

UNIT-I

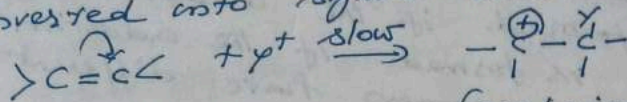
①

ADDITION TO CARBON-CARBON AND CARBON-HETERO MULTIPLE BONDS:-

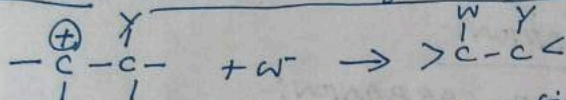
Electrophilic Addition:-

STEP I:- Addition of electrophile:- AE

A positive electrophilic species approaches the double or triple bond and  $\pi$  bond is converted into sigma bond.

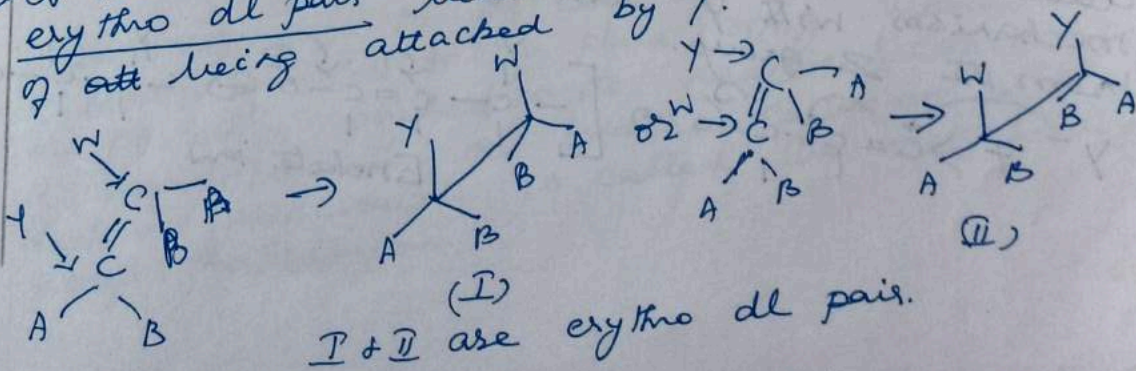


STEP II:- Addition of nucleophile AN:- (Carbanionism)

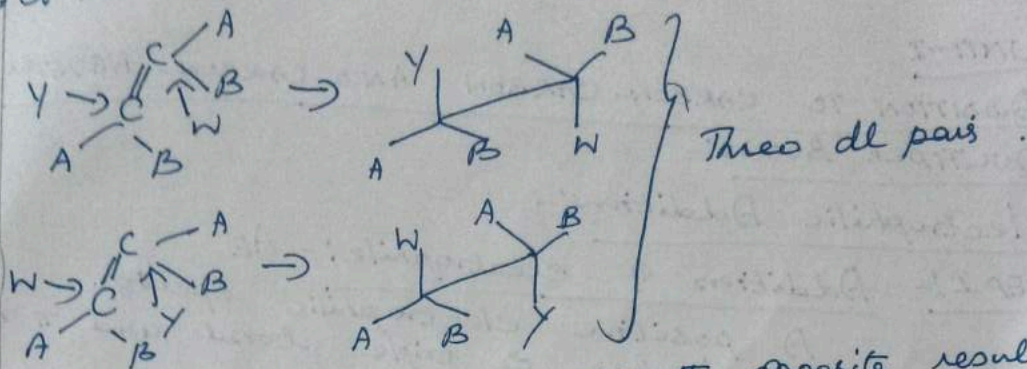


Stereochemistry of the reaction:-

- ① The two carbons of the double bond and the four atoms immediately attached to them are all in a plane.
- ② There are thus 3 possibilities:-
  - (a)  $Y+W$  may enter from the same side of the plane. In this case, addition is stereospecific & syn.
  - (b)  $Y+W$  may enter from the opposite side of the plane. In this case, addition is stereospecific & anti.
  - (c) The reaction may be non-stereospecific of experiment is often done to determine which of these possibilities may be followed.
- ③ The following type of cis & trans isomers of the olefin of the form  $ABC=CBA$ , we may use cis-olefin as an example.
- ④ If the addition is syn, the product will be the erythro dl pair because each carbon has a chance of being attached by Y.



⑥ At the addition is anti, theo dl pair is formed.

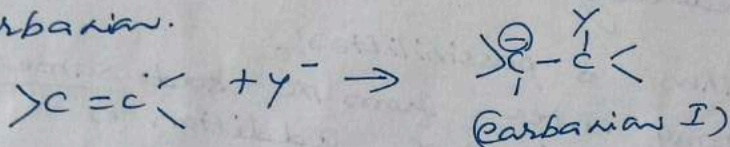


⑦ The trans isomer will give the opposite results. The threo pair is formed if the addition is syn and the erythro pair is formed if the addition is anti. The threo + erythro isomers have different physical and chemical properties.

② NUCLEOPHILIC ADDITION:-

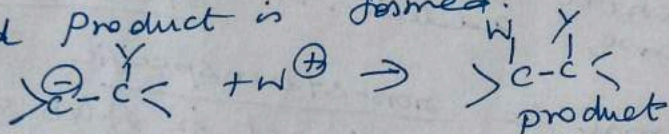
STEP I:- FORMATION OF CARBANION:-

A nucleophile brings its pair of electrons to one carbon atom of double/triple bond creating a carbanion.



STEP II:-

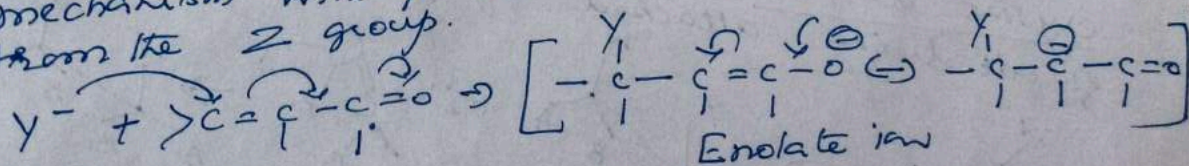
Carbanion (I) combines with the positive species and product is formed.

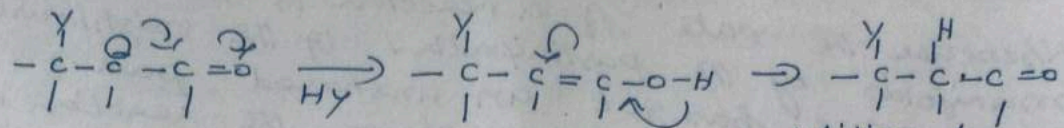


① The mechanism is similar to simple electrophilic one except that the charges are reversed.

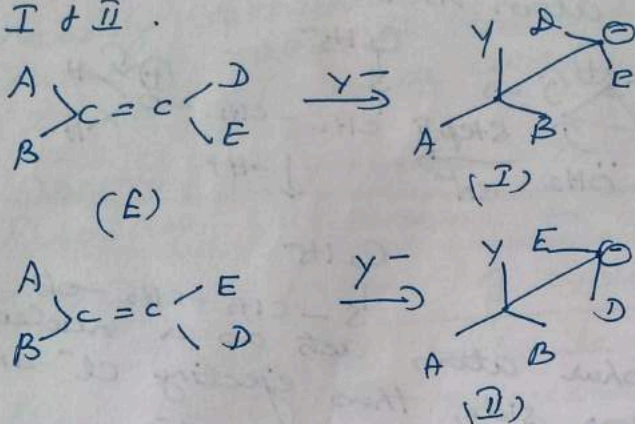
(AN + AE)

② Addition of H<sub>2</sub> to a substrate of the form  $-C=C-Z$ , where  $Z = CHO, COOR, CN, NO_2, SO_2$  etc, addition nearly always follows nucleophilic mechanism with  $Y^-$  bonding with the carbon away from the Z group.





- ③ Net result of this reaction is addition to carbon-carbon double bond, the mechanism is 1,4-nucleophilic addition to the  $>C=C-C=O$  or similar system.
- ④ If the mechanism for nucleophilic addition is the simple carbanion mechanism, the addition should be non-stereospecific, though it will be stereoselective.
- ⑤ E & Z forms of an olefin  $ABC=CDE$  would give I & II.



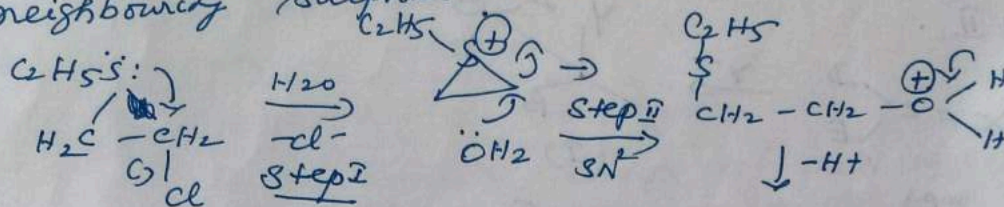
- ⑥ If the carbanion has even short lifetime, I & II will assume the most favourable conformation before the attack of W. This is of course the same for both and when W attacks, the same product will result from each.
- ⑦ One of the two possible diastereoisomers is formed and so the reaction is stereoselective since cis & trans isomers do not give rise to same different isomers.

NEIGHBOURING GROUP PARTICIPATION:-

Definition:-

"A group which is attached to the carbon atom, adjacent to the carbon, where nucleophilic substitution is taking place, may become bonded or partially bonded to the reaction centre to form a non-classical or bridged carbonium ion. Such a participation is called the neighbouring group participation."

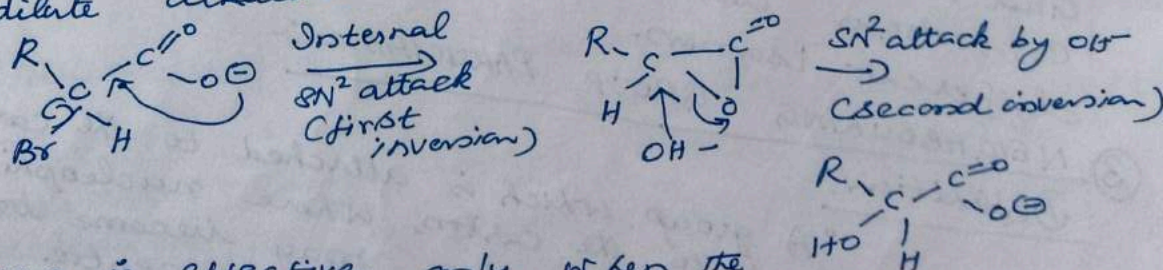
- ① Whenever the rate of a reaction is increased manifold by the participation of the neighbouring group, which has got an unshared pair of electrons or a negative charge, the reaction is said to be anchimerically assisted.
- ② For this, the neighbouring group must be stereochemically suited to interact with the carbon atom undergoing substitution. i.e. it must have trans configuration to the group being ejected.
- ③ ethyl-β-chloro-ethyl sulphide  $C_2H_5SCH_2CH_2Cl$  is hydrolysed in aqueous dioxan 1000 times faster than its ether analogue,  $C_2H_5OCH_2CH_2Cl$ . This has been explained due to the participation of neighbouring sulphur atom in the former case.



④ In step (2), the sulphur atom acts as a nucleophile attacking from the rear side, thus ejecting  $Cl^-$  and causing internal inversion of configuration.

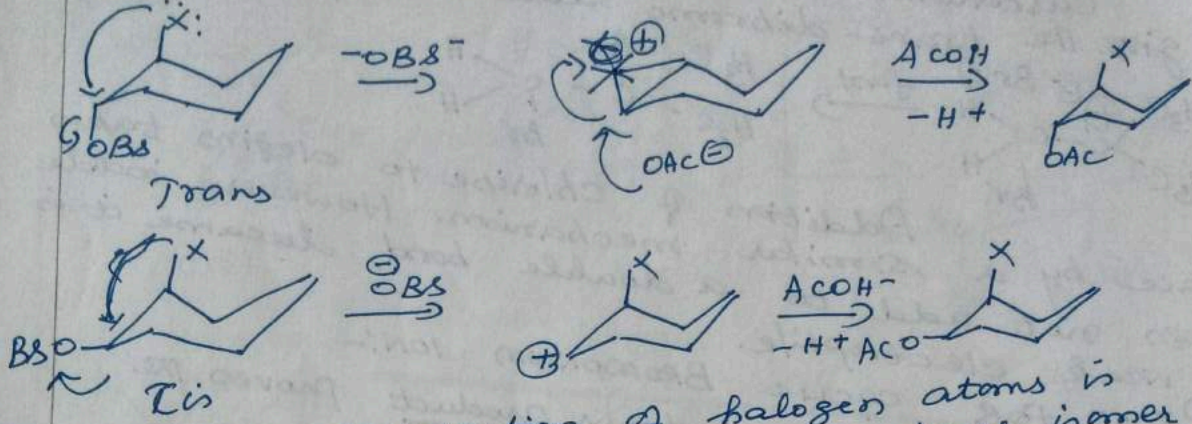
⑤ In step (1), the three membered ring is opened by the normal  $SN^2$  attack of water molecule and thus again inversion takes place. So overall change involves apparent retention of configuration.

⑥ A similar apparent retention of configuration is observed in the hydrolysis of  $\alpha$ -halogen acids in dilute alkaline solution.



⑦ NGP is effective only when the interaction involves the apparent ~~change~~ formation of 3, 4, 5 or 6 membered rings.

8) Halogen atoms can form cyclic ions to offer achimeric assistance in the acetolysis of cis & trans -2-halogenocyclohexyl-bromylates (I & II)



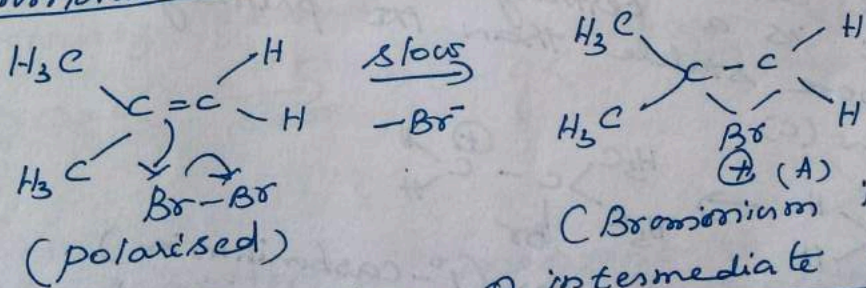
9) Since the participation of halogen atoms is readily available in the case of trans isomer, relative rates of trans and cis isomers are  $2.7 \times 10^6$  & 1 in the case of iodides.

IV ADDITION OF HALOGEN TO OLEFINS:-

Addition of bromine to 2-methylpropene:-

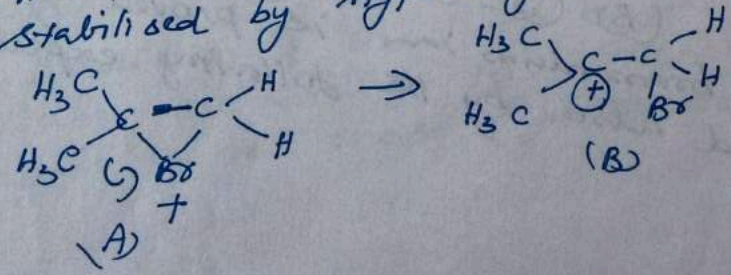
STEP I:- Formation of cyclic bromonium ion:-

Bromine molecule ( $Br_2$ ) on colliding with alkene molecule polarised and the formed bromine cation attacks the alkene and cyclic bromonium ion is formed.



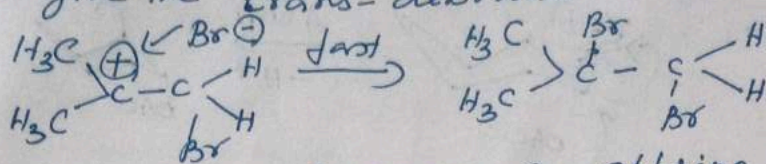
STEP II:- Formation of intermediate carbanion:-

The most stable cyclic bromonium ion (A) rearranges to cyclic carbanion ion (B), which is stabilised by hyperconjugation: (B) is an intermediate.



STEP iii:- Formation of trans product:-

Carbanium ion (B) is attacked by bromide anion to give the trans-dibromo addition product.

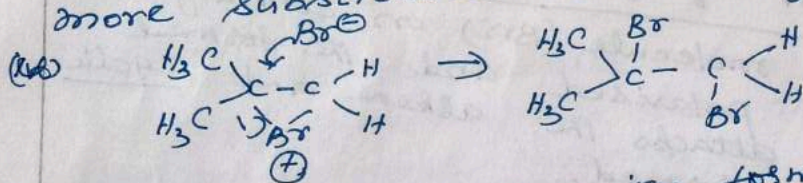


Addition of chlorine to olefins takes place by a similar mechanism. However iodide does not add to a double bond, because it is a weak electrophile.

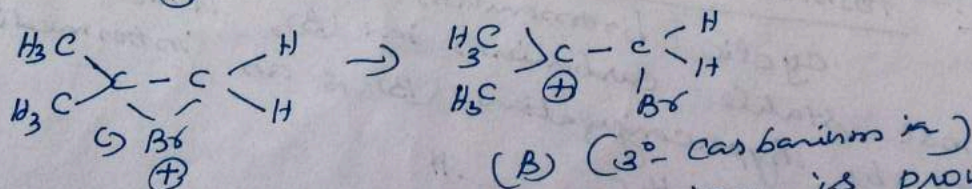
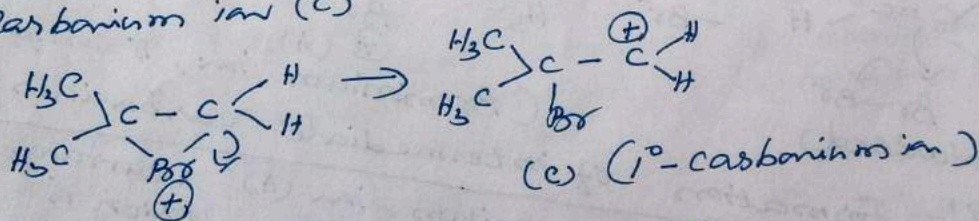
PROOF FOR CYCLIC BROMONIUM ION:-

- (i) Exclusive formation of trans product proves the formation of cyclic bromonium ion.
- (ii) Attack of bromide ion on this intermediate can only occur from the opposite side, resulting in the exclusive formation of trans addition product.

(iii) Since the carbanium ion (B) is formed from unsymmetrical alkenes, the Br<sup>-</sup> ion attacks the more substituted carbon only.

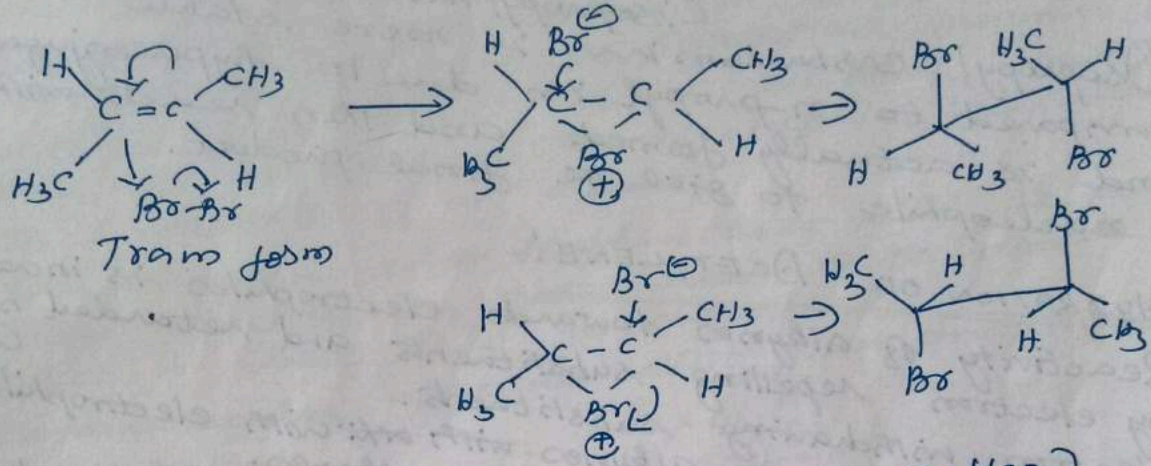
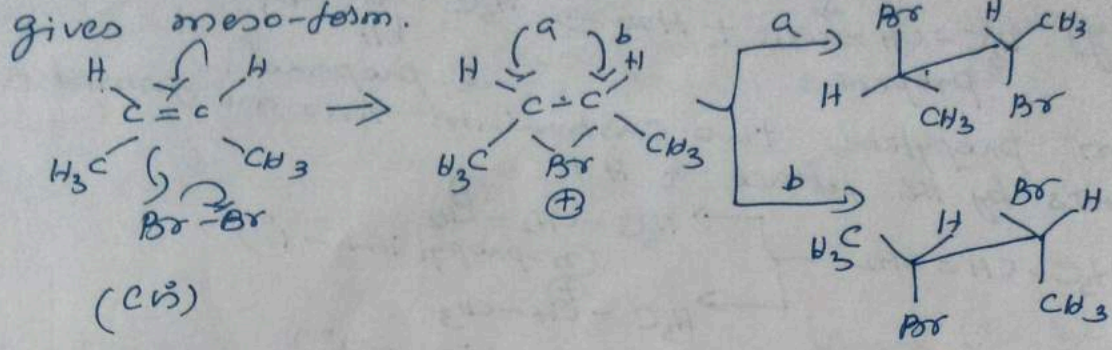


(iv) Because the carbanium ion formed from the cyclic intermediate is a tertiary carbanium ion (B) which is more stable than the primary carbanium ion (C)



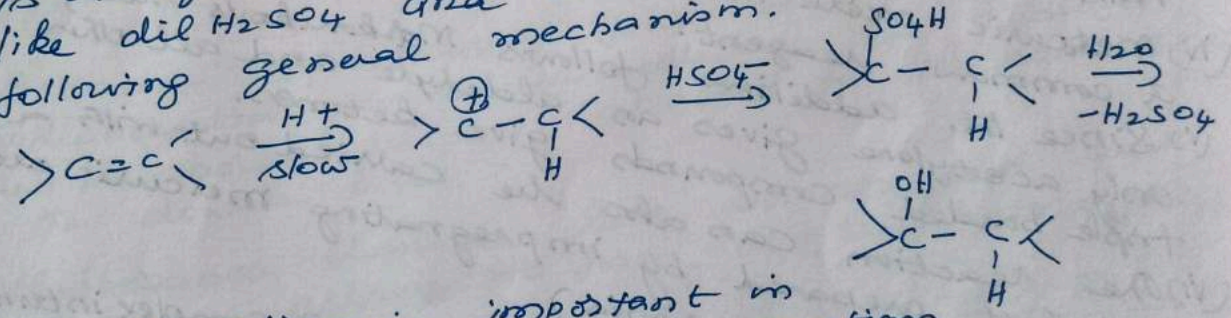
(v) The intermediate bromonium ion is proved by NMR studies and also by the following experiment.

(vi) cis-butene on bromination gives d/l-2,3-dibromo butane and trans butene on bromination gives meso-form.



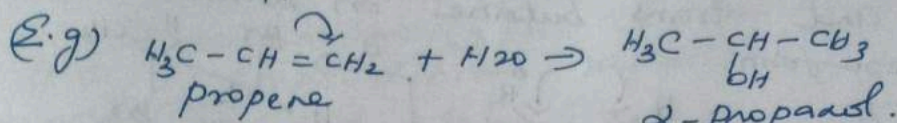
V HYDRATION OF OLEFINS:- (Addition of H<sub>2</sub>O)

(i) Hydration of carbon-carbon double bond is always carried out in the presence of acids like dil H<sub>2</sub>SO<sub>4</sub> and takes place by the following general mechanism.

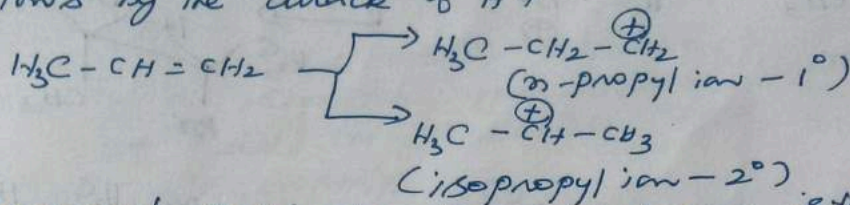


- (ii) This reaction is important in converting lower petroleum fractions into alcohols.
- (iii) The orientation of hydration reaction is always trans to olefin occurs by Markovnikov's rule, according to which the hydrogen atom adds to the most hydrogenated end and OH-

adds to the least hydrogenated end of the double bond.



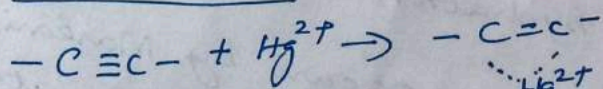
(V) From propylene, two carbanion ions are formed as follows by the attack of  $\text{H}^+$



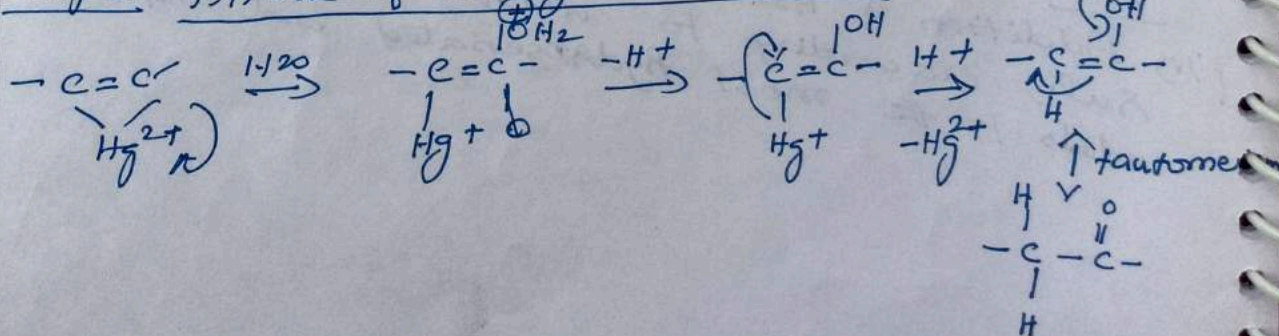
(VI) Isopropyl carbanion ion is more stable compared to n-propyl ion due to hyperconjugation and is actually formed and then reacts with a nucleophile to give the final product.

### VI HYDRATION OF ACETYLENE:-

- (i) Reactivity of alkynes towards electrophiles is increased by electron repelling substituents and retarded by electron withdrawing substituents.
- (ii) Reaction rates of alkynes with  $\text{H}^+$  with electrophiles are rather less than those of alkenes.
- (iii) Hydration of triple bonds is generally carried out with mercuric ion salts as catalysts.
- (iv) Mercuric oxide in the presence of an acid is also a common reagent.
- (v) Since the addition follows Markovnikov's rule, only acetylene gives an aldehyde and all other triple bonded compounds give ketones.
- (vi) The reaction can also be carried out with a catalyst prepared by impregnating mercuric oxide onto Nafion-H (a resin).
- (vii) Mechanism:- Step I:- Formation of complex intermediate:-



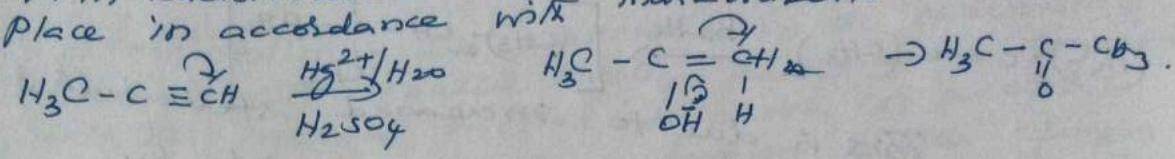
Step II:- Attack of  $\text{H}_2\text{O}$  by  $\text{S}_\text{N}^2$  mechanism:-





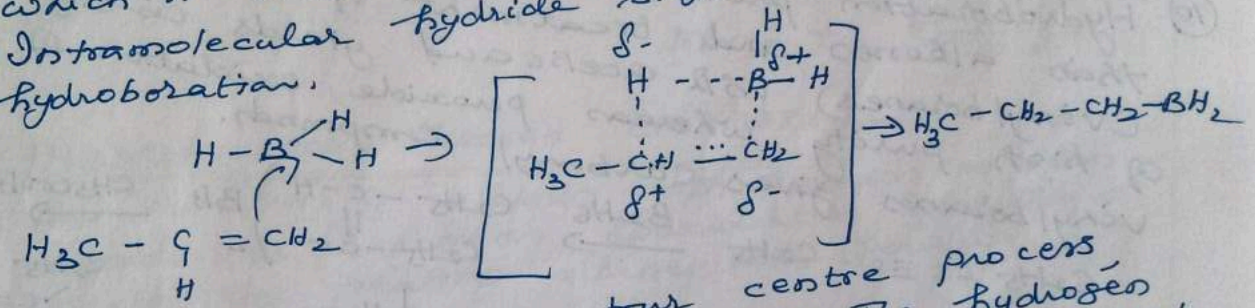
(viii) A spectrum of enol was detected by flash photolysis when phenylacetylene was hydrated photolytically. (2)

(ix) With substituted alkynes, addition of water takes place in accordance with Markovnikov's rule.



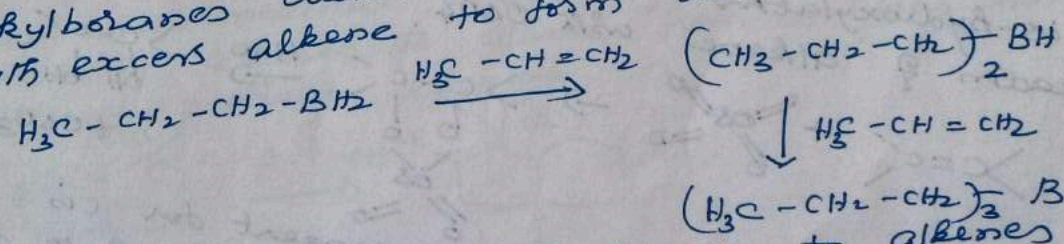
VII HYDROBORATION:-

- ① Borane itself is unknown, but its dimer (B<sub>2</sub>H<sub>6</sub>) functions as if it were the hypothetical monomer borane.
- ② Because of the vacant orbital on boron, borane may be regarded as an electrophile and attacks the π electrons of an alkene.
- ③ In accordance with Markovnikov's rule, the positive charge develops on that carbon of the double bond which is best able to support it.
- ④ Intramolecular hydroboration.



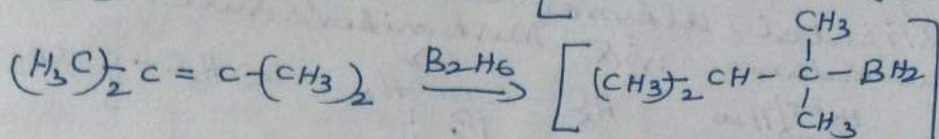
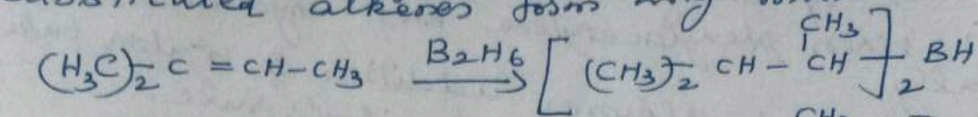
- ⑤ Because of one-step four centre process, hydroboration is a cis-addition. The hydrogen and the boron become attached to the same side of the double bond.

⑥ Alkylboranes behave like boranes and react with excess alkene to form di + trialkylboranes.



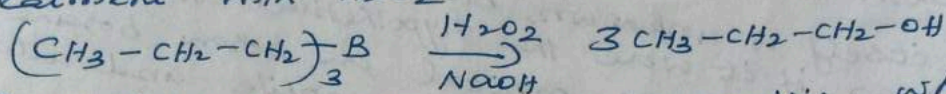
- ⑦ The rate of addition of borane to alkenes decreases with increase in the number of alkyl substituents on the double bond. Trisubstituted

Alkenes normally give dialkylboranes and tetra substituted alkenes form only monoalkyl boranes.

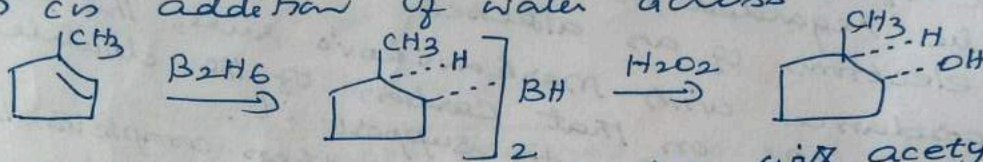


This is due to increased steric bulk of the substituents.

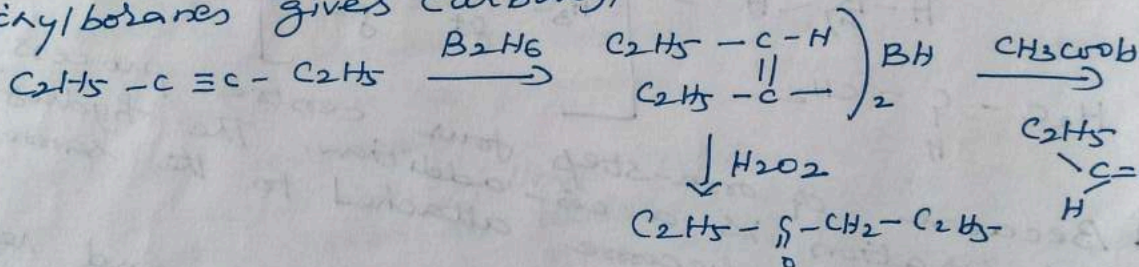
8) Di-alkylboranes can be oxidised to alcohols by treatment with  $H_2O_2$



9) The whole process is stereospecific, which results in cis addition of water across a double bond.

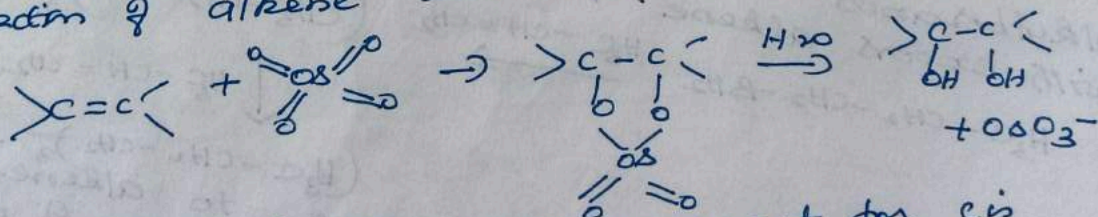


10) Hydroboration proceeds faster with acetylenes than alkenes and treatment of the product (vinylboranes) with acetic acid yields cis-olefins of high purity whereas peroxide oxidation of vinylboranes gives carbonyl compounds.

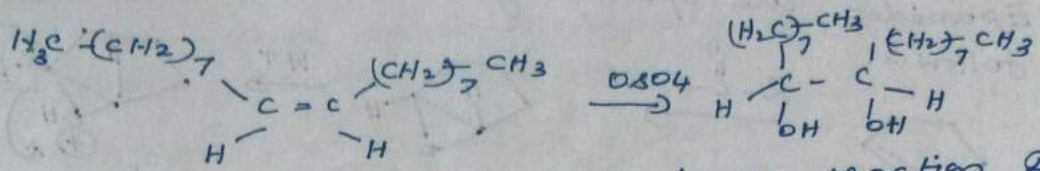


### VIII HYDROXYLATION:-

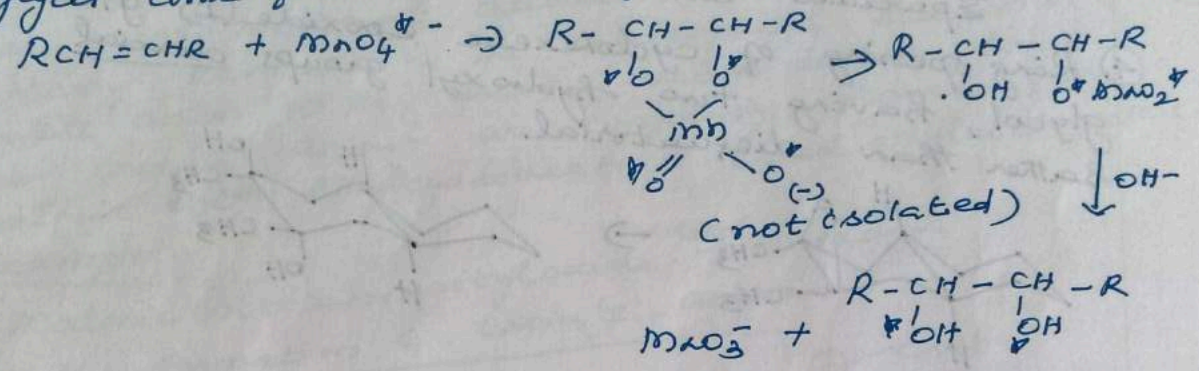
1) cis-Hydroxylation can be better achieved by the reaction of alkene with  $OsO_4$ .



2)  $OsO_4$  is a highly specific reagent for cis hydroxylation on the less hindered side of the alkene.

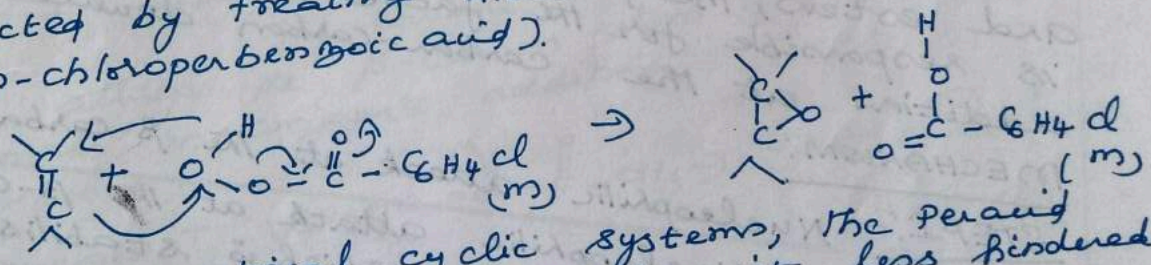


③ A cis-diol can be obtained by the reaction of alkene with alkaline  $KMnO_4$ . The reaction proceeds with the ~~intermediate~~ initial formation of a cyclic manganate ester which undergoes further changes in alkaline conditions.  $^{18}O$  labelling experiments have demonstrated that both oxygens of the resulting glycol come from the permanganate ion.

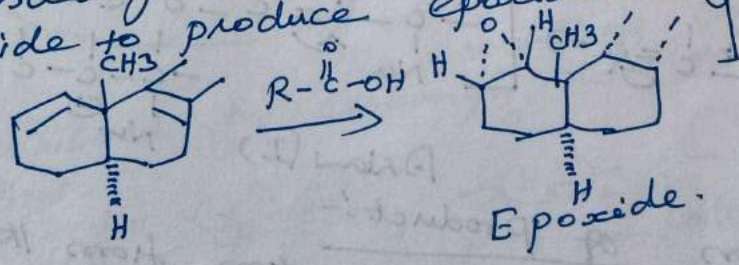


IX HYDROXYLATION THROUGH EPOXIDATION:-

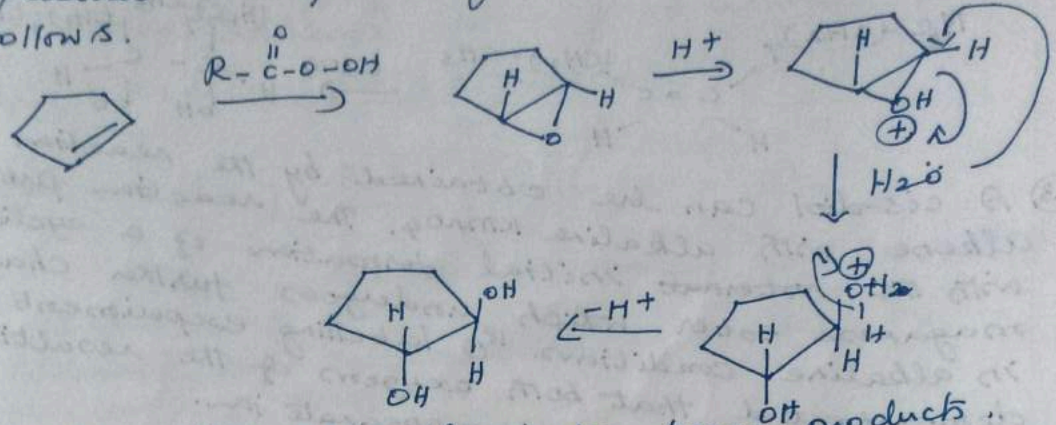
(i) The reaction of alkenes with peracids to form epoxides is known as epoxidation and this is effected by treating alkene with peracid (m-chloroperbenzoic acid).



(ii) In unsymmetrical cyclic systems, the peracid usually attacks the alkene from its less hindered side to produce epoxide.

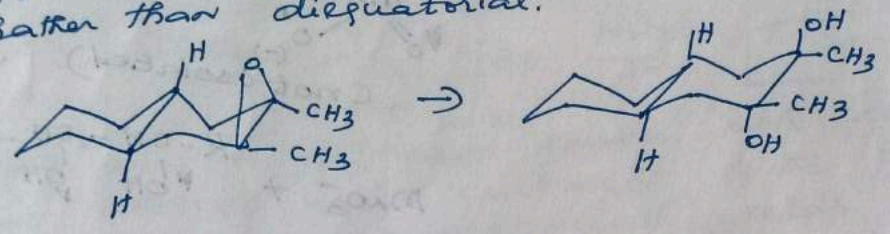


③ Epoxides are opened by acid catalyst as follows.



Epoxides can lead to trans products.

④ Ring opening of cyclohexene epoxide (I) yields a glycol, having two hydroxyl groups diaxial rather than diequatorial.



X MICHAEL ADDITION:-

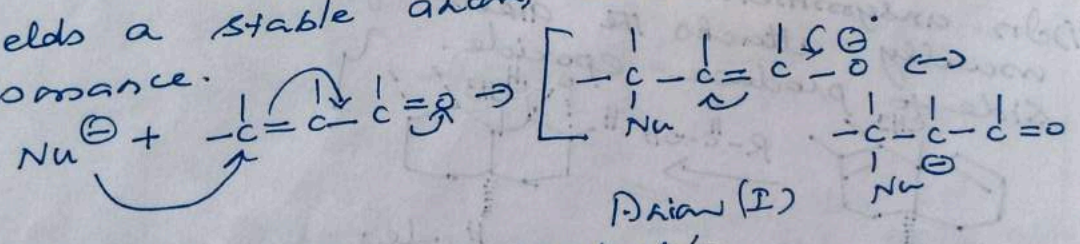
Definition:-

In  $\alpha, \beta$ -unsaturated aldehydes, ketones and esters, the presence of carbonyl group is responsible for the facile nucleophilic addition at the carbon-carbon double bond.

MECHANISM:-

STEP I:- Nucleophilic attack at the  $\beta$ -carbon:-(Conjugate addition)

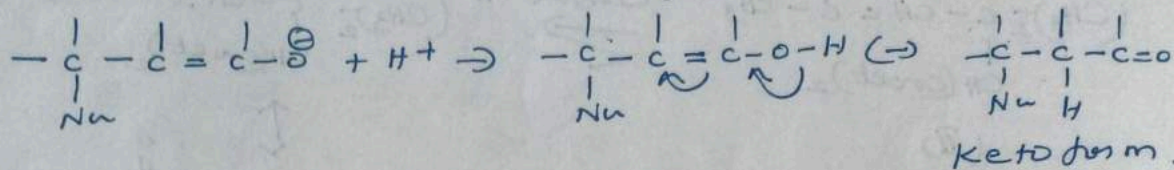
yields a stable anion, which is stabilised by resonance.



STEP II:- Formation of product:-

Enan (I) abstracts proton from the solvent to produce either the keto/enol form ②

the addition product. The enol form is usually less stable and so it is rapidly equilibrated to the more stable keto form. (14)



(i) The  $\alpha, \beta$ -unsaturated compounds used in this reaction include any unsaturated system having an electron withdrawal group capable of stabilising the intermediate anion.

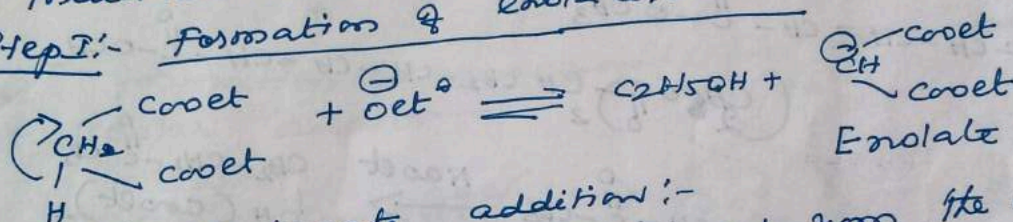
(ii) The most important addition reaction of  $\alpha, \beta$ -unsaturated carbonyl compounds is the nucleophilic addition of enolate anion to the carbon-carbon double bond.

(iii) The enolate anions are commonly produced from malonic ester, ethylcyanoacetate and ethylacetoacetate.

Example!:-

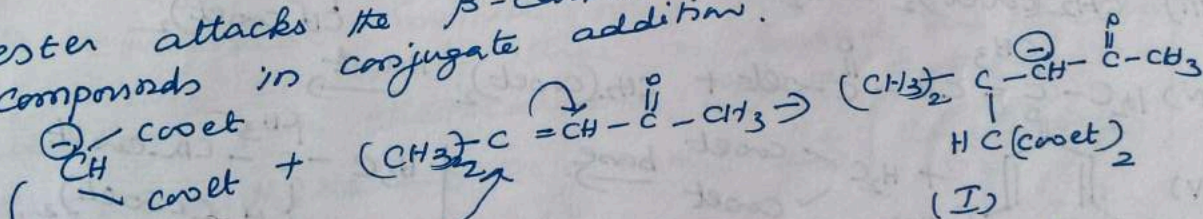
Malonic ester + mesityloxide  $\xrightarrow{\text{dimedone}}$

Step I:- formation of enolate:-

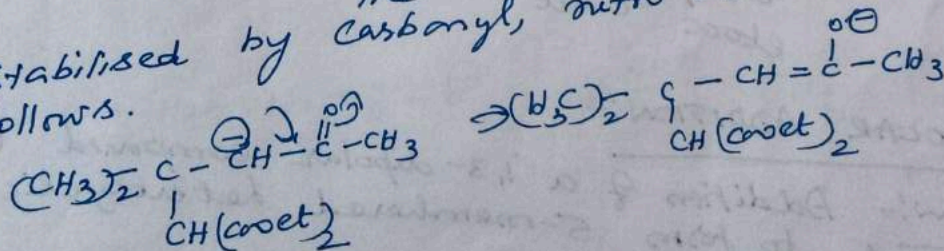


STEP II:- conjugate addition:-

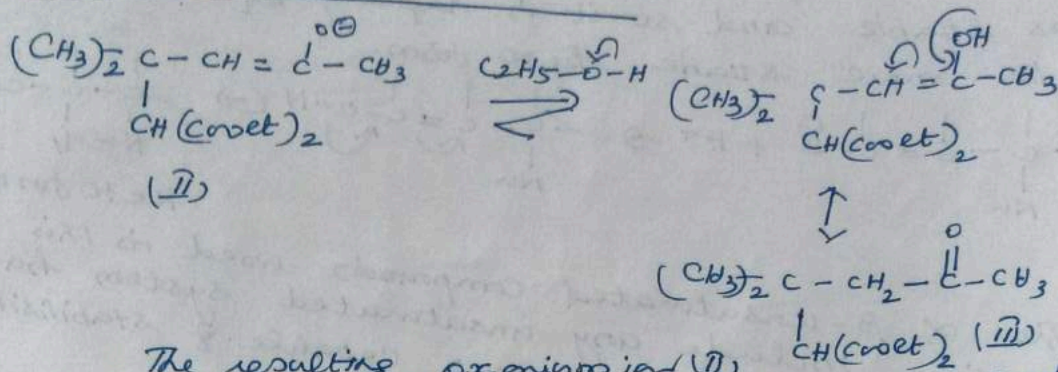
The enolate derived from the malonic ester attacks the  $\beta$ -carbon atom of  $\alpha, \beta$ -unsaturated compounds in conjugate addition.



The resulting carbanion (I) is stabilised by carbonyl, nitro or nitrile group as follows.



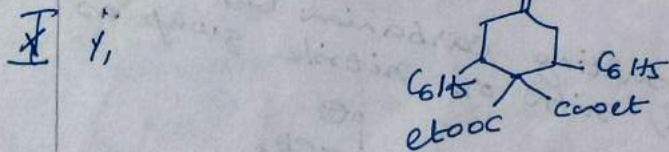
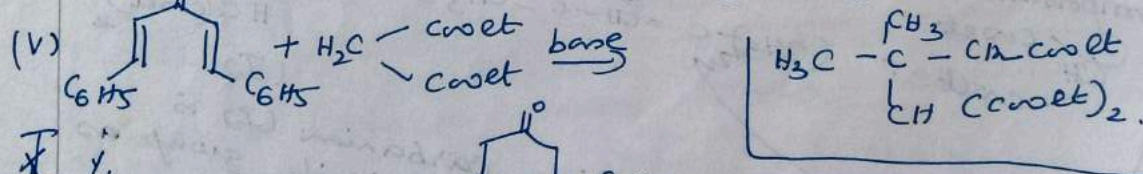
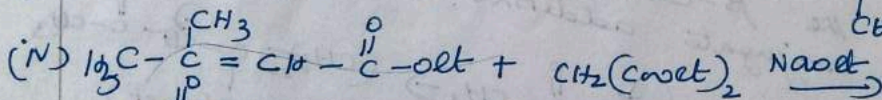
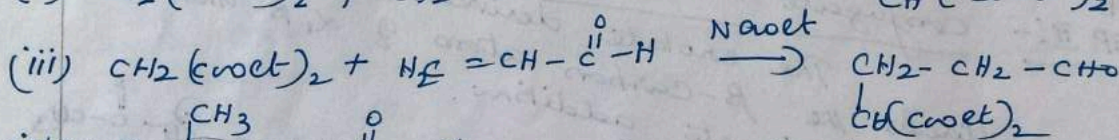
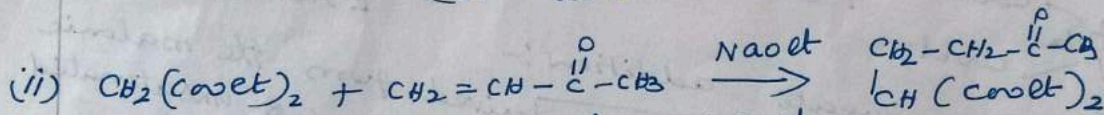
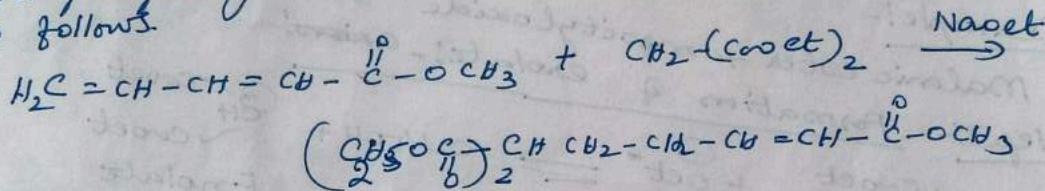
STEP II:- FORMATION OF PRODUCT:-



The resulting oxonium ion (II) abstracts a proton from ethanol to give the product (III) and ethoxide ion.

Applications:-

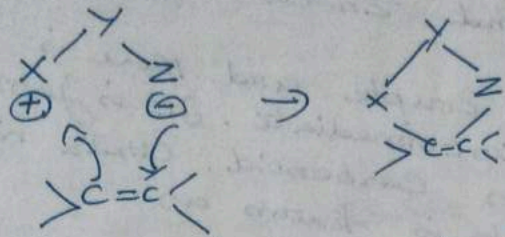
(i) Compounds containing two double bonds conjugated with a carbonyl group react with active methylene compounds to give 1,6-addition product. Thus methylvinylacrylate condenses with diethylmalonate as follows.



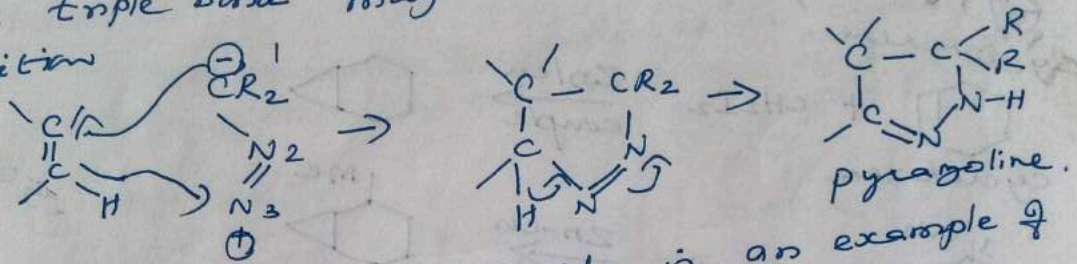
XI 1,3-DIPOLAR ADDITION:-

(i) Definition:- Addition of a 1,3-dipolar compound to a double bond to form 5-membered heterocyclic

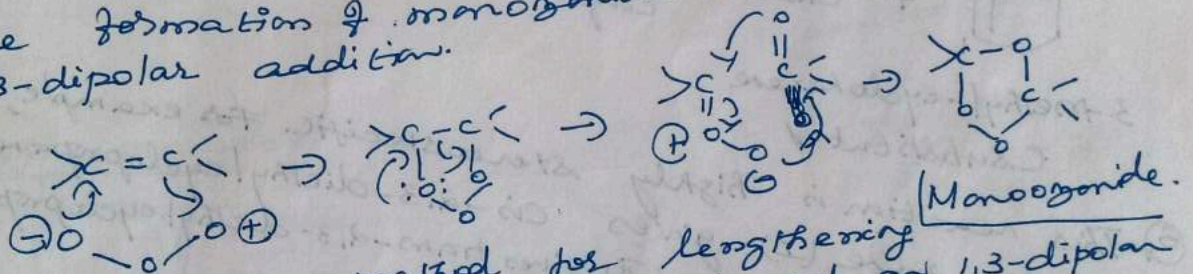
compounds. This type of addition may be regarded as [2+3] cycloaddition.



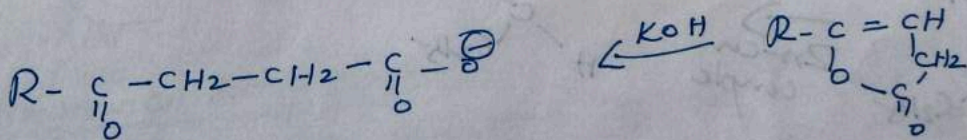
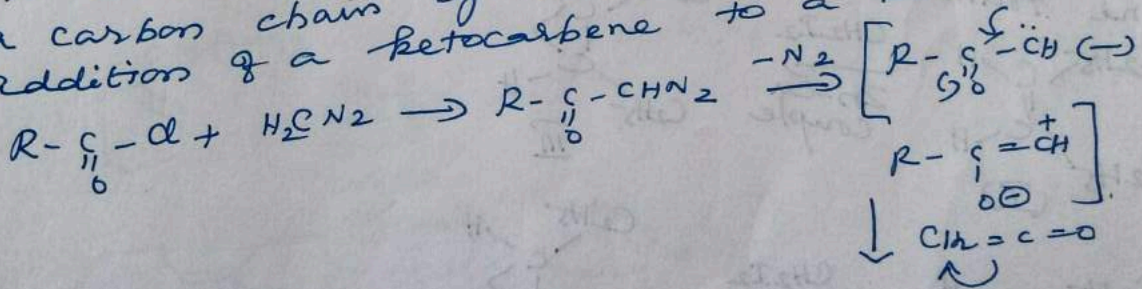
- (ii) X has 6 electrons in the outer shell and Z has at least one pair of unshared electrons. (Eg) diazoalkanes, alkylazides and azoxy compounds.
- (iii) All these compounds add to double bond, forming various heterocyclic compounds.
- (iv) C-C triple bond may also undergo 1,3-dipolar addition



- (v) The formation of monoazide is an example of 1,3-dipolar addition.



- (vi) A convenient method for lengthening a carbon chain by three is based on 1,3-dipolar addition of a ketocarbene to a ketene.

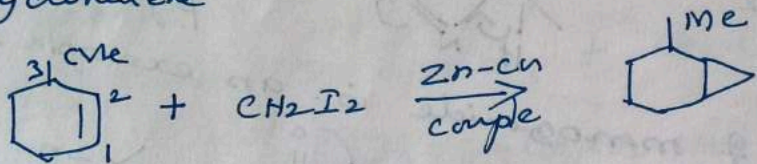
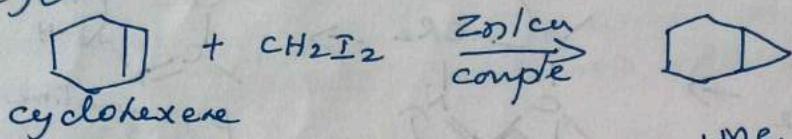


## XII SIMON-SMITH REACTION:-

Definition:- Treatment of olefinic compound with diiodomethane ( $\text{CH}_2\text{I}_2$ ) and Zn-Cu couple, leads to cyclopropane derivative.

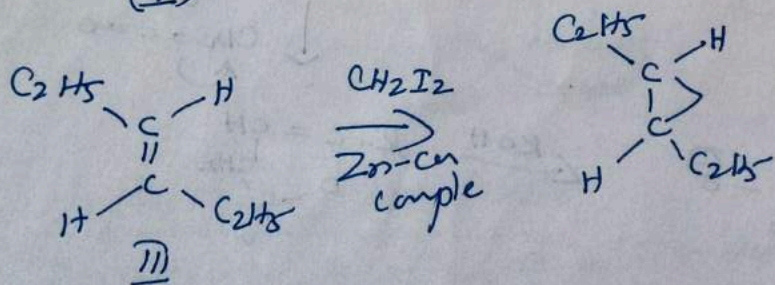
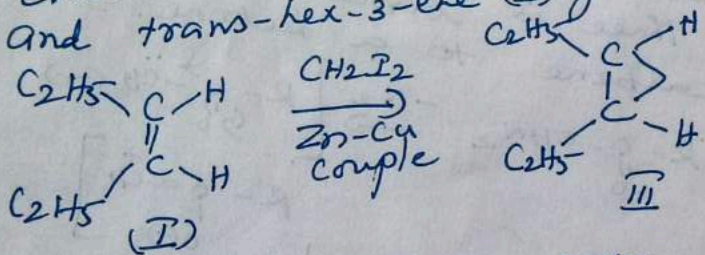
①  $\text{CH}_2\text{I}_2$  reacts with Zn-Cu couple and there is formation of organoionic intermediate. It is just like carbene and is known as carbenoid.  $\text{CH}_2\text{I}_2$  in the presence of Zn-Cu couple is known as SIMON-SMITH reagent.

② Substituted alkenes react faster than non-substituted alkenes.  
 (e.g.) 3-methylcyclohexene reacts faster than cyclohexene.



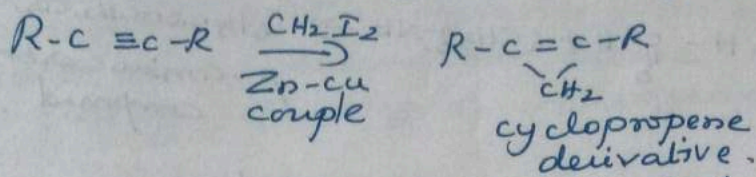
3-methyl-cyclohexene  
 C substituted

③ This reaction is highly stereospecific. For example, cis-hex-3-ene (I) gives cis-2,3-dimethylcyclopropane (III) and trans-hex-3-ene (II) gives trans-2,3-dimethylcyclopropane (IV).

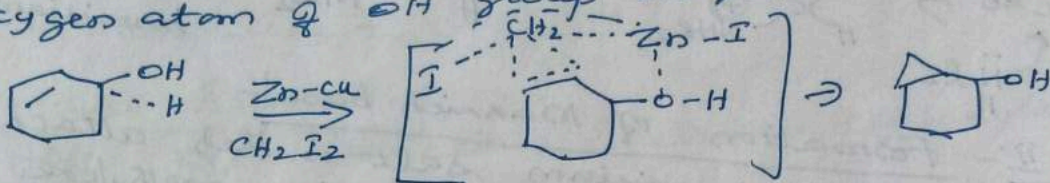




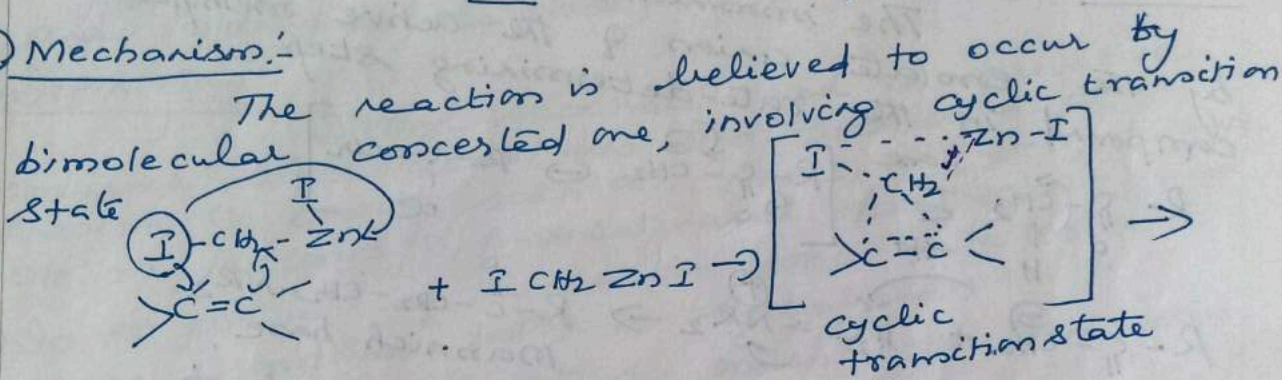
④ Non-terminal alkynes also undergo Simon-Smith reaction, but the yield is very poor.



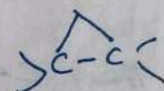
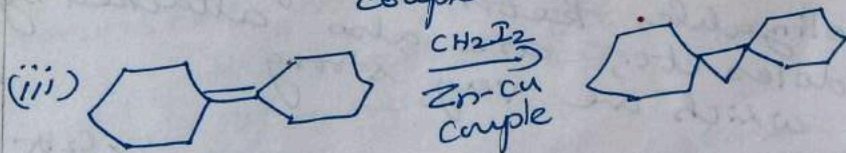
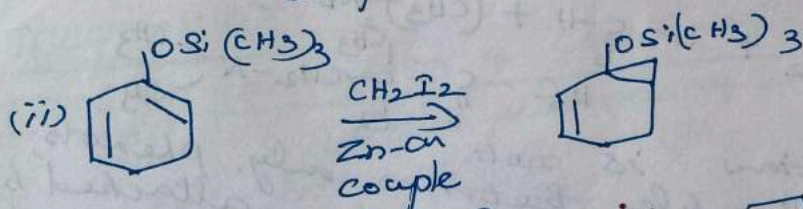
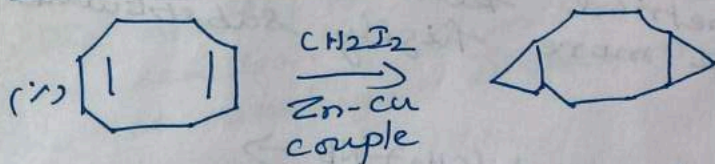
⑤ If hydroxyl group is substituted in the neighbouring carbon atom to double bond, the reaction rate is increased due to coordination of zinc to oxygen atom of OH group as follows.



⑥ Mechanism:-



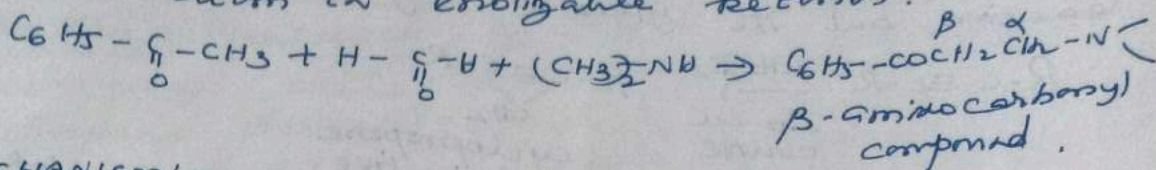
⑦ Other examples:-



### XIII MANNICH REACTION:-

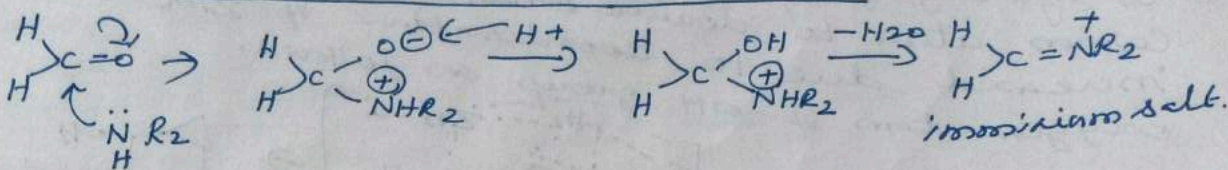
Definition:- The reaction of an active methylene compound with formaldehyde and an amine to form a  $\beta$ -amino carbonyl compound (Mannich base) is known as Mannich reaction.

It is a very convenient method for introducing a carbon atom in enolizable ketones.



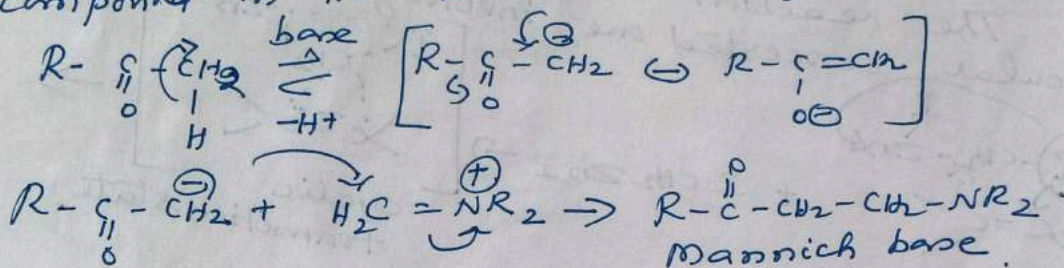
MECHANISM:-

STEP I:- Formation of iminium salt:-

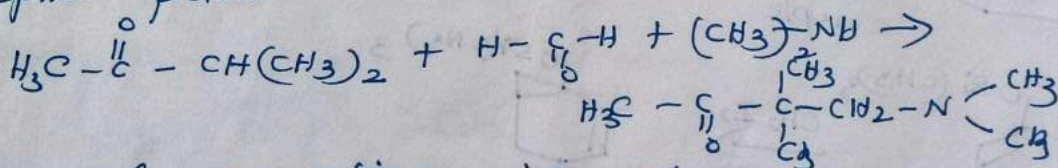


STEP II:- Formation of Mannich base:-

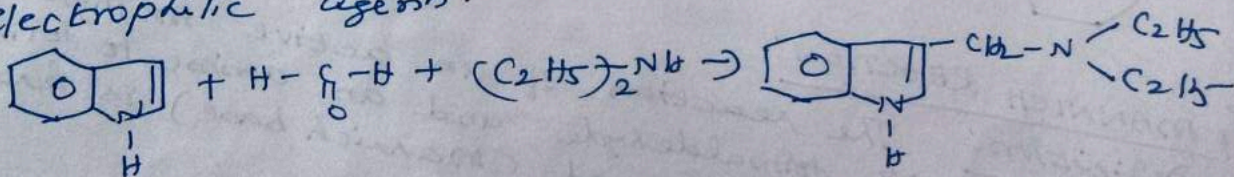
The iminium salt is then attacked by the enolate anion of the active methylene compound in the rate-determining step.



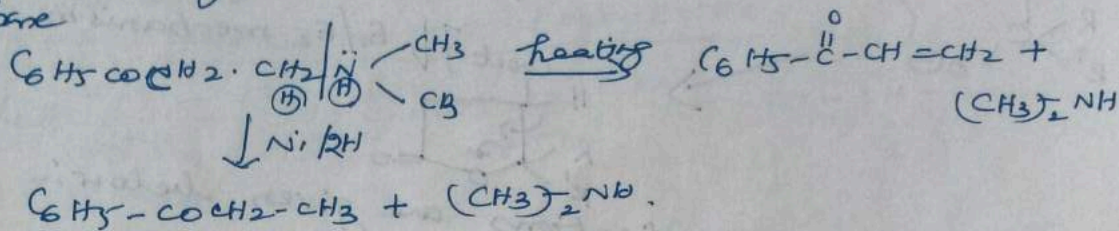
(i) Since the ease of formation of enol is increased by the presence of alpha-alkyl substituents, the following unsymmetrical ketone reacts predominantly at the more highly substituted alpha position.



(ii) Mannich reaction is not confined to enolizable ketones only. Phenols, nitroalkanes, indoles etc., are also attacked by iminium salts which are very strong electrophilic agents.



iii) The synthetic use of Mannich reaction lies in the facile conversion of a Mannich base into various products. For instance, an  $\alpha, \beta$ -unsaturated ketone or a saturated ketone may readily be obtained by heating or hydrogenating a Mannich base



#### XIV STOBBE REACTION:-

(Aldol type reactions between carboxylic esters and aldehydes/ketones)

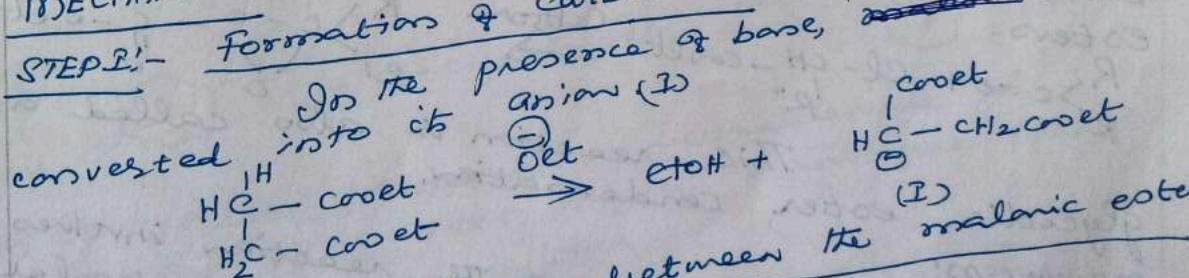
#### Definition:-

Diethyl succinate and its derivatives condense with aldehydes and ketones in the presence of bases such as NaOEt, NaH etc., to give olefins/lactones/ $\alpha, \beta$ -unsaturated half esters.

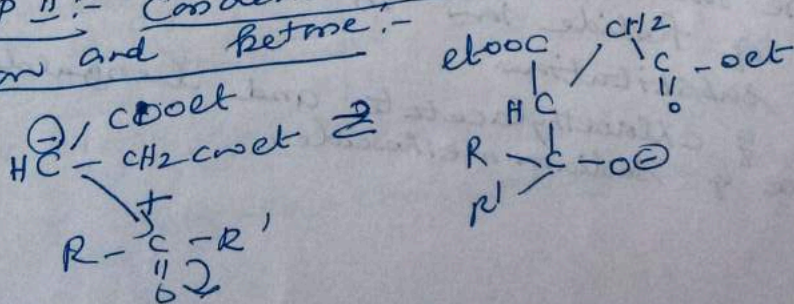
- (i) In the course of the reaction, one of the ester groups (sometimes both) is hydrolysed.
- (ii) Succinic ester reacts so much better than others.
- (iii) One ester group is always cleaved.
- (iv) The alcohol is not the product, but the olefin.
- (v) The reaction is limited to those esters which do not undergo Dieckmann condensation.

#### MECHANISM:-

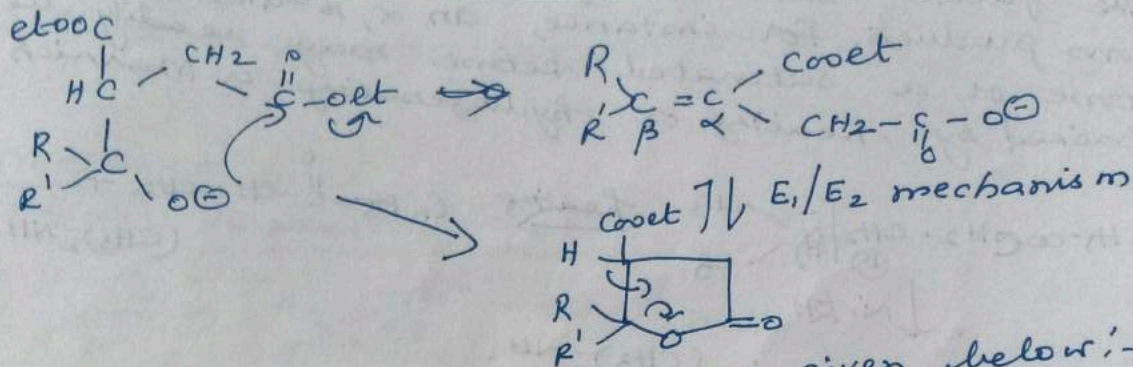
##### STEP I:- Formation of carbanion:-



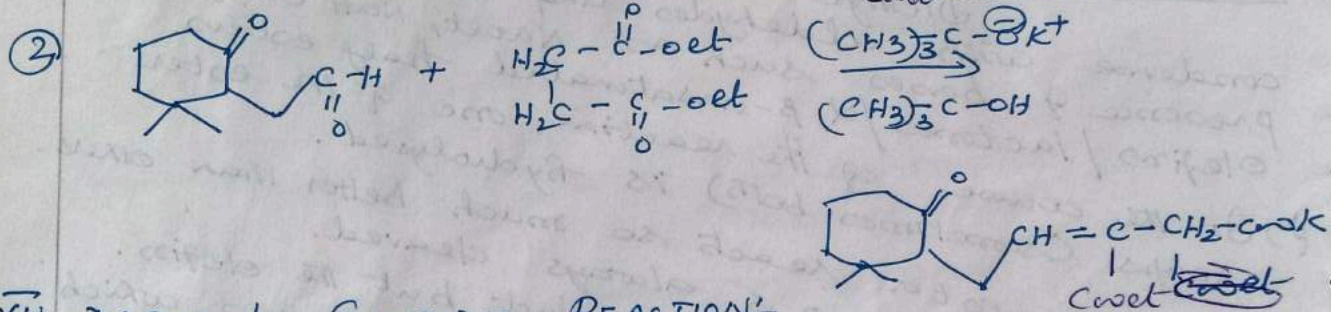
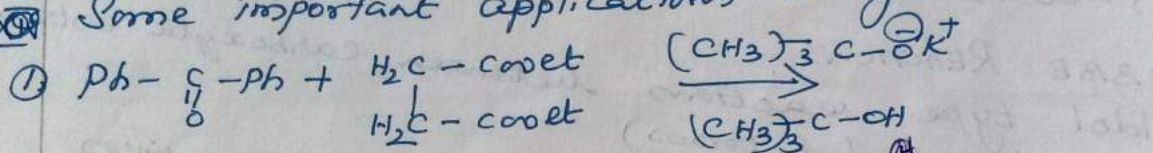
##### STEP II:- Condensation between the malonic ester anion and ketone:-



STEP III:- RING CLOSURE REACTION & FORMATION OF PRODUCT:-



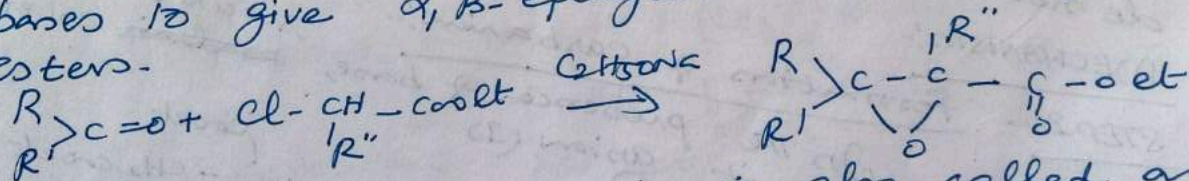
Some important applications are given below:-



XIV DARZEN'S GLYCIDIC REACTION:-

Definition:-

Aldehydes & ketones (mostly aromatic) condense with  $\alpha$ -haloesters in the presence of bases to give  $\alpha, \beta$ -epoxyesters called glycidic esters.



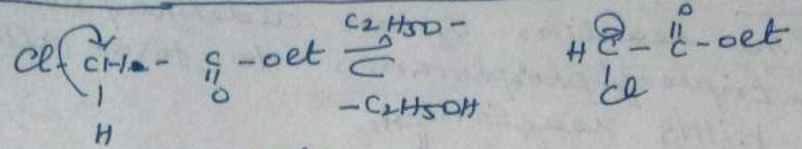
This reaction is also called as glycidic ester condensation.

MECHANISM:-

The mechanism of the reaction involves the displacement of halide ion in an intramolecular nucleophilic substitution.

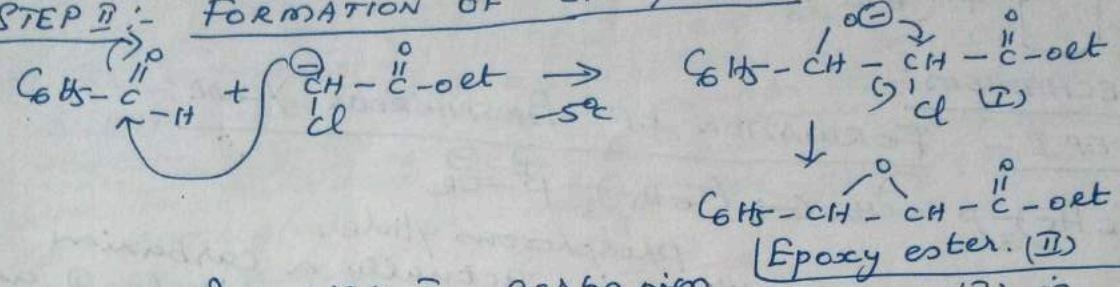
(E.g) Reaction of chloroethylacetate and benzaldehyde in the presence of sodium methoxide.

STEP I:- Formation of carbanion:-



Chloroethylacetate.

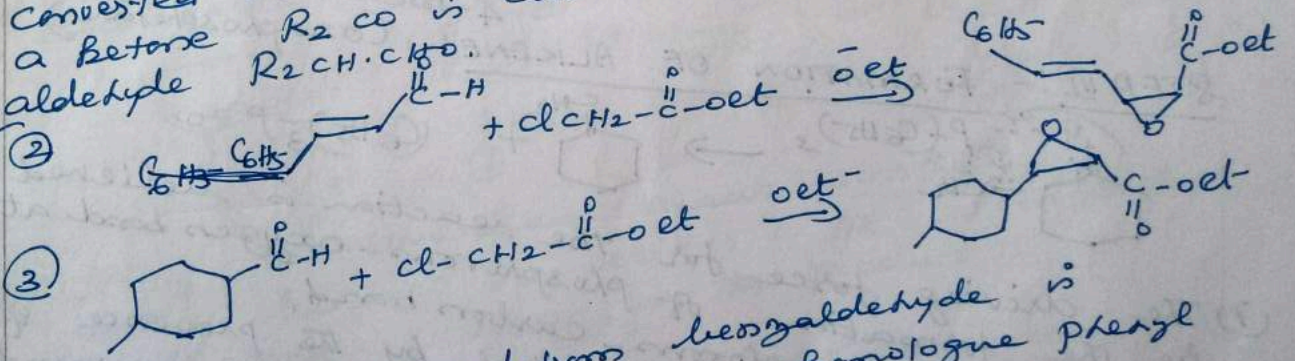
STEP II:- FORMATION OF EPOXY ESTER:-



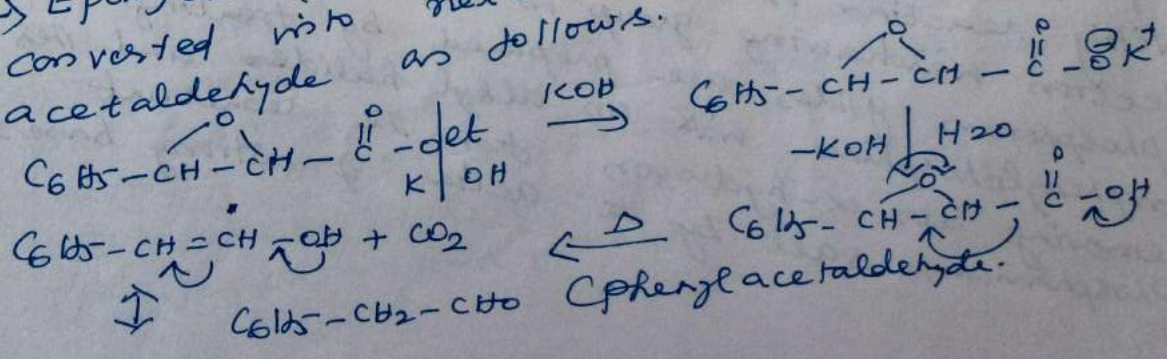
In step II carbanion adds to benzaldehyde and oxycanion (I) is formed. From (I), displacement of Cl<sup>-</sup> takes place by internal S<sub>N</sub>2 reaction.

Applications:-

1) Glycidic esters formed are useful for the synthesis of aldehydes + ketones. They undergo alkaline hydrolysis gives glycidic acid, which undergoes decarboxylative rearrangement in the presence of acid to an aldehyde/ketone. The overall process involves the addition of one or more carbons converted into longer chain homologue RCH<sub>2</sub>CHO is converted into longer chain a ketone R<sub>2</sub>CO is converted into longer chain aldehyde R<sub>2</sub>CH.CHO.

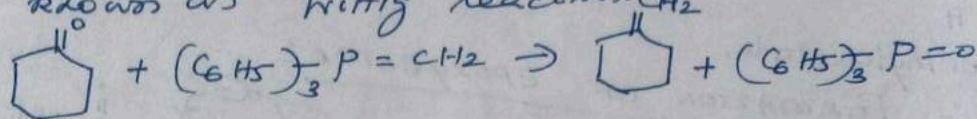


Epoxy ester (II) formed from benzaldehyde is converted into next higher homologue phenyl acetaldehyde as follows.



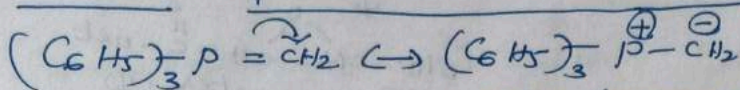
# XV WITTIG REACTION:-

Definition:- The reaction of an aldehyde/ketone with alkylidene triphenyl phosphoranes to form alkenes is known as Wittig reaction.



## MECHANISM:-

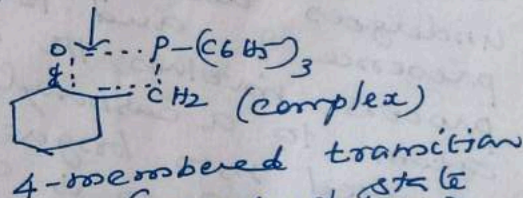
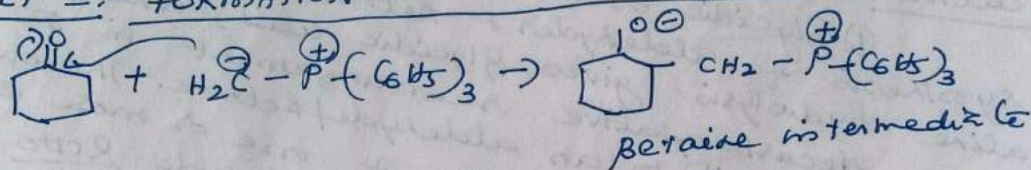
### STEP I:- FORMATION OF PHOSPHOROUS YLIDE:-



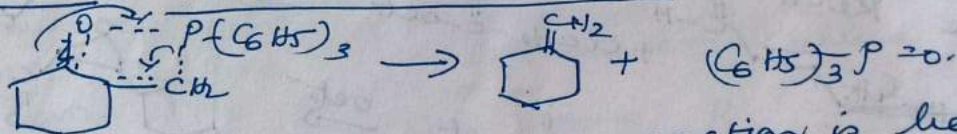
Phosphorous ylide.

Phosphorous ylide is actually a carbanion stabilised by resonance with the d orbitals of an adjacent phosphonium cation on the carbonyl carbon of the ketone.

### STEP II:- FORMATION OF COMPLEX WITH KETONE:-

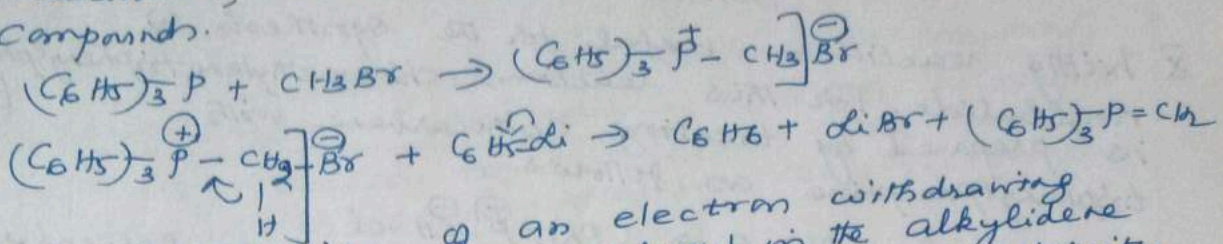


### STEP III:- FORMATION OF ALKENE:- (Oxaphosphetane)

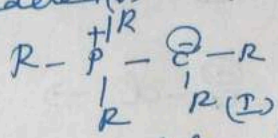


- (i) The driving force for the reaction is believed to be the formation of phosphorus-oxygen bond at the expense of phosphorus-carbon bond.
- (ii) Wittig reaction is accelerated by the presence of electron withdrawing group in the carbonyl compounds.
- (iii) phosphorous ylides are prepared by treating triphenyl phosphine with an alkyl halides and then removing an  $\alpha$ -hydrogen from the resultant phosphonium salt by the action of strong bases.

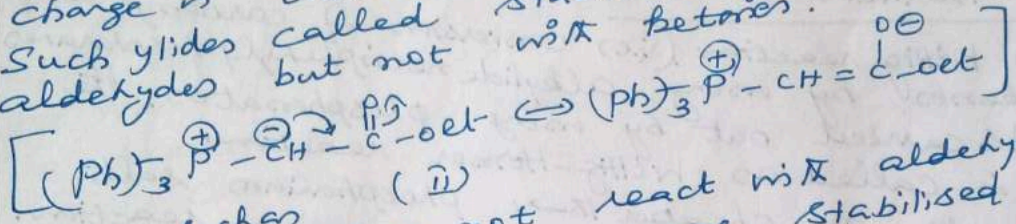
sodamide, sodium hydride or organolithium compounds. (19)



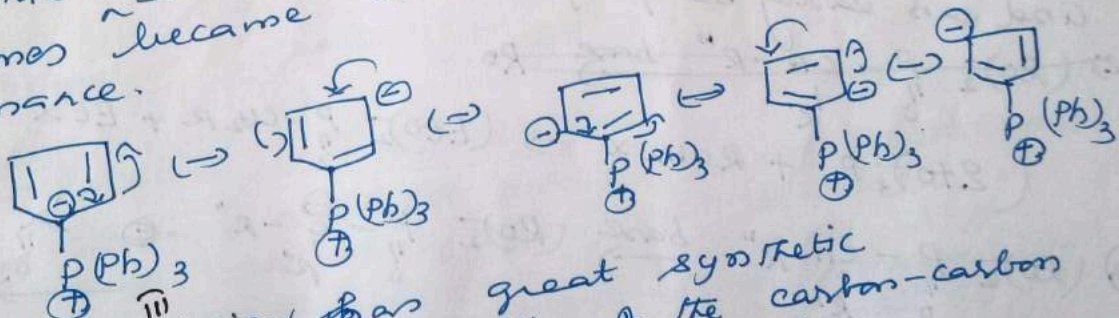
(iv) The introduction of an electron withdrawing substituent such as carbonyl in the alkylidene portion of the ylide decreases its nucleophilicity and the ylide becomes stable by resonance. The carbonyl compound is somewhat hindered. Simple ylide (i) is highly reactive.



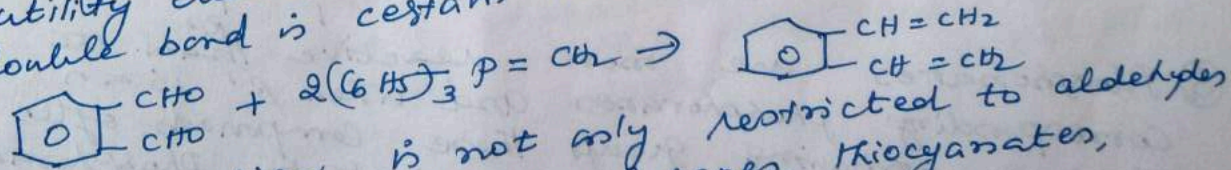
(vi) Ylide (ii) is more stable because negative charge is delocalised by the ester group. Such ylides called stabilised ylides, react with aldehydes but not with ketones.



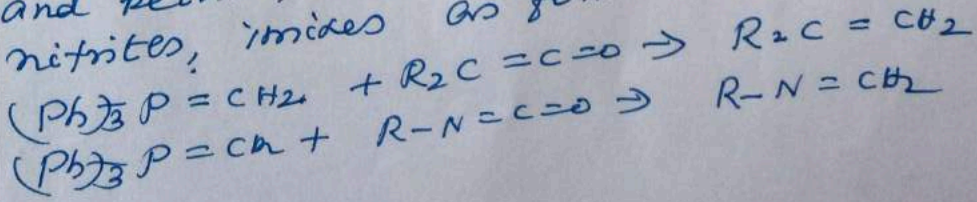
(vii) Ylide (iii) does not react with aldehydes and ketones because it is more stabilised by resonance.

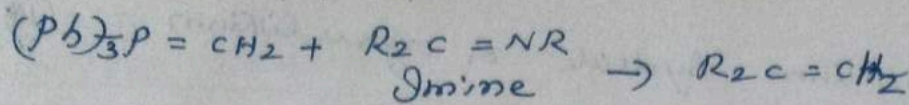


(viii) Wittig reaction has great synthetic utility because the position of the carbon-carbon double bond is certain in the product.

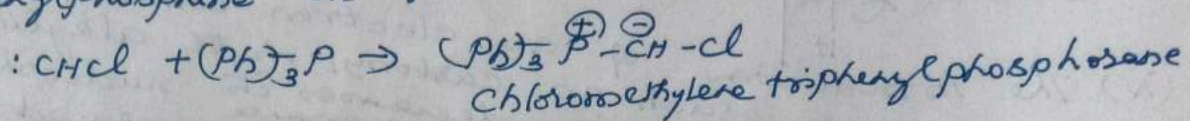


(ix) This reaction is not only restricted to aldehydes and ketones, but also to nitriles, thiocyanates, nitrites, imides as follows

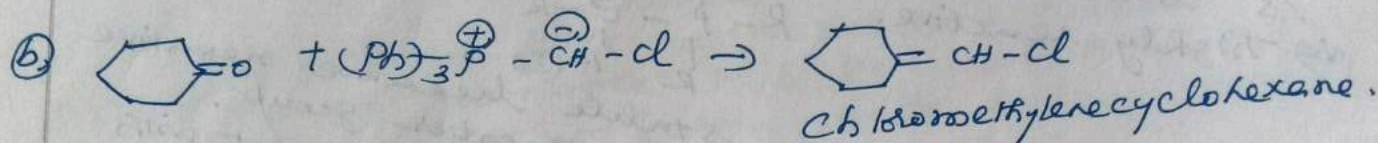
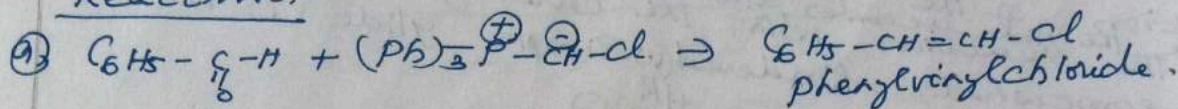




Ⓐ Wittig reaction is useful for the synthesis of vinyl halide. For this reaction, chloromethylene triphenylphosphorane is prepared by treating chlorocarbene with triphenylphosphine as follows.



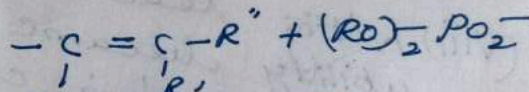
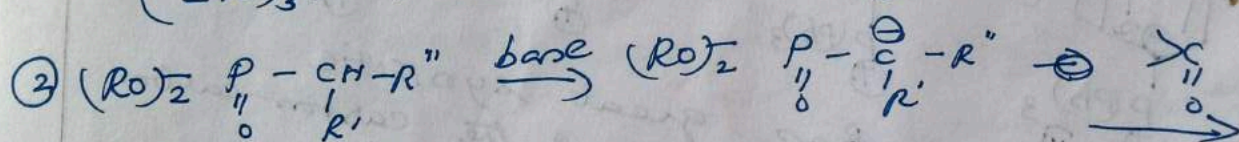
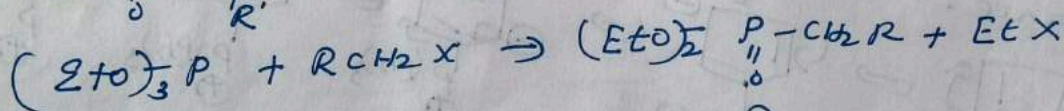
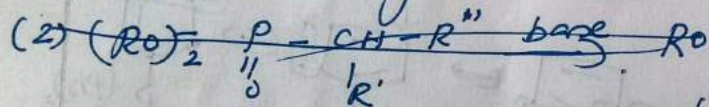
Reactions:-



(XVI) WITTIG - HORNER REACTION:-

Wittig reaction (i.e.) conversion of carbonyl compounds into alkenes by using alkylidene triphenylphosphoranes, if it is carried out by using phosphonates, the method is called as Wittig-Horner reaction.

(1) Phosphonates are cheaper than phosphonium salts and can easily be prepared by Arbuzov reaction.



(3) Phosphonates are more reactive than the corresponding phosphoranes and when  $R'$  is an electron withdrawing group these compounds often react with ketones that are inert to phosphoranes.



XVII  
CARBENES:-

Definition:-

Carbenes can be defined as neutral, divalent, carbon intermediates in which a carbon covalently bonded to two atoms and has two non-bonded orbitals containing two electrons in between them.

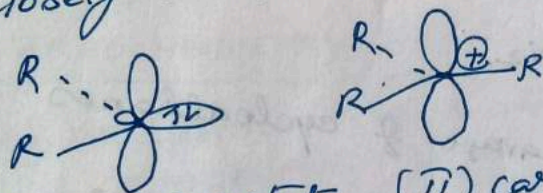
STRUCTURE:-

(i) Theoretical consideration suggests that there are two possible kinds of carbenes, singlet and triplet carbenes.

(ii) In the singlet state, a carbon atom is presumed to approximate  $sp^2$  hybridisation.

(ii) Two of the three  $sp^2$  hybrid orbitals are utilized in forming two covalent bonds whereas the third hybrid orbital contains the unshared pair of electrons.

(iv) The remaining p-orbital remains vacant. Thus singlet carbene (I) resembles carbanion<sup>origin</sup> ion, very closely as follows

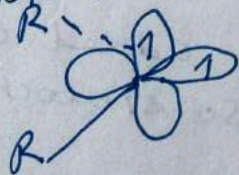


(I) Singlet state (II) Carbanion ion

(v) Carbon atom of a triplet carbene is  $sp$  hybridized and it is a linear or a non-linear species.

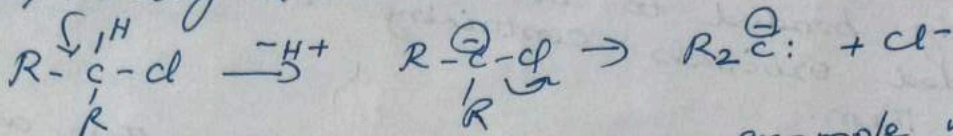
(vi) These two hybrid orbitals are involved in the bond formation with two groups and the remaining two electrons are placed one in each in the equivalent, mutually perpendicular  $p_y$  &  $p_z$  orbitals.

(vii) These electrons have parallel spins and a carbene triplet state. This structure is referred to as triplet state.

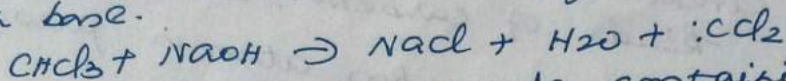


## GENERATION OF CARBENES:-

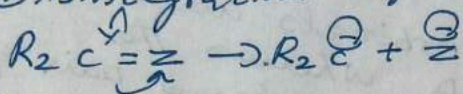
Carbenes are chiefly formed in two ways.  
 (i) In  $\alpha$ -elimination, a carbon loses a group without its e-pair, usually a proton and then a group with its pair, usually a halide ion.



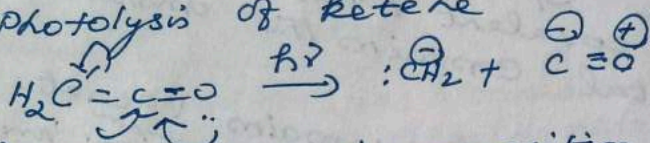
The most common example is formation of dichlorocarbene by treatment with  $\text{CHCl}_3$  with a base.



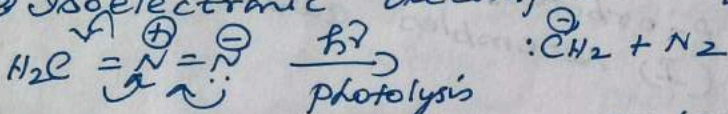
(ii) Disintegration of compounds containing double bonds



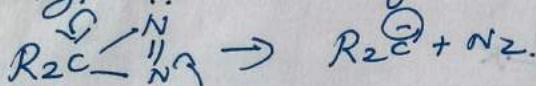
(Eg) (a) Photolysis of ketene



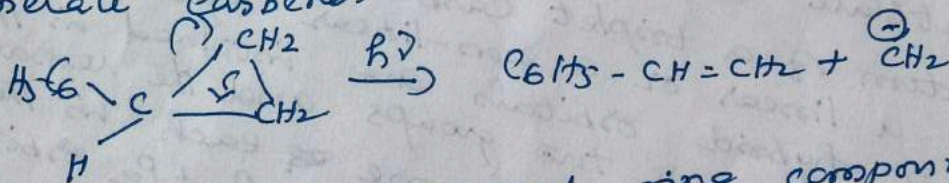
(b) Isoelectronic decomposition of diazomethane



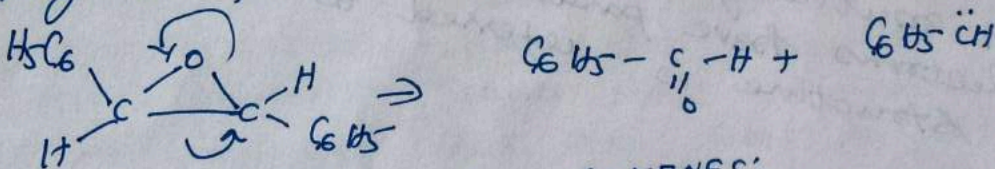
(c) Diazirines also give carbenes.



(iii) Photochemical/thermal cleavage of cycloalkanes generate carbenes.



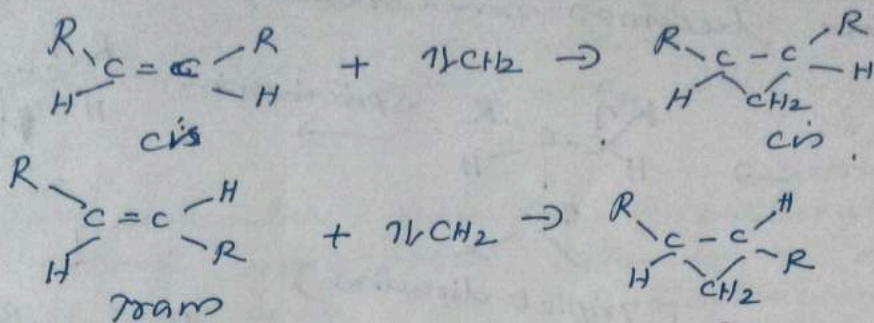
(iv) Oxiranes, three membered ring compounds decompose easily to produce a carbene and a carbonyl compound.



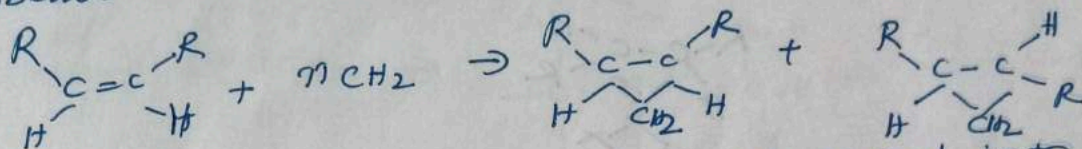
## ADDITION REACTIONS WITH ALKENES:-

(1) CYCLOADDITION:- Singlet carbene, when it is added to alkenes, the reaction is stereospecific. So stereochemistry

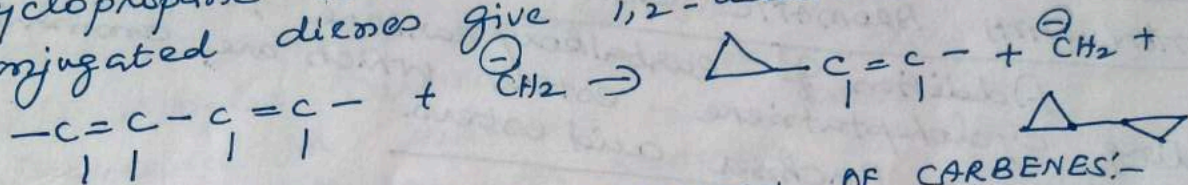
of the alkene is retained.



In contrast, the addition of triplet carbenes to alkenes takes place non-stereospecific

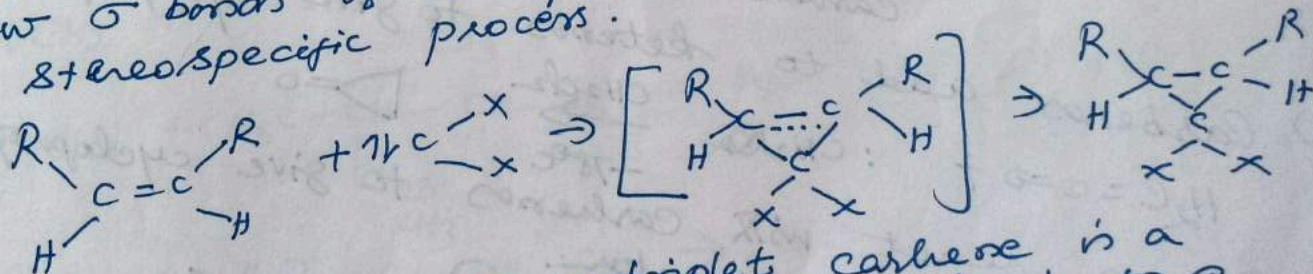


- ② Olefins of all types can be converted into cyclopropane derivatives by this reaction. Conjugated dienes give 1,2-addition.



### STEREOCHEMISTRY OF CYCLOADDITION OF CARBENES:-

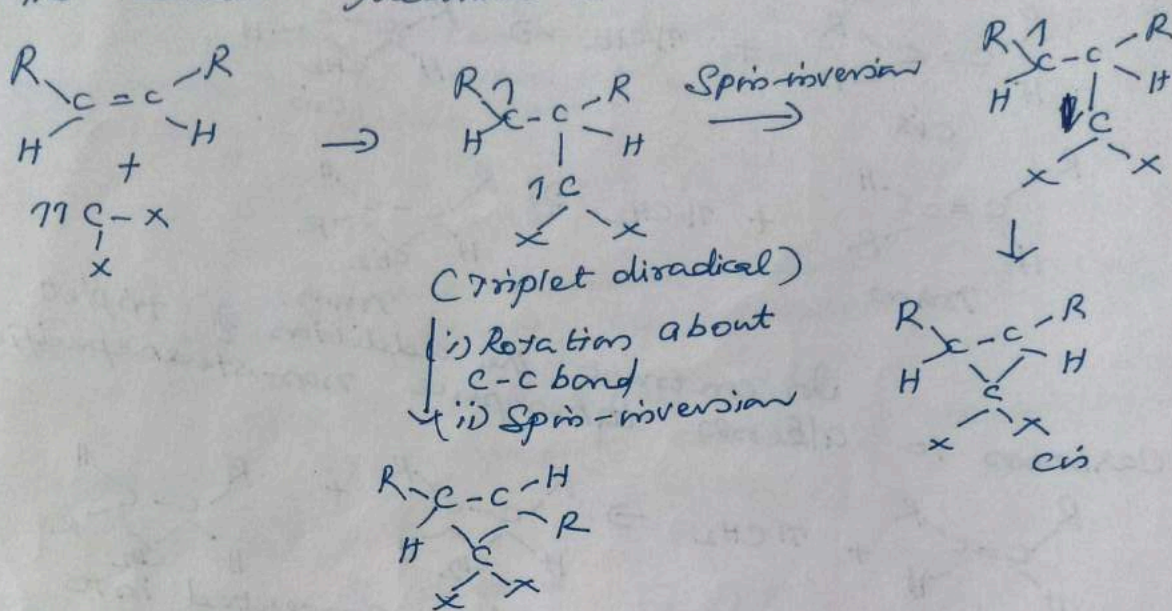
- (i) The addition of a singlet carbene to an alkene is a concerted process as there is no spin restriction on the simultaneous formation of two new  $\sigma$  bonds of the cyclopropane and hence it is a stereospecific process.



- (ii) The cycloaddition of a triplet carbene is a step-wise process. The first step leads to a triplet diradical which will have to undergo spin-inversion before it collapses to cyclopropane.

- (iii) Since this diradical has c-c single bond, there is a possibility of free rotation about the bond.

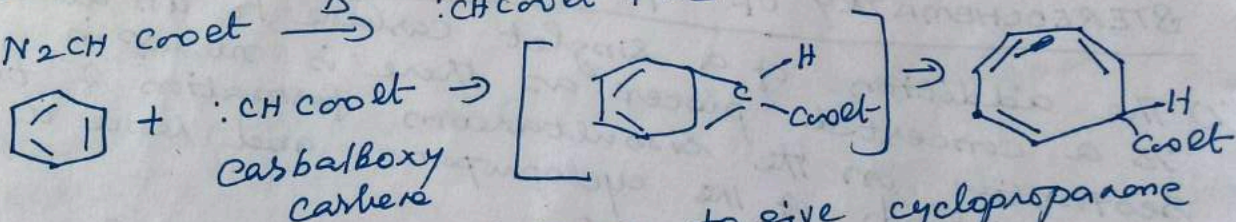
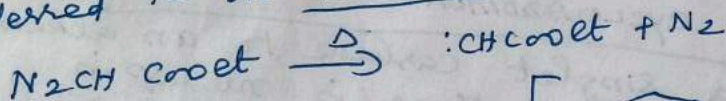
(iv) This rotation is faster than spiro-inversion  
 as the reaction becomes non-stereospecific.



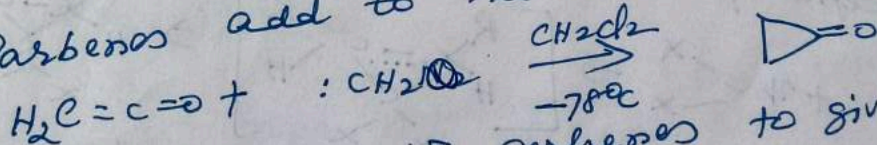
### ③ OTHER ADDITION REACTIONS:-

#### (i) ADDITION WITH AROMATIC SYSTEM:-

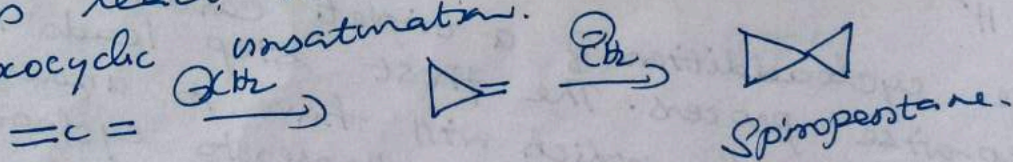
Addition of carbonyl carbene to benzene, yielding cycloheptatriene esters which are commonly referred to as Bucherer acid esters.



(ii) Carbenes add to ketones to give cyclopropanone

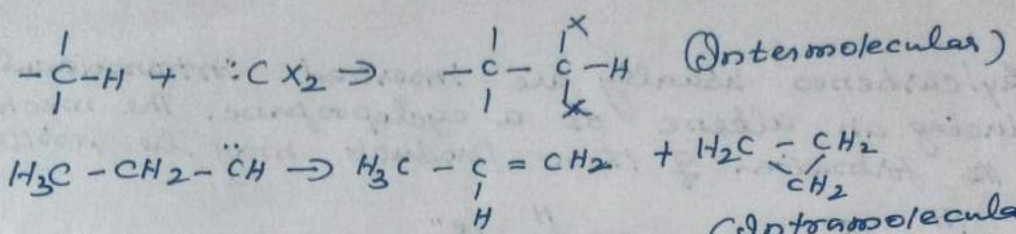


(iii) Allenes react with carbenes to give cyclopropanes

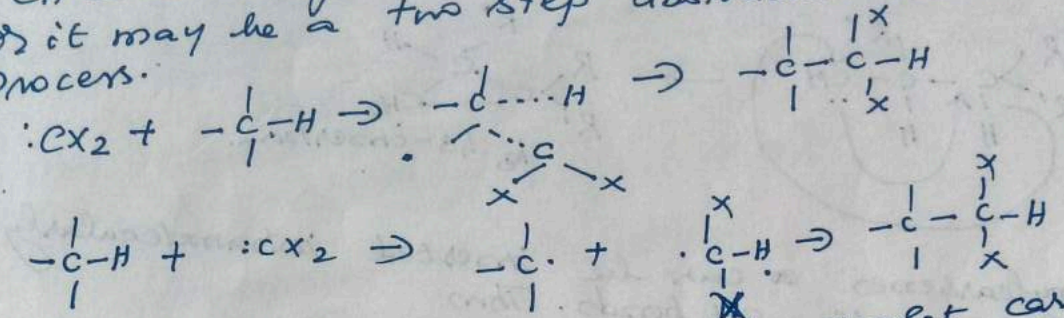


#### INSERTION REACTIONS OF CARBENES:-

Carbenes can be inserted to a C-H bond, the reaction may be inter/intramolecular.

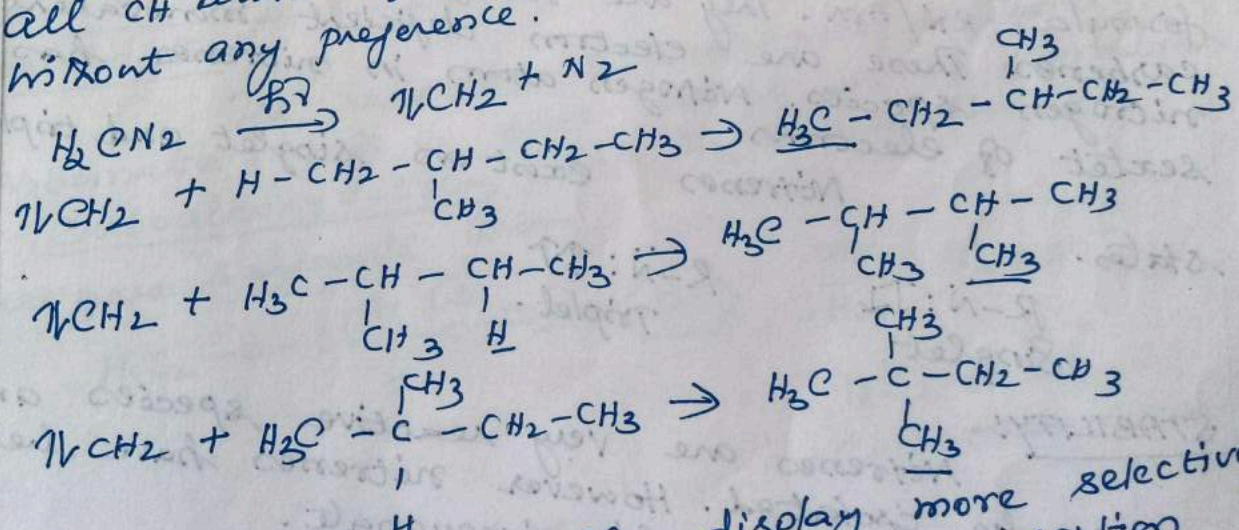


(i) Intermolecular insertion of carbenes into a CH bond may occur either by a one-step process or it may be a two-step abstraction-recombination process.



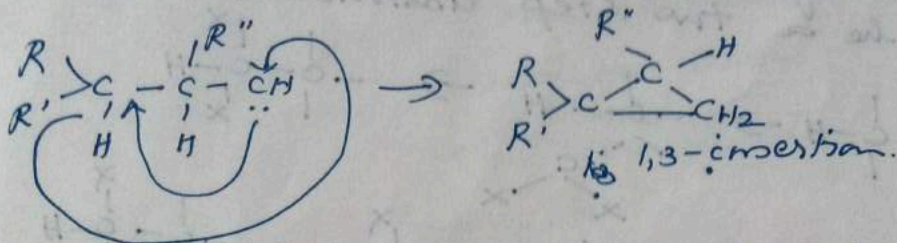
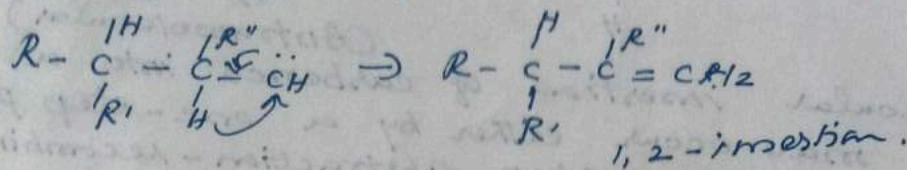
(ii) In cycloaddition reactions, the carbene undergoes concerted insertion whereas singlet carbenes are inserted via two-step process.

(iv) A singlet carbene does not show any preference for insertion to a particular position. Singlet methylene for example is inserted into all CH bonds of 2-methylbutane without any preference.

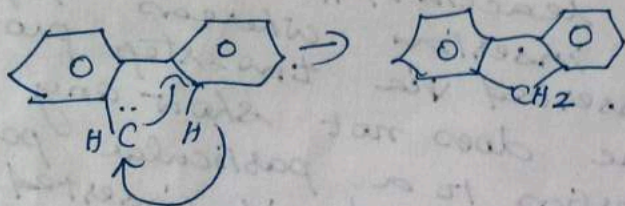


(v) Triplet carbenes usually display more selectivity for a more particular position in insertion reactions. Triplet methylene shows prim : sec : tert selectivity 4.4 : 1.6 : 1.0.

(vi) Alkylcarbenes usually are inserted intramolecularly producing an alkene or a cyclopropane. The mechanism for the formation of these products may be written as



(vii) Arylcarbenes can be inserted intramolecularly into aromatic C-H bonds. Thus

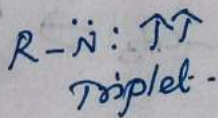
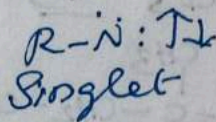


### XVIII

#### NITRENES:-

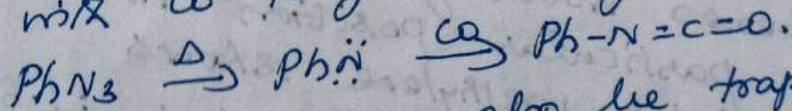
Definition:- Nitrenes are organic species, having general formula  $RN/ArN$ . They are nitrogen analogues of carbenes. These are electron deficient monovalent nitrogen species. Nitrogen atom in nitrenes has a sextet of electrons.

Nitrenes exist as singlet and triplet states.



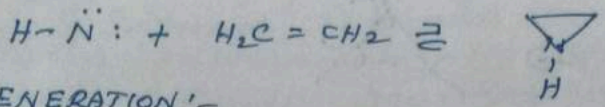
#### STABILITY:-

Nitrenes are very reactive species and cannot be isolated. However nitrenes have been trapped with CO to yield isocyanate.



Nitrenes can also be trapped in the presence of ethylene.

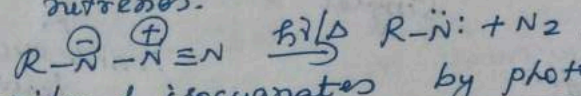
molecularly  
mechanism  
written as



GENERATION:-

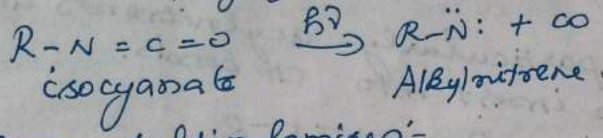
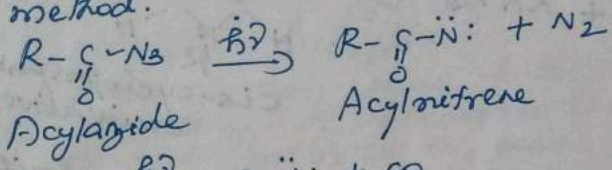
① Form Azides:-

Thermal / photolytic decomposition of azides give nitrenes.



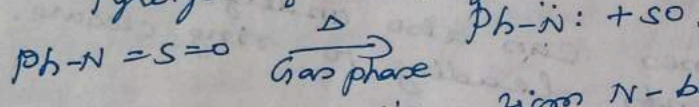
② Form acylazides & isocyanates by photolysis:-

Acyl and alkyl nitrenes can be obtained by this method.



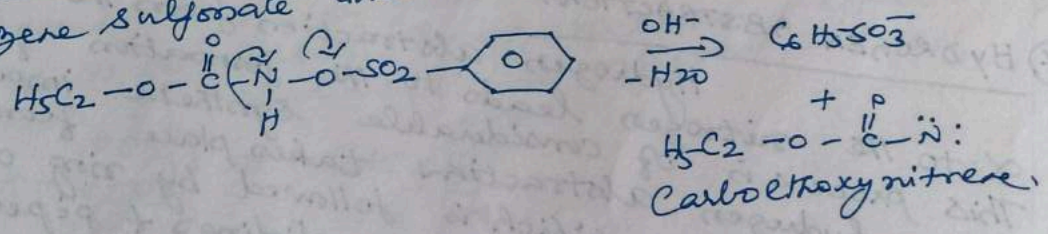
③ Form Sulfonylamines:-

Pyrolysis of sulfonylamines generate nitrenes.



④ Elimination reaction from N-benzene sulfonyl carbamates:-

The reaction of N-benzene sulfonyl carbamate with a base results in the formation of Carboalkoxy nitrene with the elimination of benzene sulfonate anion.

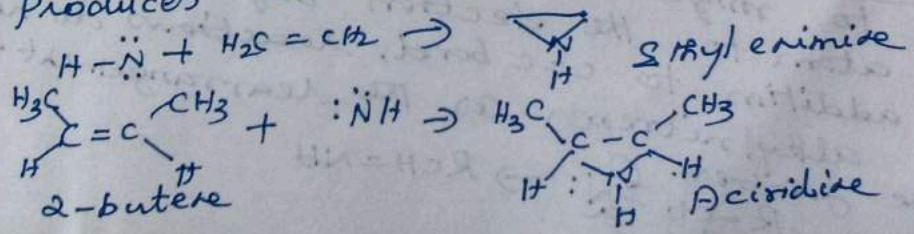


REACTIONS OF NITRENE:-

① Addition to >C=C< bonds

(i) The addition of nitrenes to C=C bond is stereospecific with singlet and non-stereospecific with triplet nitrenes.

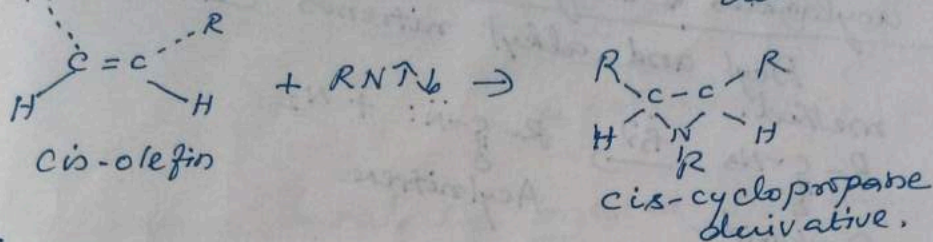
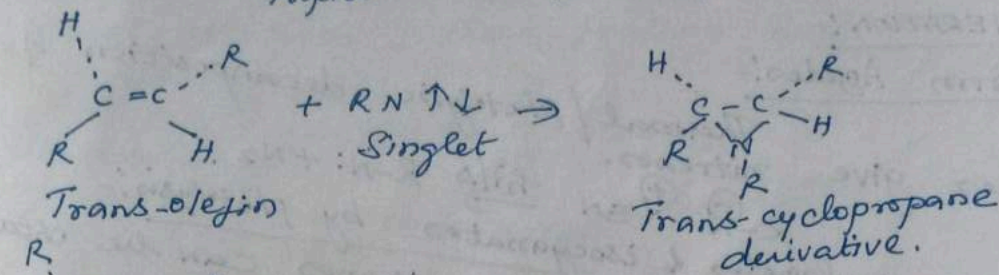
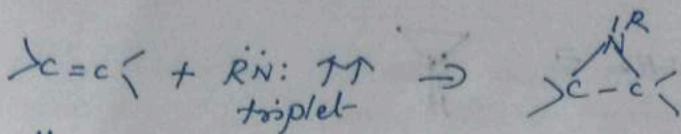
(ii) cycloaddition of nitrenes to alkenes produces acridines.



early

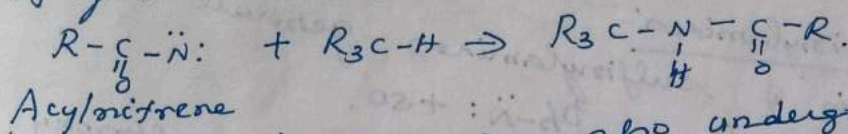
general  
of  
valent  
has a  
triplet

and  
been



## ② INSERTION:-

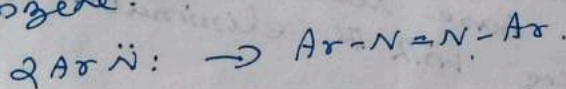
Nitrenes, particularly acylnitrenes and sulfonyl nitrenes can insert into C-H bonds.



Nitrenes can also undergo insertion into C-H single bonds leading to ring closure.

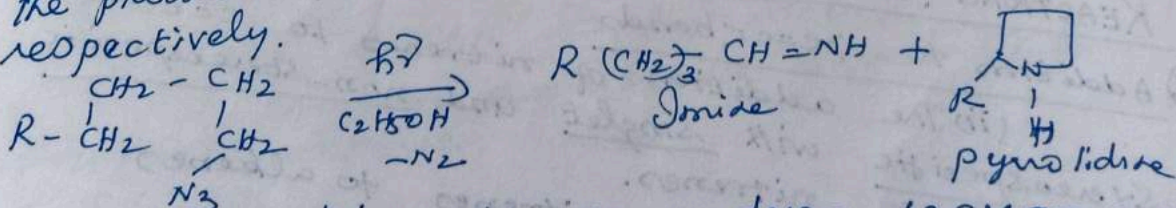
## ③ DIMERISATION:-

Dimerisation of aryl nitrenes give azobenzene.

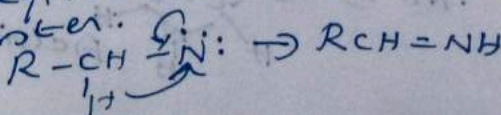


## ④ HYDROGEN ABSTRACTION:-

Hydrogen abstraction from the carbon  $\alpha$  to the nitrogen leads to the formation of imines. This process is of considerable synthetic importance. When hydrogen abstraction takes place from 4<sup>th</sup>/5<sup>th</sup> position, which is followed by ring closure, the product formed are pyrrolidines + piperidines respectively.

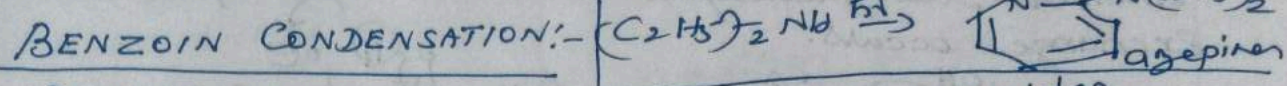


⑤ Rearrangements:- Nitrenes undergo rearrangements also due to migration of a group from adjacent atom to the electron deficient nitrogen. Insertion + addition to C-C bond, reactions do not proceed in alkyl nitrenes as the rearrangement is much more faster.



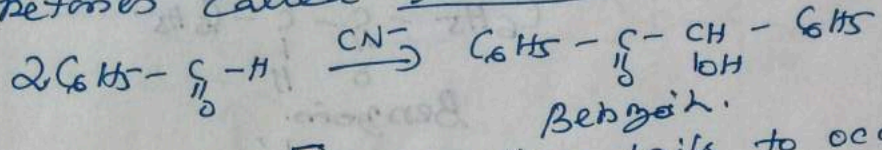


6) Ring enlargement: - Amepines are prepared by ring enlargement of phenylamide.  $\rightarrow$  (24)  
 Nitrenes can also be obtained as reaction intermediate in Hofmann, Curtius, Schmidt & Lossen rearrangements.



Definition: -

In the presence of alkali cyanides, aromatic aldehydes (benzaldehyde and its derivatives) often dimerize to form  $\alpha$ -hydroxy ketones called benzoin.

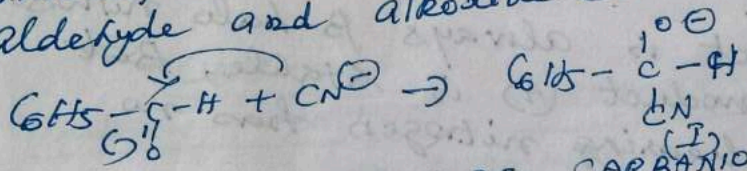


The reaction fails to occur, when either strongly e-attracting or electron releasing groups are present in ortho or para positions to the aldehyde group.

MECHANISM: -

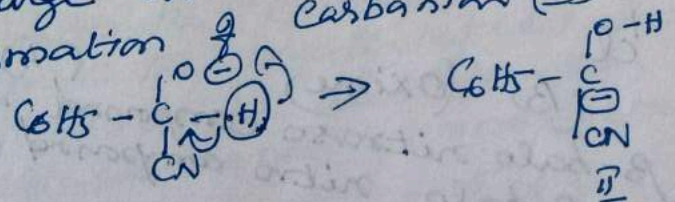
STEP I: - FORMATION OF ALKOXIDE ION: -

Cyanide ion, which is a very strong nucleophile and a very weak base attacks the aldehyde and alkoxide (I) is formed.

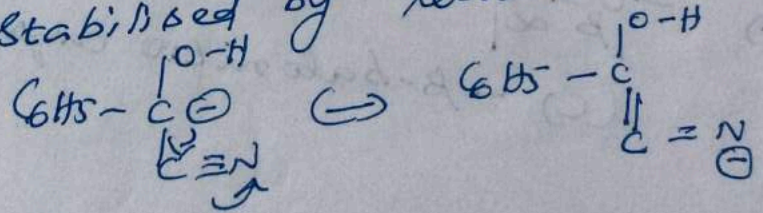


STEP II: - FORMATION OF CARBANION: -

Internal exchange of proton occurs and carbon attains negative charge and carbanion (II) is formed. Cyanide group delocalize the negative charge on the carbon through mesomeric effect and carbanion (II) is assisted.

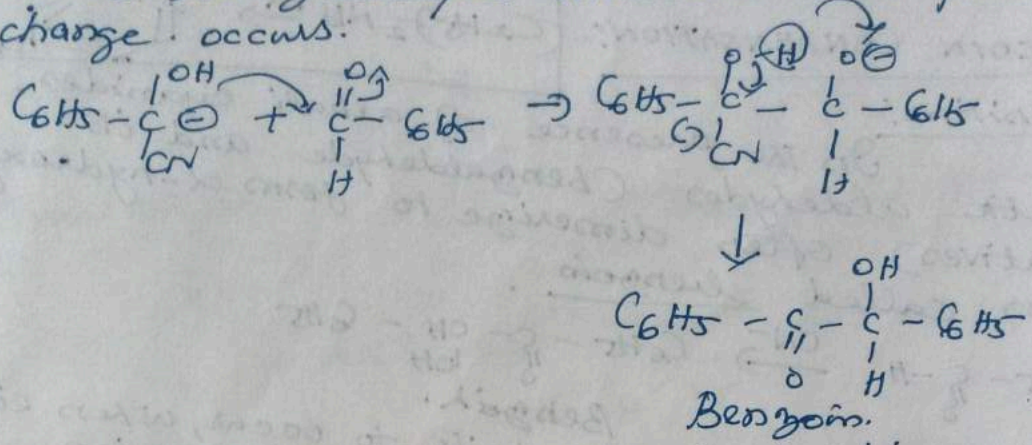


The newly formed carbanion (II) is stabilized by resonance as follows.



STEP III :- FORMATION OF BENZOIN :-

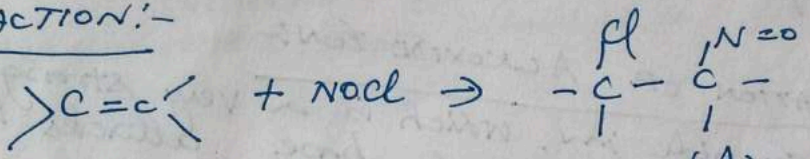
The carbanion (II) formed attacks another benzaldehyde molecule and proton exchange occurs.



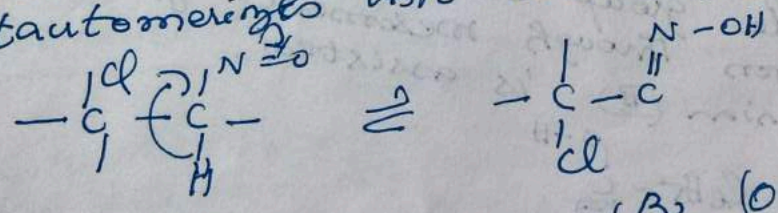
XX ADDITION OF NOCl to double bond :-

Nitroso-chloro addition :-

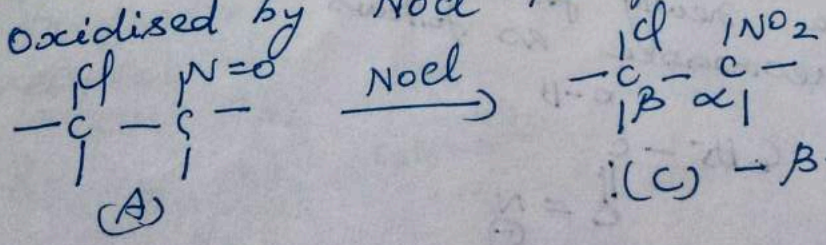
REACTION :-



- (i) There are three possible products when NOCl is added to alkenes.
- (ii) The initial product is always  $\beta$ -halo nitroso compound (A). But product (A) is stable, ~~but~~ if the carbon bearing nitrogen has no hydrogen atom.
- (iii) If that carbon has hydrogen atom, product (A) tautomerises into oxime (B)



- (iv) With some alkenes,  $\beta$ -halo nitroso compound (A) is oxidised by NOCl to  $\beta$ -halo nitro compound (C)



(C) -  $\beta$ -halo nitro compound.