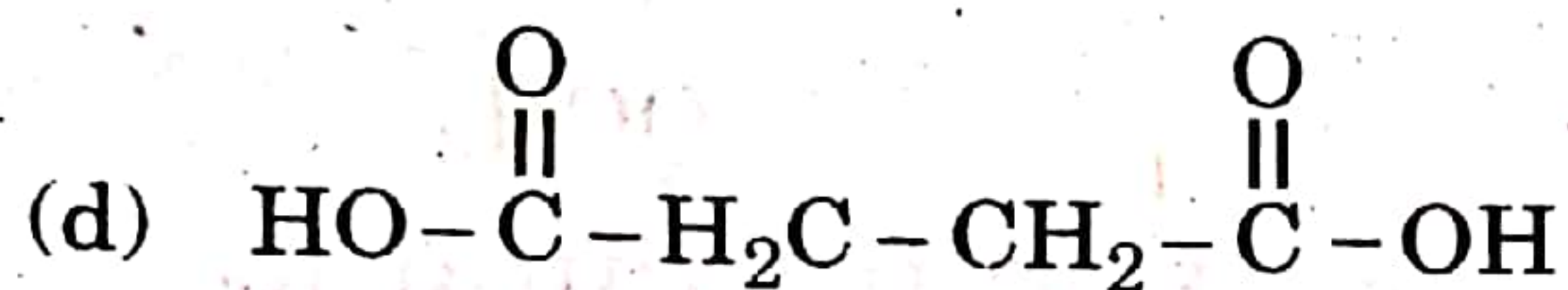
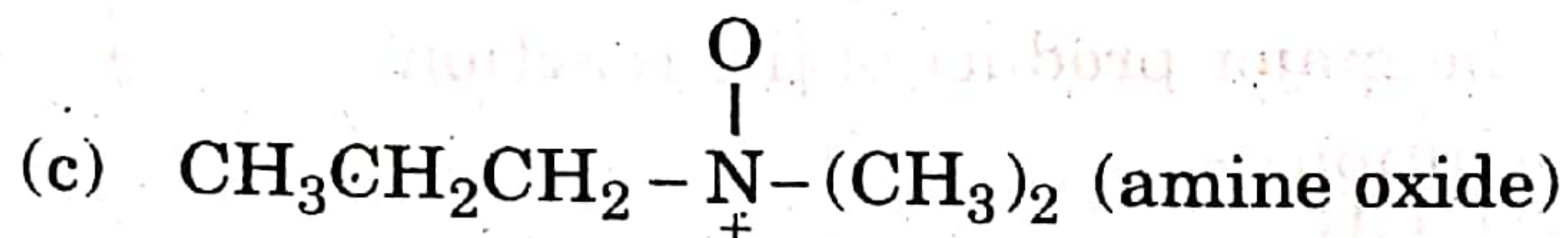
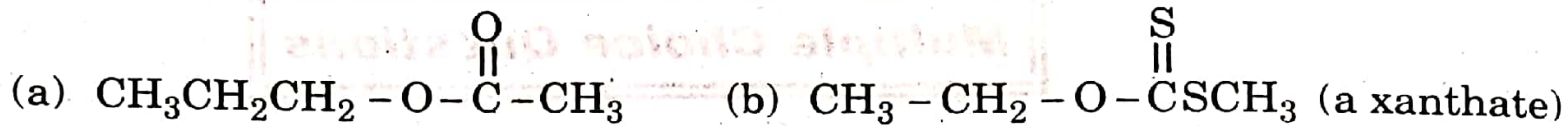
(a) 1,2-ethanediol	(b) 1,2-propanediol	(c) propanal	(d) propane-2-ol <b>Ans: (b)</b>
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- Which of the following alkenes has the greatest stability?
 

<p>(a) <math>\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad / \\ \text{C}=\text{C} \\ / \quad \diagdown \\ \text{CH}_3 \quad \text{CH}_3 \end{array}</math></p> <p>(c) <math>\text{CH}_3-\text{CH}=\text{CH}_2</math></p>	<p>(b) <math>\text{CH}_2=\overset{\text{CH}_3}{\underset{ }{\text{C}}}-\text{CH}_3</math></p> <p>(d) <math>\text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CH}_3</math>     <b>Ans: (a)</b></p>
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- Propene on treatment with diborane followed by oxidation with alkaline  $\text{H}_2\text{O}_2$  gives:
 

(a) 2-propanol	(b) 1-propanol	(c) propanal	(d) propanone <b>Ans: (b)</b>
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- Which of the following alkenes is the most stable?
 

(a) propene	(b) 1-butene	(c) cis-2-butene	(d) trans-2-butene <b>Ans: (d)</b>
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9. Addition of Br<sub>2</sub> in an inert solvent to propene gives:  
 (a) 3-bromopropene (b) 1-bromopropene  
 (c) 1,2-dibromopropane (d) 2-bromopropene **Ans: (c)**
10. Which of the following compounds does not undergo pyrolytic elimination to form alkene?

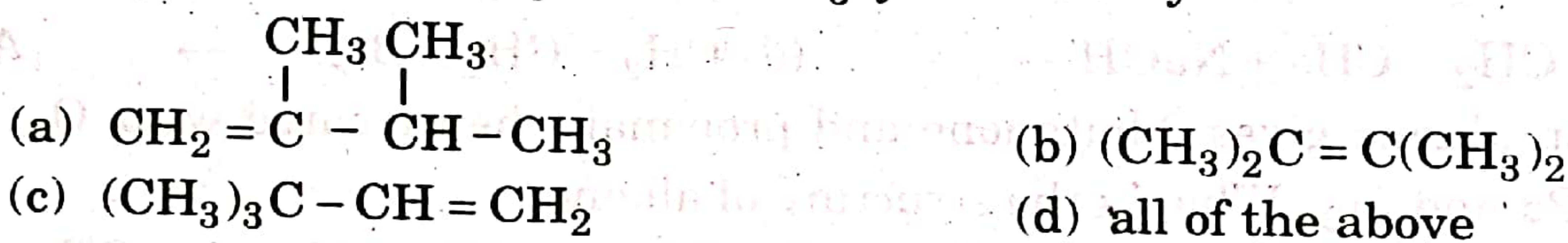
**Ans: (d)**

11. A reaction in which an aldehyde or ketone is treated with a phosphorus ylide to yield an alkene is called

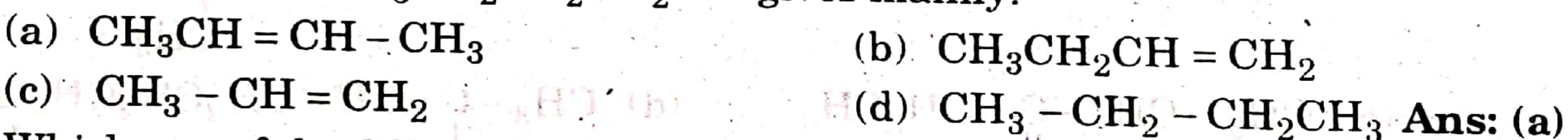
- (a) Wittig reaction (b) Hofmann reaction  
 (c) Chugaev reaction (d) Cope reaction

**Ans: (a)**

12. Dehydration of  $(\text{CH}_3)_3\text{CCHOHCH}_3$  yields mainly:

**Ans: (b)**

13. Dehydration of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$  gives mainly:

**Ans: (a)**

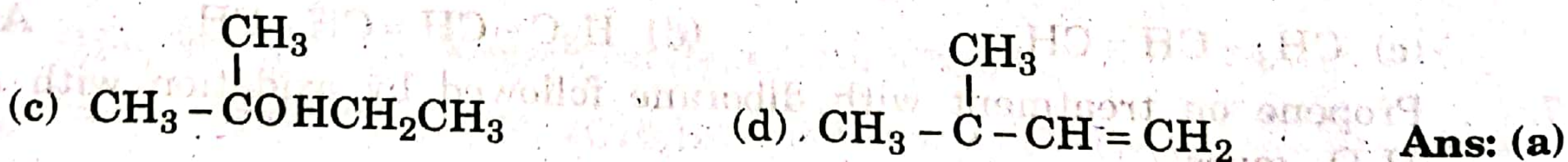
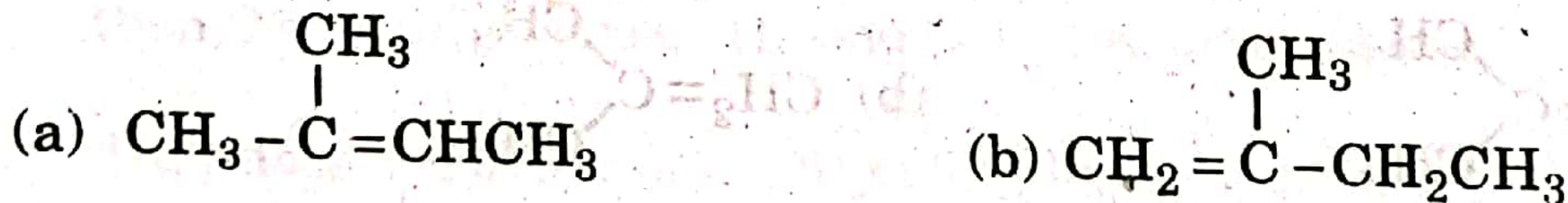
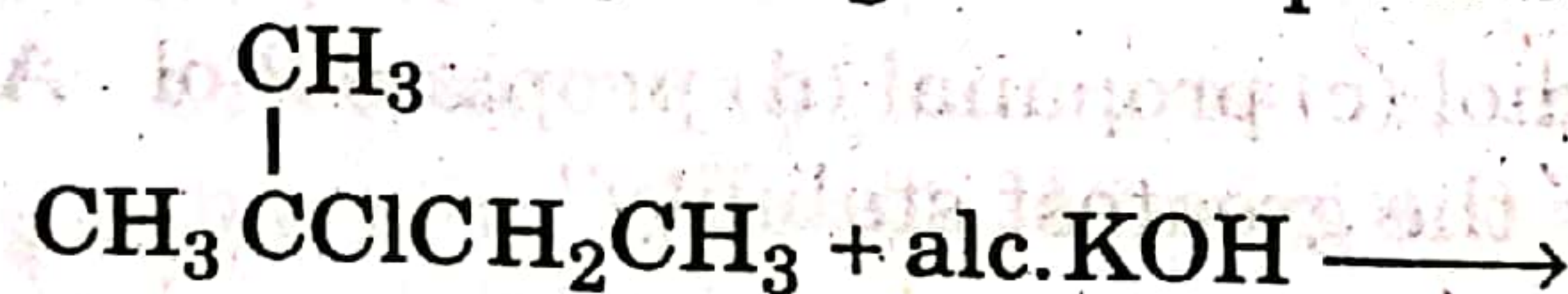
14. Which one of the following butenes is the most stable?

- (a) 1-butene (b) trans-2-butene (c) isobutylene (d) cis-2-butene **Ans: (c)**

15. Which of the following hydrogen halides on addition to unsymmetric alkenes will give anti-Markovnikov products in the presence of peroxides?

- (a) HF (b) HCl (c) HBr (d) HI **Ans: (c)**

16. Which principal organic compound is formed in the reaction:



17. Which one of the following is called Lindlar's catalyst?

- (a) Pd deposited on BaSO<sub>4</sub> poisoned by quinoline (b) Na/liq NH<sub>3</sub>  
 (c) Ni-Al alloy in NaOH (d) Na/H<sub>2</sub>O

**Ans: (a)**

18. Which one of the following will form white ppt. with ammonical solution of  $\text{AgNO}_3$ ?  
 (a) 2-butyne (b) propene (c) 1-butyne (d) ethene **Ans: (c)**
19. Which of the following will form red ppt. with ammonical  $\text{Cu}_2\text{Cl}_2$  solution?  
 (a) Ethyne (b) propyne (c) 1-butyne (d) all of the given **Ans: (d)**
20. Propyne on treatment with  $\text{H}_2\text{O}$  in the presence of  $\text{HgSO}_4$  and  $\text{H}_2\text{SO}_4$  yields.  
 (a) propanol (b) propanone  
 (c) Ethanal (d) propanal and propanone **Ans: (b)**
21. The reaction of  $\text{O}_3$  with propyne followed by hydrolysis with water gives.  
 (a) acetic acid (b) acetic acid and formic acid  
 (c) formic acid (d) acetic acid and  $\text{CO}_2$  **Ans: (b)**
22. The oxidation of  $\text{CH}_3\text{C}\equiv\text{CCH}_2\text{CH}_3$  with alkaline  $\text{KMnO}_4$  followed by hydrolysis with  $\text{H}_3\text{O}^+$  gives.  
 (a)  $\text{CH}_3\text{COOH} + \text{CH}_3\text{CH}_2\text{COOH}$  (b)  $\text{CH}_3\text{CH}_2\text{COOH} + \text{CO}_2$   
 (c)  $\text{CH}_3\text{CH}_2\text{COOH} + \text{HCOOH}$  (d)  $\text{CH}_3\text{COOH}$  **Ans: (a)**
23. How many acidic hydrogen atom does contain 2-butyne?  
 (a) zero (b) six (c) three (d) two **Ans: (a)**
24. The reaction of borane with propyne followed by oxidation with alkaline  $\text{H}_2\text{O}_2$  yields:  
 (a) propanone (b) propanol (c) propanal (d) all of the given **Ans: (c)**
25. Addition of  $\text{HCl}$  to acetylene in the presence of  $\text{HgCl}_2$  produces:  
 (a) 1,1-dichloroethane (b) 1,2-dichloroethane  
 (c) polyvinyl chloride (d) ethylene chloride **Ans: (c)**
26. Which of the following statements is not true for a carbocation?  
 (a) A carbocation may combine with a negative ion.  
 (b) Rearrange to form a more stable carbocation  
 (c) Eliminate a hydrogen ion to form an alkene.  
 (d) Not remove a hydride ion from an alkane **Ans: (d)**
27.  $\text{CH}_2 = \text{CH}_2 + \text{CH}_3\text{CH} = \text{CH}_2 \xrightarrow{\Delta} \text{X}$ ; the product X in the reaction is:  
 (a) methylcyclobutane (b) 1-pentene  
 (c) pentane (d) no reaction occurs **Ans: (d)**
28. Which of the following is not a free radical process?  
 (a) Cracking of alkanes (b)  $\text{Alkene} + \text{Br}_2 \longrightarrow \text{dibromoalkane}$   
 (c) Photochemical isomerization of alkenes  
 (d) High temperature polymerization of ethylene **Ans: (b)**
29. A reaction in which an acid is added to a carbon-carbon double bond of an alkene and the hydrogen of the acid attaches itself to the carbon holding the

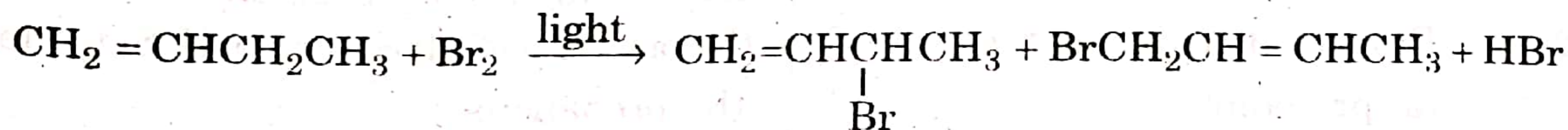


greater number of hydrogens. The phenomenon is referred to as:

- (a) the Saytzeff's rule (b) Markovnikov's rule  
 (c) electrophilic addition to C-C double bond involving a carbocation.  
 (d) Both choices b and c are correct.

Ans: (d)

30. What kind of reactive intermediate is formed in the reaction:



- (a) Carbocation (b) Carbanion (c) Bromide ion (d) Free radical

Ans: (d)

31. Addition of HBr to propene in the presence of peroxide gives:

- (a) Markovnikov's product (b) 2-bromopropane  
 (c) Anti-Markovnikov's product (d) 1,2-dibromopropane

Ans: (c)

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