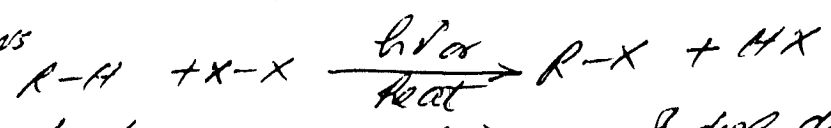


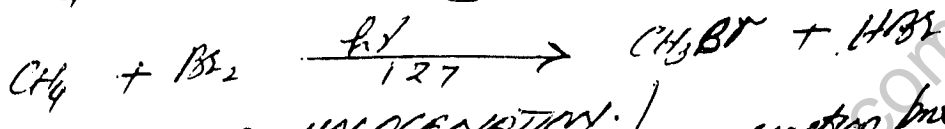
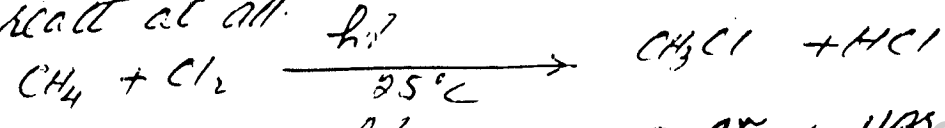
PREPARATION OF ALKYL HALIDES:-

HALOGENATION OF ALKANES

The replacement of hydrogen of an alkane by a halogen group is called Halogenation. The reaction is carried out by reacting chlorine or bromine with an alkane at 200-400°C or in presence of U.V. light. The ~~the~~ reaction does not occur at room temperature or in dark. The general reaction can be shown as follows



The order of reactivity is  $F_2 > Cl_2 > Br_2$ . Iodine does not react at all.

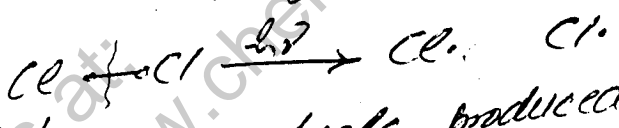


MECHANISM OF HALOGENATION.

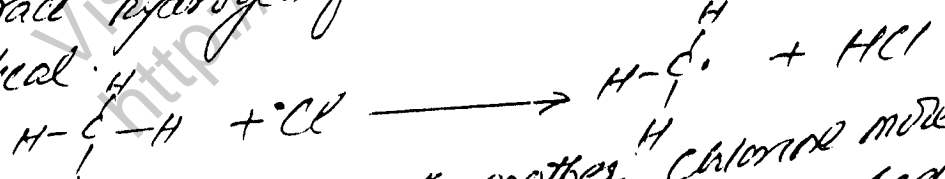
Free radical mechanism:

The reaction proceeds through following steps:

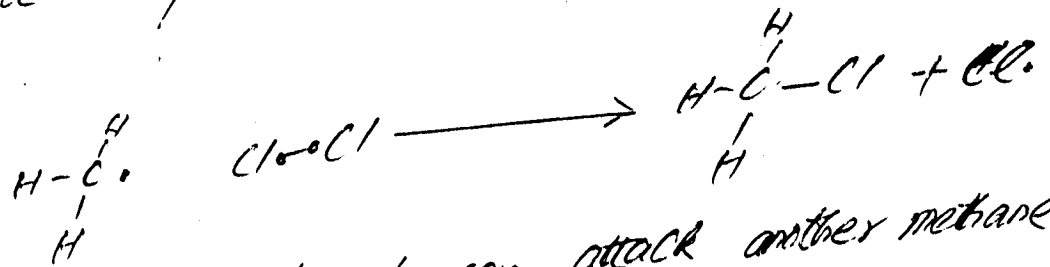
1) INITIATION STEP:- In this step free radicals are produced by light or heat.



PROPAGATION STEP | The free radicals produced in first step abstract hydrogen from any alkane producing an alkyl radical.

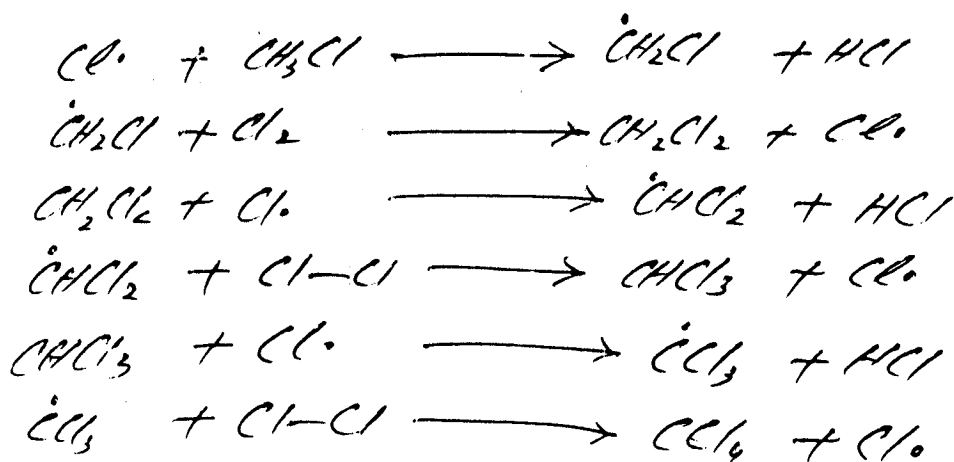


The methyl radical react with another chlorine molecule to produce methyl chloride and another chlorine radical.

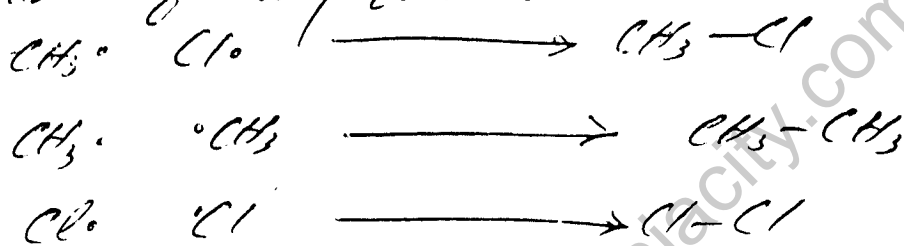


Chlorine radical produced can attack another methane molecule, and reaction continues.

As the reaction proceeds the concentration of methane decreases and concentration of methyl chloride increases. The possibility of Cl radical to attack  $\text{CH}_3\text{Cl}$  increases which leads to dichloro, trichloro, and tetrachloro products

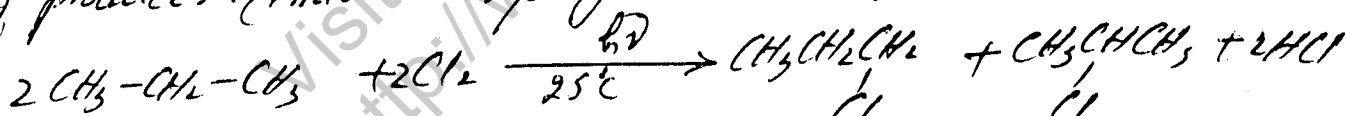


TERMINATION STEP The termination may occur due to collision of any two radicals.



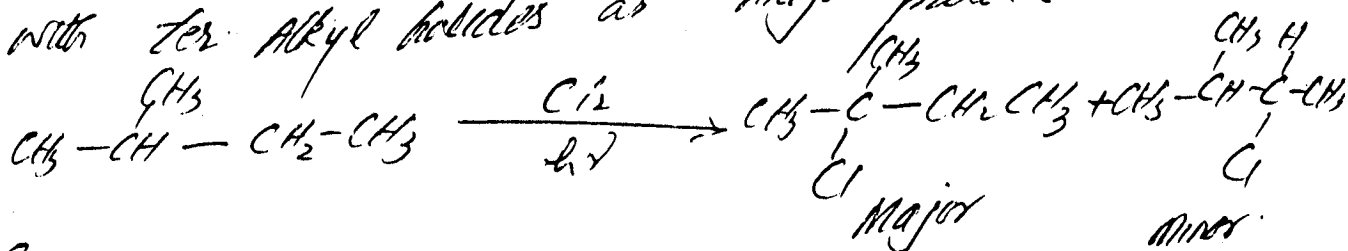
The polyhalogenation can be minimized by use of halogen excess of <sup>alkane</sup> ~~halogen~~ and limited quantity of ~~alkane~~.

Halogenation of long chain alkanes produces mixture of products. Thus all hydrogens can be replaced by halogen



Pentane can produce three possible products on monohalogenation.

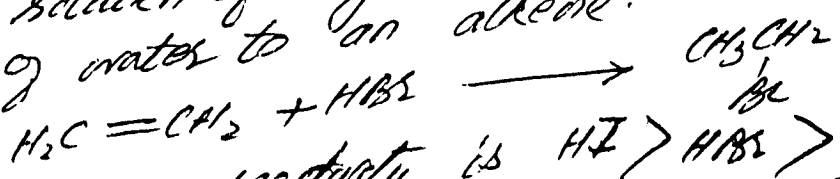
Branched alkanes produce a mixture of alkyl halide with ter-alkyl halides as major product



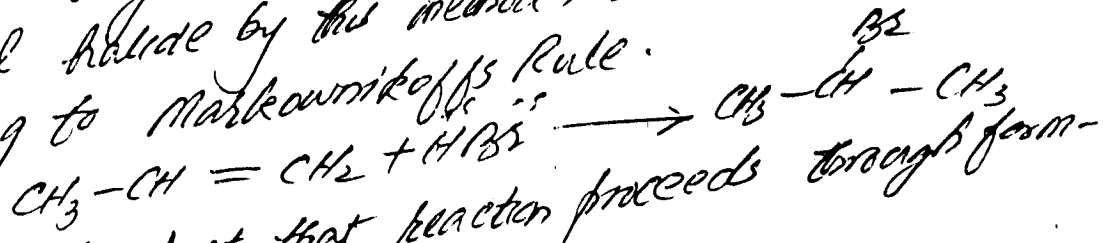
Since halogenation of alkanes produces a mixture of product it is not a good method for preparation of alkyl halides

FROM ALKENES

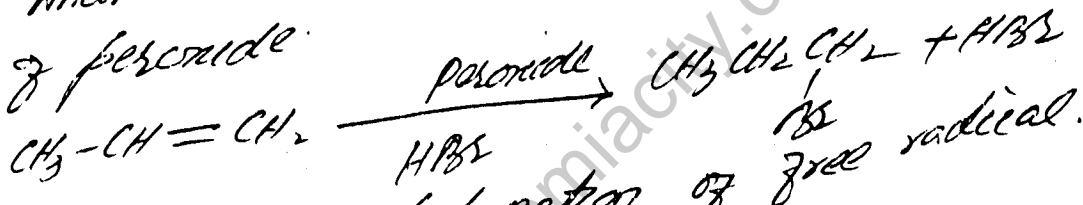
Addition of halogen acids to an alkene produces alkyl halide. Dry gaseous halogen acid is passed through alkene to get alkyl halide. Aqueous solution of halogen acid is not used to avoid addition of water to an alkene.



The order of reactivity is  $HI > HBr > HCl$ . When an unsymmetrical alkene is converted to an alkyl halide by this method, addition takes place according to Markownikoff's Rule.



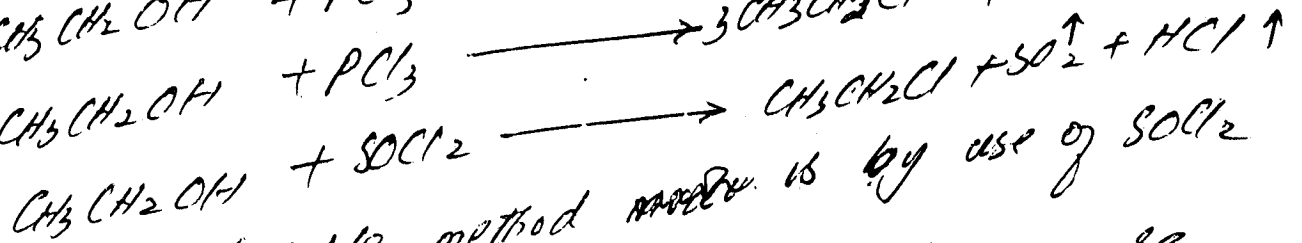
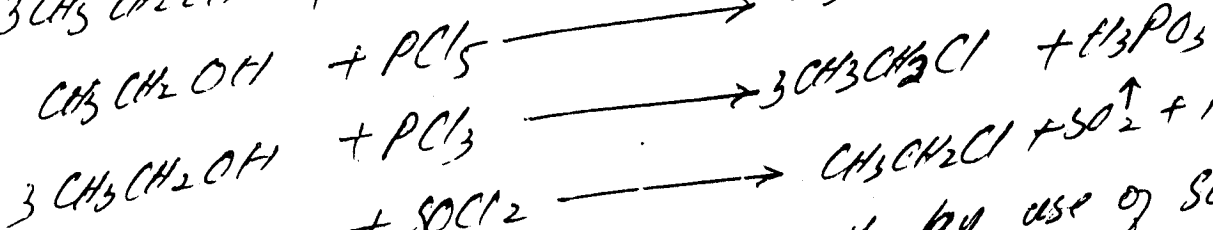
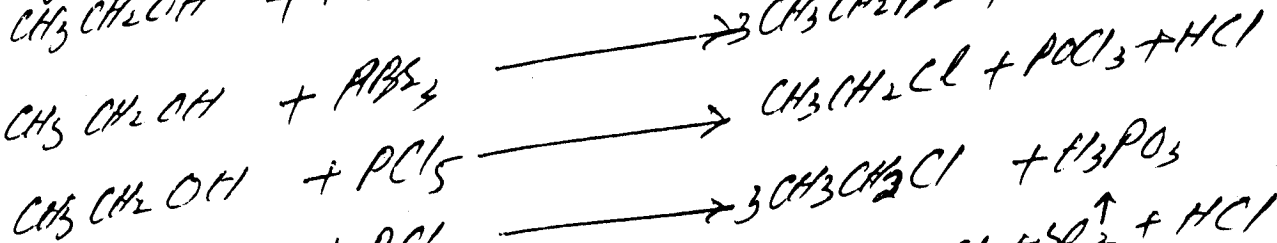
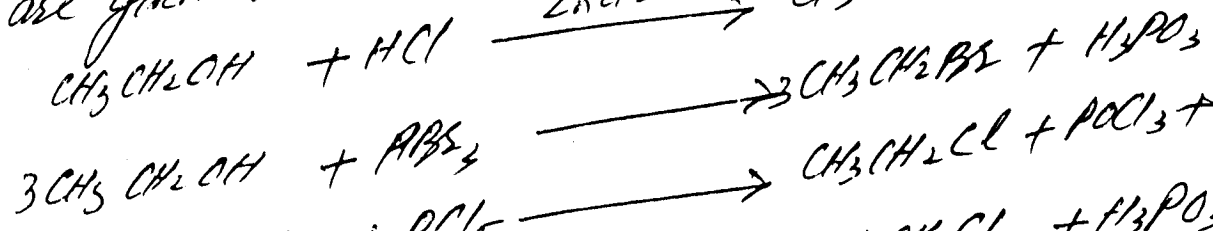
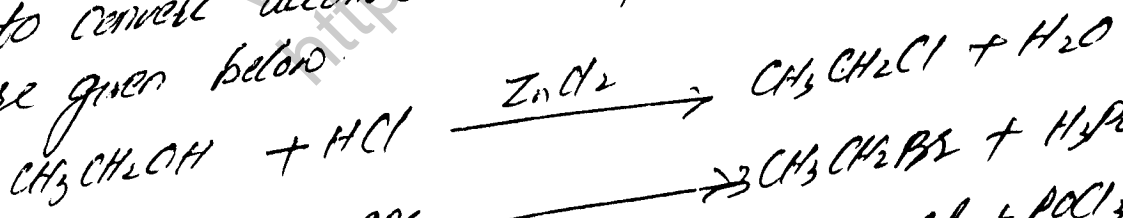
This is due to the fact that reaction proceeds through formation of carbocation ion. However Anti-Markovni addition can take place in presence of peroxide.



This reaction proceeds through formation of free radical.

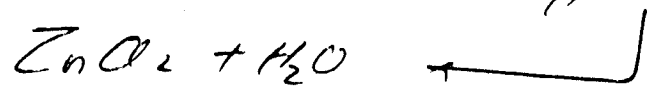
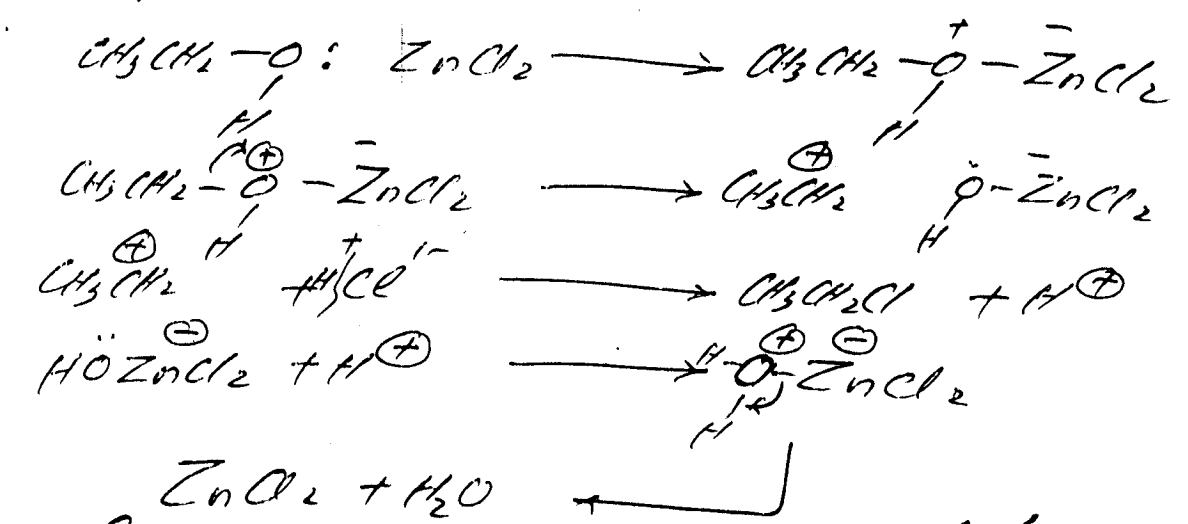
FROM ALCOHOLS

Alkyl halides are mostly prepared from alcohols. A variety of methods are available to convert alcohol into alkyl halide. Some of these are given below.

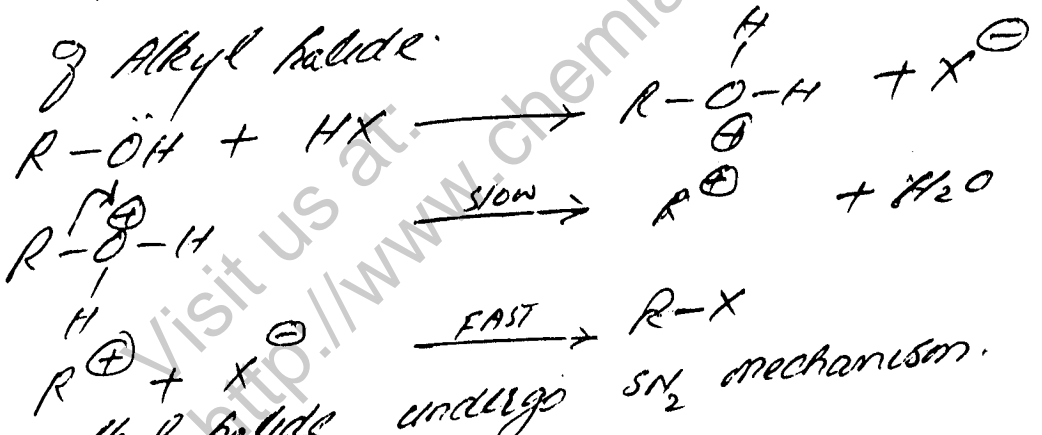


The best possible method is by use of  $SOCl_2$  because side products  $SO_2$  and  $HCl$  are removed as gases.

MECHANISM | The reaction of alcohol with halogen acid involves formation of carbocation ion. So order of reactivity is  $3^{\circ} > 2^{\circ} > 1^{\circ}$ . The catalyst used is  $ZnCl_2$ .

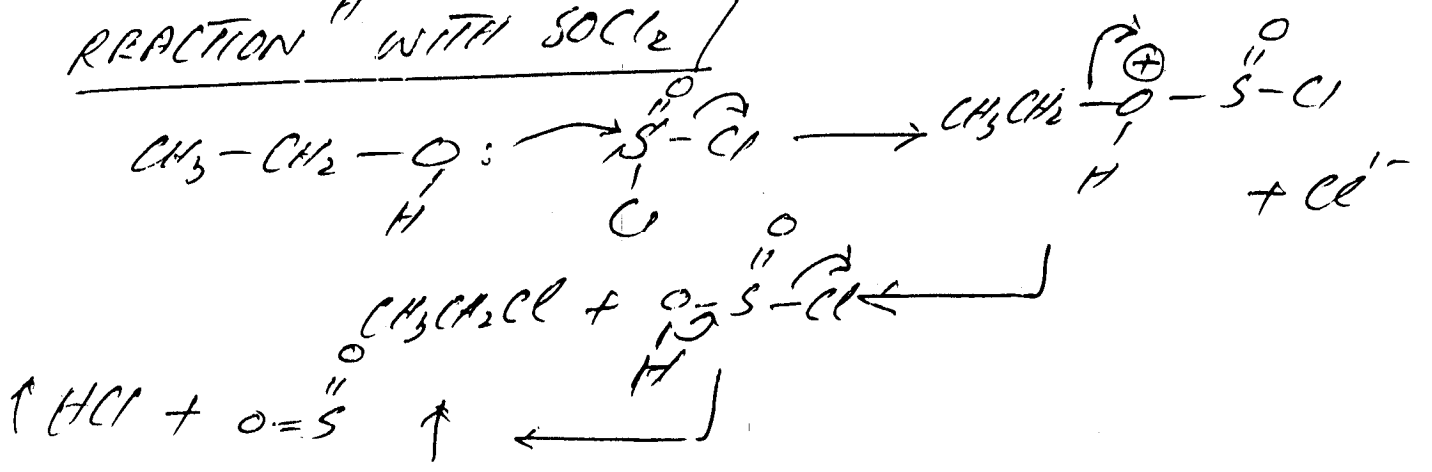


However since the reaction proceeds through formation of carbocation ion so there are always chances of rearrangement.  $HBr$  and  $HI$  being more reactive react without catalyst. The reaction may proceed through  $S_N1$  or  $S_N2$  mechanism depending upon the nature of alkyl halide.



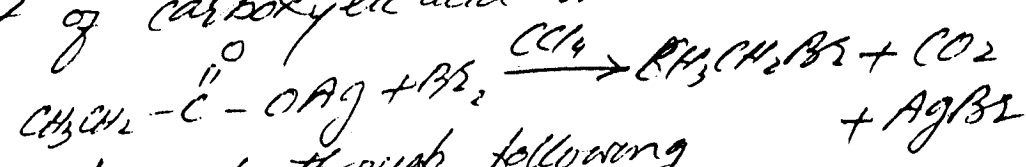
Primary alkyl halide undergo  $S_N2$  mechanism.  
 $R-OH_2^+ + X^- \xrightarrow{slow} R-X + H_2O$

REACTION WITH  $SOCl_2$

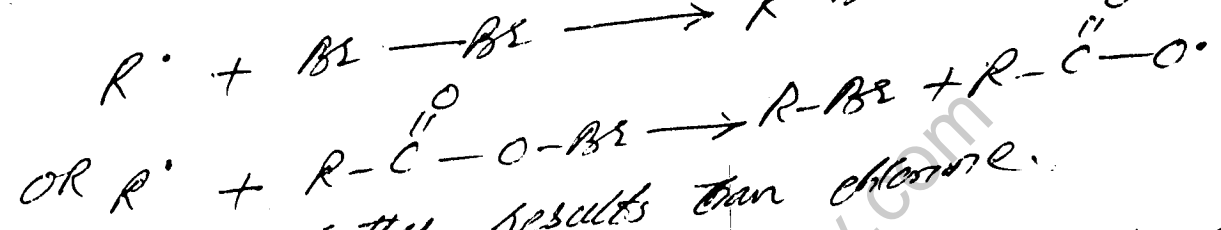
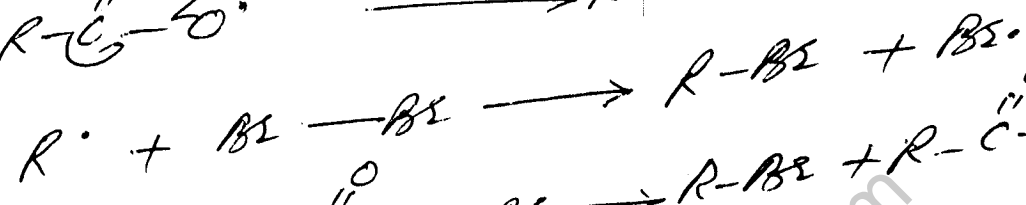
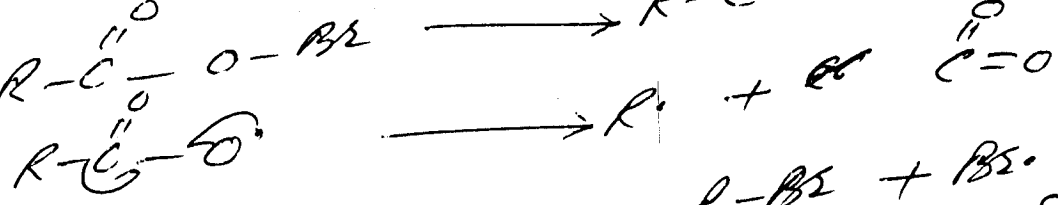
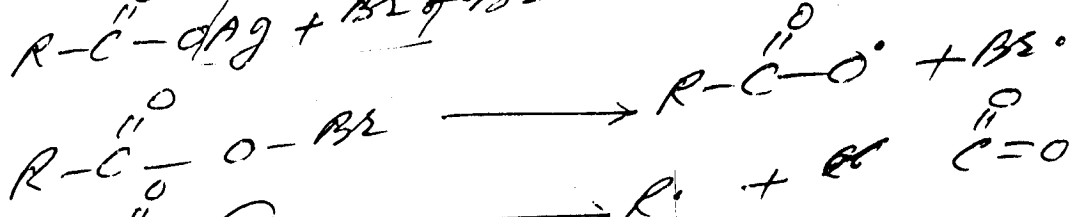
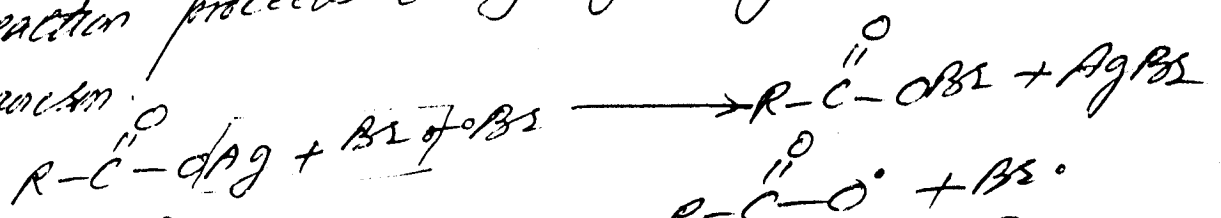


FROM SILVER SALT OF CARBOXYLIC ACID

Alkyl halides can also be produced by reaction of silver salt of carboxylic acid with chlorine or bromine

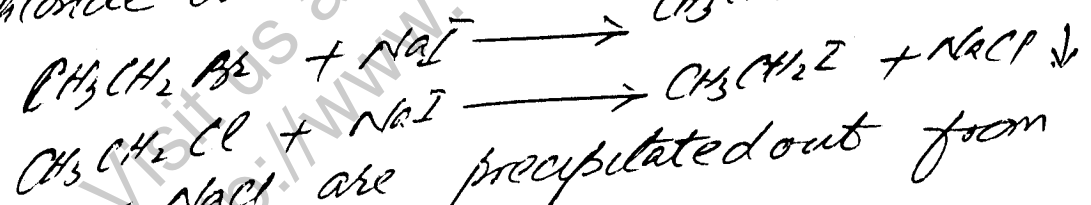
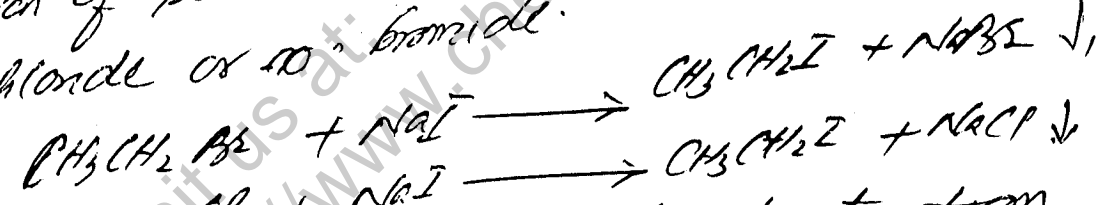


The reaction proceeds through following mechanism:



Bromine gives better results than chlorine.

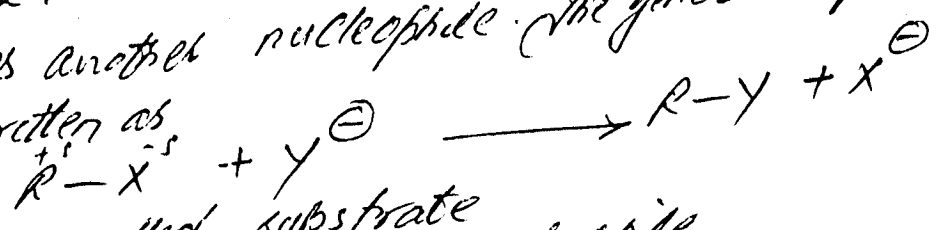
HALIDE EXCHANGE | Alkyl iodides can be produced by reaction of sodium iodide with corresponding alkyl chloride or so. bromide.



The NaBr or NaCl are precipitated out from solution.

Q WRITE A NOTE ON SN REACTIONS.

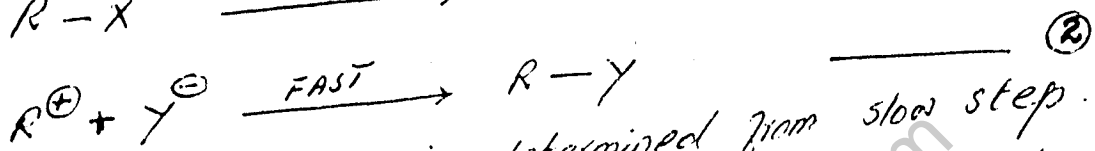
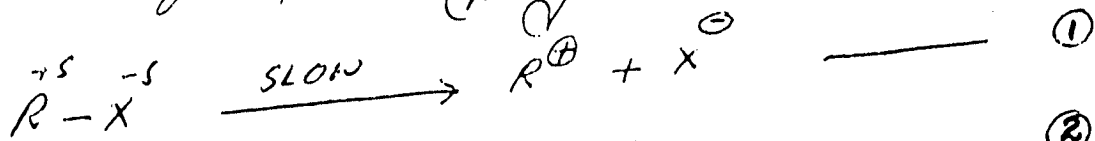
Nucleophilic substitution reactions are called SN reactions. In these reactions, one nucleophile (nucleus loving species) replaces another nucleophile. The general expression could be written as



- R-X is called substrate
- Y<sup>-</sup> is called Attacking nucleophile
- X<sup>-</sup> is called leaving group
- R-Y is called product.

The attacking nucleophile is mostly negatively charged or it may be a neutral molecule with a lone pair of electron. These reactions are further divided into two categories (i)  $S_N1$  - REACTIONS. (ii)  $S_N2$  - REACTIONS.

**$S_N1$  - REACTIONS:-** Nucleophilic substitution unimolecular reactions are called  $S_N1$  - REACTIONS. These are two step reactions. In first step leaving group leaves and carbocation ion is formed. In second step attacking nucleophile attacks to form product. The general mechanism is shown



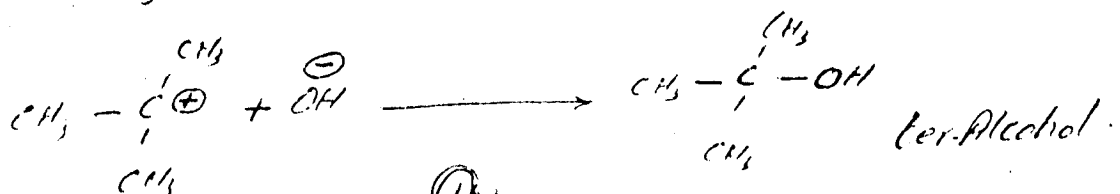
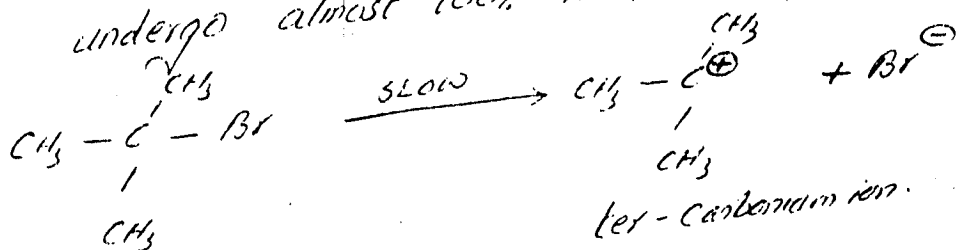
The rate of reaction is determined from slow step. According to Law of mass action from 1st step.

$$\text{Rate} \propto [R-X]$$

$$\text{Rate} = k[R-X] \quad \text{--- (3)}$$

The rate expression involves only one molecule so it is called unimolecular reaction (first order reaction). The rate of  $S_N1$  reaction depends upon following factors.

**EFFECT OF SUBSTRATE:-**  $S_N1$  reactions proceed through formation of carbocation ion. The greater the stability of carbocation ion the greater are chances of  $S_N1$  reactions. Ter-alkyl halides produce ter carbocation ion, which is most stable carbocation ion. So ter-alkyl halides undergo almost 100%  $S_N1$  reactions.



(91)

Sec. carbonium ion is less stable than ter. carbonium ion but more stable than p. carbonium ion. So sec-alkyl halides undergo 50% SN<sub>1</sub> reactions. Primary carbonium ion is least stable, so p-alkyl halides generally donot undergo SN<sub>1</sub> - REACTIONS.

**KINETIC OF SN<sub>1</sub> REACTIONS:- (Conc. Effect.)**

The rate of SN<sub>1</sub> reaction is given by

$$\text{Rate} \propto [R-X]$$

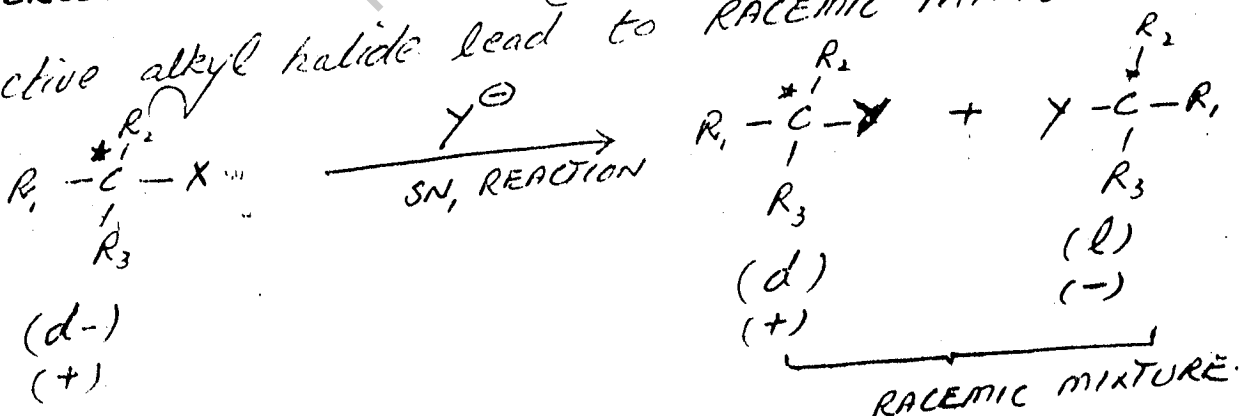
$$\text{Rate} = k[R-X]$$

So rate of reaction only depends upon concentration of substrate only. The rate of reaction is independent of concentration of attacking nucleophile. The rate of SN<sub>1</sub> reaction is not effected by increase or decrease in concentration of attacking nucleophile.

**SOLVENT EFFECT:-** The SN<sub>1</sub> reactions proceed through formation of charged intermediate (CARBONIUM ION). The carbonium ion is more stable in polar solvent. Thus SN<sub>1</sub> reactions are favoured in polar solvents.

For example sec. Alkyl halides undergo more than 50% SN<sub>1</sub> reaction mechanism in polar solvent but more than 50% SN<sub>2</sub> reaction mechanism in Non polar solvent.

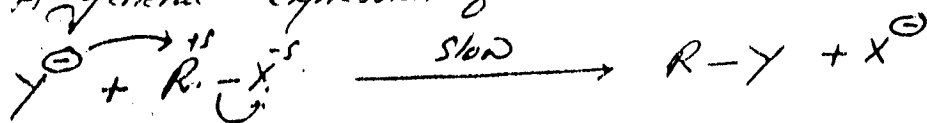
**STEREOCHEMICAL EVIDENCE:-** The SN<sub>1</sub> reaction of an optically active alkyl halide lead to RACEMIC MIXTURE.



**SN<sub>2</sub> - REACTIONS:-** Nucleophilic substitution bimolecular reactions are called SN<sub>2</sub> - Reactions. These are one step REACTIONS.



A general expression for  $S_N2$  - reaction is



These are one step reactions which is slow and rate determining step. Rate of reaction according to law of mass action could be written as

$$\text{Rate} \propto [R-X][Y^-]$$

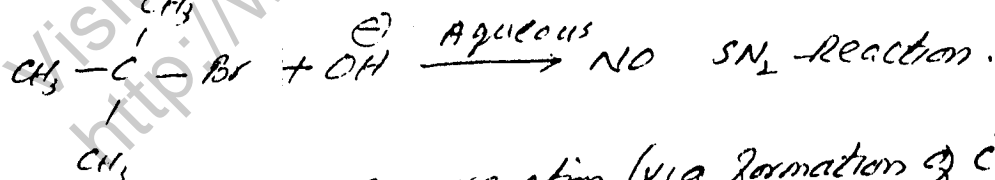
$$\text{Rate} = k[R-X][Y^-]$$

The rate expression involves molar concentration of two molecules i.e. substrate and attacking nucleophile. So it is a bimolecular reaction.

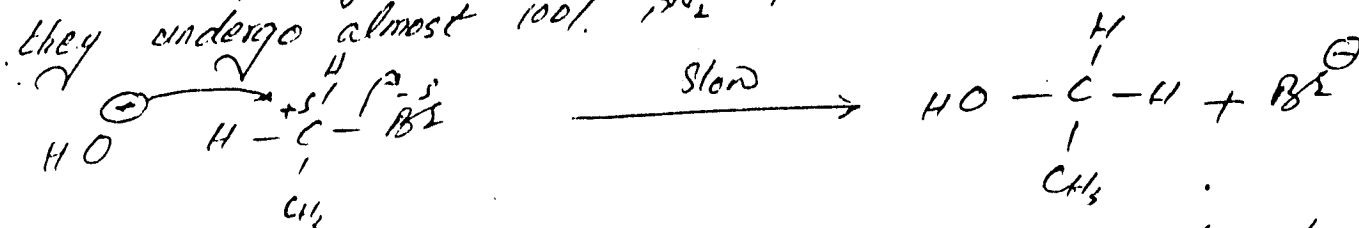
**KINETIC EVIDENCE:** - The rate of  $S_N2$  reaction is effected both by concentration of attacking nucleophile and substrate. Rate of reaction increases by increasing conc. of substrate and attacking nucleophile. The rate of  $S_N2$  reaction is independent of conc. of attacking nucleophile.

**SUBSTRATE EFFECT:** - In  $S_N2$  reactions attacking nucleophile always attacks from backside. So reaction is affected by steric hindrance on backside.

Ter. alkyl halides have maximum steric hindrance on back side due to bulky groups. So ter. alkyl halides don't undergo  $S_N2$  - reaction.



These alkyl halide undergo  $S_N1$  - reaction (via formation of  $C^+$  ion).  $\rho$  alkyl halides have least steric hindrance so they undergo almost 100%  $S_N2$  - reaction.



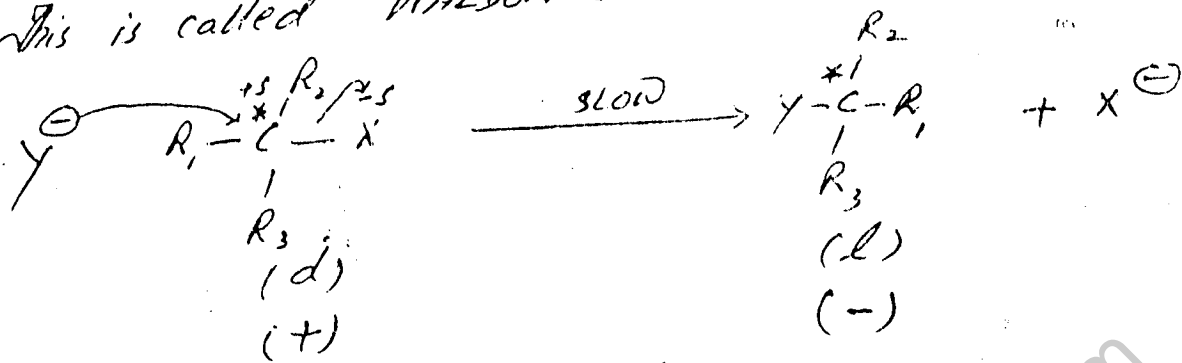
Sec. alkyl halides undergo almost 50%  $S_N2$  reaction due to moderate steric hindrance (less than ter- but more than  $\rho$  alkyl halides) (b)



## SOLVENT EFFECT:-

$S_N2$ -reaction does not involve formation of charged intermediate (carbonium ion) So these reactions are favoured in NON-POLAR SOLVENTS, ~~the~~ which inhibit formation of carbonium ion. These reactions are carried out in NON-POLAR SOLVENTS like cyclohexane, n-Hexane, ethers etc.

**STEREOCHEMICAL EVIDENCE:-** If an optically active alkyl halide is used,  $S_N2$ -reactions lead to Inversion of configuration. This is called WALDON INVERSION.



## Compare $S_N1$ & $S_N2$ Reactions.

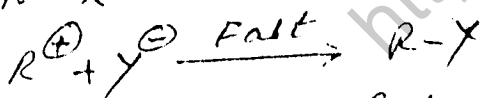
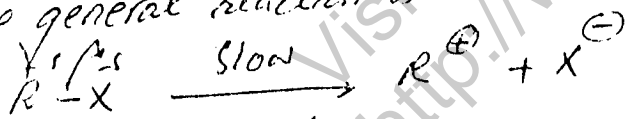
Nucleophilic substitution reactions are called  $S_N$ -REACTIONS. These are of two types.  $S_N1$  &  $S_N2$  Reactions.

### $S_N1$ -REACTIONS

These are nucleophilic substitution unimolecular reactions.

These are completed in TWO STEPS.

The general reaction is



Rate expression is first order

$$\text{Rate} = k[\text{R}-\text{X}]$$

Reaction rate is not effected by conc. of attacking nucleophile.

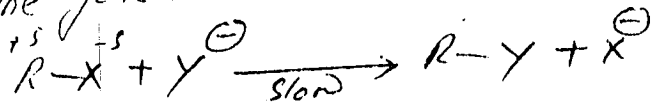
Reaction proceeds through formation of carbonium ion.

### $S_N2$ -REACTIONS

These are nucleophilic substitution bimolecular reactions.

These are completed in ONE STEP

The general reaction is written as



Rate expression is bimolecular second order

$$\text{Rate} = k[\text{R}-\text{X}][\text{Y}^-]$$

Reaction rate is effected by conc. of attacking nucleophile.

No CARBONIUM ion is formed.

7 The order of ease of  $S_N1$  reaction is  $ter > sec > p$ .

8 These reactions are favoured in polar solvents.

9 The  $S_N1$ -reactions lead to RACEMIZATION.

10 Powerful nucleophile is not required for  $S_N1$ -reactions.

11 A good leaving group is required for  $S_N1$ -reactions.

The order of ease of  $S_N2$  reaction is  $p > sec > ter$ .

These reactions are favoured in non-polar solvents.

The  $S_N2$ -reactions lead to WALDEN INVERSION.

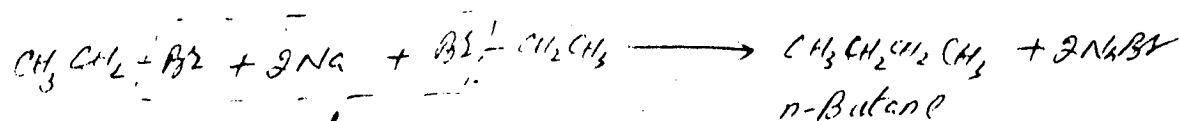
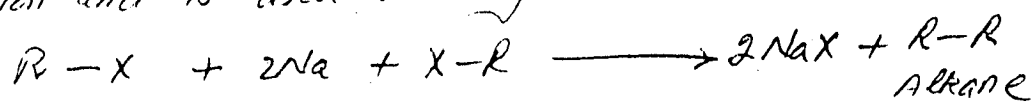
A powerful attacking nucleophile is required for  $S_N2$ -reactions.

A good leaving group is not required for  $S_N2$ -reactions.

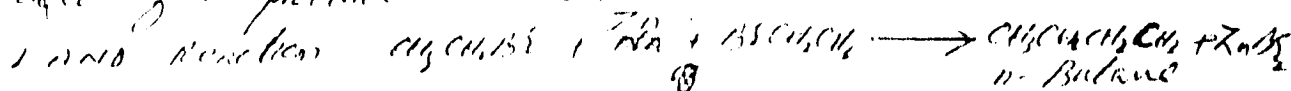
Show that alkyl Halides are Important organic Compounds in Synthetic chemistry.

Alkyl halides are quite reactive compounds and a large number of organic compounds can be prepared from alkyl halides. So these are very important starting material in synthetic chemistry. Some general reactions are given below.

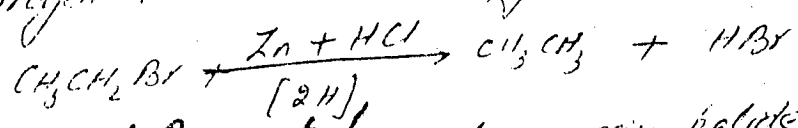
Wurtz Reaction: When an alkyl halide is heated with sodium an alkane is produced. This reaction is called Wurtz Reaction and is used to lengthen carbon chain.



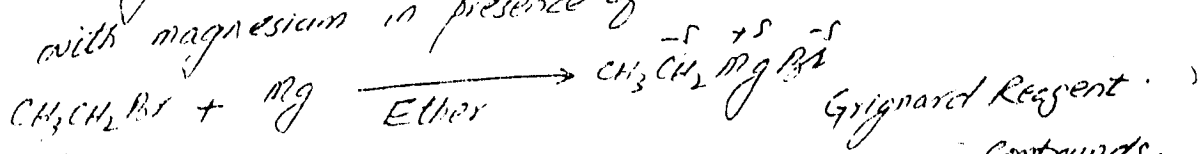
Frankland Reaction - Alkyl halide on treatment with granulated zinc produce alkane. This reaction is called FRANKLAND reaction.



Reduction of Alkyl Halides: When an alkyl halide is treated with a mixture of Zinc and HCl, an alkane is produced. The Zinc and HCl mixture produces nascent hydrogen which reduces alkyl halide to alkane.

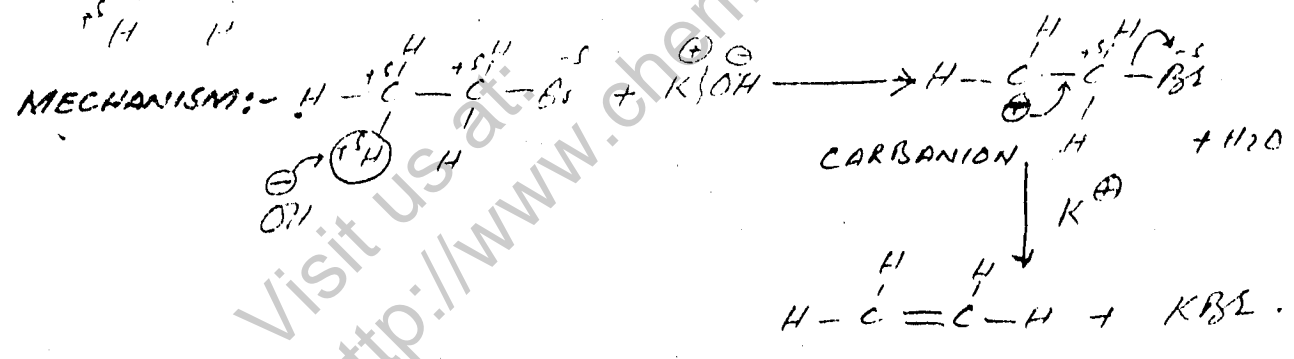
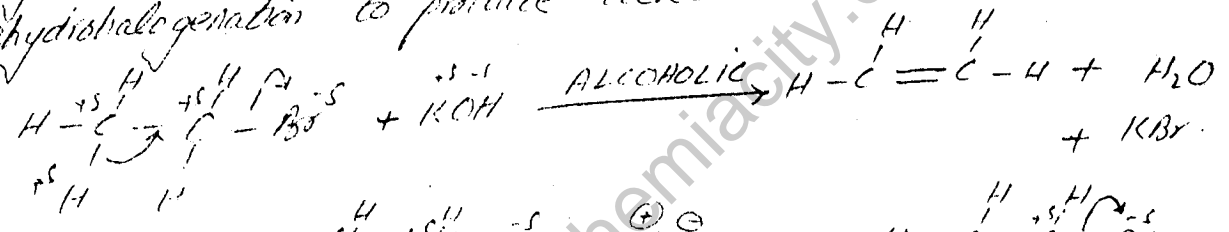


Grignard Reagent: Alkyl magnesium halide is commonly called Grignard reagent. It is produced by reaction of an alkyl halide with magnesium in presence of ether.



G.R. can be used to prepare a number of other organic compounds.

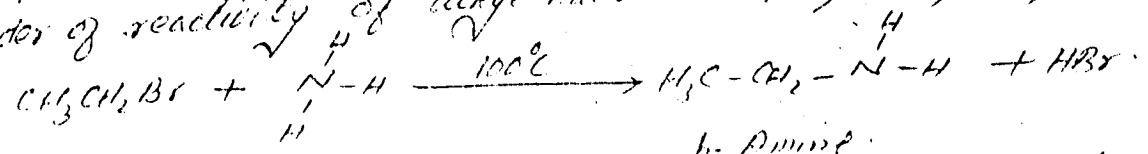
Dehydrohalogenation: The removal of hydrogen and halogen from two adjacent carbons is called dehydrohalogenation. Alkyl halides on treatment with alcoholic KOH undergo dehydrohalogenation to produce alkene.



If aqueous KOH is used elimination reaction competes with  $S_N2$  reaction, and an alcohol may be formed.

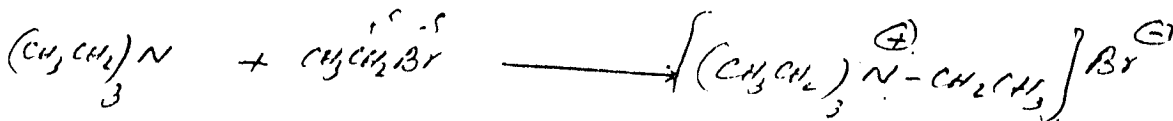
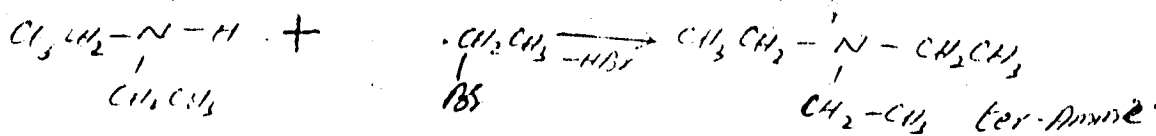
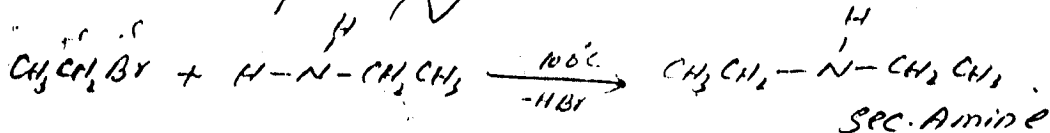
Reaction with Ammonia (HOFFMAN REACTION).

Alkyl halides react with ammonia to form amines. The order of reactivity of alkyl halides is  $RI > RBr > RCl > RF$



But reaction does not stop at p-amine stage and

goes on till quaternary ammonium salt is formed.



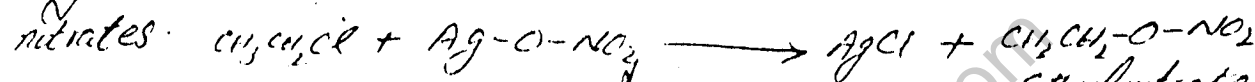
### Reaction with silver sulphate:

Alkyl halides react with silver sulphate to form alkyl sulphate.



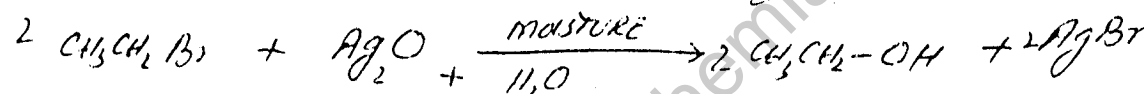
### Reaction with silver nitrate:

Alkyl halides react with silver nitrate to form alkyl nitrates.

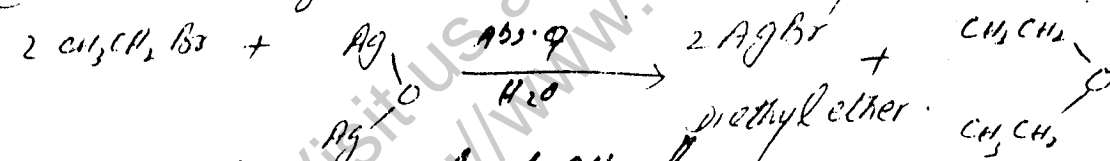


### Reaction with silver oxide:

The product of this reaction depend upon presence or absence of moisture.



In absence of moisture ethers are produced.



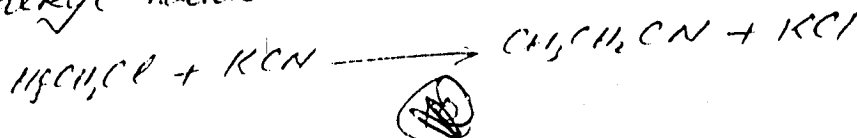
### Reaction with sodium lead Alloy:

The alkyl halides react with sodium lead alloy to form tetraalkyl lead. The compound is used as an antiknock.



### Reaction with KCN:

Alkyl cyanides are produced by reaction of alkyl halide with KCN.



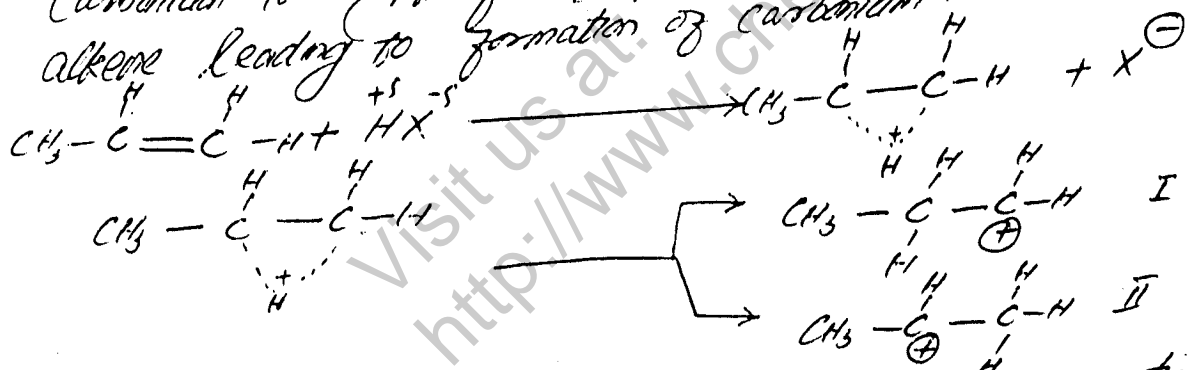
**WRITE A NOTE ON MARKOVNIKOFF'S RULE.**

The Rule states that, "when a halogen acid is added to an unsymmetrical alkene, the hydrogen atom will attach to that carbon which has maximum number of hydrogen atoms. However Markovnikoff's Rule holds good for all additions of unsymmetrical ionic reagents to unsymmetrical alkene.

Thus Markovnikoff's Rule in general form can be stated as follows

When an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of reagent will attach to that carbon atom which has least number of hydrogen atoms. In other words when an unsymmetrical reagent is added to an unsymmetrical alkene, the positive end of reagent will attack double bond such that it produces most stable carbocation ion.

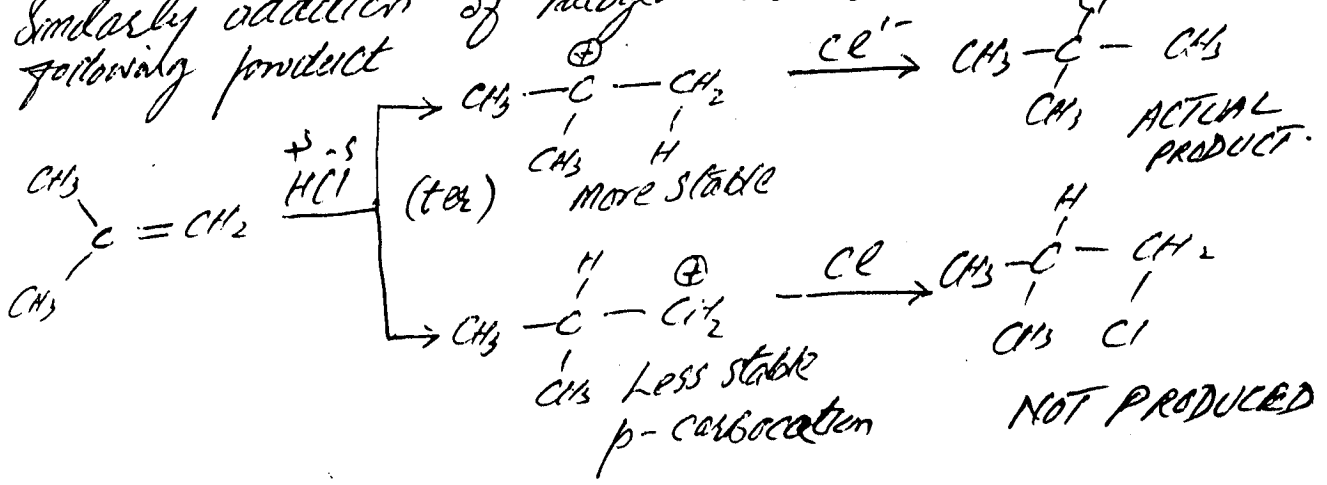
**MECHANISM:** The reaction proceeds through formation of carbocation ion. The first step is attack of electrophile to alkene leading to formation of carbocation ion.



The "II" produces stable carbocation ion (Sec. carbocation). Thus sec. carbocation ion will be attacked by halide ion



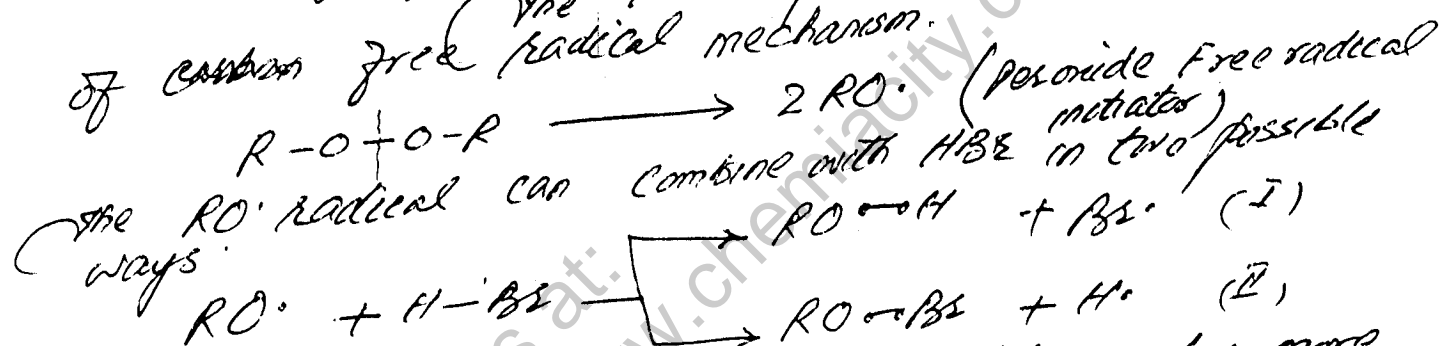
Similarly addition of halogen acid to isobutylene produces following product



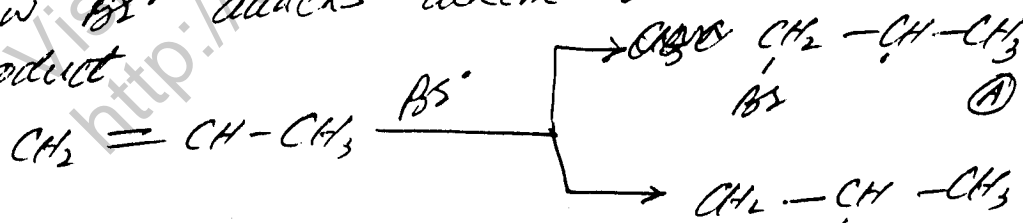
The addition of HCl and HI to alkene always takes place according to Markownikoff's Rule. But addition of HBr depends upon presence or absence of peroxide. In absence of peroxide addition follows Markownikoff's Rule but in presence of peroxide addition takes place opposite to Markownikoff's Rule (Anti-Markownikoff's Rule).

ANTI-MARKOWNIKOFF'S RULE: According to this rule, "When an unsymmetrical reagent is added to unsymmetrical alkene in presence of peroxide, hydrogen attach to that carbon which has minimum number of hydrogen atoms." It can be stated in another way, when HBr is added to an unsymmetrical alkene, the bromine (larger atom) will attach to less hindered site (more number of hydrogen atoms).

The reaction proceeds through formation of carbon free radical mechanism.

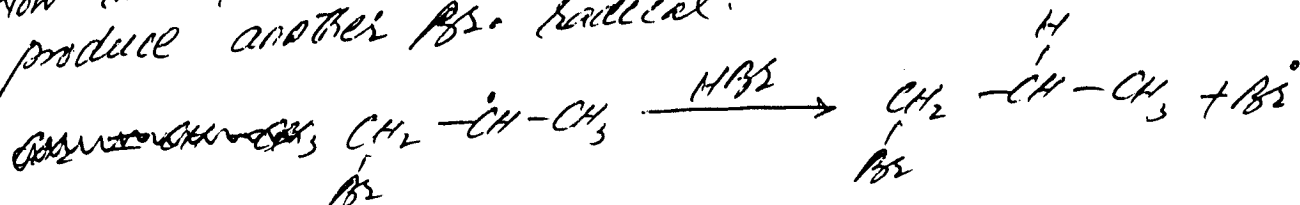


Since  $Br\cdot$  is more stable thus possibility I has more chances. Now  $Br\cdot$  attacks alkene and determines the rate of product.



In first case (A), sec. radical is produced.  $Br\cdot$  (B) which is more stable than p-radical produced second case (B).

Thus " $Br\cdot$ " attach to least hindered site. Now this sec. radical reacts with another HBr to produce another  $Br\cdot$  radical.

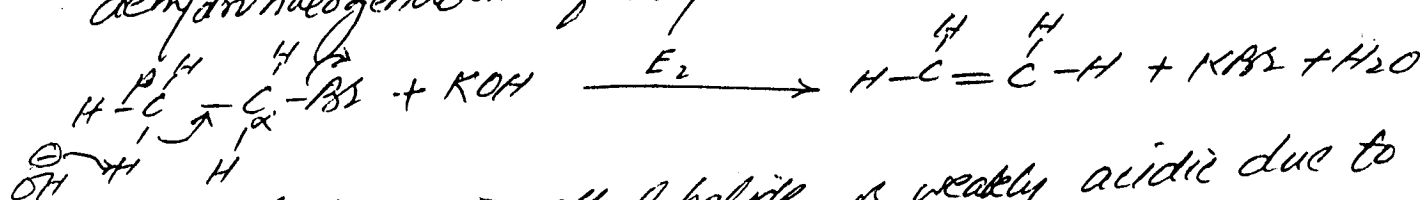


" $Br\cdot$ " can continue the chain reaction.

WRITE A NOTE ON ELIMINATION REACTIONS

The reactions in which two atoms or groups of atoms are removed from two adjacent atoms leading to formation of double bond are called Elimination Reactions. Since one atom is always removed from  $\beta$ -carbon, so these are called  $\beta$ -eliminations.

An example of elimination reaction is dehydrohalogenation of alkyl halides with Alcoholic KOH.



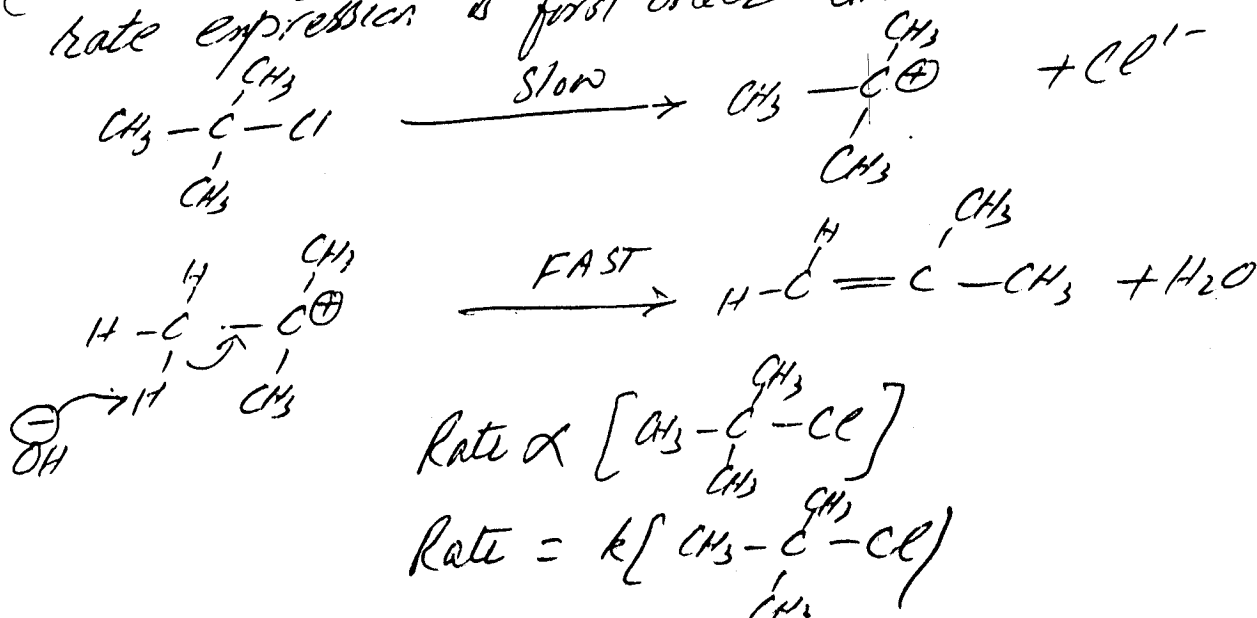
The  $\beta$ -hydrogen of alkyl halide is weakly acidic due to electron withdrawing inductive effect of halogen atom.

Thus  $\beta$ -hydrogen can be removed as proton by a base. The loss of proton from  $\beta$ -carbon and removal of halide ion from  $\alpha$ -carbon takes place simultaneously forming a double bond between " $\alpha$ " and " $\beta$ " carbon.

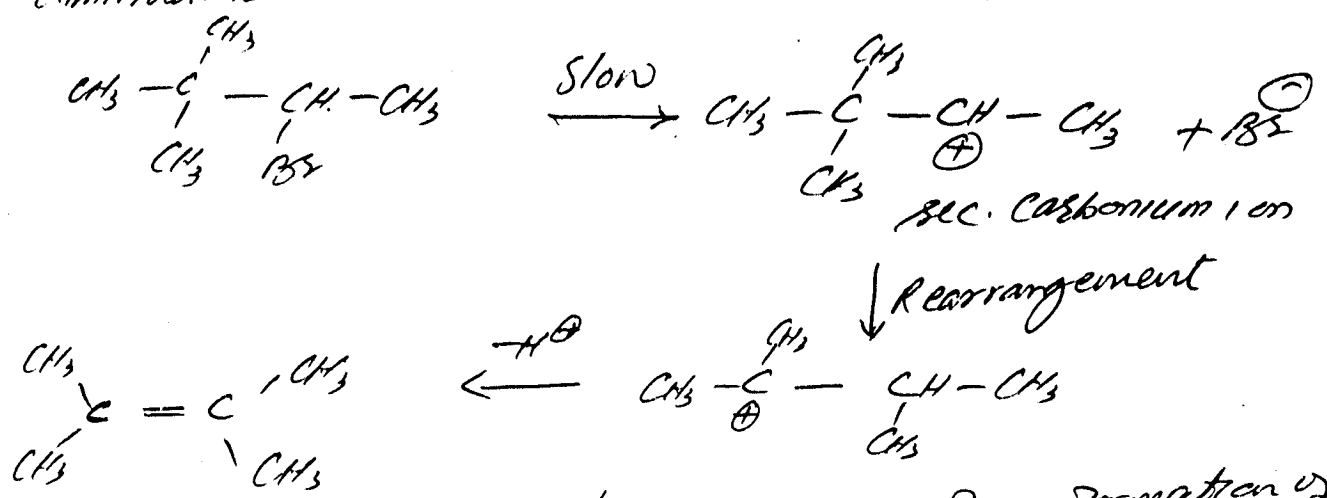
The elimination reactions are basically divided into two categories on the basis of kinetics of reaction.

- (i)  $\text{E}_1$  - Elimination      (ii)  $\text{E}_2$  - ELIMINATIONS.

$\text{E}_1$  - ELIMINATIONS / It is unimolecular elimination reaction. This elimination occurs in two step. The first step is slow and formation of carbonium ion takes place. The second step is fast and proton is removed from  $\beta$ -carbon. The rate of reaction depends upon slow step. Thus rate expression is first order unimolecular.



Since "E<sub>1</sub>" elimination reactions involve formation of carbocation ion so rearranged products are mostly formed in E<sub>1</sub> eliminations.



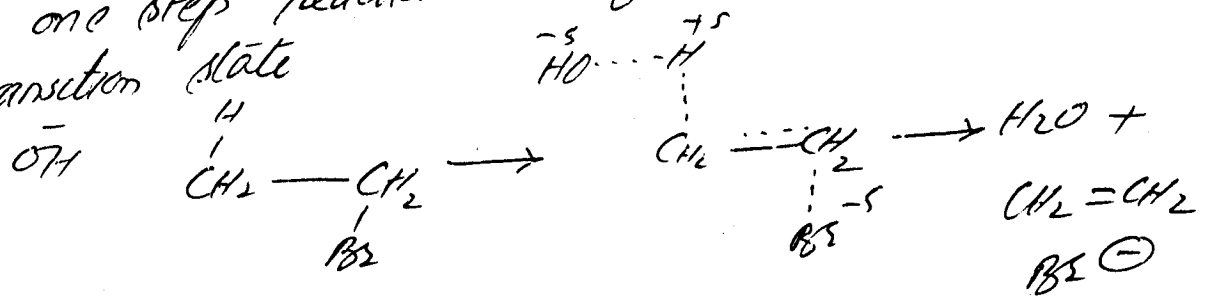
EFFECT OF SUBSTRATE | Since E<sub>1</sub> involves formation of carbocation ion so ter. Alkyl halides mostly undergo "E<sub>1</sub>" reaction. Secondary alkyl halides can undergo E<sub>1</sub> or E<sub>2</sub> mechanism depending upon conditions. However ter. Alkyl halides can also undergo elimination by E<sub>1</sub> mechanism.

EFFECT OF BASE | In E<sub>1</sub> reactions an external base is generally not required. The solvent itself acts as a base when weak base is used in low conc. "E<sub>1</sub>" mechanism is observed in low conc. ter. alkyl halide.

EFFECT OF LEAVING GROUP | A good leaving group favours E<sub>1</sub> elimination and vice versa.

EFFECT OF SOLVENT | E<sub>1</sub> reaction involves an ionic intermediate & thus these are favoured in polar solvents.

E<sub>2</sub> - ELIMINATIONS | Are eliminations in which pulling of proton from β-carbon and departure of leaving group occurs simultaneously or called E<sub>2</sub> - Eliminations. These are one step reactions. All five atoms are involved in transition state.



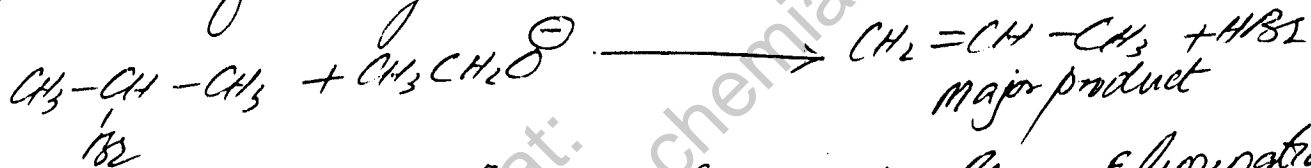


The  $E_2$ -reaction always competes with  $S_N2$ -reaction. The difference between two pathways is that if reagent with unshared electron pair attacks hydrogen atom (acts as base) then reaction is " $E_2$ "- and if reagent attacks carbon atom then it is  $S_N2$  reaction.

EFFECT OF SUBSTRATE: ON  $E_2$ -REACTIONS

$\beta$ -Alkyl halides favour  $E_2$  reaction. In case of secondary substrate the reaction may be  $E_1$  or  $E_2$  depending upon condition. Tertiary substrate can also undergo  $E_2$ -reaction because, the base attacks hydrogen of  $\beta$ -Carbon which is not effected by steric hindrance

EFFECT OF BASE | The strong base or high concentration of base favours  $E_2$ -reaction. For example consider following reaction.



Strong base favour  $E_2$  over  $E_1$  and also Elimination over substitution.

LEAVING GROUP | A poor leaving group favours  $E_2$  reactions. rather than  $E_1$ .

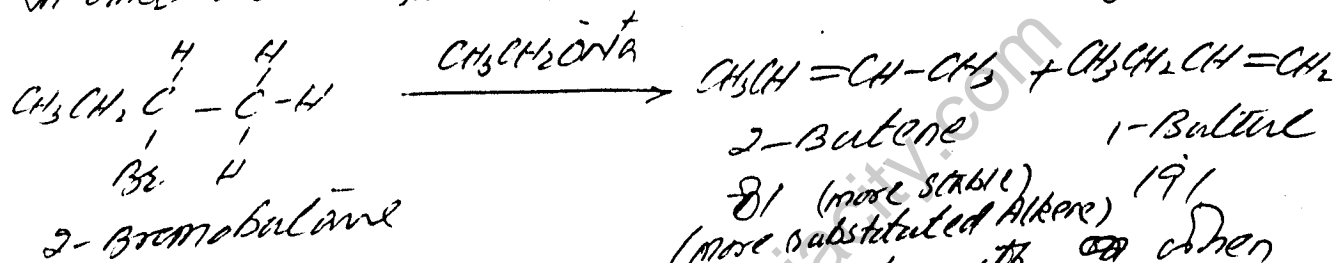
SOLVENT EFFECT | The  $E_1$ -reactions are favoured in nonpolar solvent. The elimination of substrate is favoured over substitution by decreasing polarity of solvent. For example alcoholic KOH is used to get major elimination product rather than substitution product

WRITE A NOTE ON SAYTZEFF RULE &

HOFFMAN RULE (ORIENTATION OF DOUBLE BOND)

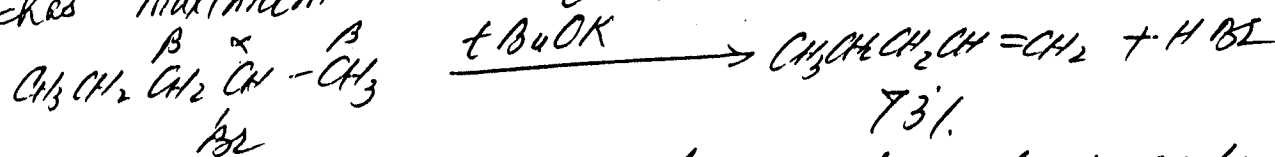
ANS:- In case of elimination reactions the hydrogen is removed from  $\beta$ -carbon. When there are more than one different  $\beta$ -carbons each having  $\beta$ -hydrogen then a mixture of products is expected to be obtained. There are two rules in this regard.

SAYTZEFF RULE | According to this rule if there are more than one different  $\beta$ -carbons, then in  $E_1$ -reaction, the hydrogen is removed from that  $\beta$ -carbon which has least number of hydrogen atoms. In other words most substituted alkene is favoured.



However Saytzeff rule is favoured when smaller size base is used and substrate contains an uncharged leaving group (-X, -OH etc.).

HOFFMAN RULE | According to this rule, if the substrate has charged leaving group (that is removed as neutral molecule) and larger size base is used, the least substituted alkene is major product. In other words hydrogen is removed from that  $\beta$ -carbon which has maximum number of hydrogen atoms.



It is due to the fact that larger base prefers to remove  $\beta$ -hydrogen which is less sterically hindered. The  $\beta$ -carbon which has all hydrogens attached to it is least hindered site.

WRITE PREPARATION, STRUCTURE AND REACTIONS OF GRIGNARD REAGENT.

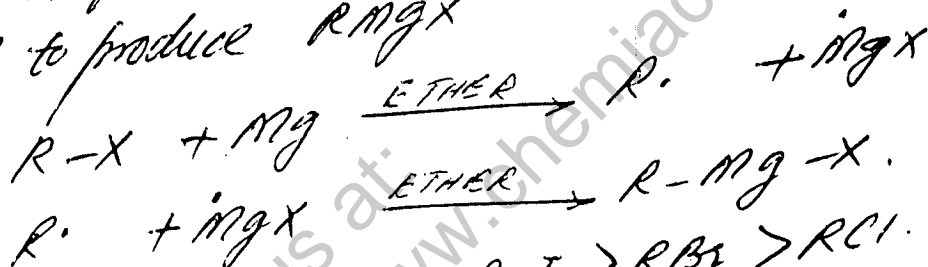
ANS:- Alkyl magnesium halide is most commonly used organo-metallic compound. It is called Grignard Reagent "RMgX".

PREPARATION Grignard reagent is generally prepared by stirring a mixture of <sup>"1M"</sup> solution of alkyl halide (R-X) in ether, and magnesium turnings (M) for 6-8 hours. The ethereal solution is not isolated but directly used for further reactions.

This is a heterogeneous reaction. The reaction occurs in two steps.

In first step alkyl halide reacts with surface of "Mg" to produce alkyl radical R<sup>•</sup> and "MgX" radical.

In second step R<sup>•</sup> radical combines with "MgX" radical to produce RMgX



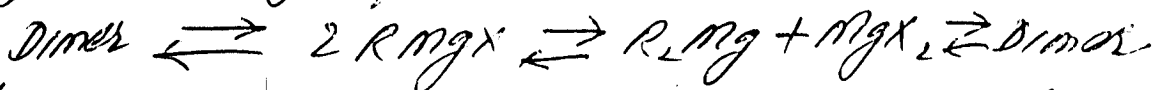
The order of reactivity is R-I > R-Br > R-Cl. Alkyl chlorides react quite slowly while R alkyl iodides are quite expensive. So G.R. is mostly prepared by alkyl bromides.

The synthesis of G.R. becomes difficult with increasing size of alkyl group CH<sub>3</sub>I > CH<sub>2</sub>I > C<sub>3</sub>H<sub>7</sub>I...

The solvent used may be ether, T.H.F or ter. amine. T.H.F is best solvent because it increases reactivity of R-X towards Mg. G.R. of vinyl and aryl halides is prepared by using T.H.F solvent. The reaction must be carried out in anhydrous conditions.

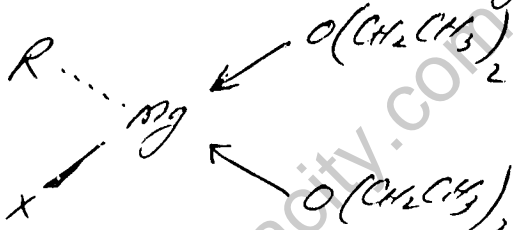
## STRUCTURE OF G.R.

According to Ashby the composition of G.R. in ether can be represented by following equilibrium.

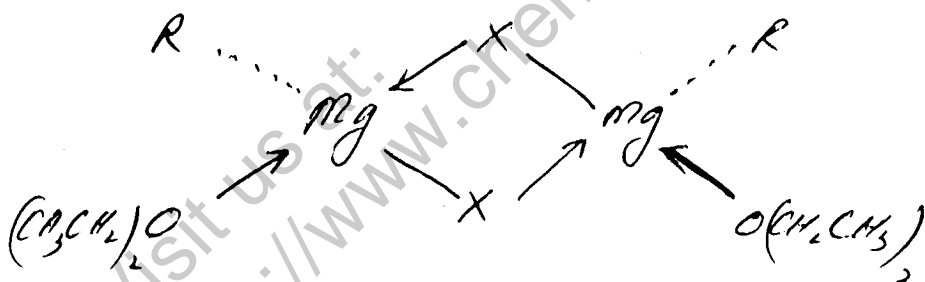


The position of equilibrium temp depends upon nature of alkyl halide, temperature, conc. etc. In low conc. of alkyl iodides and bromides and ether as solvent RMgX is major product.

Crystalline G.R. has been obtained by cooling ethereal solution. It is found in following crystallized form.



In concentrated solution it exists as dimer.



Complete removal of ether by evaporation at 100°C in vacuum favours  $\text{R}_2\text{Mg} + \text{MgX}_2$ .

### REACTIVITY OF GRIGNARD REAGENT

Grignard reagent is highly reactive species. The reactivity of G.R. is due to the fact that carbon bonded to "Mg" acquires partial negative charge (carbanion character). It is due to greater electropositivity of magnesium.

$\overset{-\delta}{\text{R}} - \overset{+\delta}{\text{Mg}} - \overset{-\delta}{\text{X}}$ . Thus in most of reactions the G.R. act as nucleophile and attack a positive centre. Reactions of G.R. are basically divided into two categories

- (i) Reactions with Compounds having

active hydrogen e.g.  $H_2O$ ,  $H \equiv C-H$ ,  $ROH$ , etc.

Reactions with compounds other having multiple bonds  
Aldehydes, ketenes etc.

REACTIONS OF GRIGNARD REAGENT (ALKANE PREPARATION)

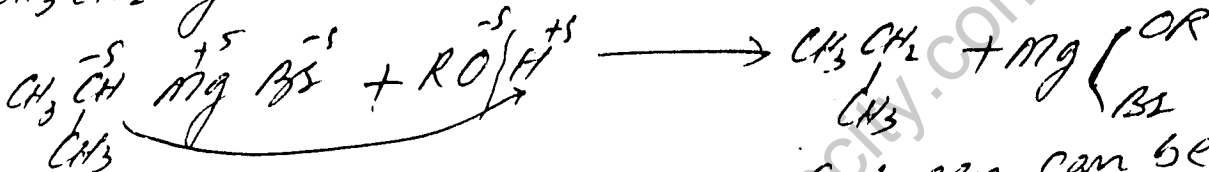
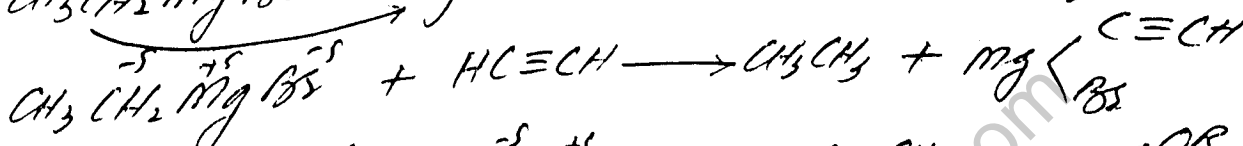
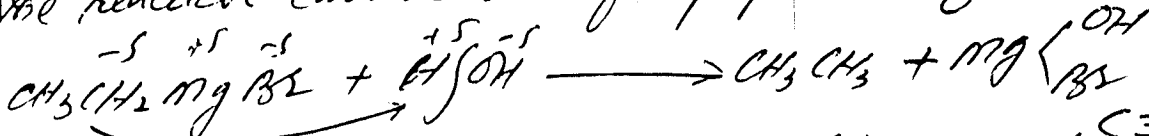
(i) REACTION WITH COMPOUNDS HAVING ACTIVE HYDROGEN

Grignard reagent can react with compounds having weakly acidic hydrogen like  $H_2O$ , alcohol, amines



Alkane.

The reaction can be used for preparation of Alkane.



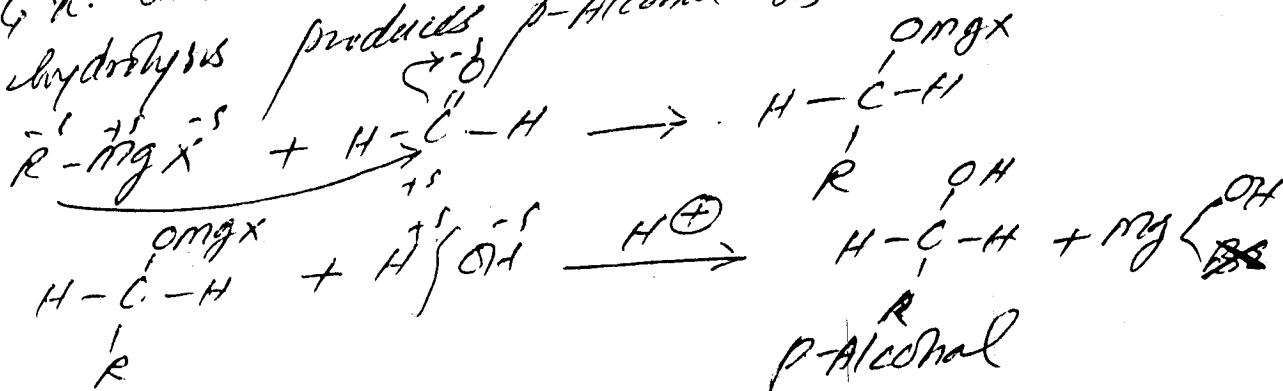
The reaction of G.R. with active hydrogen can be used to determine number of active hydrogens in a compound. For this purpose  $CH_3MgI$  is used and the volume of  $CH_4$  liberated is measured.

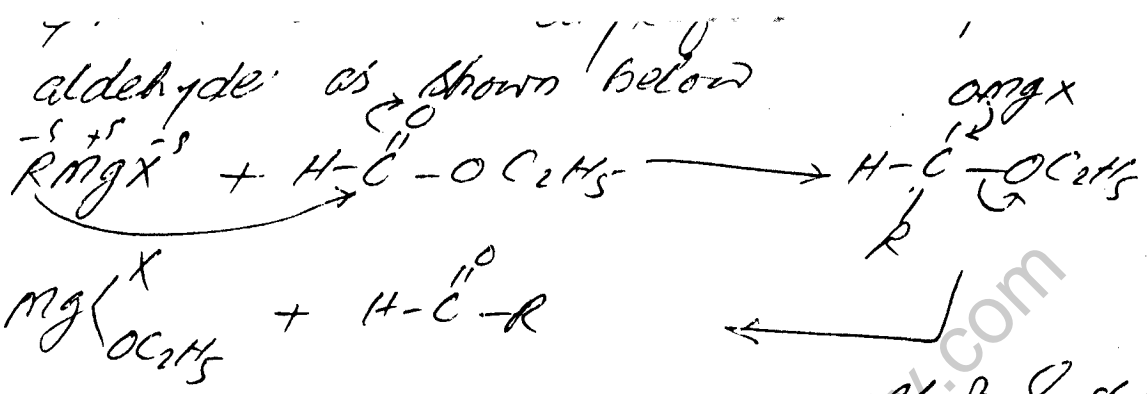
REACTION WITH CARBONYL COMPOUNDS

Grignard Reagent react with carbonyl compounds producing a wide variety of compounds. The reaction involves attack of negatively charged alkyl group on carbonyl carbon.

PREPARATION OF p-ALCOHOL (REACTION WITH "HCHO")

G.R. on reaction with formaldehyde, followed by hydrolysis produces p-Alcohol as shown below.

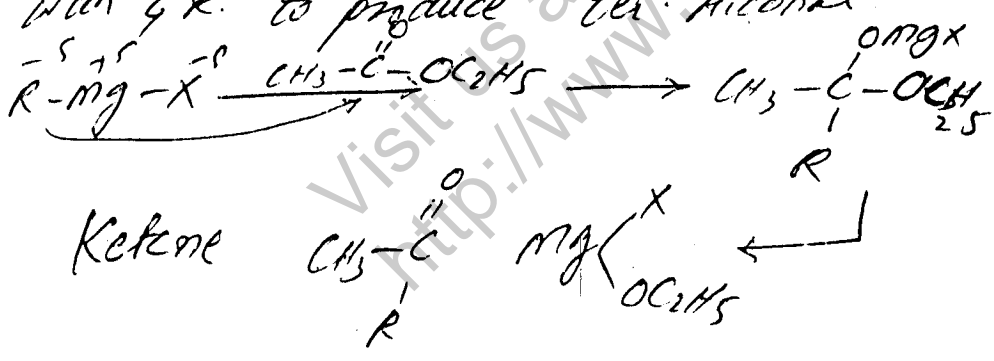


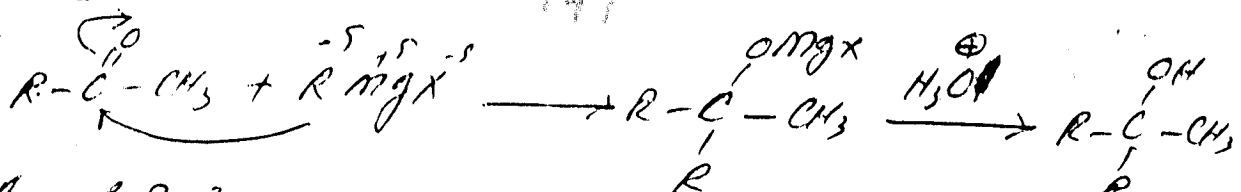


However if G.R. is in excess sec. Alcohol is produced.

REACTION WITH ETHYL ACETATE

G.R reacts with ethyl acetate to produce ketone which reacts further with G.R. to produce ter. Alcohol.

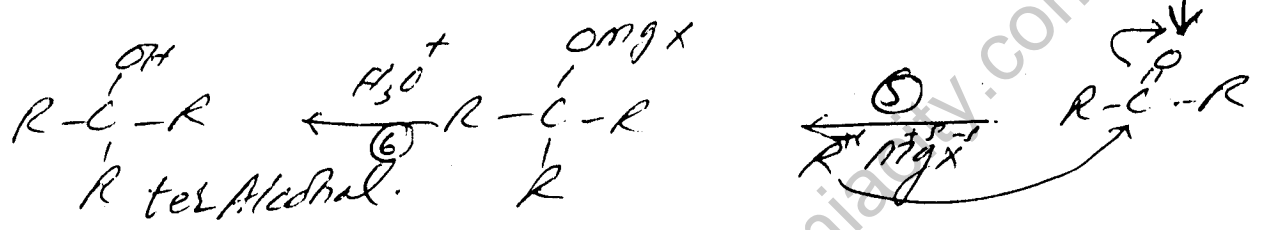
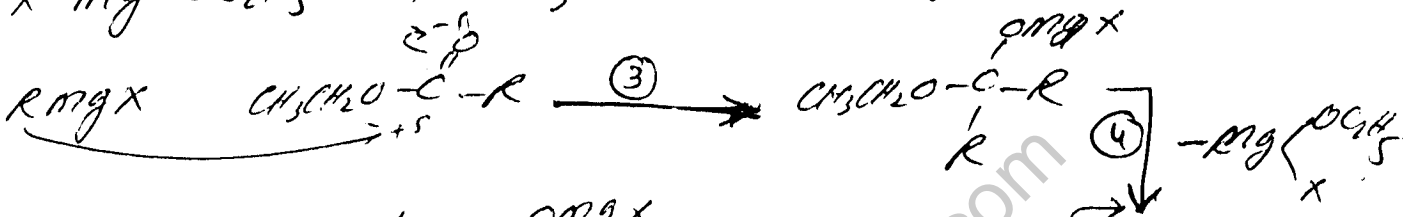
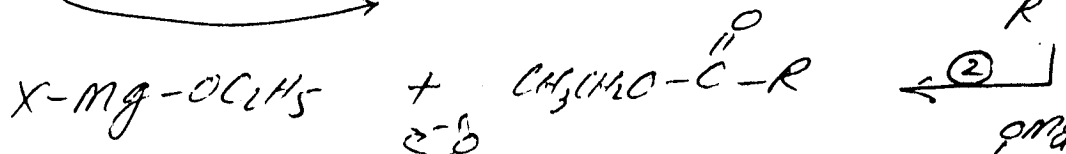
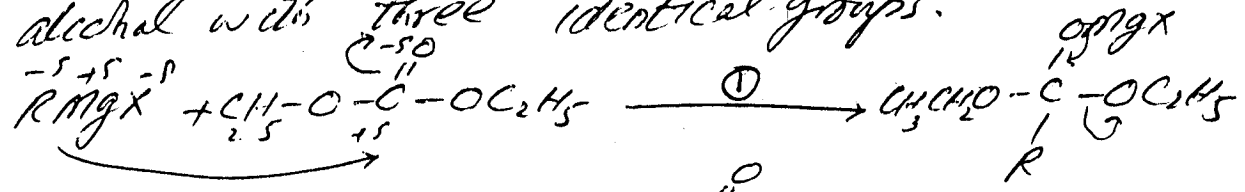




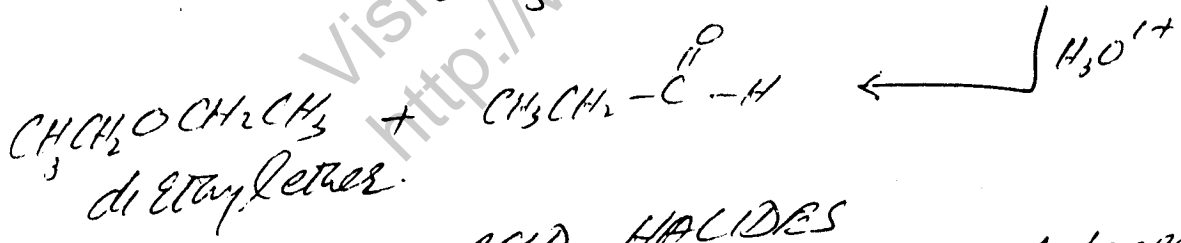
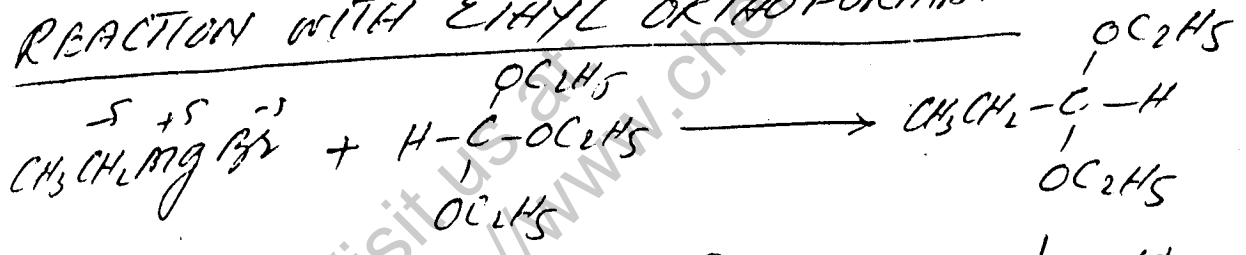
An alcohol with two identical groups is obtained by this reaction. ter Alcoh.

REACTION WITH ETHYL CARBONATE

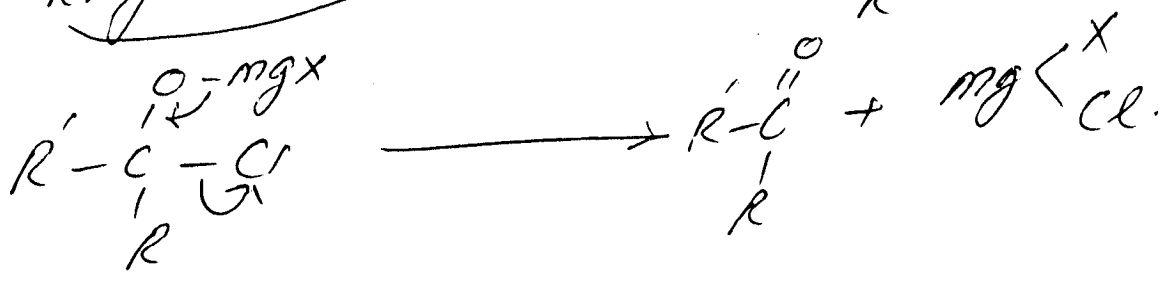
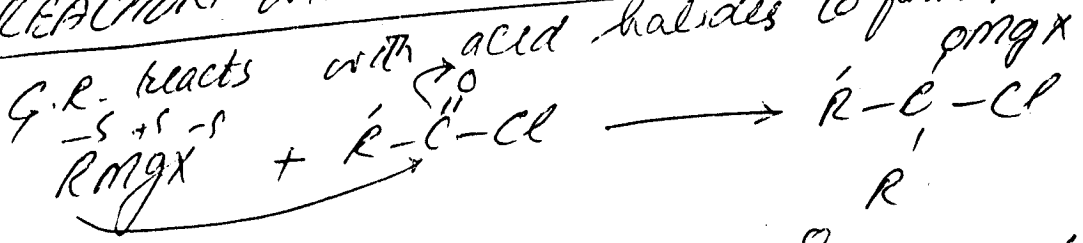
G.R. reacts with ethyl carbonate to produce an alcohol with three identical groups.



REACTION WITH ETHYL ORTHOFORMATE

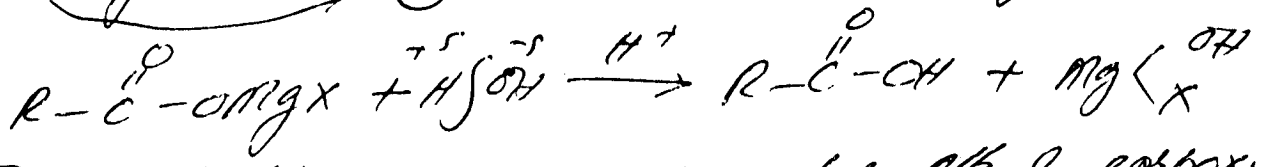
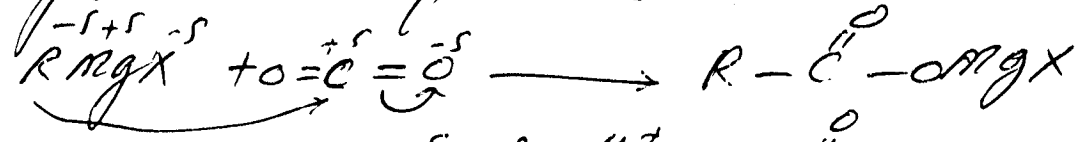


REACTIONS WITH ACID HALIDES to form ketones

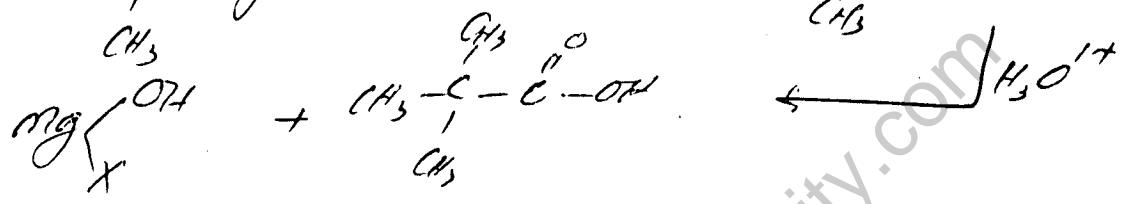
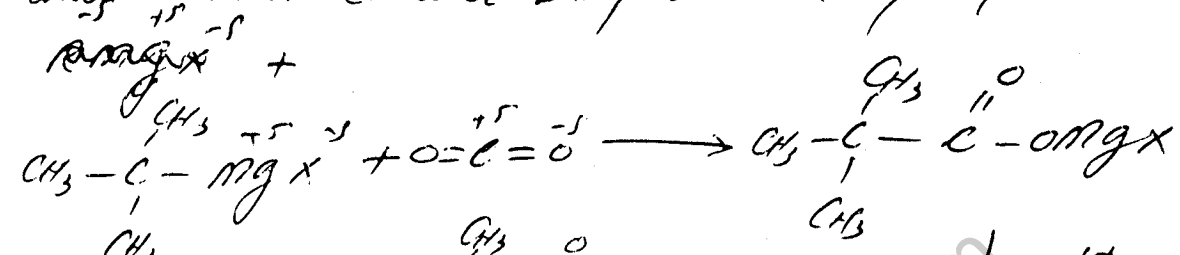


REACTION WITH CO<sub>2</sub> / PREPARATION OF CARBOXYLIC ACIDS

G.R. reacts with "CO<sub>2</sub>" followed by acid hydrolysis to produce carboxylic acids.

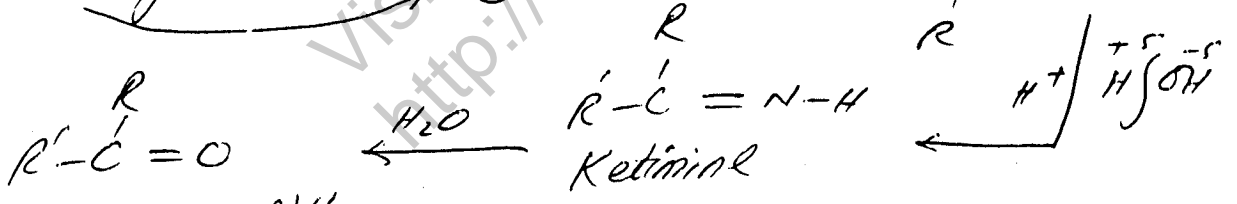
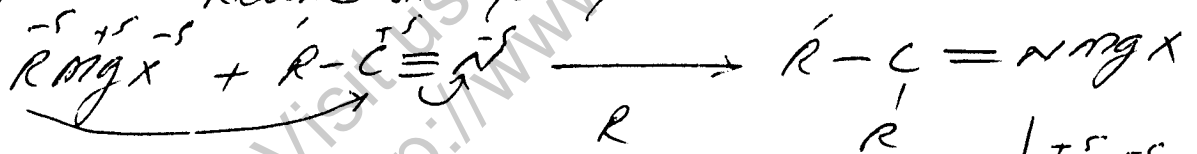


This method is used to produce ter-alkyl carboxylic acids which cannot be produced by cyanide method.



REACTION WITH NITRIL GROUP / Grignard Reagent

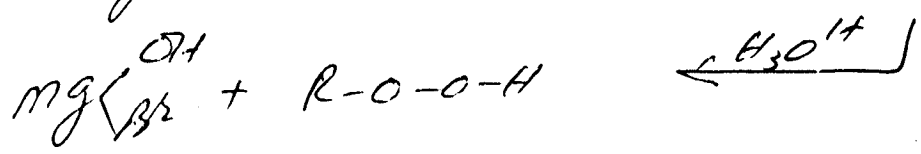
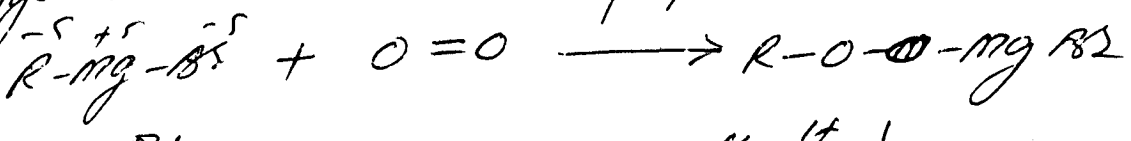
reacts with nitril compounds just like ketones, producing ketimine on hydrolysis. Ketimine is unstable and it produces ketone on hydrolysis



Ketone. NH<sub>3</sub>

REACTION WITH OXYGEN / The reaction of G.R. with

oxygen at -70°C is used to prepare hydroperoxides

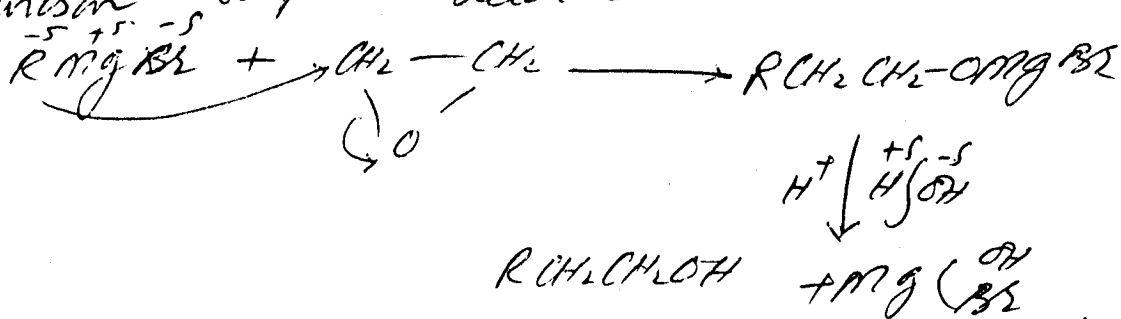


The reaction of G.R. with oxygen is so vigorous that they self inflame in air.



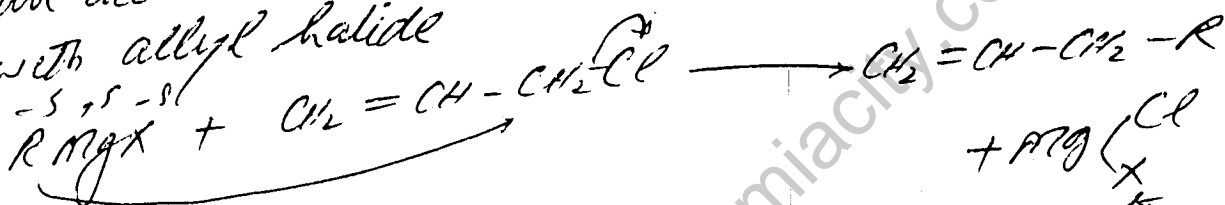
REACTION WITH SMALL RING COMPOUNDS

G.R. reacts with small ring cyclic ethers by SN2 mechanism to produce alcohols.



Straight six and five membered rings do not react with G.R. However this is quite useful method for preparation of  $\beta$ -Alcohol with two carbons more than alkyl halide.

DISPLACEMENT REACTION / The alkyl group of G.R. can act as nucleophile and undergo SN2 reaction with allyl halide



All these reactions show that G.R. is a quite important compound in chemistry and used to prepare a number of organic compounds

ASSIGNMENT

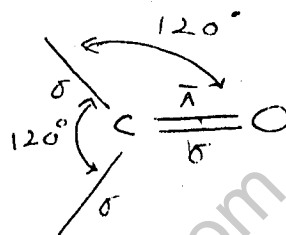
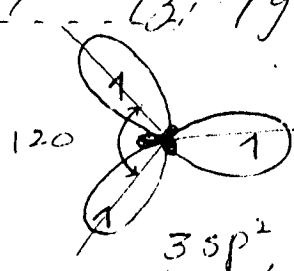
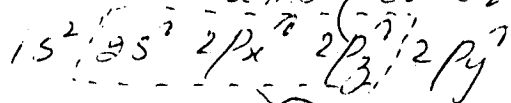
ATTEMPT Q NO: 15 Text Book of BSc by M. Younis.

# B.Sc. (Organic) ALDEHYDES AND KETONES

## STRUCTURE AND REACTIVITY:

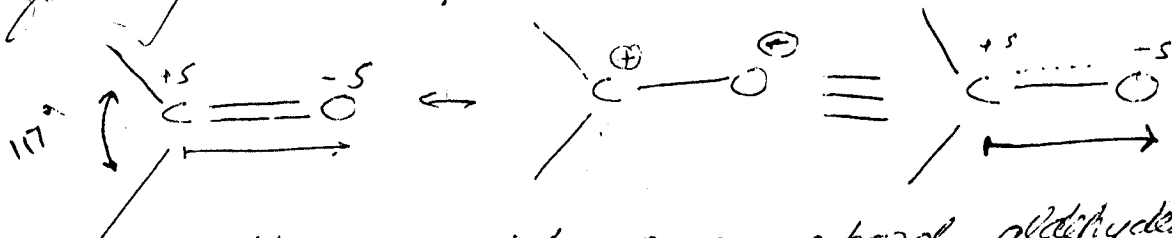
The carbonyl carbon of aldehydes and ketones is  $sp^2$  hybridized. Thus three  $sp^2$  hybridized orbitals are produced which are situated at an angle of  $120^\circ$  from each other. These three hybrid orbitals are planar and used in sigma bond formation.

One  $sp^2$  is used to form sigma bond with oxygen and other two are used to form sigma bonds with two more atoms (either hydrogen or carbons).



The unhybridized  $p$ -orbital of carbon overlaps with  $p$  orbital of oxygen to form a  $\pi$ -bond. Thus there is a double bond between C and oxygen.

Due to greater E.N. of oxygen, it acquires  $\delta^-$  charge and carbon acquires  $\delta^+$  charge. Thus carbon is  $\delta^+$  electrophilic centre (electron deficient) and oxygen is electron rich. The  $C=O$  is polarized having dipole moment (2.2 to 3.0 D). Its polar nature can also be explained on the basis of following canonical forms



As a result of polarity of  $C-O$  bond aldehydes and ketones have higher B.P. than corresponding hydrocarbons.