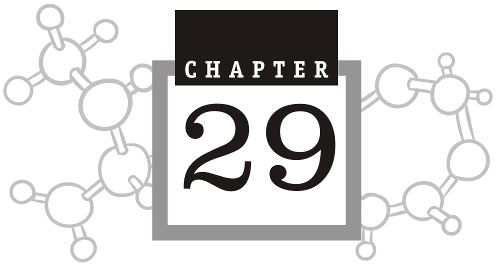


CHAPTER 29

Alkene

◎ Introduction

Unsaturated hydrocarbons are hydrocarbons that contain one or more carbon carbon double or triple bonds. There are three classes of unsaturated hydrocarbons : alkenes, alkynes and aromatic hydrocarbons.

Alkenes are the unsaturated hydrocarbons that contain one double bond. They have the general formula C_nH_{2n}, and the double bond is known as the 'olefinic bond' or 'ethylenic bond' (*i.e.* oleum, oil + fines, forming) because lower alkene react with halogens to form oily substances.

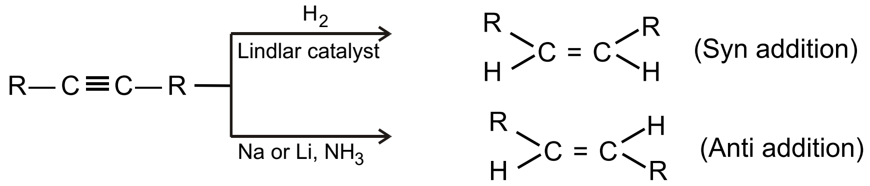
◎ PHYSICAL PROPERTIES

At room temperature alkenes differs in their physical state depending upon the number of carbon atom.

C_2 — C_4	:	Gases
C_5 — C_{17}	:	Liquids
C_{18}— Onwards	:	Solids

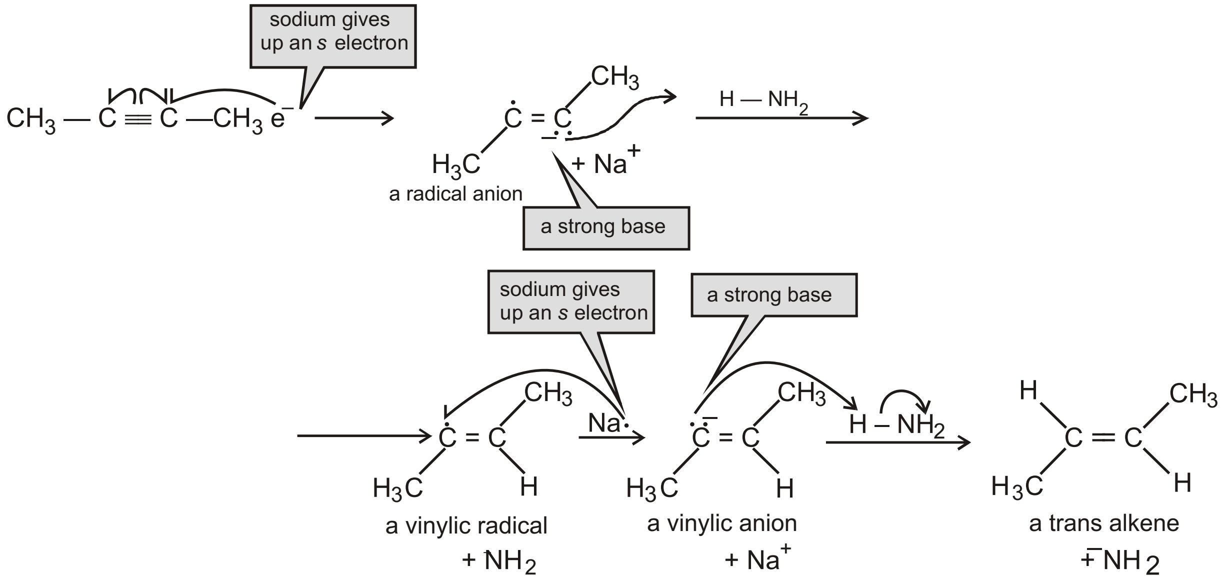
◎ Methods of Preparation of Alkenes

1. Reduction of Alkynes



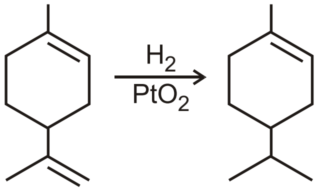
Metallic palladium deposited conditioned with lead acetate and quinoline is *Lindlar's catalyst*. It reduces alkynes to cis alkenes whereas trans alkenes are obtained predominantly by reduction with sodium or lithium in liquid ammonia.

MECHANISM FOR THE CONVERSION OF AN ALKYNE TO A TRANS ALKENE

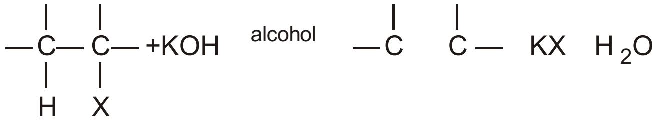


An arrowhead with a double barb signifies the movement of two electrons.

In polyenes that contain differently substituted C C double bonds, it is often possible to hydrogenate chemoselectively the least hindered C C double bond or unstable double bond:



2. Dehydrohalogenation of Alkyl Halides



$$-\underset{\substack{|\\H}}{\overset{|}{C}}-\underset{\substack{|\\X}}{\overset{|}{C}}-+KOH \quad \overset{\text{alcohol}}{} \quad -\overset{|}{C}\quad \overset{|}{C}-\quad KX\quad H_2O$$

Dehydrohalogenation belongs to a general class of reactions called 1,2 - elimination reactions.

Such elimination reactions are characterised by the following:

(a) The substrate should contain a leaving group (an atom or group that leaves the molecule, taking its electron pair with it).

(b) The substrate should have an atom or a group in a position beta to leaving group (nearly always hydrogen) that can be extracted by a base, leaving its electron pair behind.

(c) The reaction is brought about by a base. It can be a basic anion like hydroxide or an alkoxide derived from alcohol like ethoxide, $C_2H_5O^-$ and tert-butoxide, $(CH_3)_3CO$.

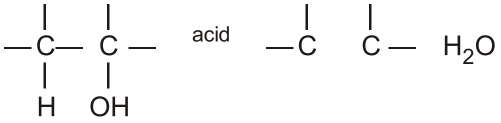
3. Dehydration of Alcohols

Alcohols form alkenes on dehydration by

(a) reaction with conc. H_2SO_4 at 100 C

(b) reaction with phosphoric acid at 200 C

(c) passing alcohol vapour over a lumina (Al_2O_3), P_2O_5 or anhydrous $ZnCl_2$ at 350 — 400 C H_2O



$$-\underset{H}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}- \quad \text{acid} \quad -\overset{|}{C}\quad\overset{|}{C}- \quad H_2O$$

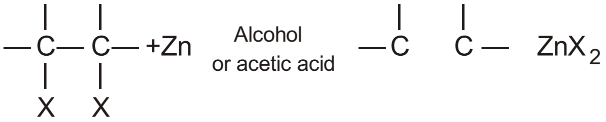
Note : *The carbo-cation intermediate may undergo rearrangement (if possible) before forming an alkene*.

Reactivity of Alcohols in Dehydration

3° alcohol > 2° alcohol > 1° alcohol

Experimental conditions like temperature and acid concentration are harshest for primary alcohols and extremely mild for tertiary alcohols.

4. **Dehalogenation of Vicinal Dihalides**

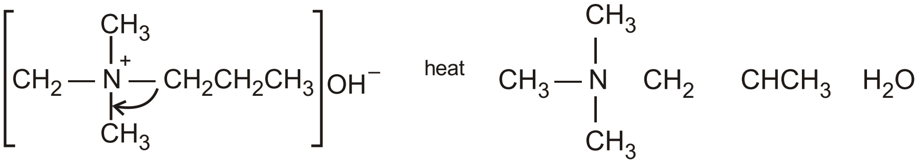


$$-\underset{X}{\overset{|}{\underset{|}{C}}}-\underset{X}{\overset{|}{\underset{|}{C}}}-+Zn \quad \begin{array}{c}\text{Alcohol}\\\text{or acetic acid}\end{array} \quad -\overset{|}{C}\quad\overset{|}{C}- \quad ZnX_2$$

Vicinal dihalides are compounds having two halide atoms on adjacent carbon atoms. Compounds having two halide atoms on same carbon atom are called geminal (or gem) dihalides.

5. **Hoffmann's Elimination of Quaternary Ammonium Hydroxides**

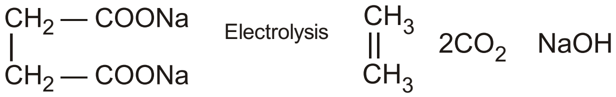
A compound having the structure R_4N+ OH– is called a quaternary ammonium hydroxide (the four alkyl groups attached to nitrogen may be same or different). When a quaternary ammonium hydroxide is heated strongly (to 125°C or higher), it decomposes to yield water, a tertiary amine, and an alkene. For example,



$$\left[CH_2-\underset{CH_3}{\overset{CH_3}{\overset{+}{N}}}-CH_2CH_2CH_3\right]OH^- \quad \text{heat} \quad CH_3-\underset{CH_3}{\overset{CH_3}{N}} \quad CH_2 \quad CHCH_3 \quad H_2O$$

Trimethyl-*n*-propylammonium hydroxide

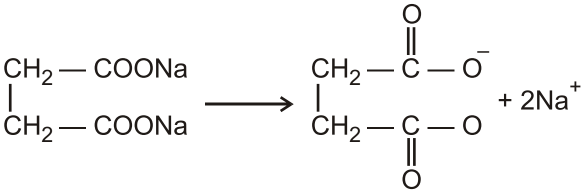
6. **Kolbe's Electrolytic Decarboxylation:** Electrolysis of aqueous solutions of sodium salts of vicinal dicarboxylic acids leads to the decarboxylation of the compound leading to the formation of alkenes.



$$\begin{array}{l}CH_2-COONa\\|\\CH_2-COONa\end{array} \quad \text{Electrolysis} \quad \begin{array}{c}CH_3\\||\\CH_3\end{array} \quad 2CO_2 \quad NaOH$$

Sod. Succinate

Mechanism

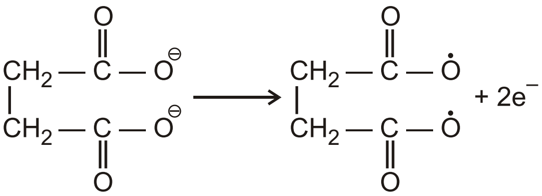


$$\begin{array}{l}CH_2-COONa\\|\\CH_2-COONa\end{array}\longrightarrow\begin{array}{l}CH_2-\overset{\overset{O}{||}}{C}-O^-\\|\\CH_2-\underset{\underset{O}{||}}{C}-O\end{array}+2Na^+$$

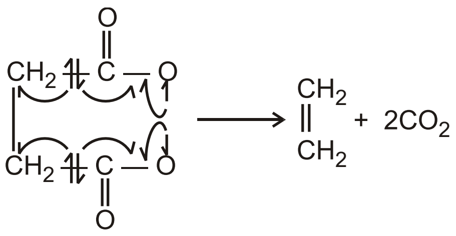
At Cathode $H_2O \quad H \quad OH$

$2H \quad 2e \quad H_2$

At Anode

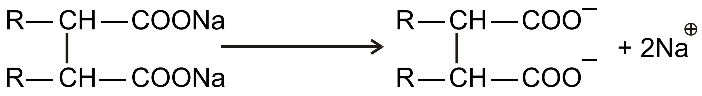


$$\begin{array}{l}CH_2-\overset{\overset{O}{||}}{C}-O^{\ominus}\\|\\CH_2-\underset{\underset{O}{||}}{C}-O^{\ominus}\end{array}\longrightarrow\begin{array}{l}CH_2-\overset{\overset{O}{||}}{C}-\dot{O}\\|\\CH_2-\underset{\underset{O}{||}}{C}-\dot{O}\end{array}+2e^-$$



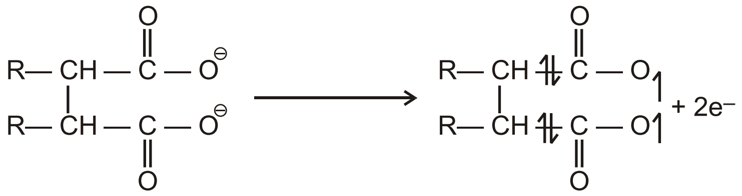
The solution hence contains Na and OH there by becoming more and more basic. Here no other side product is formed because the elimination of CO_2 takes place without the formation of new free Radical.

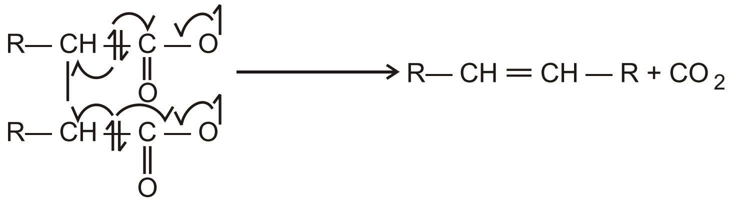
Solved Example



$$H_2O \longrightarrow H^+ + OH^{\oplus}$$

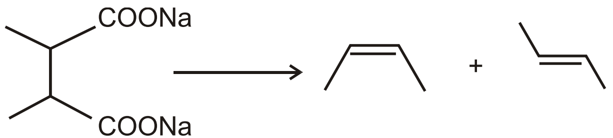
At Anode



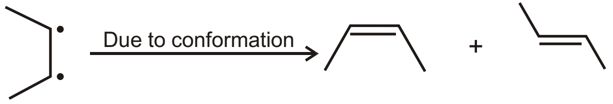


(i) PhCOONa Ph– Ph

(ii)



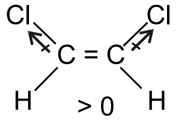
Hint:

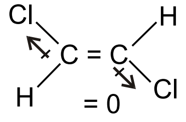


Structure And Physical Properties

1. **Physical Properties**
   - (a) Alkenes containing two to four carbon atoms are gases, those containing five to seventeen are liquids and higher alkenes are solids
   - (b) These are insoluble in water but soluble in organic Solvents.
   - (c) The boiling points of cis alkenes are higher where as melting points of trans-alkenes are more.

e.g.





As Cis isomers being more polar, boils at a higher temperature, where as trans isomers being more symmetrical fits well into the crystal lattice and have higher melting point.

2. **Structure**

   (a) The characteristic feature of the alkene structure, is the carbon carbon double bond. It is thus the functional group of alkenes and as the functional group, it determines the characteristic reactions that alkenes undergo.

   These reactions are of two kinds.

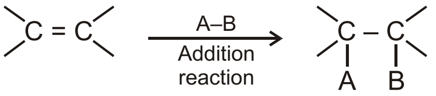
   (b) First, there are those that take place at the double bond itself and, in doing this, destroy the double bond.

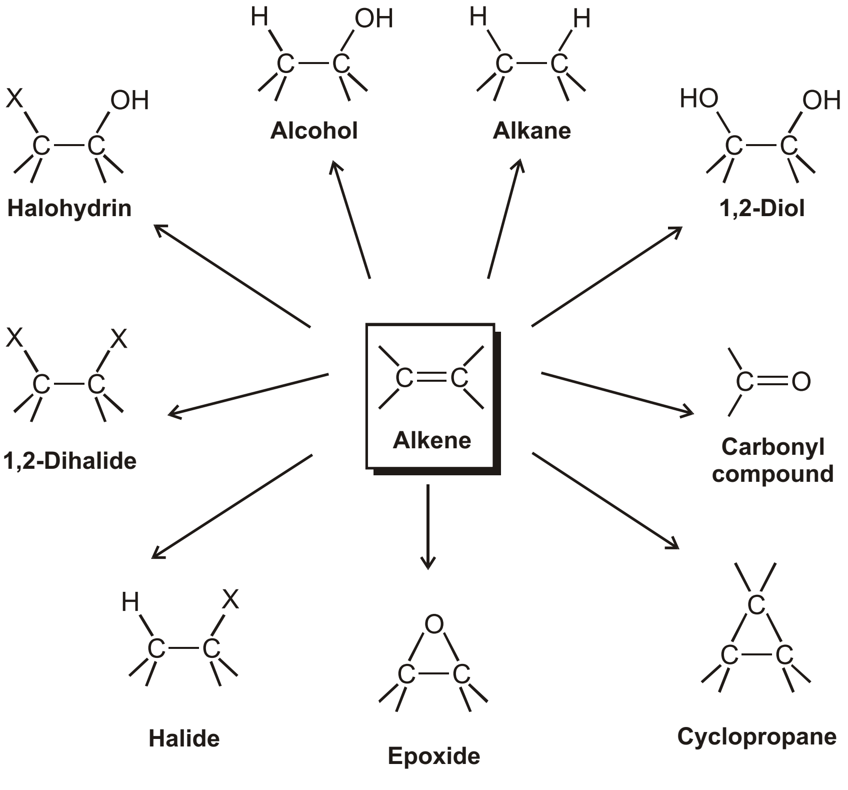
   (c) There are the reactions that take place, not at the double bond, but at certain positions having special relationships to the double bond. Outwardly the double bond is not involved; it is found intact in the product. Yet it plays an essential, though hidden, role in the reaction : it determines how fast reactions take place and by which mechanism or whether it takes place at all.

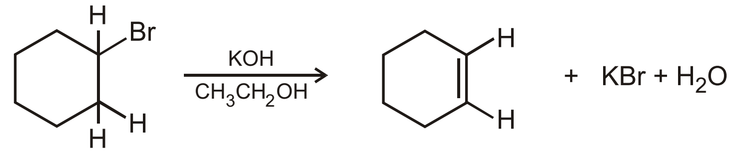
◎ CHEMICAL PROPERTIES

Alkene addition reactions occur widely, both in the laboratory and in living organisms. Although we've studied only the addition of HX thus far, many closely related reactions also take place. In this chapter, we'll see briefly how alkenes are prepared and we'll discuss further examples of alkene addition reactions. Particularly important are the addition of a halogen to give a 1,2-dihalide, addition of a hypohalous acid to give a halohydrin, addition of water to give an alcohol, addition of hydrogen to give an alkane, addition of a single oxygen to give a three-membered cyclic ether called an epoxide, and addition of two hydroxyl groups to give a 1,2-diol.

General reaction of alkene :







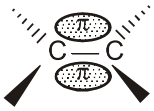
Bromocyclohexane Cyclohexene (81%)

Addition Reactions :

Reactions at the carbon–carbon double bond. : The double bond consists of a strong bond and a weak bond; we expect, therefore, that reaction would involve breaking of this weaker bond. This expectation is correct; the typical reactions of the double bond are of the sort where the bond is broken and two strong bonds are formed in its place.

$$-\overset{|}{C}\quad\overset{|}{C}- \qquad EZ \qquad -\underset{\underset{E}{|}}{\overset{|}{C}}-\underset{\underset{Z}{|}}{\overset{|}{C}}-$$

A reaction in which two molecules combine to yield a single molecule or product is called an addition reaction. The reagent is simply added to the substrate. Addition reactions are necessarily limited to compounds that contain atoms sharing more than one pair of electrons, that is, to compounds that contain multiple bonded atoms. Formally, addition is the opposite of elimination; just as elimination generates a multiple bond, addition destroys it.



In the structure of the bond there is a cloud of electrons above and below the plane of the atoms. These electrons are less involved than the electrons in holding together the carbon nuclei.

As a result, they are themselves held less tightly. These loosely held electrons are particularly available to a reagent that is seeking electrons. It is not surprising, then, that in many of its reactions the carbon–carbon double bond serves as a source of electrons : that is, it acts as a base. The compounds with which it reacts are those that are deficient in electrons, that is, are acids. These acidic reagents that are seeking a pair of electrons are called electrophilic reagents. The typical reaction of an alkene is electrophilic addition, or, in other words, addition of acidic reagents.

Reagents of another kind *i.e.*, free radicals also seek electrons–or, rather, seek an electron. And so we find that alkenes also undergo free-radical addition.

Electrophilic Addition Reaction – Mechanism

Addition of the acidic reagent, HZ, involves two steps : (Z may be — Cl, — Br, — I, — CN, — OH, — OSO_3H etc.)

Step (1) the first step involves the addition of H leading to the formation of carbocation.

Step (2) is the combining of the carbocation with the base : Z.

The evidence for this mechanism includes.

(a) The rate of reaction depends upon the concentration of both the alkene and the reagent HZ.

(b) Where the structure permits, reaction is accompanied by rearrangements. In addition, the mechanism is consistent with structures :

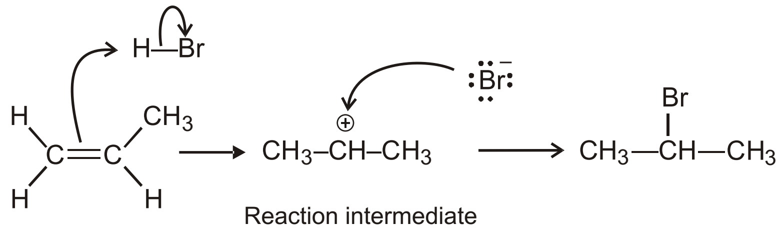
(c) The orientation of addition; and

(d) The relative reactivities of alkenes.

1. **Hydrohalogenation (addition of H–X) :**

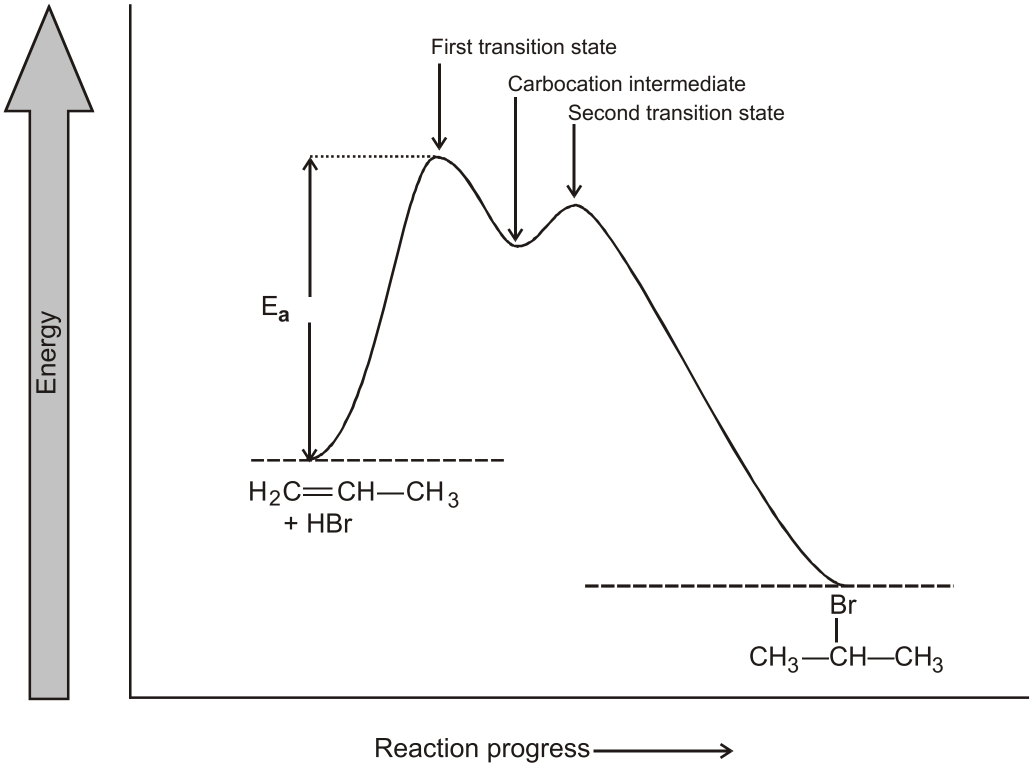
Describing a Reaction: Intermediates :

How can we describe the carbocation formed in the first step of the reaction of ethylene with HBr? The carbocation is clearly different from the reactants, yet it isn't a transition state and it isn't a final product.



We call the carbocation, which exists only transiently during the course of the multistep reaction, a **reaction intermediate**. As soon as the intermediate is formed in the first step by reaction of ethylene with H , it reacts further with Br in a second step to give the final product, bromoethane. We can picture the second transition state as an activated complex between the electrophilic carbocation intermediate and the nucleophilic bromide anion, in which Br donates a pair of electrons to the positively charged carbon atom as the new C–Br bond just starts to form.

A complete energy diagram for the overall reaction of ethylene with HBr is shown. In essence, we draw a diagram for each of the individual steps and then join them so that the carbocation product of step 1 is the reactant for step 2. As indicated, the reaction intermediate lies at an energy minimum between steps. Because the energy level of the intermediate is higher than the level of either the reactant that formed it or the product it yields, the intermediate can't normally be isolated. It is, however, more stable than the two transition states that neighbour it.

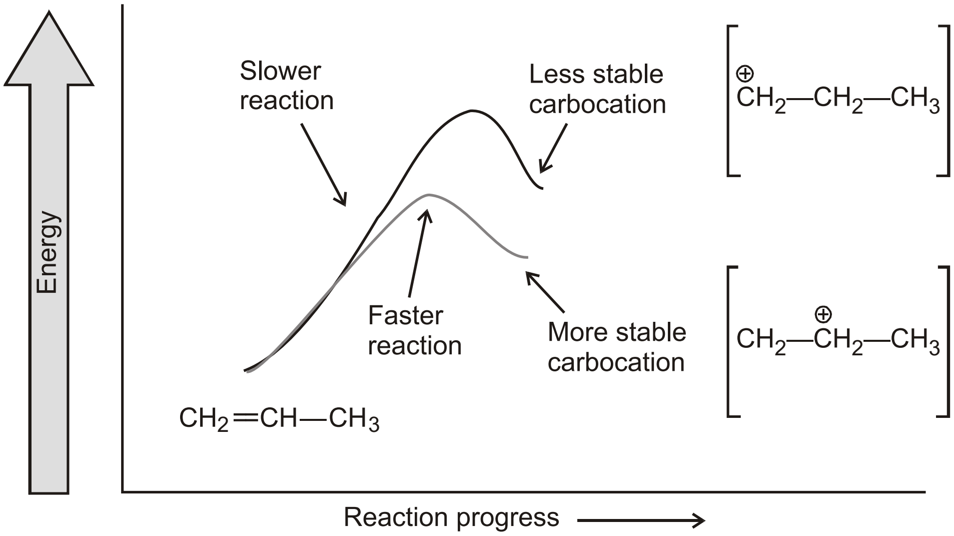


An energy diagram for the reaction of propylene with HBr.

Hammond postulate

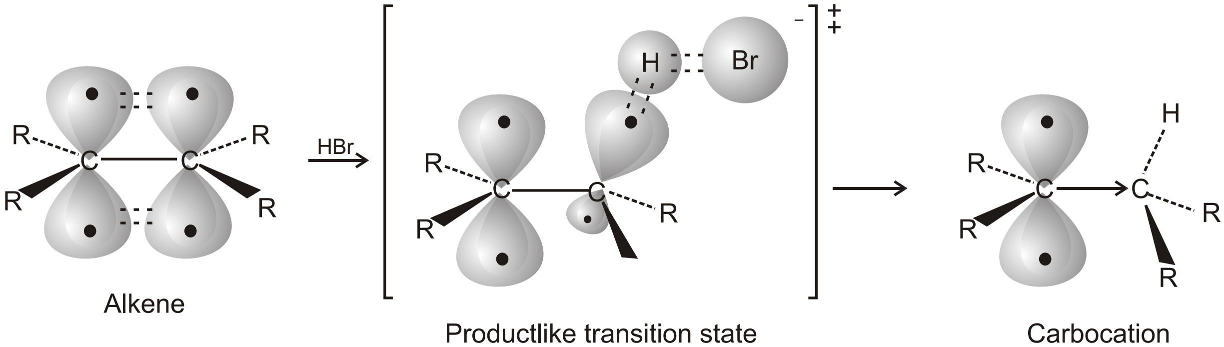
The structure of a transition state resembles the structure of the nearest stable species. Transition states for endergonic steps structurally resemble products, and transition states for exergonic steps structurally resemble reactants.

How does the Hammond postulate apply to electrophilic addition reactions? The formation of a carbocation by protonation of an alkene is an endergonic step. Thus, the transition state for alkene protonation structurally resembles the carbocation intermediate, and any factor that stabilizes the carbocation will also stabilize the nearby transition state. Since increasing alkyl substitution stabilizes carbocations, it also stabilizes the transition states leading to those ions, thus resulting in a faster reaction. More stable carbocations form faster because their greater stability is reflected in the lower-energy transition state leading to them



Energy diagrams for carbocation formation.

The more stable tertiary carbocation is formed faster because its increased stability lowers the energy of the transition state leading to it.



Alkene

Productlike transition state

Carbocation

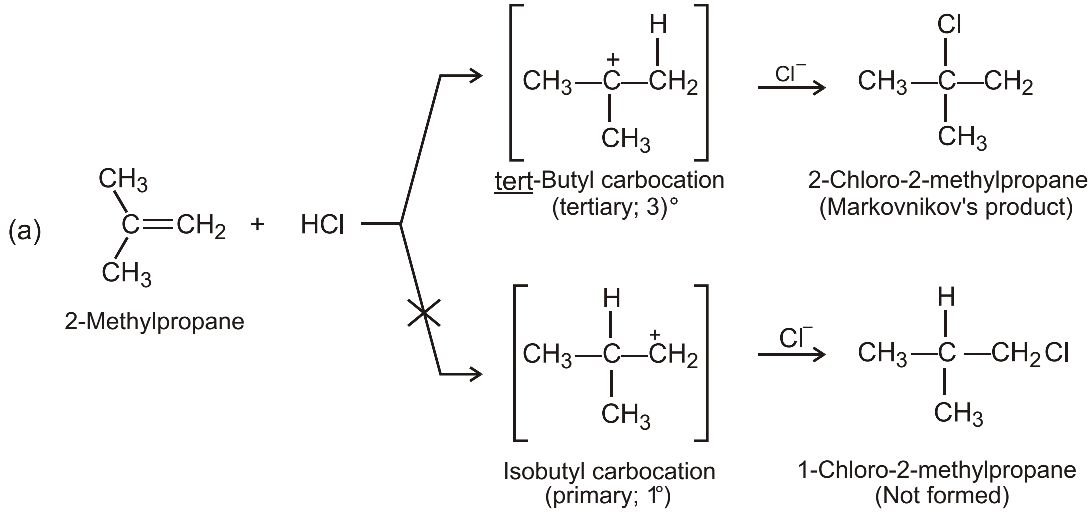
The hypothetical structure of a transition state for alkene protonation. The transition state is closer in both energy and structure to the carbocation than to the alkene. Thus, an increase in carbocation stability also causes an increase in transition-state stability, thereby increasing the rate of its formation.

Markovnikov's Rule and Regioselectivity :

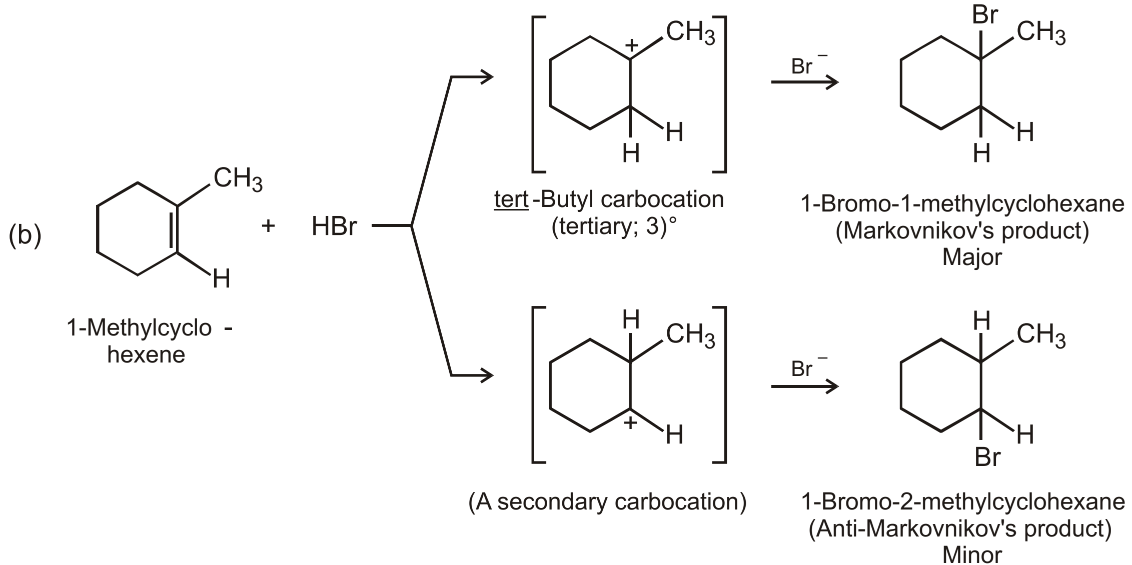
Markovnikov's rule is applicable on unsymmetric alkenes and alkynes. According to it, in electrophilic addition reactions, H+(an electrophile) attacks on least substituted carbon or the carbon having more number of hydrogens present. Product obtained in accordance with above rule, is called Markovnikov product.

A reaction in which two or more constitutional isomers could be obtained as products, but one of them predominates, is called a **regioselective reaction.**

There are degrees of **regioselectivity** : a reaction can be moderately regioselective, highly regioselective, or completely regioselective. For example,

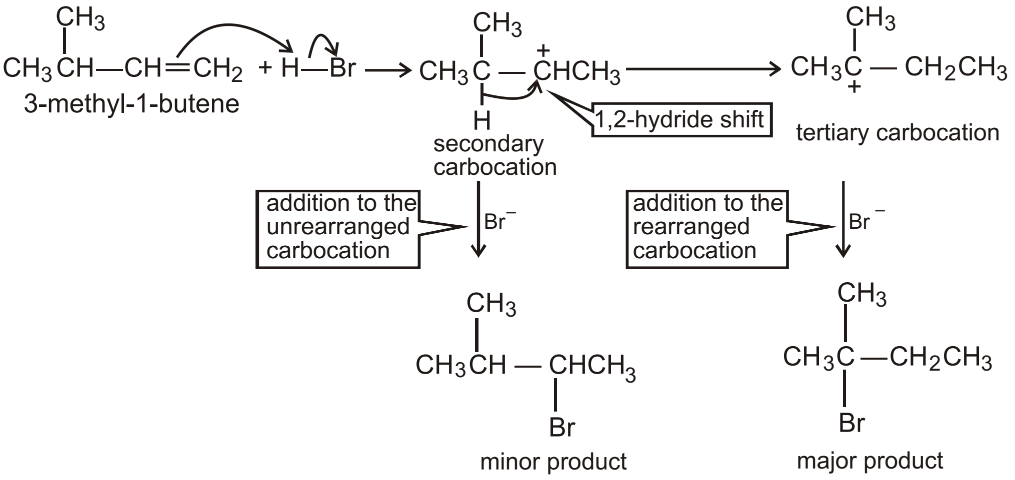


This is highly regioselective reaction.



This is moderately regioselective reaction.

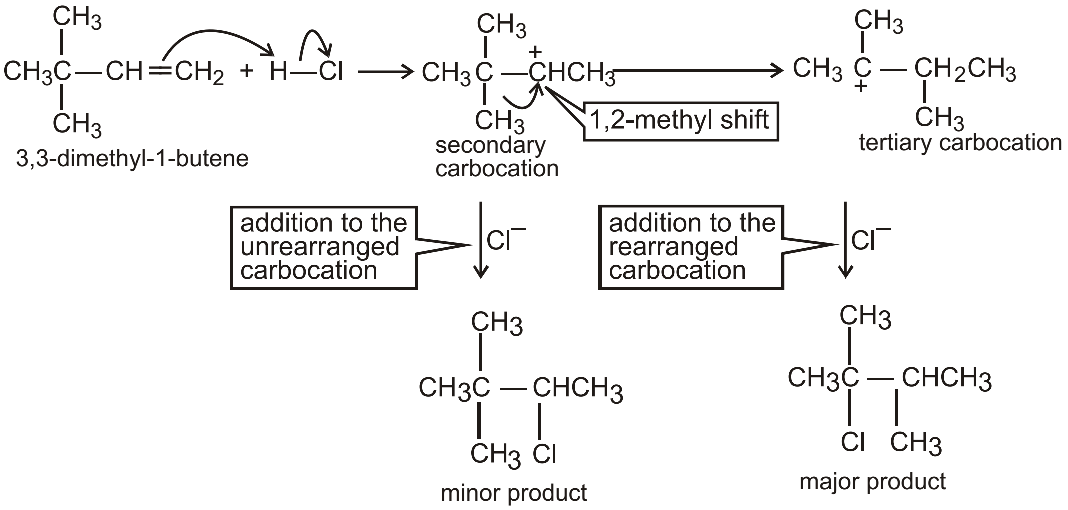
Rearrangement in electrophilic addition reactions :



Because a hydrogen shifts with its pair of electrons, the rearrangement is called a hydride shift. (Recall that - is a hydride ion.) More specifically, it is called a **1,2- hydride shift** because the hydride ion moves from one carbon to an adjacent carbon.

As a result of the **carbocation rearrangement**, two alkyl halides are formed, one from adding the nucleophile to the unrearranged carbocation and one from adding the nucleophile to the rearranged carbocation. The major product results from adding the nucleophile to the rearranged carbocation.

In the second reaction, again a secondary carbocation is formed initially. Then one of the methyl groups, with its pair of electrons, shifts to the adjacent positively charged carbon to form a more stable tertiary carbocation. This kind of rearrangement is called a **1,2-methyl shift** —the methyl group moves with its electrons from one carbon to an adjacent carbon. Again, the major product is the one formed by adding the nucleophile to the rearranged carbocation.



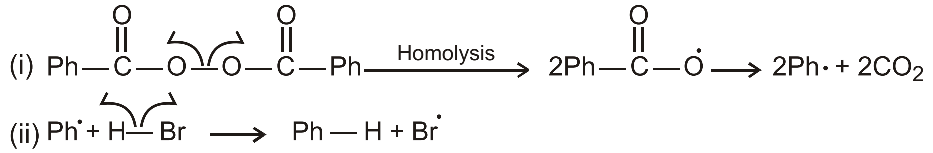
◎ Peroxide Effect or Kharash effect or Anti Markownikov's rule

In presence of peroxide Anti Markownikov's addition takes place

$$CH_3-CH\quad CH_2\ \overset{HBr}{\underset{Peroxide}{\quad}}\ CH_3CH_2-CH_2-Br$$

Mechanism: Peroxide effect proceeds via free radical mechanism as given below.

Initiation

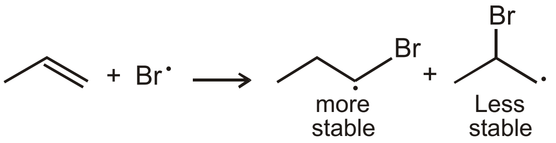


$$\text{(i) } Ph-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-Ph \xrightarrow{\text{Homolysis}} 2Ph-\overset{O}{\overset{\|}{C}}-\dot{O} \longrightarrow 2Ph\cdot + 2CO_2$$

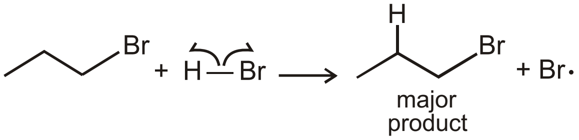
$$\text{(ii) } Ph^{\cdot} + H-Br \longrightarrow Ph-H + Br^{\cdot}$$

Propagation :

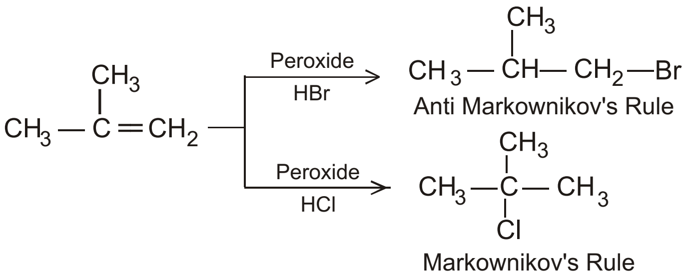
(i)



(ii)



SPECIAL PROBLEM



Peroxide effect is not observed in addition of HCl, HI, HF. This may be due to the fact that both. Propagation step must be exothermic for continuous chain reaction which is only observed by HBr not by HF, HCl, HI.

1. Consider the reaction of an alkene with HBr:

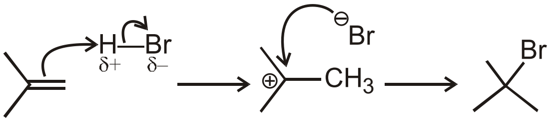
(a) Write the mechanism for the reaction.

(b) Why do the bond electrons attack the hydrogen end of HBr ?

(c) Briefly explain why the addition of HBr gives the product shown instead of the primary alkyl halide.

Sol.

(a)



(b) The hydrogen was attacked because it is less electronegative than bromine and bears the in the HBr bond (Vacant anti-bonding of H–Br).

(c) In looking at the mechanism in 3a, we can see that the formation of the carbocation is the first step. The formation of a more stable carbocation has a lower energy of activation (E_{act}). A tertiary carbocation is much more stable than an isomeric primary carbocation, so the E_{act} for the formation of the tertiary carbocation is lower than the Eact for the formation of the primary carbocation.

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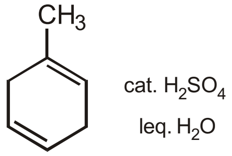
2. Consider the reaction of a nonoconjugated diene with aqueous sulfuric acid :



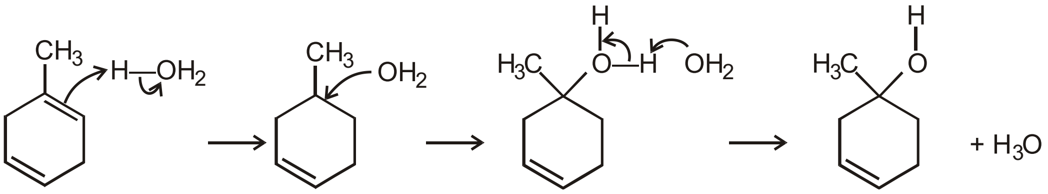
(a) Show the major product for the following reaction and provide a detailed mechanism for the reaction.

(b) Show the product if a second equivalent of H_2O is added.

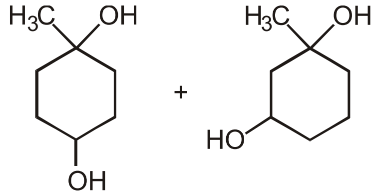
(c) What happens if no acid catalyst is added ?

Sol.

(a)



(b)

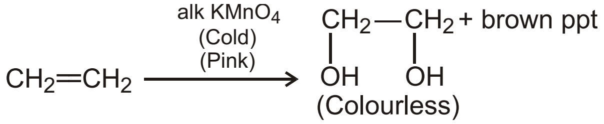


(c) Water by itself is a poor electrophile, as the magnitude of charge on the hydrogen atoms is not great enough for the reaction to proceed. Protonation of the water oxygen makes this oxygen atom more electron poor, thus amplifying the magnitude of the on hydrogen. Hydronium ion is sufficiently electrophilic to undergo the energetically expensive reaction with the alkene p bond to form a carbocation. In the absence of acid catalyst, the reaction does not proceed at a useful rate.

---

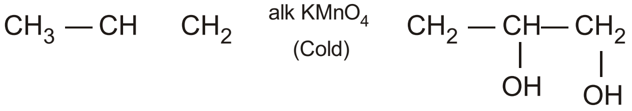
2. **Hydroxylation :**

 (i) With Bayers Reagent : When an alkene is reacted with dilute alkaline $KMnO_4$ solution in cold condition then the alkene is converted to vicinal dihydroxy compound.



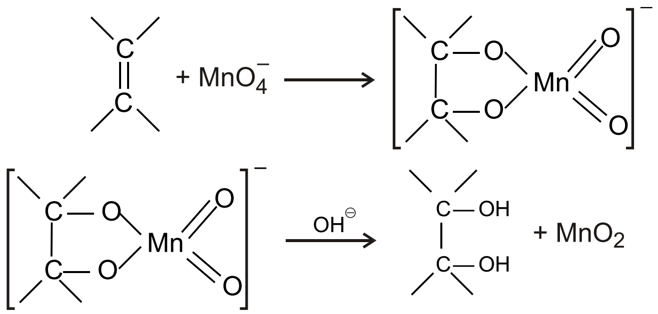
$$CH_2{=}CH_2 \xrightarrow[\text{(Pink)}]{\text{alk KMnO}_4\ \text{(Cold)}} \underset{OH}{CH_2}-\underset{OH}{CH_2} + \text{brown ppt}$$

(Colourless)



$$CH_3-CH\quad CH_2 \quad \underset{\text{(Cold)}}{\overset{\text{alk KMnO}_4}{}} \quad CH_2-\underset{OH}{CH}-\underset{OH}{CH_2}$$

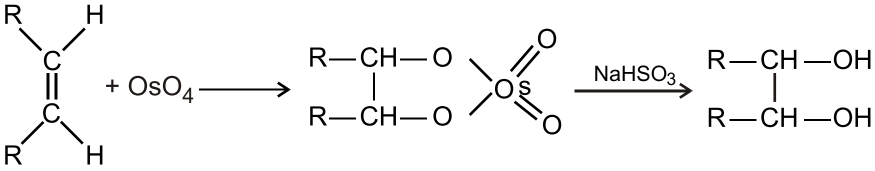
Mechanism



This reaction which gives rise to vicinal diols and is a SYN–ADDITION reaction.

This is supported by the mechanism that the oxygen atoms of OH group in the diol formed are from the permanganate ions which add to the alkene molecule from the same side.

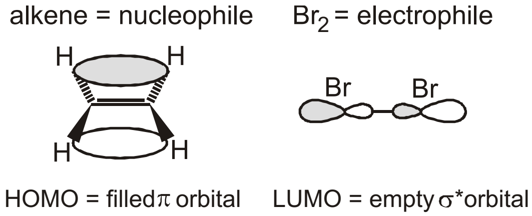
(ii) With OsO_4 (Osmium tetraoxide)



This is again a SYN–ADDITION reaction

3. **Halogenation :**

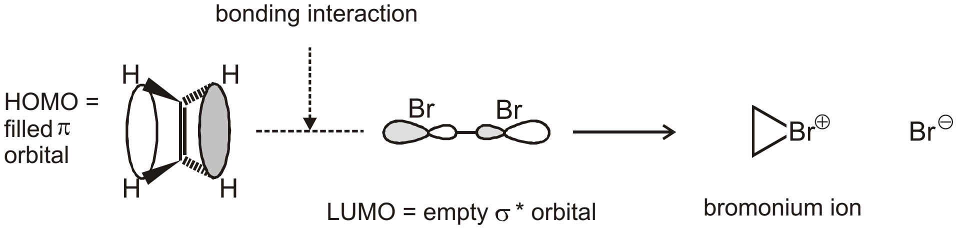
When it reacts with Br_2, the alkene's filled orbital (the HOMO)



will interact with the bromine's empty * orbital to give a product. But what will that product be? Look at the orbitals involved.

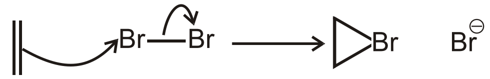
The highest electron density in the orbital is right in the middle, between the two carbon atoms, so this is where we expect the bromine to attack. The only way the HOMO can interact in a bonding manner with the * LUMO is if the Br_2 approaches end-on—and this is how the product forms. The symmetrical three-membered ring product is called a bromonium ion.

electrophilic attack by Br_2 on ethylene



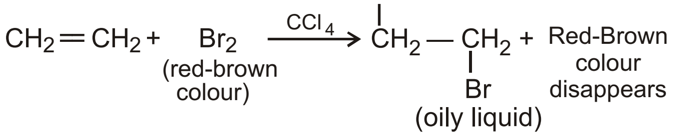
How shall we draw curly arrows for the formation of the bromonium ion? We have a choice. The simplest is just to show the middle of the p bond attacking Br–Br, mirroring what we know happens with the orbitals.

But there is a problem with this representation: becauseonly one pair of electrons is moving, we can't form two new C–Br bonds. We should really then represent the C–Br bonds as partial bonds. Yet the bromonium ion is a real intermediate with two proper C–Br bonds So an alternativeway of drawing the arrows is to involve a lone pair on bromine. We think the first way represents more accurately the key orbital interaction involved, and we shall use that one, but the second is acceptable too.



Of course, the final product of the reaction isn't the bromonium ion. The second step of the reaction follows on at once: the bromonium ion is an electrophile, and it reacts with the bromide ion lost from the bromine in the addition step. We can now draw the correct mechanism for the whole reaction, which is termed electrophilic addition to the double bond, because bromine is an electrophile. Overall, the molecule of bromine adds across the double bond of the alkene.

Alkenes react with halogens (x_2 / CCl_4) to give vicinal-dihalide, an oily liquid. Halogen (Cl_2, Br_2, I_2) acts as an electrophilc and halogen molecule adds on alkene and p-bond is destroyed. It is anti-addition-

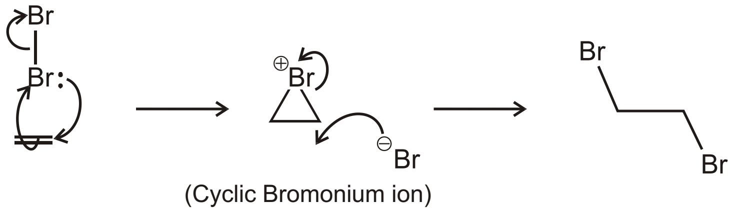


$$CH_2{=}CH_2 + \underset{\text{(red-brown colour)}}{Br_2} \xrightarrow{CCl_4} \underset{\text{(oily liquid)}}{\overset{Br}{\overset{|}{C}H_2} - \underset{Br}{\underset{|}{C}H_2}} + \text{Red-Brown colour disappears}$$

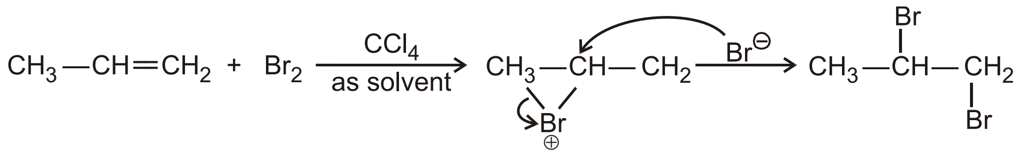
This reaction is used as a tool to detect whether a p-bond is present or not in an unknown organic compound (Test of unsaturation).

Mechanism :

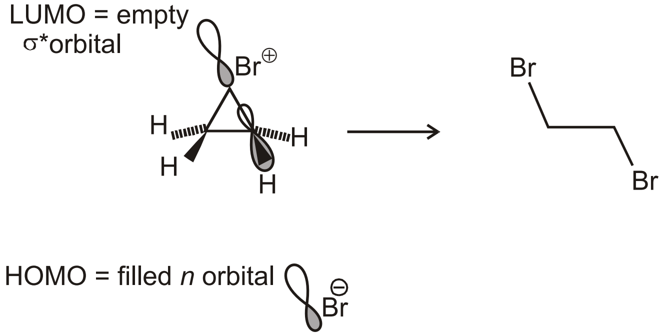
electrophilic addition of bromine to ethylene



Reaction intermediate is non-classical carbocation in which charge is delocalized over all three atoms.In unsymmetric non-classical carbocation, Br attacks on that carbon where charge is relatively more stabilized.



Attack of Br on a bromonium ion is a normal S_N2 substitution—the key orbitals involved are the HOMO of the bromide and the * of one of the two carbon–bromine bonds in the strained three-membered ring. As with all S_N2 reactions, the nucleophile maintains maximal overlap with the * by approaching in line with the leaving group but from the opposite side, resulting in inversion at the carbon that is attacked. The stereochemical outcome of more complicated reactions (discussed below) is important evidence for this overall reaction mechanism.

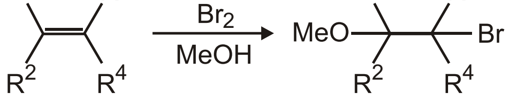


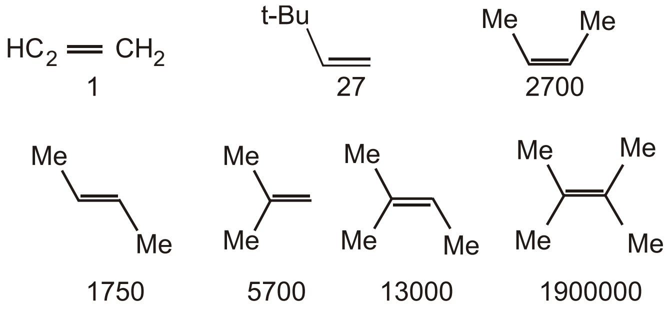
Why doesn't the bromine simply attack the positive charge and re-form the bromine molecule ? Well, in fact, it does and the first step is reversible.

Rates of bromination of alkenes

The pattern you saw for epoxidation with peroxyacids (more substituted alkenes react faster) is followed by bromination reactions too. The bromonium ion is a reactive intermediate, so the rate-determining step of the brominations is the bromination reaction itself. The chart shows the effect on the rate of reaction with bromine in methanol of increasing the number of alkyl substituents from none (ethylene) to four. Each additional alkene substituent produces an enormous increase in rate. The degree of branching (Me versus n-Bu versus t-Bu) within the substituents has a much smaller, negative effect (probably of steric origin) as does the geometry (E versus Z) and substitution pattern (1,1-disubstituted versus 1,2-disubstituted) of the alkene.

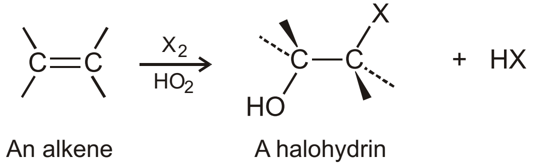
Relative rates of reaction of alkenes with bromine in methanol solvent.



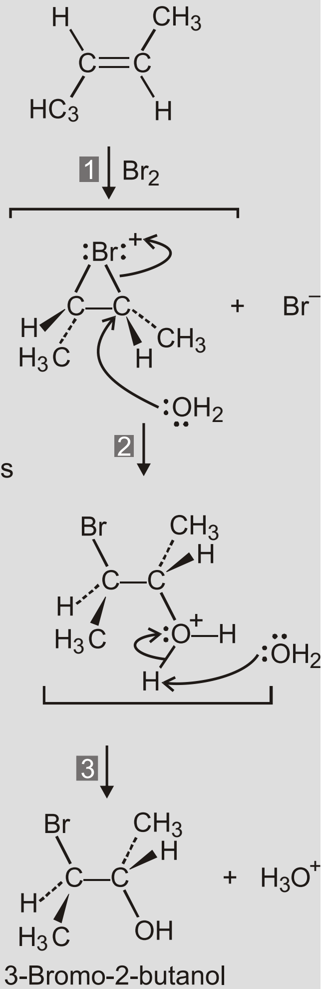


4. Halohydrins from Alkenes : Addition of HOX :

Another example of an electrophilic addition is the reaction of alkenes with the hypohalous acids HO–Cl or HO–Br to yield 1,2-halo alcohols, called halohydrins. Halohydrin formation doesn't take place by direct reaction of an alkene with HOBr or HOCl, however. Rather, the addition is done indirectly by reaction of the alkene with either Br_2 or Cl_2 in the presence of water.



1. Reaction of the alkene with Br yields a bromonium ion intermediate, as previouslydiscussed.



2. Water acts as a nucleophile, using a lone pair of electrons to open the bromonium ion ring and form a bond to carbon. Since oxygen donates its electrons in this step, it now has the positive charge.

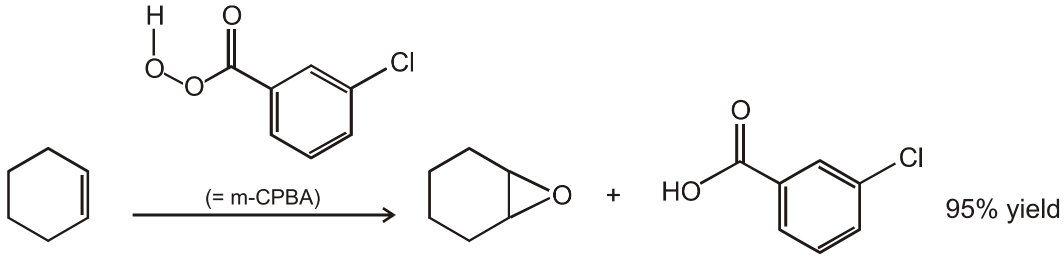
3. Loss of a proton (H) from oxygen then gives H_3O and the neutral bromohydrin addition product.

3-Bromo-2-butanol
(a bromohydrin)

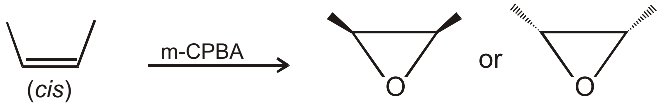
5. Epoxidation :

An alkene on reaction with peroxy-acid gives 3-membered cyclic ether (*i.e.* epoxide).

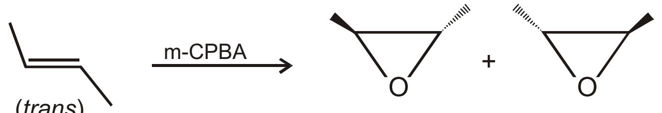
The most commonly used peroxy-acid is known as m-CPBA, or meta-Chloro Peroxy Benzoic Acid. m-CPBA is a safely crystalline solid. Here it is, reacting with cyclohexene, to give the epoxide in 95% yield. It is syn-additon.



Because both new C–O bonds are formed on the same face of the alkene's p bond, the geometry of the alkene is reflected in the stereochemistry of the epoxide. The reaction is therefore stereospecific. Here are two examples demonstrating this: cis-alkene gives cis-epoxide and trans-alkene gives transepoxide.



(1-Product only)

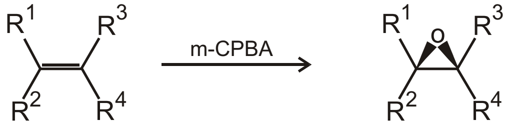


(2-Products)

More substituted alkenes epoxidize faster

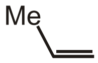
Peracids give epoxides from alkenes with any substitution pattern but the chart alongside shows how the rate varies according to the number of substituents on the double bond. Not only are more substituted double bonds more stable , but they are more nucleophilic. We showed you that alkyl groups are electrondonating because they stabilize carbocations.

Relative rates of reaction of alkenes with m-CPBA



$H_2C{=}CH_2$

1



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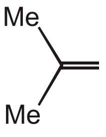
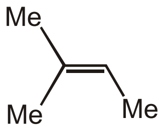


500



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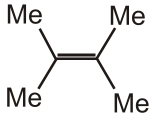
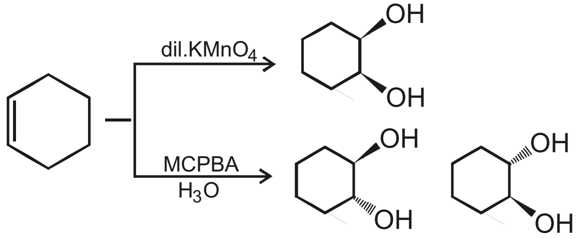


>6500

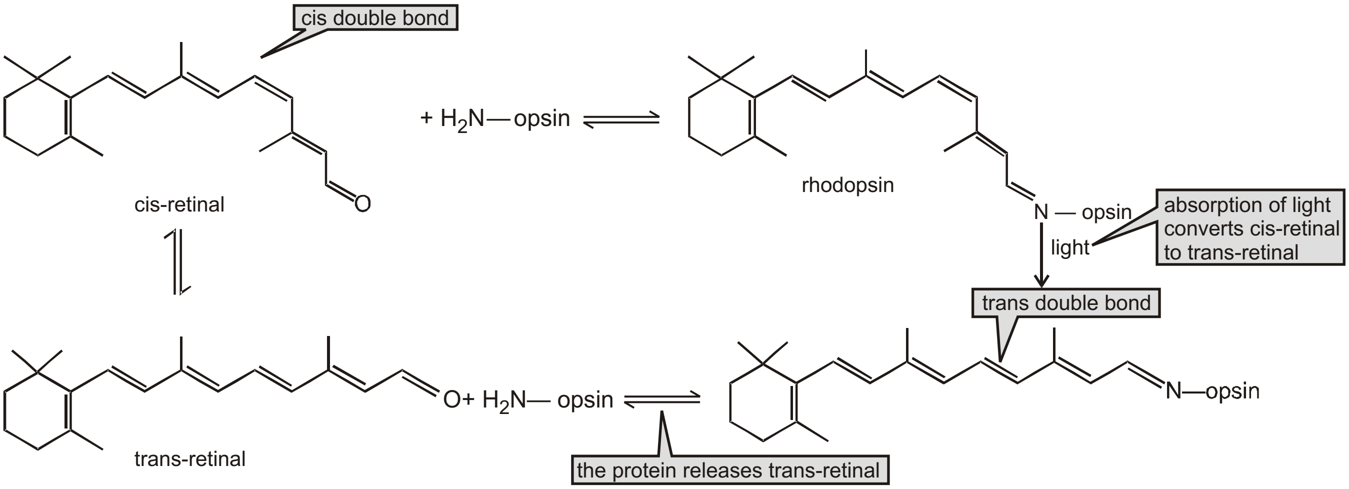
Solved Example



SPECIAL PROBLEM

cis-trans **Interconversion in Vision :**

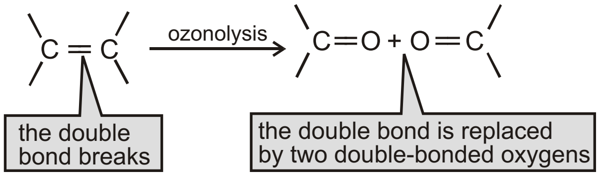
Our ability to see depends in part on an interconversion of cis and trans isomers that takes place in our eyes. A protein called opsin binds to cis-retinal (formed from vitamin A) in photoreceptor cells (called rod cells) in the retina to form rhodopsin. When rhodopsin absorbs light, a double bond interconverts between the cis and trans configurations, triggering a nerve impulse that plays and important role in vision. trans-Retinal is then released from opsin. trans-Retinal isomerizes back to cis-retinal and another cycle begins. To trigger the nerve impulse, a group of about 500 rod cells must register five to seven rhodopsin isomerizations per cell within a few tenths of a second.



◎ 6. THE ADDITION OF OZONE TO AN ALKENE: OZONOLYSIS

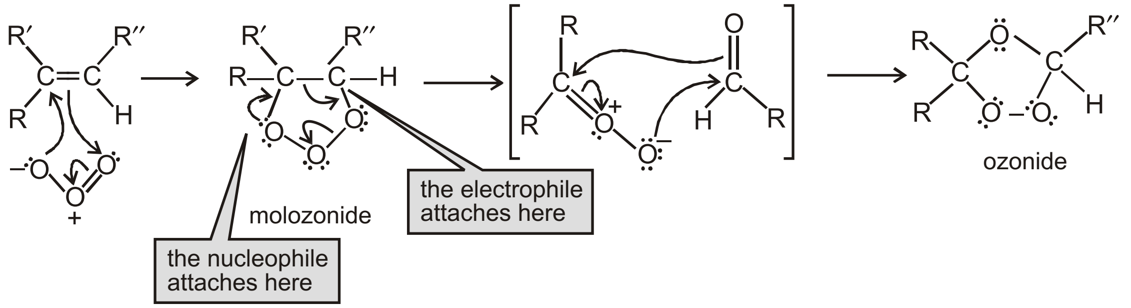
When an alkene is treated with ozone (O_3) at a low temperature, both the sigma and pie bonds of the double bond break and the carbons that were doubly bonded to each other are now doubly bonded to oxygens instead.

This is an oxidation reaction—called **ozonolysis** — because the number of C—O bonds increases.



Ozonolysis is an example of **oxidative cleavage** —an oxidation reaction that cleaves the reactant into pieces (***lysis*** is Greek for “breaking down”).

MECHANISM FOR OZONIDE FORMATION

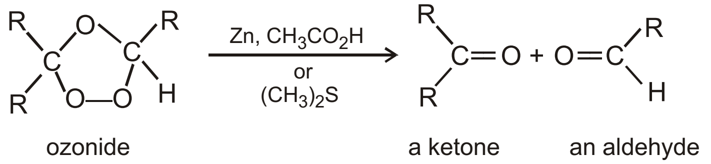


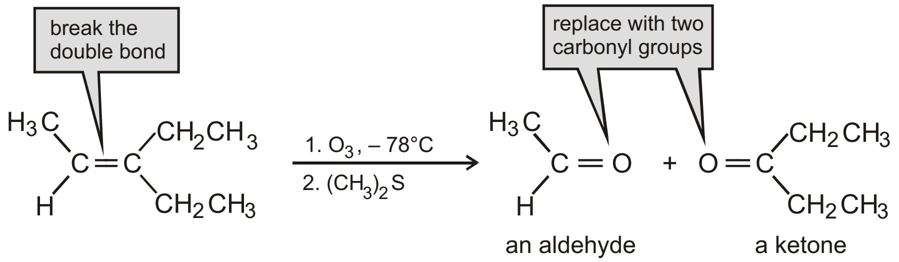
The electrophile (an oxygen at one end of the ozone molecule) adds to one of the sp^2 carbons, and a nucleophile (the oxygen at the other end) adds to the other sp^2 carbon.

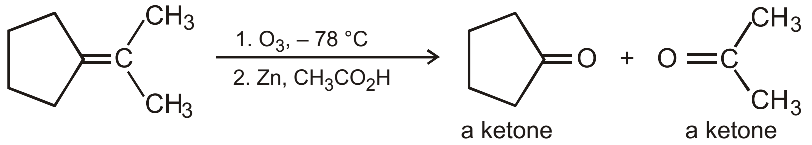
The product is a molozonide.

- The molozonide is unstable because it has two O—O bonds; it immediately rearranges to a more stable ozonide.

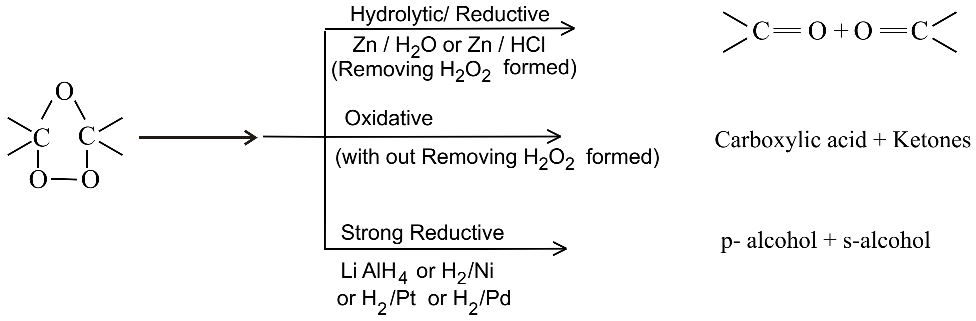
Because ozonides are explosive, they are not isolated. Instead, they are immediately conver ted to ketones and/or aldehydes by dimethyl sulfide (CH_3SCH_3) or zinc in acetic acid (CH_3CO_2H).





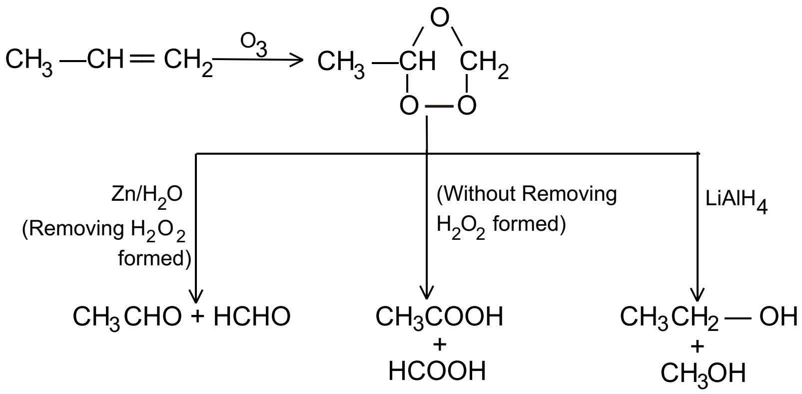


Such Ozonides may be cleaved in 3-ways

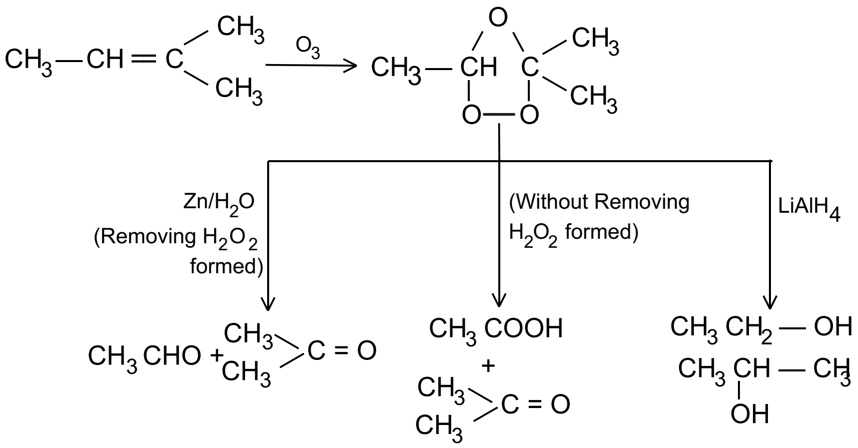


Solved example

(a) Ozonolysis of Propene

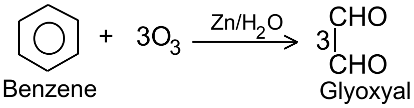


(b) Ozonolysis of 2-Methyl but-2-ene



Note Only
CH_3CHO gets converted to acid
i.e. aldehydic part gets converted to carboxylic acid

(c) Addition of ozone – Benzene adds up three molecules of ozone forming glyoxal.

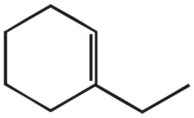


PROBLEM-SOLVING STRATEGY

Determing the Products of Oxidative Cleavage

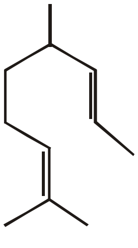
What products would you would expect to obtain when the following compounds react with ozone and then with dimethylsulfide?

(a)

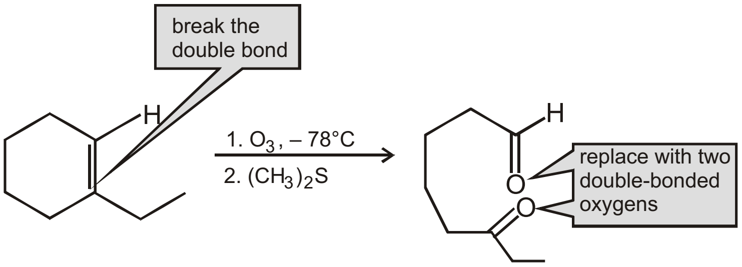


(b) $CH_3CH_2CH = CHCH_2CH_3$

(c)



Sol. (a) Break the double bond and replace it with two double-bonded oxygens.



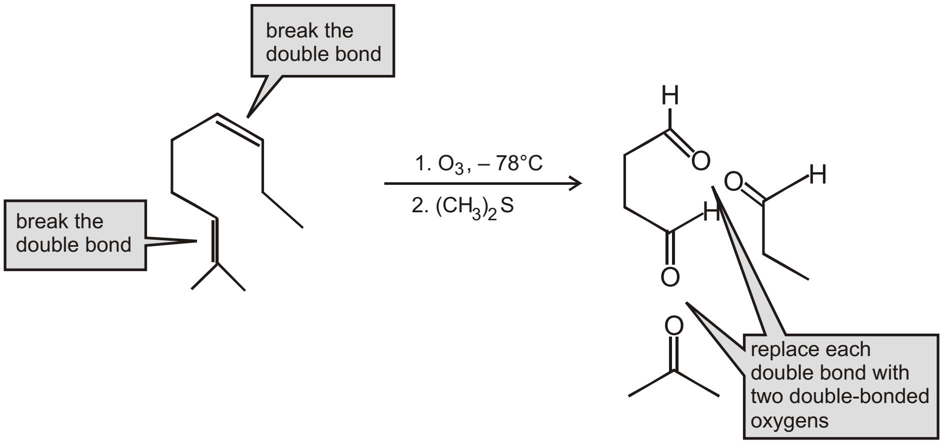
Sol. (b) Break the double bond and replace it with two double-bonded oxygens. Because the alkene is symmetrical, only one product is formed.

$$CH_3CH_2CH = CHCH_2CH_3 \xrightarrow[2.\ (CH_3)_2S]{1.\ O_3 - 78°C} CH_3CH_2CH = O\ \ O = CH_2CH_3CH$$

break the double bond

replace the double bond with = O and O =

Sol. (c) Since the reactant has two double bonds, each one must be replaced with two double-bonded oxygens.



Sol. Because only one product is obtained, the reactant must be a cyclic alkene.

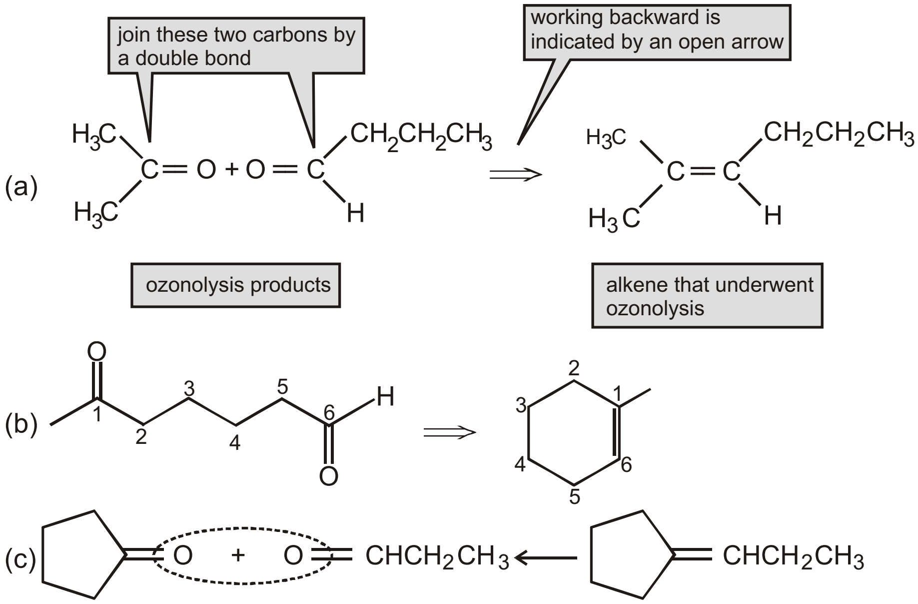
Numbering the product shows that the carbonyl groups are at C-1 and C-6, so the double bonds must be between C-1 and C-6.

Predicting the Reactant in an Ozonolysis Reaction

Ozonolysis can be used to determine the structure of an unknown alkene. If we know what carbonyl compounds are formed by ozonolysis, we can mentally work backward to deduce the structure of the alkene. In other words, delete the "O and O" and join the carbons by a double bond. (Recall that working backward is indicated by an open arrow.)

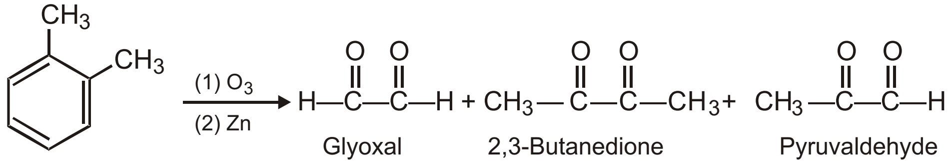
Strategy :

Reaction of an alkene with ozone, followed by reduction with zinc, cleaves the C C bond and gives two carbonyl-containing fragments. That is, the C C bond becomes two C O bonds. Working backward from the carbonyl-containing products, the alkene precursor can be found by removing the oxygen from each product and joining the two carbon atoms to form a double bond.



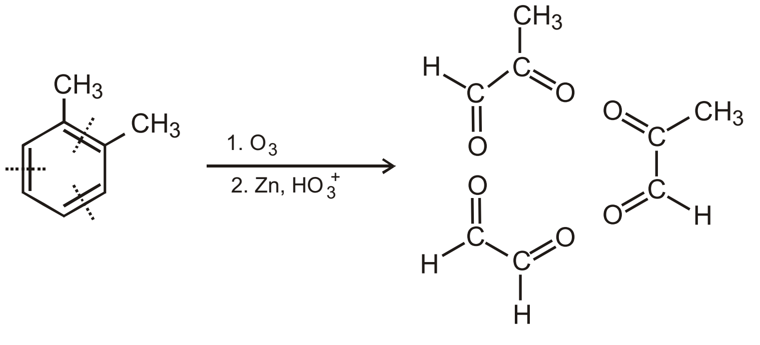
Solved example

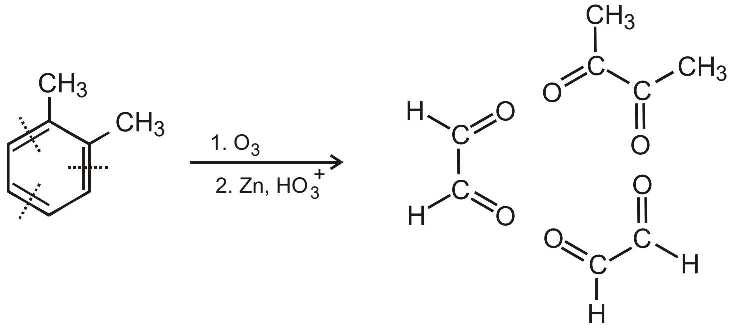
- In 1932, A. A. Levine and A. G. Cole studied the ozonolysis of o-xylene and isolated three products: glyoxal, 2,3-butanedione, and pyruvaldehyde:



In what ratio would you expect the three products to be formed if o-xylene is a resonance hybrid of two structures? The actual ratio found was 3 parts gly-oxal, 1 part 2,3-butanedione, and 2 parts pyruvaldehyde. What conclusions can you draw about the structure of o-xylene?

Sol.



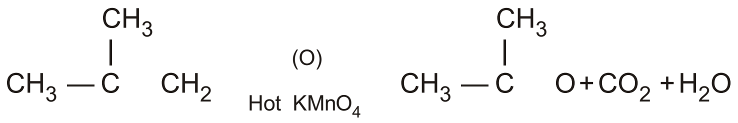


Solved example

- With HOT $KMnO_4$: Alkenes on reaction with hot alkaline $KMnO_4$ give a mixture of carboxylic acid and ketones or only ketones or carboxylic acids.

$$CH_2 \quad CH_2 \quad \underset{\text{Hot KMnO}_4}{\overset{(O)}{\qquad}} \quad 2HCOOH \quad \overset{(O)}{\quad} \quad 2$$

$$CH_3 - CH \quad CH_2 \quad \underset{\text{Hot KMnO}_4}{\overset{(O)}{\qquad}} \quad CH_3COOH + CO_2 \quad H_2O$$

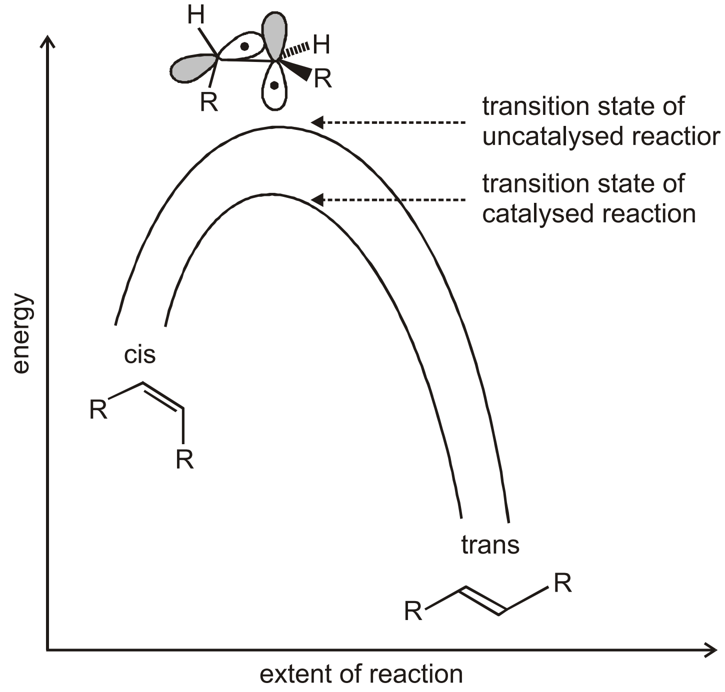


$$\underset{CH_3 - \overset{|}{C}}{\overset{CH_3}{}} \quad CH_2 \quad \underset{\text{Hot KMnO}_4}{\overset{(O)}{\qquad}} \quad \underset{CH_3 - \overset{|}{C}}{\overset{CH_3}{}} \quad O + CO_2 + H_2O$$

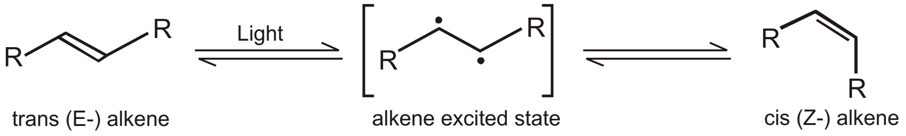
SPECIAL PROBLEM

◎ How to catalyse the isomerization of alkenes

The rate at which a reaction occurs depends on its activation energy—quite simply, if we can decrease this, then the reaction rate will speed up. There are two ways by which the activation energy may be decreased: one way is to raise the energy of the starting materials; the other is to lower the energy of the transition state. In the cis/trans isomerization of alkenes, the transition state will be halfway through the twisting operation—it has *p* orbitals on each carbon at right angles to each other. It is the most unstable point on the reaction pathway.

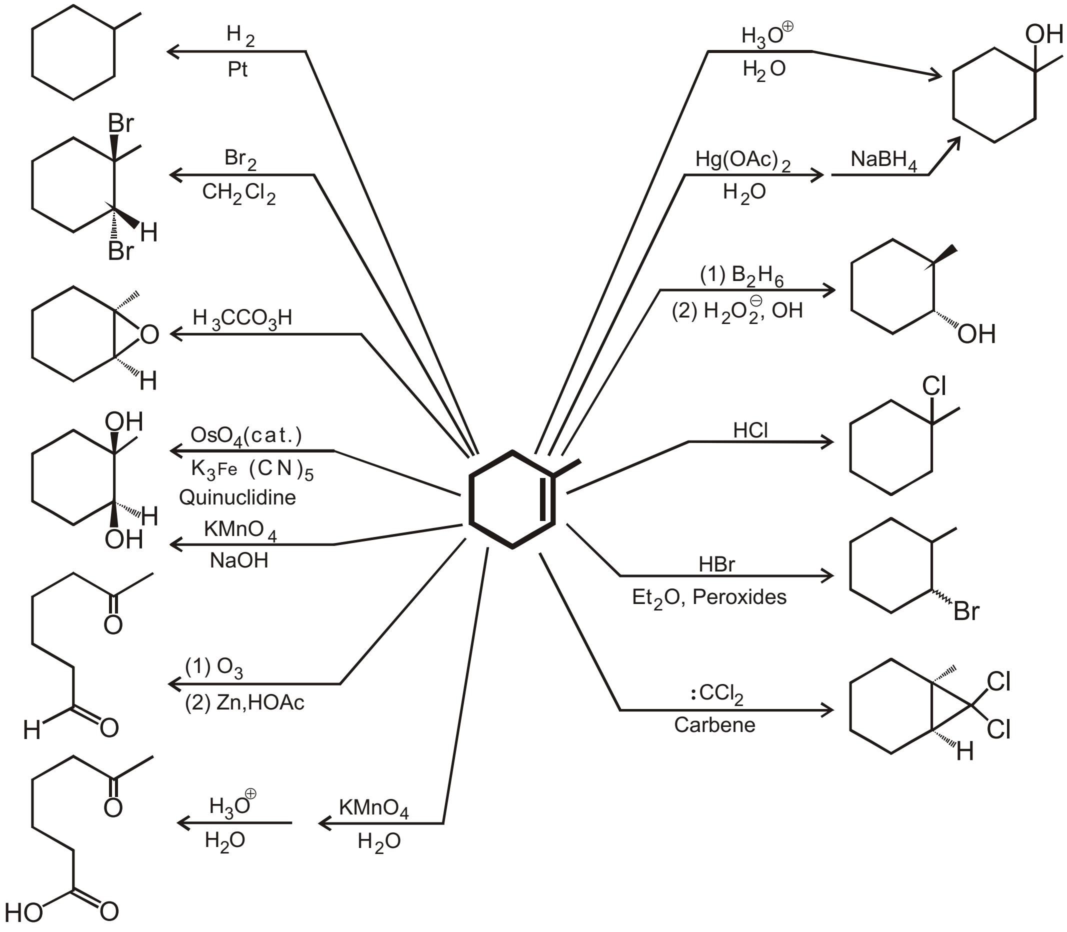


Lowering the energy of the transition state means stabilizing it in some way or other. For example, if there is a separation of charge in the transition state, then a more polar solvent that can solvate this will help to lower the energy of the transition state. Catalysts generally work by stabilizing the transition states or intermediates in a reaction. It can be catalyzed by the light.



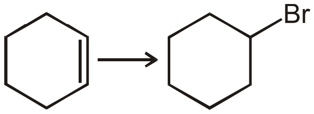
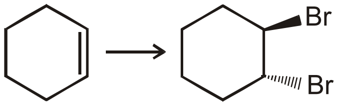
Another approach to alkene isomerization would be to use a catalyst. Base catalysis is of no use as there are no acidic protons in the alkene. Acid catalysis can work if a carbocation is formed by protonation of the alkene.

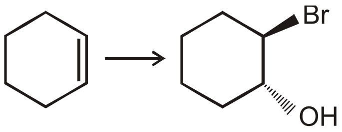
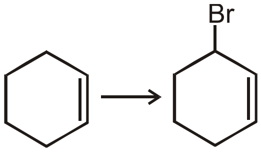
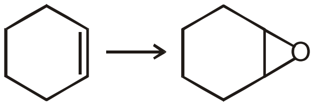
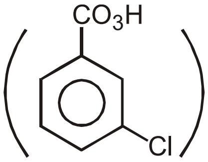
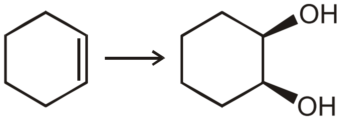
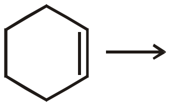
Summary :



EXERCISE

MATCH THE COLUMN

1. **Conversion**	**Reagent is used**
(A) 	(P) Br_2 / H_2O
(B) 	(Q) NBS

(C) 	(R) Br_2/CCl_4
(D) 	(S) HBr/CCl_4
(E) 	(T) MCPBA 
(F) 	(U) cold. dil. KMnO4
(G)  Adipic acid	(V) hot KMnO4

Answers

MATCH THE COLUMN

1. (A) S ; (B) R ; C P ; D Q ; E T ; F U ; G V

❑❑❑