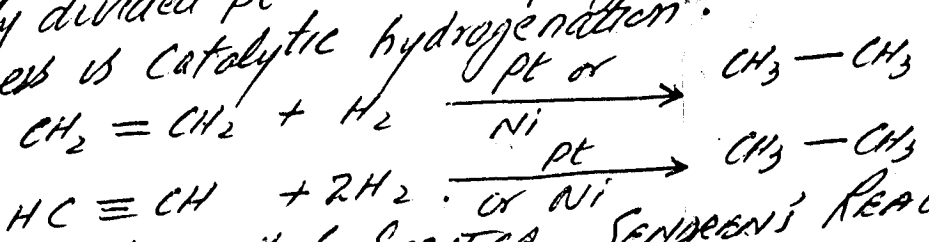


"ALKANES"

PREPARATION OF ALKANES. Alkanes occur in nature in the form of petroleum and natural gas but these can also be prepared in laboratory by following methods.

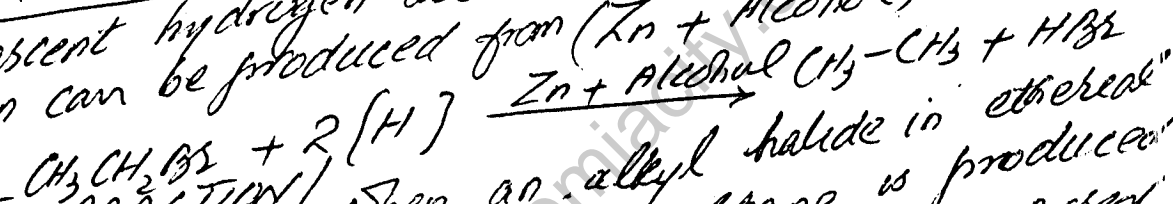
1. FROM UNSATURATED HYDROCARBONS: When a mixture of an unsaturated hydrocarbon and Hydrogen is passed over finely divided "Pt" or "Ni" hydrogenation takes place. This process is catalytic hydrogenation.



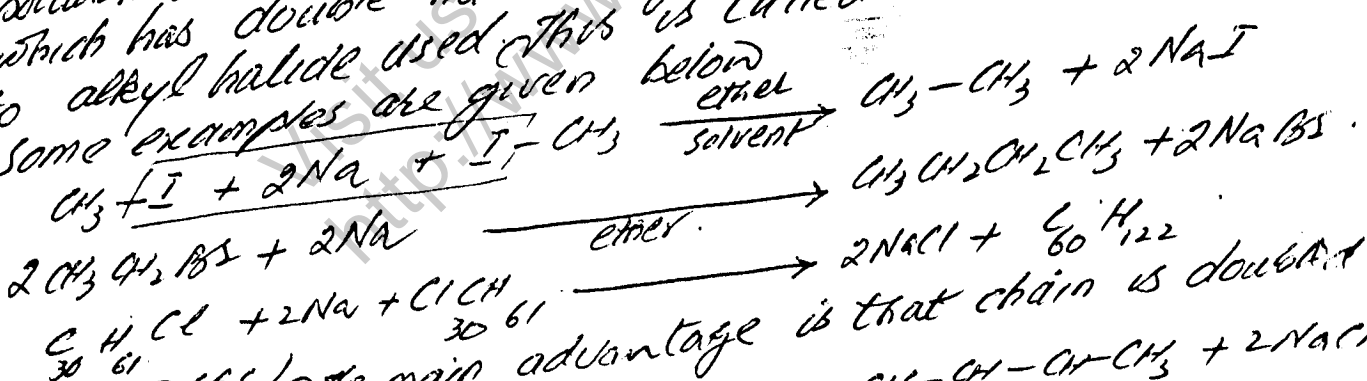
59

This is also called SABITER SENEDEEN'S REACTION.
2. FROM ALKYL HALIDES Alkyl halides are converted into alkanes by a number of methods, these are given below.

(a) REDUCTION OF ALKYL HALIDE Alkyl halides on treatment with nascent hydrogen are reduced to alkanes. Nascent hydrogen can be produced from (Zn + Alcohol) or LiAlH₄.

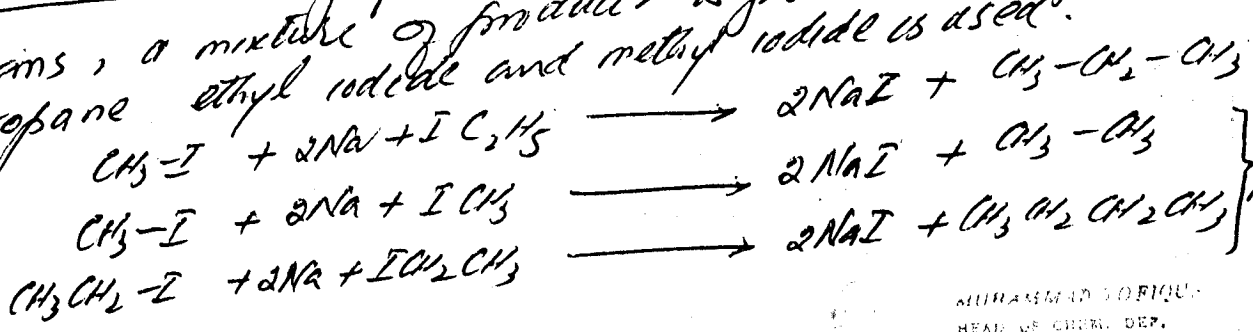


(b) WURTZ REACTION When an alkyl halide in etheral solution is treated with sodium an alkane is produced which has double number of carbon atoms as compared to alkyl halide used. This is called WURTZ REACTION. Some examples are given below.



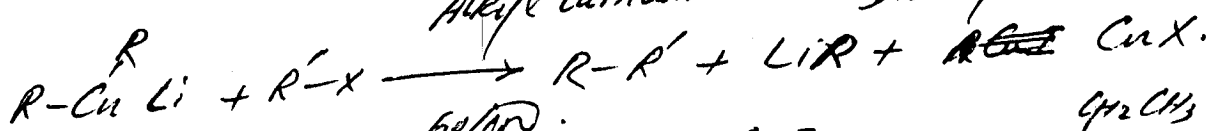
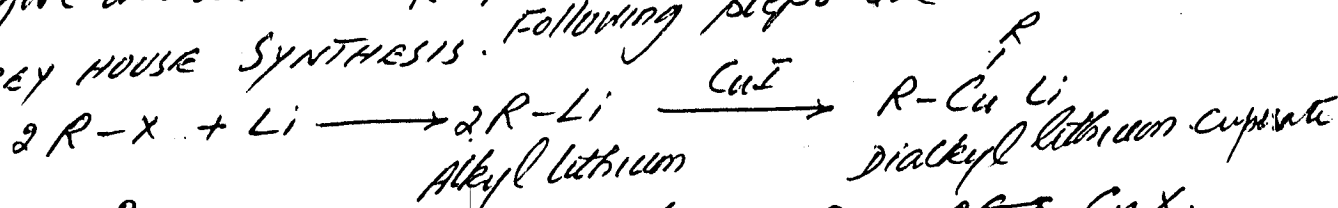
ADVANTAGES The main advantage is that chain is doubled.

DISADVANTAGE When a mixture of alkyl halide is used to prepare an alkane with odd number of carbon atoms, a mixture of products is produced. To prepare propane ethyl iodide and methyl iodide is used.

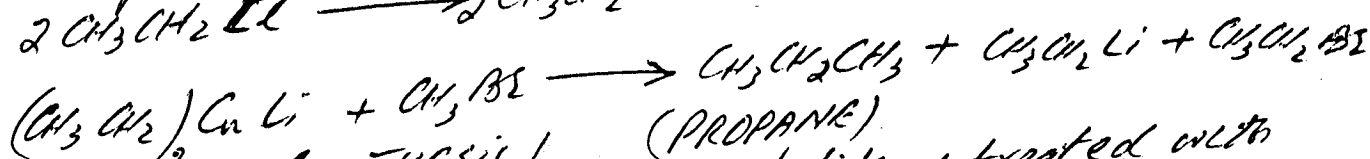
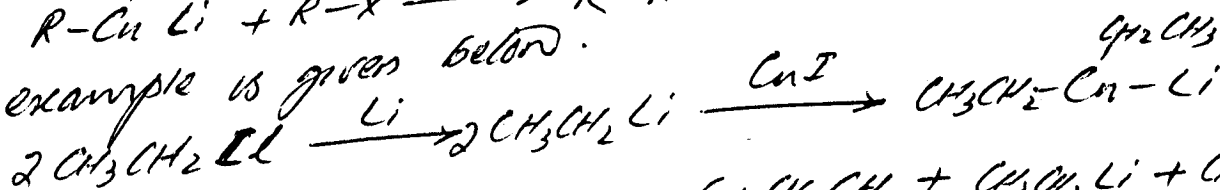


} SIDE PRODUCTS

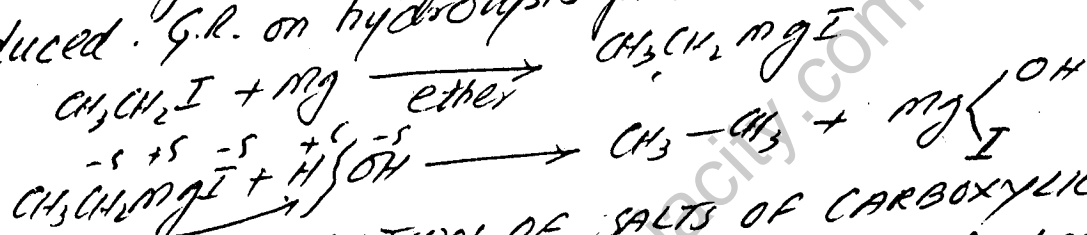
COREY HOUSE SYNTHESIS In this reaction Lithium dialkyl cuprate (R_2CuLi) is treated with an alkyl halide $R'X$ to give an alkane $R-R'$. Following steps are involved in COREY HOUSE SYNTHESIS.



An example is given below.

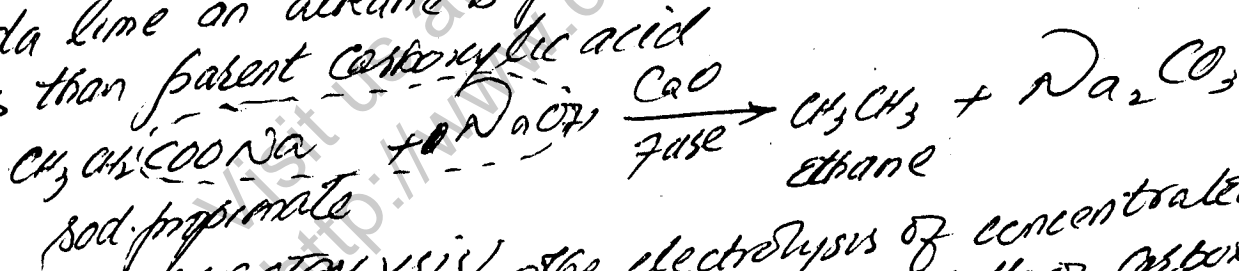


GRIGNARD SYNTHESIS When alkyl halide is treated with magnesium in presence of ether alkyl magnesium halide (G.R.) is produced. G.R. on hydrolysis produces an alkane.

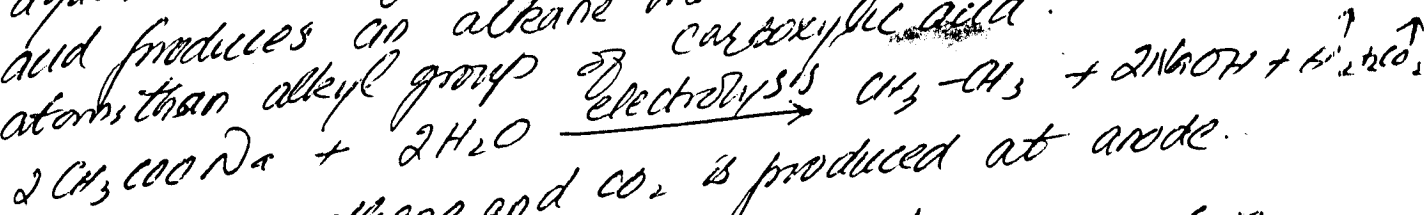


3 FROM DECARBOXYLATION OF SALTS OF CARBOXYLIC ACIDS

(a) When sodium salt of carboxylic acid is heated with soda lime an alkane is produced. It has one carbon less than parent carboxylic acid.



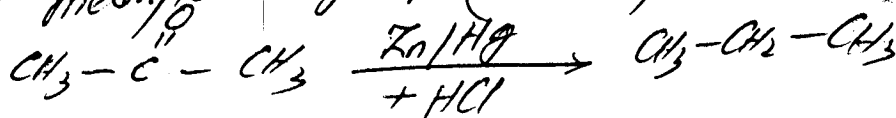
(b) KOLB ELECTROLYSIS The electrolysis of concentrated aqueous solution of sodium or potassium salt of carboxylic acid produces an alkane with double number of carbon atoms than alkyl group of carboxylic acid.



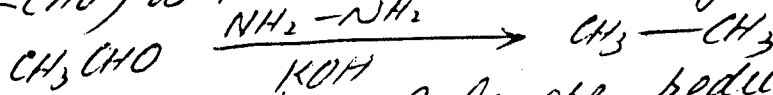
A mixture of alkane and CO_2 is produced at anode.

FROM ALDEHYDES AND KETONES There are two methods for reduction of carbonyl compounds.

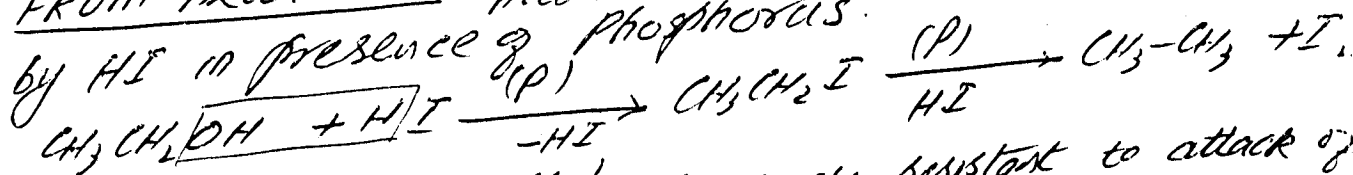
(a) CLEMENSON REDUCTION In this method ketone is treated with Zinc amalgam and HCl. Carbonyl group is reduced to methylene group ($-CH_2-$)



WOLF KISHNER REDUCTION In this method ~~an~~ aldehyde is treated with hydrazine in presence of KOH. Aldehyde group (-CHO) is reduced to -CH₃ group.

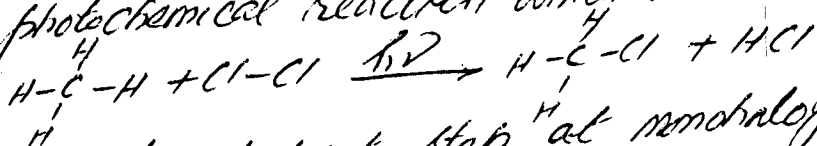


FROM ALCOHOLS Alcohols are reduced to alkane by HI in presence of phosphorus.

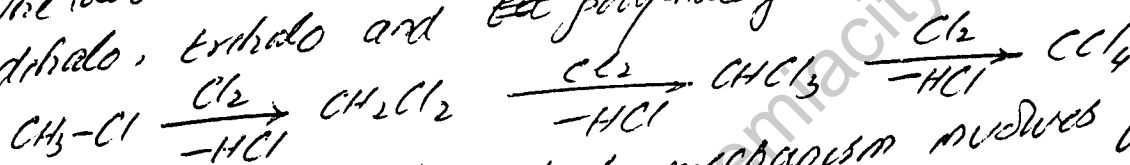


REACTIONS OF ALKANES Alkanes are resistant to attack of powerful reagents like acids, bases, K₂S₂O₇, KMnO₄ etc. Due to lack of reactivity these are called PARAFFINS. However alkanes undergo some substitution reactions under drastic conditions.

HALOGENATION: Alkanes react with halogens (Cl₂) in presence of a photochemical reaction which involves free radical mechanism.



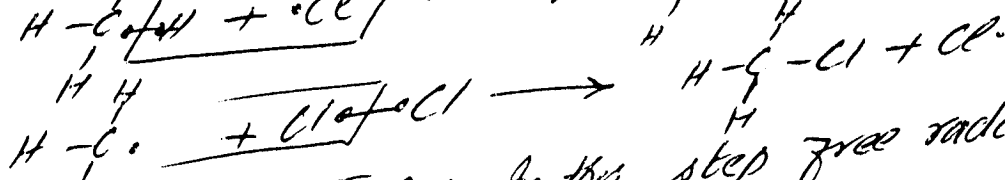
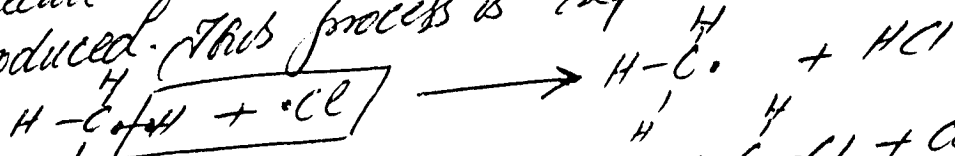
The reaction does not stop at monohalogenated state and dihalo, trihalo and tetrahalogenated compounds are formed.



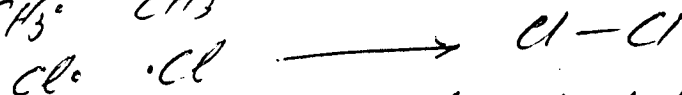
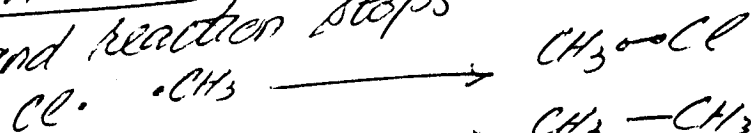
MECHANISM Free radical mechanism involves following steps

(i) INITIATION STEP In this step free radicals are produced due to action of sunlight $\text{Cl}-\text{Cl} \xrightarrow{h\nu} \text{Cl}\cdot + \text{Cl}\cdot$

(ii) PROPAGATION STEP Chlorine radical "Cl·" produced in first step reacts with methane and methyl radical is produced "·CH₃". Methyl radical abstracts "Cl" from another molecule of "Cl₂" and methyl chloride and another Cl· is produced. This process is repeated over and over again.



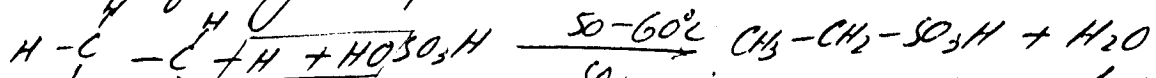
TERMINATION STEP In this step free radicals are annihilated and reaction stops



The order of reactivity of halogens is F₂ > Cl₂ > Br₂
Iodine does not react

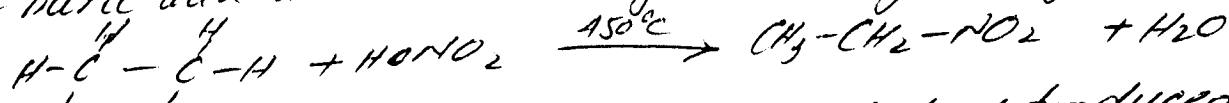
Ethane and higher alkanes produce polyhalogenated isomeric products like $\text{CH}_2\text{Cl}-\text{CH}_2\text{Cl}$ and CH_3CHCl_2 etc.

SULFONATION: Alkanes are converted into alkyl sulphonic acids with fuming sulphuric acids at $50-60^\circ\text{C}$.



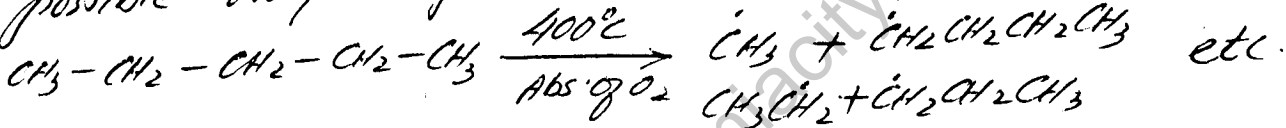
Alkyl sulphonic acids are used in detergent manufacture

NITRATION Nitration of alkanes takes place when vapours of nitric acid and alkane are passed through hot glass tube

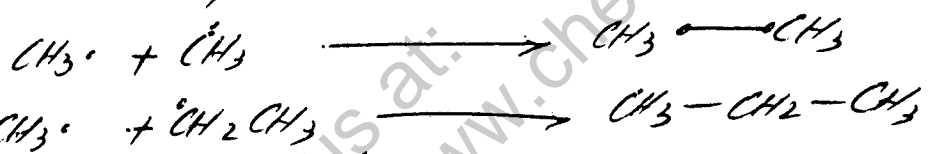


with long chain alkanes mixture of products is produced due to cracking of alkanes at such a high temp.

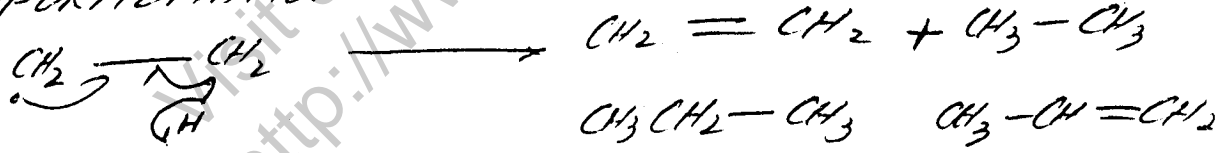
PYROLYSIS When alkane is heated in absence of oxygen above 400°C C-C bond cleaves randomly to produce alkyl radicals. These alkyl radicals may terminate in a number of possible ways to produce a mixture of products



TERMINATION BY COMBINATION OF RADICALS.

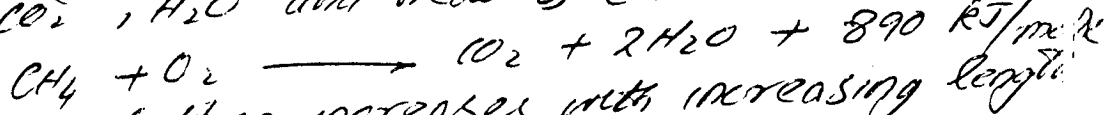


DISPROPORTIONATION



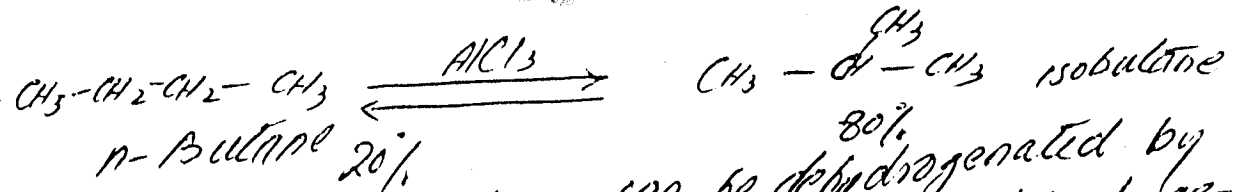
Pyrolysis is an important industrial process in petroleum industry. It is used to get smaller alkanes and alkenes.

COMBUSTION The complete oxidation of alkane with oxygen producing CO_2 , H_2O and heat is called combustion.

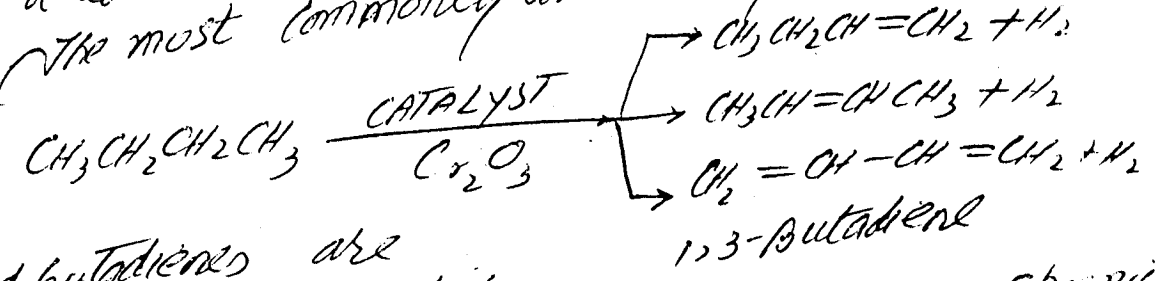


Heat of combustion increases with increasing length of carbon chain. Incomplete combustion in presence of limited supply of oxygen produces carbon black.

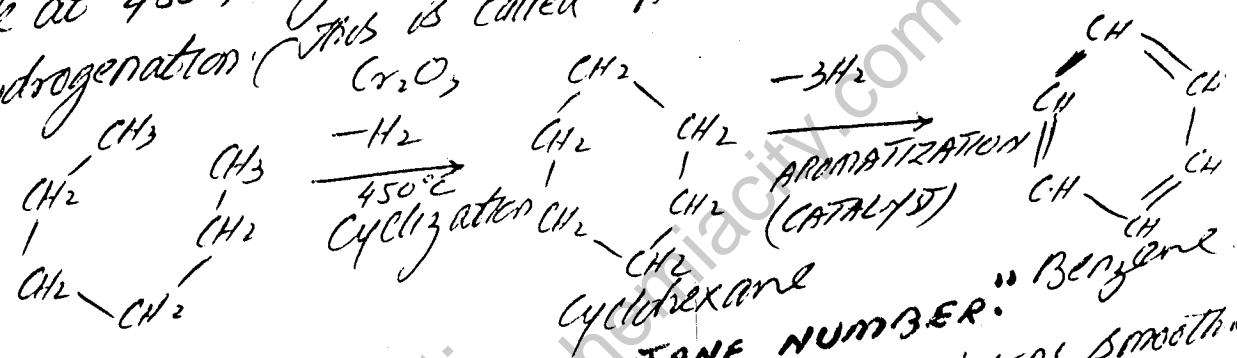
ISOMERIZATION It is reforming of straight chain alkane into branched alkane by heating in presence of Lewis acid catalyst. It is used to improve quality of fuel because branched alkanes are better fuels.



DEHYDROGENATION Alkanes can be dehydrogenated by using suitable catalyst which brings about dehydrogenation at a lower temperature than that required for pyrolysis. The most commonly used catalyst is Cr_2O_3 or V_2O_5 .



Butenes and butadienes are used in petrochemical industry. **AROMATIZATION** When n-Hexane is passed over chromic oxide at 450°C , benzene is produced by cyclization and dehydrogenation. This is called AROMATIZATION.



Q.: "WHAT IS KNOCKING AND OCTANE NUMBER?"
 A compressed mixture of alkane and air burns smoothly in the internal combustion engine. However under certain conditions (when straight chain alkane is used) the smooth explosion is replaced by knocking which reduces efficiency of engine. The problem of knocking can be reduced in two ways: (i) By using branched hydrocarbons as fuel. (ii) By use of antiknock like tetraethyl lead.
OCTANE NUMBER: The relative antiknocking tendency of a fuel is indicated by Octane Number. A scale of octane no. has been set up by with n-heptane octane no. zero and 2,2,4-trimethyl pentane "100" ratio of iso octane and n-heptane in fuel. Branched alkanes and aromatic hydrocarbons have excellent antiknocking qualities. These are produced by

cracking and reforming. Octane number can also be improved by using knock inhibitor "tetraethyl lead". But it causes air pollution by producing poisonous gases which come out of engine after combustion. Therefore its used must be discouraged.

MURAHMAS
HEAD OF CHEMISTRY
GOVT. DEGREE COLLEGE

HOME ASSIGNMENT

(1) STUDY I.U.P.A.C. RULES OF NOMENCLATURE OF ALKANES FROM TEXT BOOK AND WRITE NAMES OF FOLLOWING ALKANES

- 1 $\text{CH}_3 - \underset{\text{CH}_2}{\underset{\text{CH}_3}{\text{CH}}} - \underset{\text{CH}_3}{\text{CH}} - \text{CH}_2 - \text{CH}_3$
- 2 $(\text{CH}_3)_2 \text{CH} - \text{CH}_2 - \text{CH}_3$
- 3 $(\text{CH}_3)_2 \text{CH} - \text{CH}_2 - \text{CH}(\text{CH}_3)_2$
- 4 $\text{CH}_3 (\text{CH}_2)_3 \underset{\text{CH}_2}{\underset{\text{CH}_3}{\text{CH}}} - (\text{CH}_2)_3 \text{CH}(\text{CH}_3)_2$
- 5 $\text{CH}_3 (\text{CH}_2)_2 \text{C}(\text{CH}_3)_2 \text{CH}_2 \text{CH}(\text{CH}_3)_2$
- 6 $(\text{CH}_3)_3 \text{C} - \text{CH}_2 \text{C}(\text{CH}_3)_3$

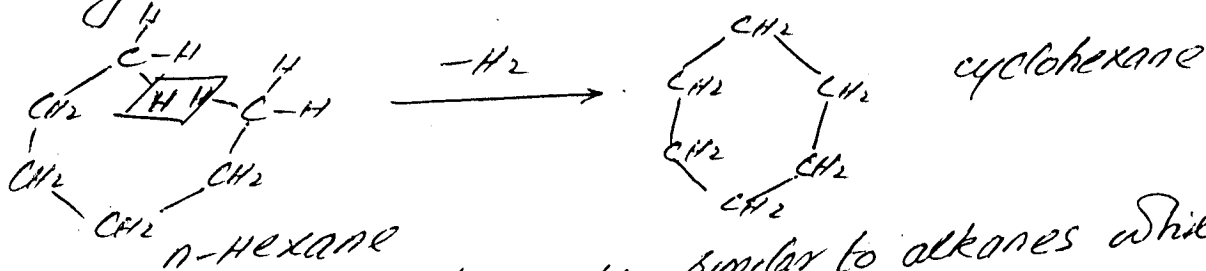
WRITE STRUCTURES OF FOLLOWING

- 1 3,4-dimethyl-4-isopropyl octane
- 2 Neopentane
- 3 All isomeric hexane.
- 4 isopentane
- 5 3-Ethyl pentane.

MURAHMAS
HEAD OF CHEMISTRY
GOVT. DEGREE COLLEGE

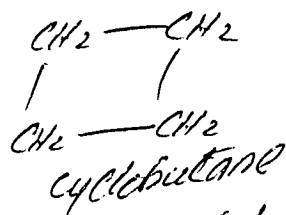
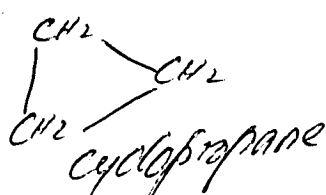
CYCLOALKANES

Cyclic hydrocarbons having C-C and C-H bonds like alkanes but general formula like that of alkenes (C_nH_{2n}) are called cycloalkanes. These are theoretically obtained by removal of two hydrogen atoms from two carbon atoms of chain and linking two carbons to form a ring.

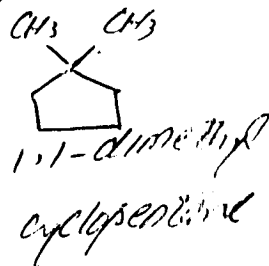
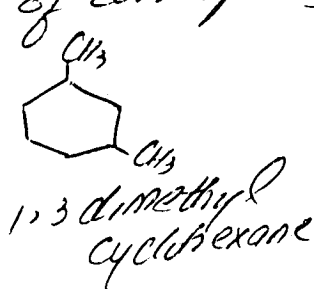
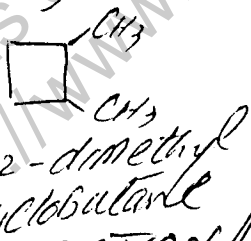


Some properties of cycloalkanes are similar to alkanes while small ring cycloalkanes behave like alkenes.

NOMENCLATURE Cycloalkanes are named by writing prefix "cyclo" before name of corresponding alkane. e.g.

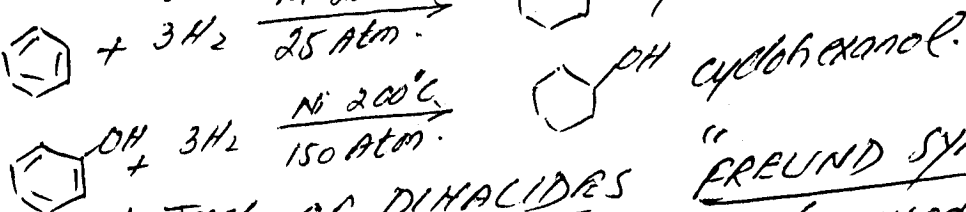
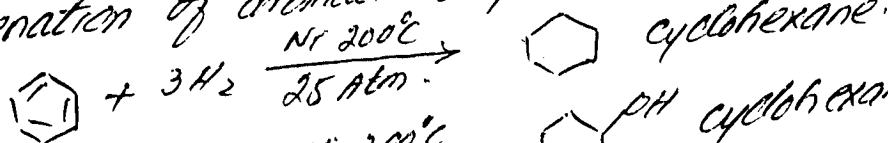


If there are more than substituents on ring, their relative position is indicated by numbers of corresponding atom.

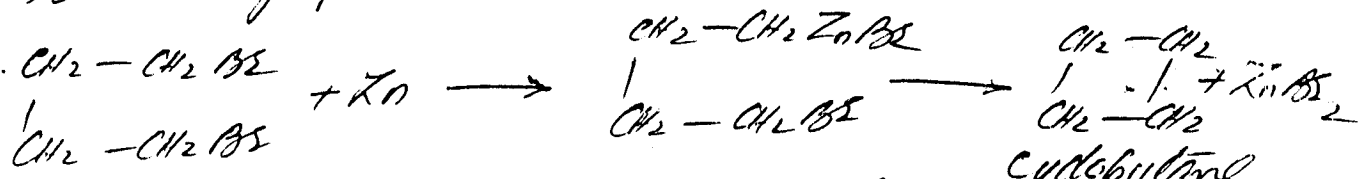
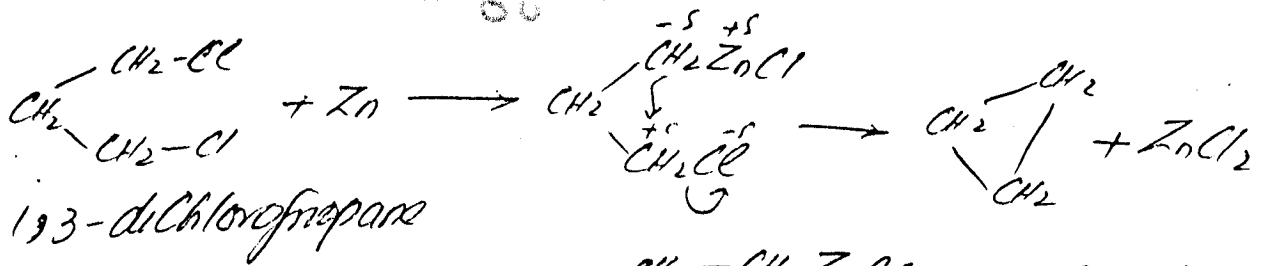


METHODS OF PREPARATION

1. CATALYTIC HYDROGENATION OF BENZENE cycloalkanes (cyclohexane) and its derivatives can be produced by catalytic hydrogenation of aromatic compounds. Consider following reactions

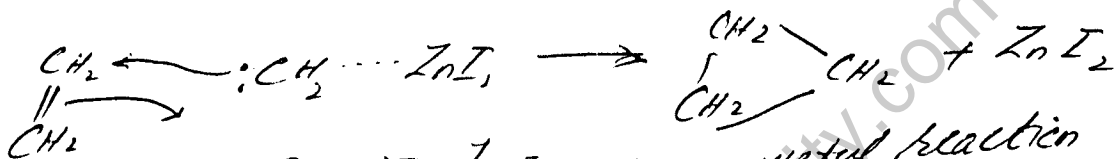
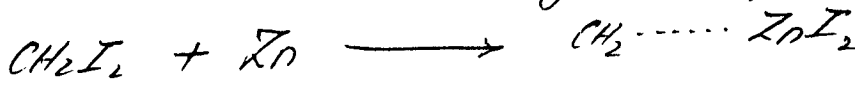


2. DEHALOGENATION OF DIHALIDES "FREUND SYNTHESIS" 1,3-dihalides or 1,4-dihalides can be used to prepare small ring cycloalkanes. One halide is converted into an organometallic compound. The second step is intramolecular cyclization. The reaction scheme is shown below

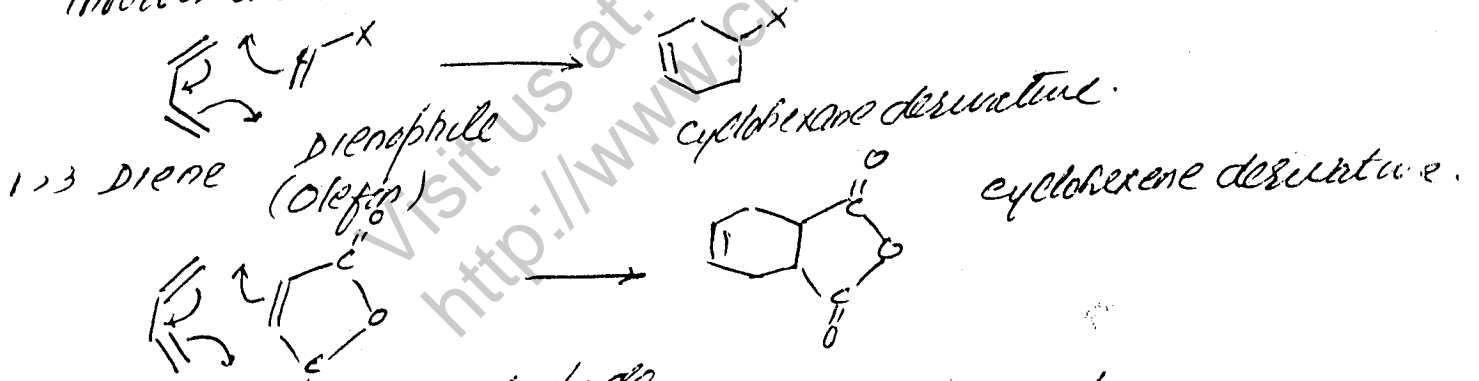


The reaction can also be carried out with "Na" but yield is quite poor.

SIMMONS SMITH REACTION cyclopropane can also be produced by treating ethene with diiodomethane in presence of Zn-Cu couple. Mechanism involves a carbene complex which adds to a π -bond to give cyclopropane.



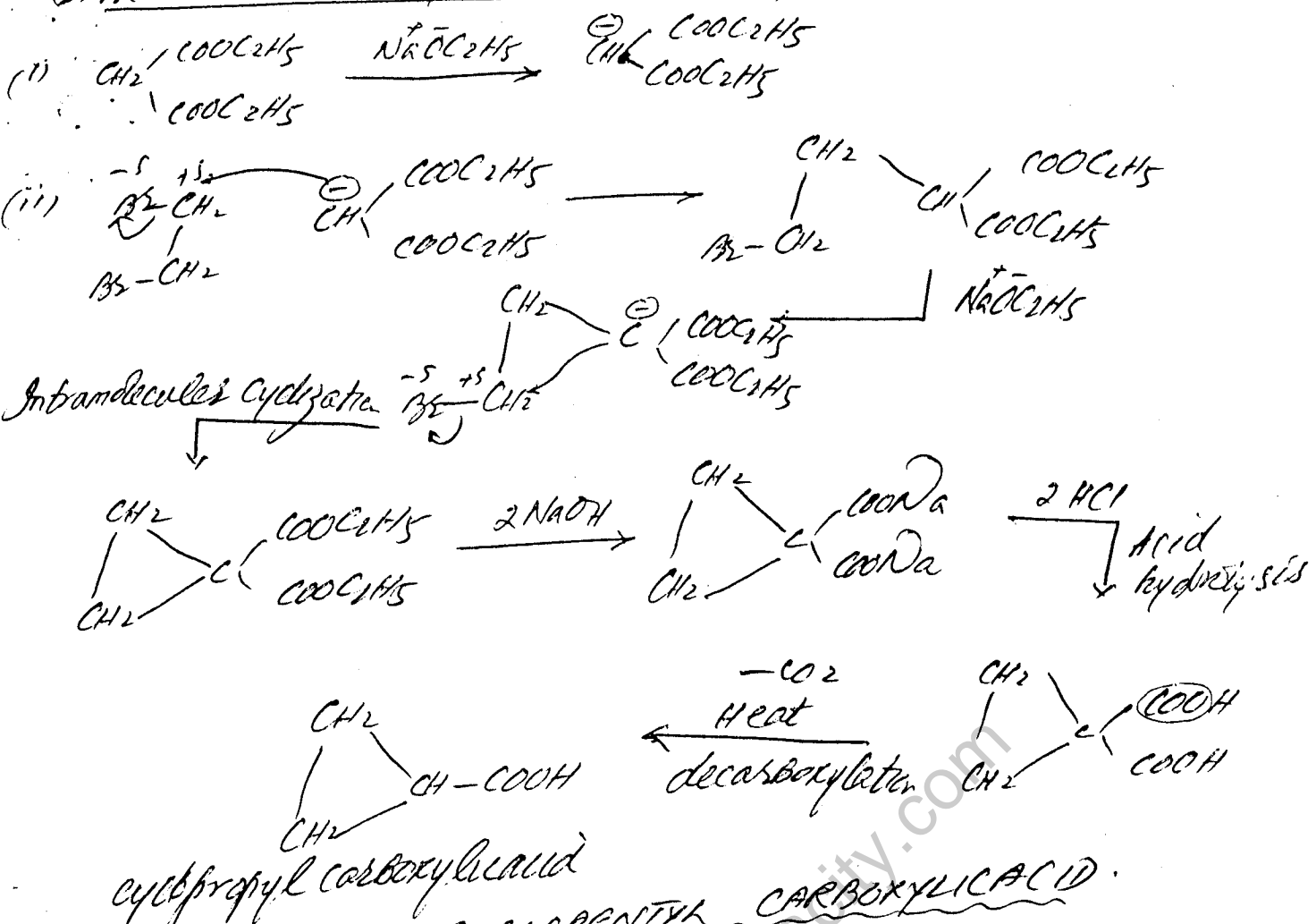
DIELS ALDER REACTION This is a useful reaction to convert an open chain compound to cyclic compound. The reaction involves thermal addition of 1,3-butadiene to an alkene.



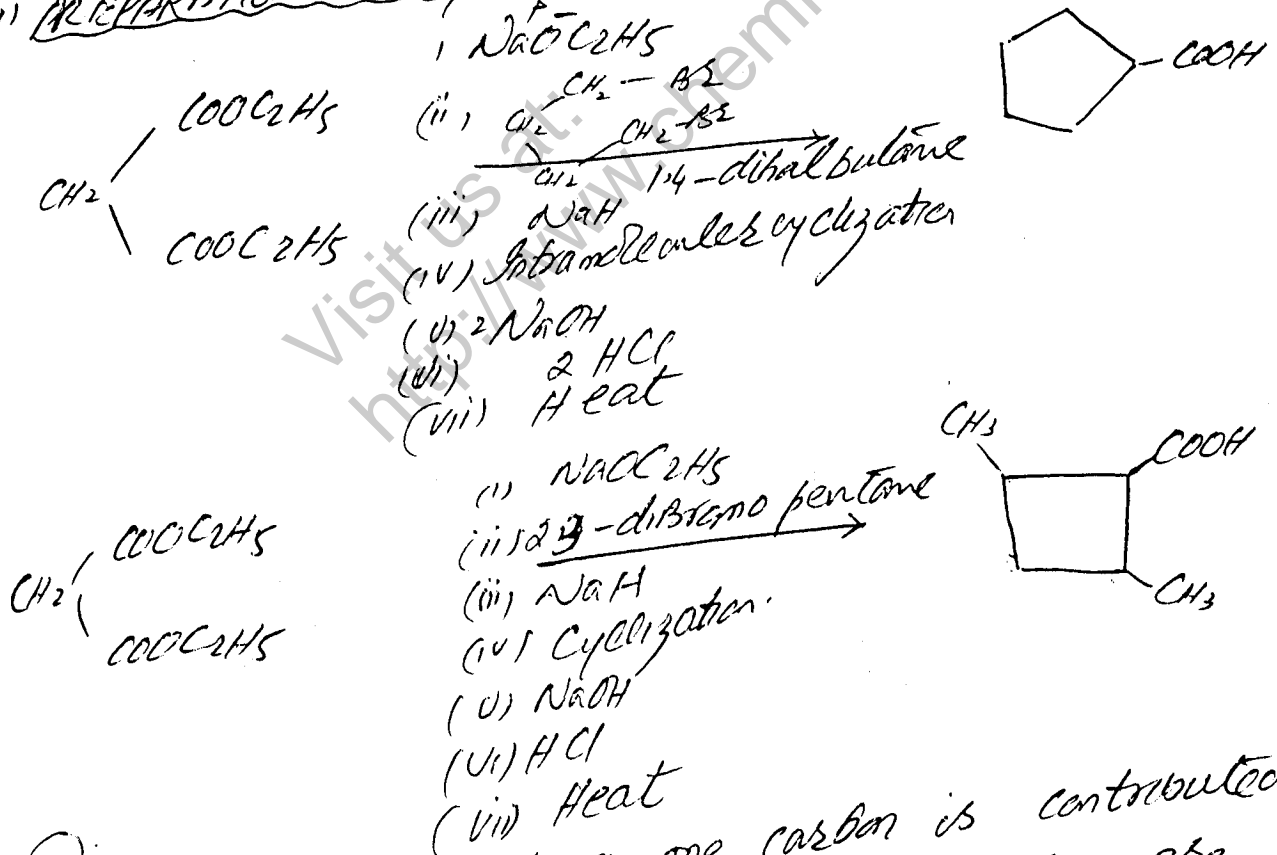
This is called PERICYCLIC or concerted reaction. PERKIN RING CLOSURE MALONIC ESTER SYNTHESIS

The preparation of cyclic compounds from Malonic ester is called Perkin ring closure. Malonic ester is an active methylene compound and its hydrogen can be removed by a strong base (NaOC_2H_5). The anion formed is alkylated with dibromide and then intramolecular cyclization takes place. The reaction scheme is shown below

(i) PREPARATION OF CYCLOPROPYL CARBOXYLIC ACID



(ii) PREPARATION OF CYCLOPENTYL CARBOXYLIC ACID



Note that out of ring one carbon is contributed by malonic ester and remaining carbons of ring are contributed by alkyl halide. Thus 1,2-dihalide produce cyclopropane, 1,3-produce cyclobutane, 1,4-produce cyclopentane and so on.

REACTIVITY AND STRUCTURE OF CYCLOALKANES

The stability and reactivity of cycloalkanes mostly depend upon size of cycloalkane. Ring compounds are basically divided into following categories on the basis of their size.

SMALL RINGS Cyclopropane & Cyclobutane (3-4 carbons)

COMMON RINGS Cyclopentane, Cyclohexane, Cycloheptane (5-7 c)

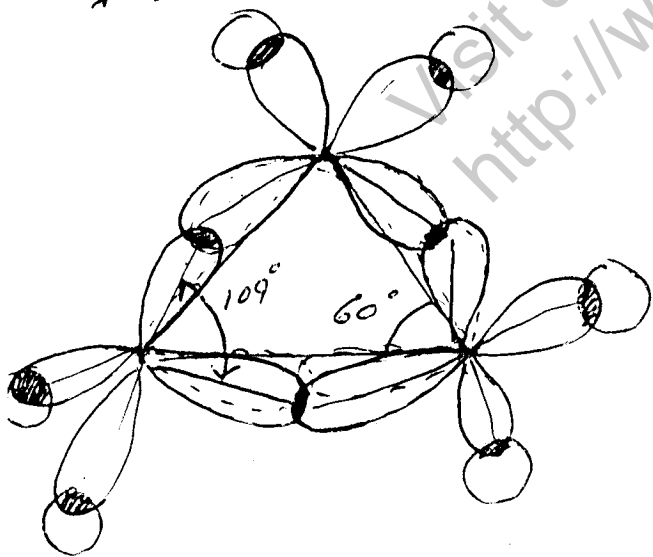
MEDIUM RINGS Cycloalkanes having 8-11 carbons.

LARGE RINGS Rings having more than 12 carbons.

The common and large rings behave like alkanes because they don't have any angular strain. It is due to the fact that these have non-planar structure.

Small and medium rings behave differently due to high angular strain.

In cyclopropane the angles must be 60° (\triangle) while sp^3 hybridized orbitals have angle 109.5° . So hybrid orbitals are not directed towards each other to have maximum overlap. The carbon-carbon bonds are considered to be bent.



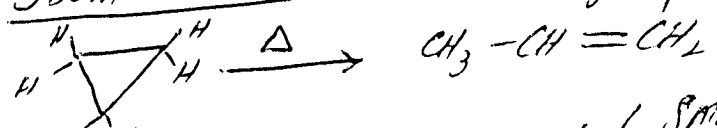
Even if no hybridization is considered "p" orbitals are oriented at an angle of 90° which is greater than 60° . What ever sort of hybridized orbitals are used, there must be angular strain in cyclopropane. Thus in most of

cases cyclopropane undergoes ring opening reactions. Cyclobutane has required bond angles 90° each. So it deviates less from

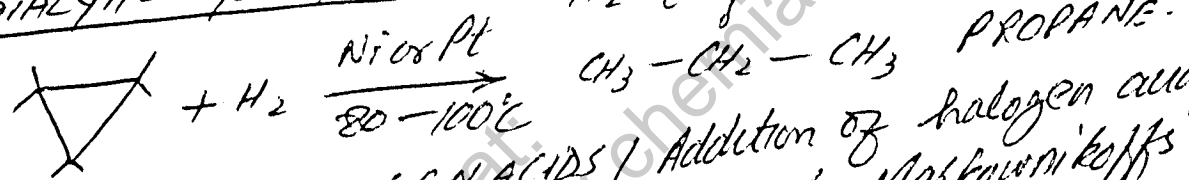
Normal angle of 109.5° of sp^3 -hybrid orbitals
 A molecule which is more strained is always less stable
 Hence small ring molecules are less stable than large molecules
 The heat of combustion decreases from cyclopropane to cyclopentane which indicates that upto cyclopentane stability increases due to decrease in angular strain.
 From cyclohexane onwards ~~stability decreases~~ heat of combustion increases by increase in length of C-chain.
 It indicates that larger cycloalkanes have no angular strain and behave like alkane.

RING OPENING REACTIONS OF CYCLOALKANES.

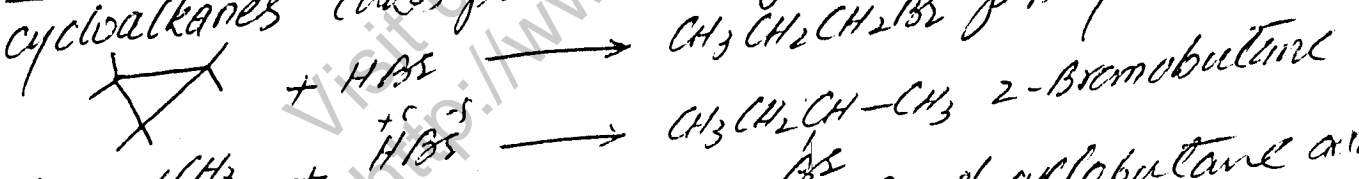
Small ring cycloalkanes behave much like alkenes and undergo addition reactions leading to ring opening.
 1) ISOMERIZATION Cyclopropane on heating opens to form propene an isomer of cyclopropane (PROPENE)



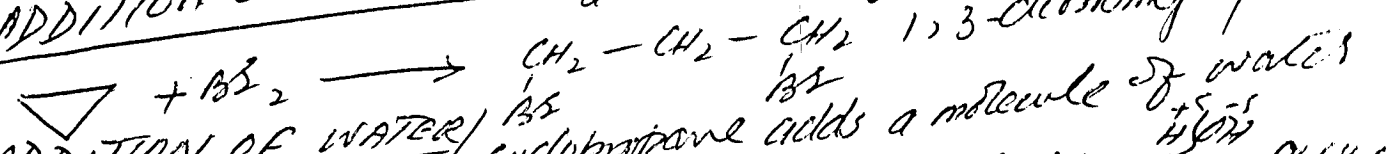
2) CATALYTIC HYDROGENATION Small rings add a molecule of H_2 to produce alkanes.



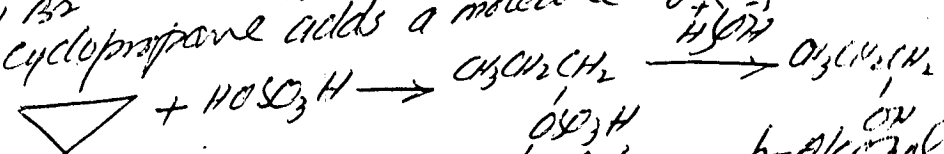
3) ADDITION OF HALOGEN ACIDS Addition of halogen acids to cycloalkanes takes place according to Markownikoff's Rule.



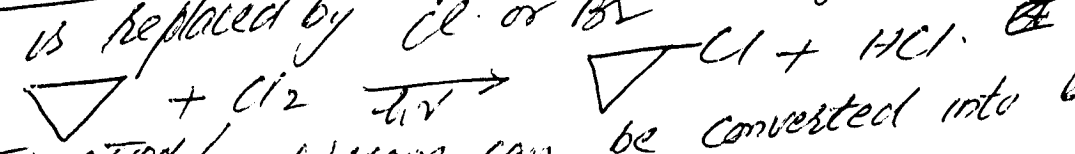
4) ADDITION OF BROMINE Cyclopropane and cyclobutane add a molecule of Br_2



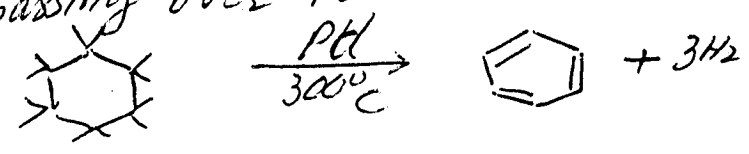
5) ADDITION OF WATER Cyclopropane adds a molecule of water in presence of H_2SO_4 .



6) SUBSTITUTION REACTIONS In presence of sunlight hydrogen is replaced by Cl or Br

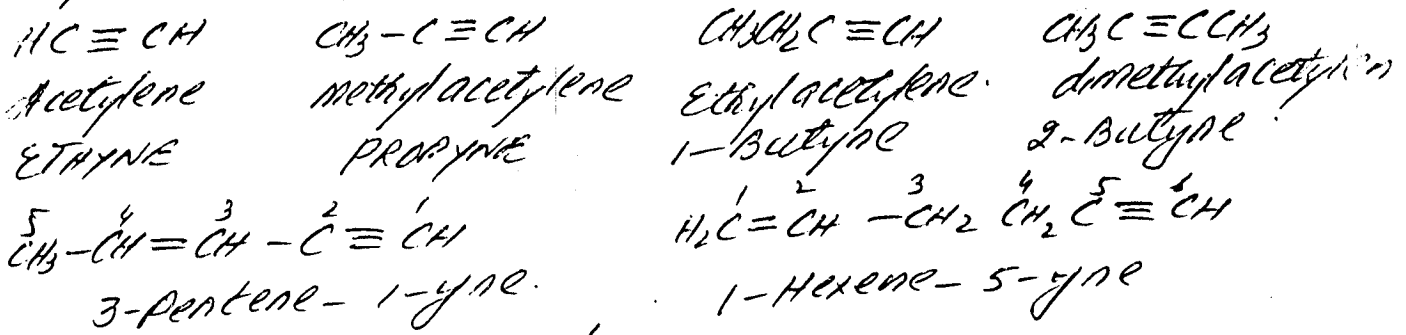


7) AROMATIZATION Cyclohexane can be converted into benzene by passing over Pd at $300^\circ C$.



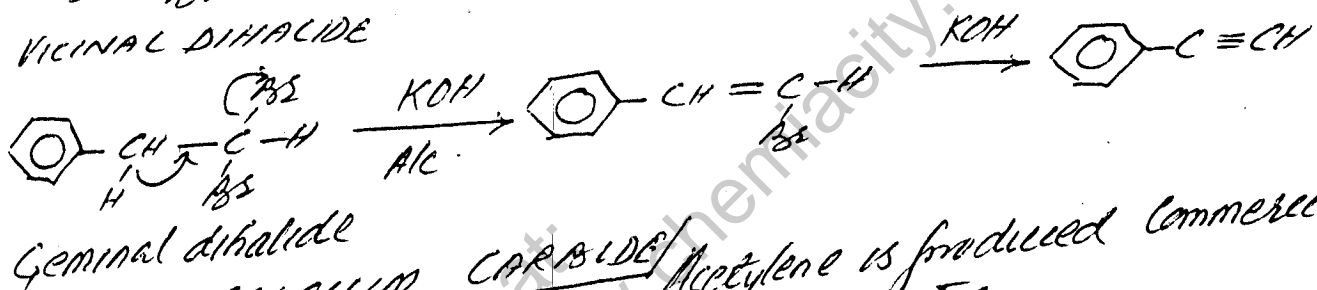
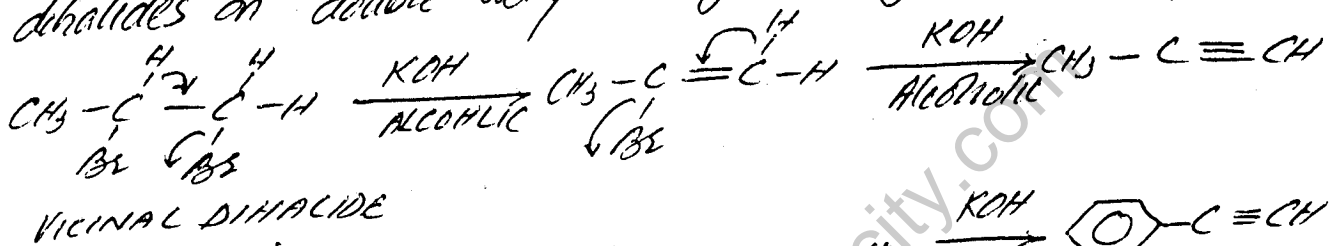
ALKYNES (HYDROCARBONS)

These are unsaturated hydrocarbons having at least one $C \equiv C$ triple bond. They have general formula $C_n H_{2n-2}$. The common name of first member of alkyne series is Acetylene. Some more common names are given below.

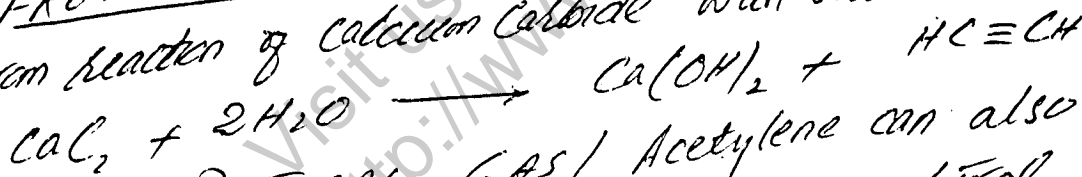


METHODS OF PREPARATION

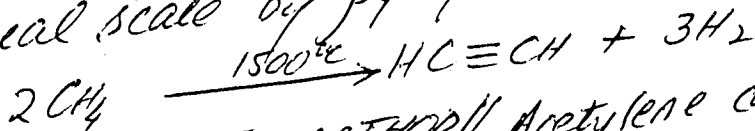
1. DOUBLE DEHYDROHALOGENATION : Geminal and vicinal dihalides on double dehydrohalogenation produce alkynes.



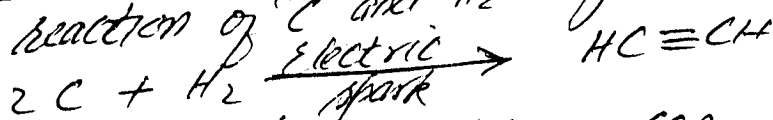
2. FROM CALCIUM CARBIDE Acetylene is produced commercially from reaction of calcium carbide with water



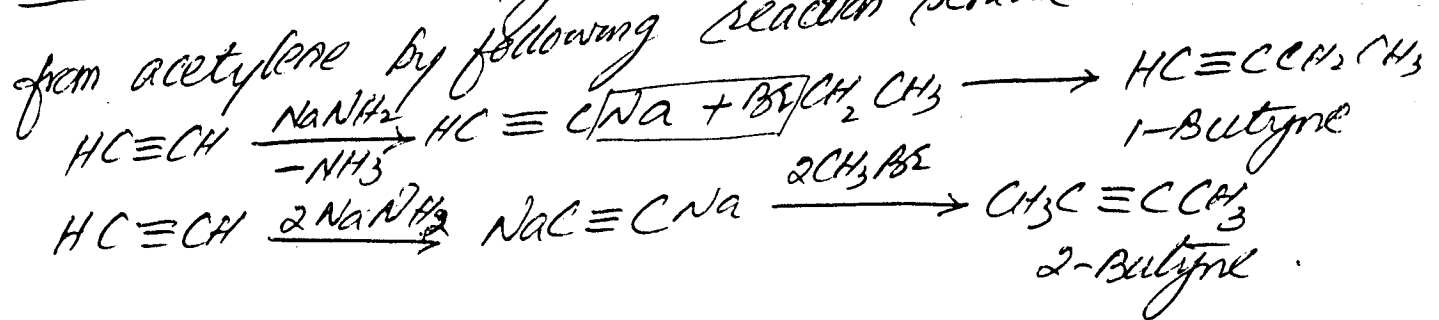
3. FROM NATURAL GAS Acetylene can also be produced on commercial scale by pyrolysis of natural gas.



4. FROM BERTHELOT METHOD Acetylene can also be prepared by reaction of "C" and H_2 in presence of electric spark



5. FROM ACETYLENE Higher alkynes can be produced from acetylene by following reaction scheme.



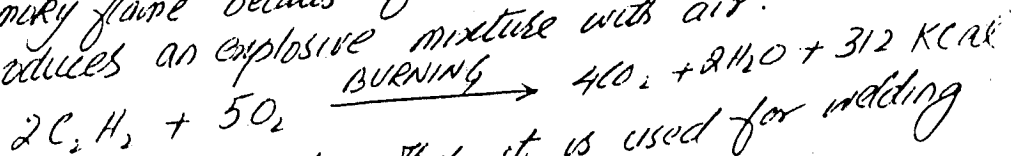
-71-

PHYSICAL PROPERTIES OF ALKYNES

The physical properties of alkynes are similar to alkenes. The lower members are gases, with boiling points somewhat higher than alkenes. Terminal alkynes like 1-Butyne has lower boiling points than isomeric alkynes like 2-Butyne. The m.p. & and B.P. increases with increase in length of C-chain.

CHEMICAL PROPERTIES OF ACETYLENE:-

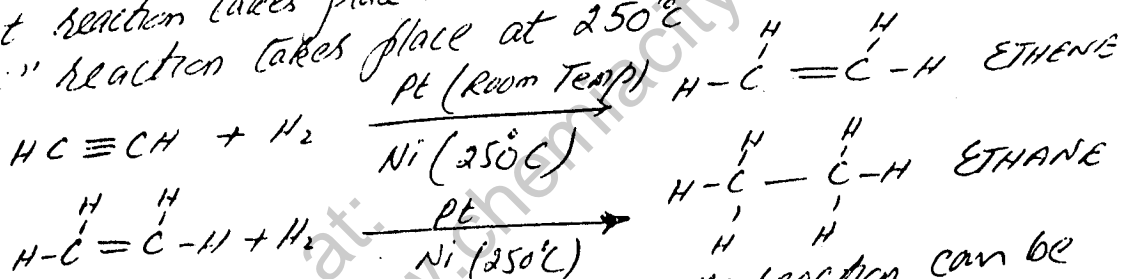
COMBUSTION | Acetylene is a non supporter of combustion. It burns with smoky flame because free carbon is produced. On burning it produces an explosive mixture with air.



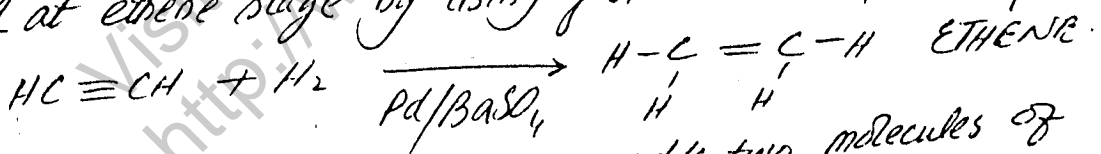
It is highly exothermic reaction. Thus it is used for welding.

SABIER SENDERENS REACTION (ADDITION OF HYDROGEN).

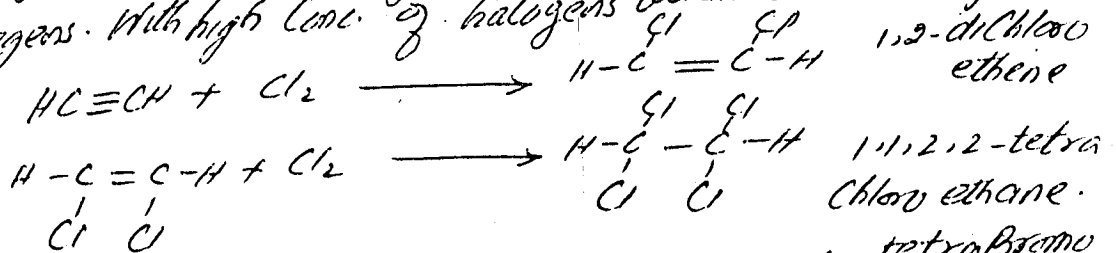
The addition of hydrogen to acetylene in presence of Pt or "Ni" is called SABIER SENDERENS Reaction. If Pt is used as catalyst reaction takes place at room temperature. In presence of "Ni" reaction takes place at 250°C.



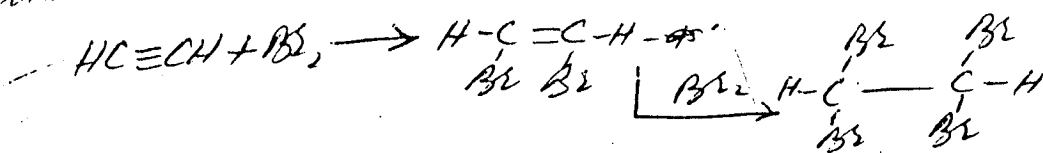
Generally reaction goes to Ethane stage. The reaction can be stopped at ethene stage by using poisoned catalyst Pd/BaSO₄.



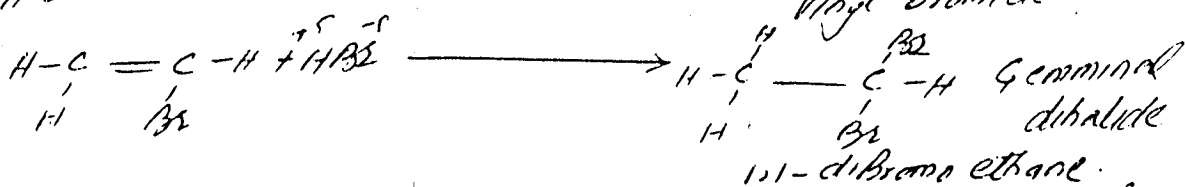
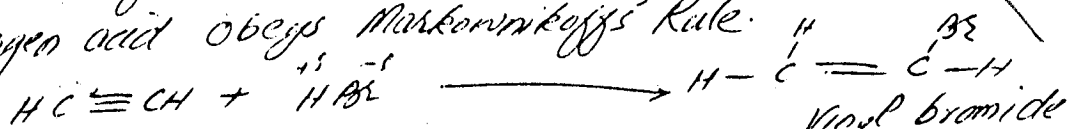
ADDITION OF HALOGENS:- Acetylene adds two molecules of halogen to form tetrahaloethane. However reaction can be stopped at dihaloethene stage by using low concentration of halogens. With high conc. of halogens tetrahaloethane is produced.



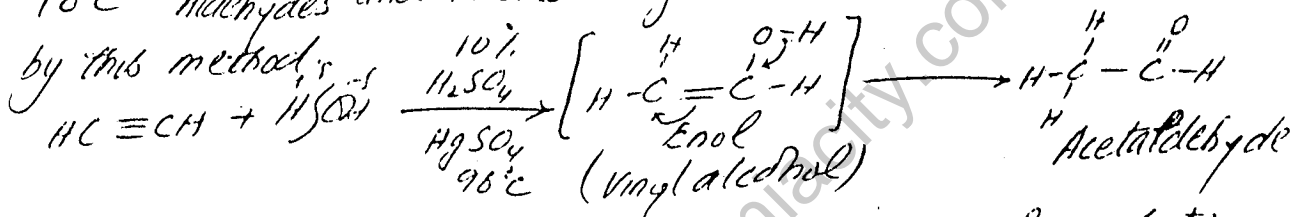
Bromine on reaction with acetylene produces 1,1,2,2-tetraBromoethane. Iodine reacts slowly.



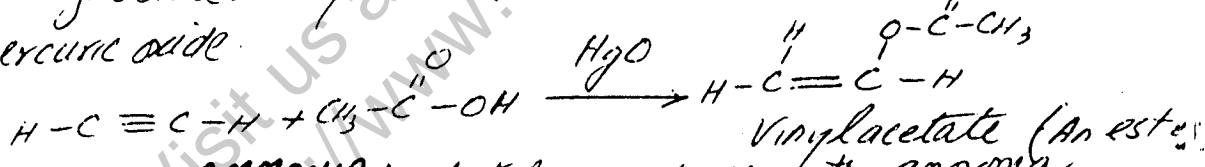
ADDITION OF HALOGEN ACIDS:- Each molecule of acetylene adds two molecules of halogen acids. In first step vinyl halide (C_2H_3X) is formed which reacts with another molecule of halogen acid and forms a Geminal dihalide. The addition of second halogen acid obeys Markownikoff's Rule.



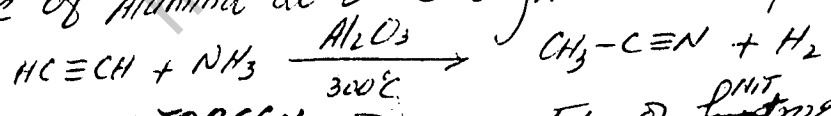
ADDITION OF WATER:- Acetylene on treatment with 10% H_2SO_4 & $HgSO_4$ adds one molecule of water to produce "ENOL". The enol rearranges to form acetaldehyde. The reaction takes place at $98^\circ C$. Aldehydes and ketenes are produced on commercial scale by this method.



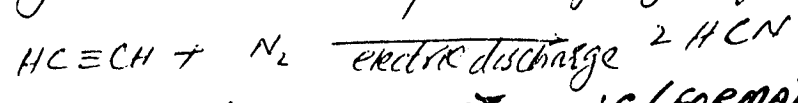
VINYLATION:- The addition of carboxylic acid to acetylene produces vinyl ester. The reaction takes place in presence of mercuric oxide.



ADDITION OF AMMONIA:- Acetylene combines with ammonia in presence of Alumina at $300^\circ C$ to produce methyl nitril.



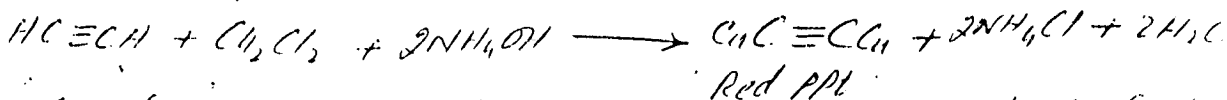
ADDITION OF NITROGEN When a mixture of hydrogen and Acetylene is subjected to electric spark, hydrogen cyanide (HCN) is produced.



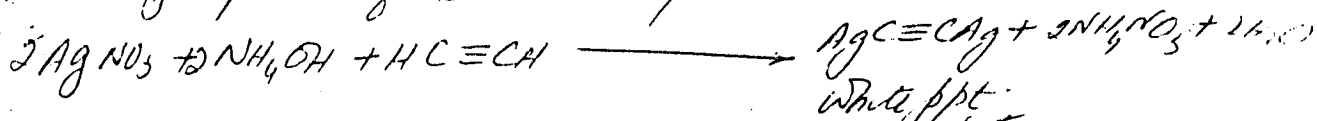
ACIDIC CHARACTER OF ACETYLENE (FORMATION OF METALLIC) ALKYNIDES

The hydrogen which can be replaced by a metal atom is called acidic hydrogen. When hydrogen of acetylene is replaced by metal the resulting salt is called metal acetylide. Let us consider following acidic reactions of acetylene.

(a) When acetylene is shaken with ammoniac cuprous chloride, a red precipitate of copper acetylide is produced.

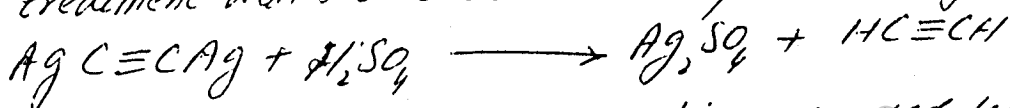


(b) Acetylene on treatment with ammoniac silver nitrate produces white precipitate of Silver acetylide.



Metallic acetylides are highly explosive in dry state.

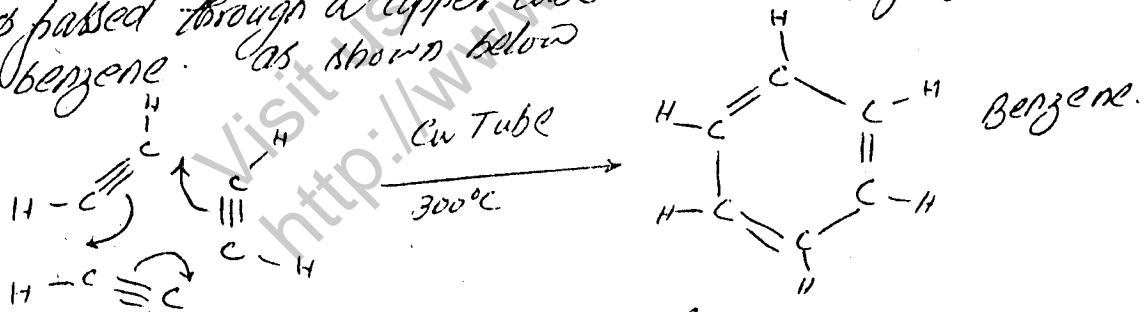
On treatment with dilute acids, acetylene is regenerated



IDENTIFICATION | The above two reactions are used for identification of acetylene. Ethene does not react with ammoniac AgNO₃ or Cu₂Cl₂.

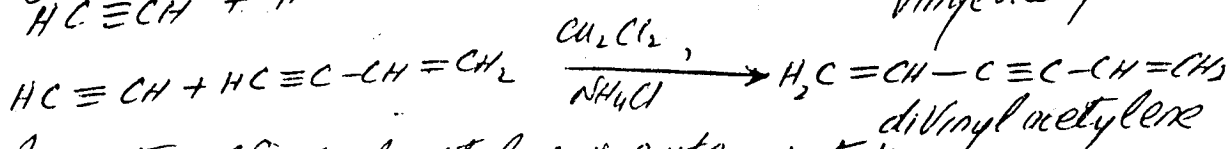
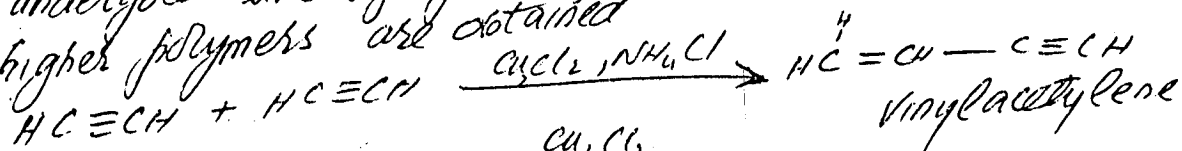
POLYMERIZATION OF ACETYLENE :- The process of formation of a large molecule of high M.Wt by combination of small molecules is called POLYMERIZATION.

(i) CONVERSION OF ACETYLENE INTO BENZENE :- When acetylene is passed through a copper tube at 300°C it polymerizes to benzene. as shown below



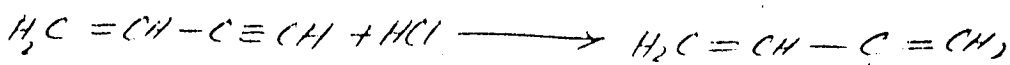
Thus benzene is a polymer of acetylene.

2. LINEAR POLYMERIZATION OF ACETYLENE when acetylene is passed through cuprous chloride and ammonium chloride it undergoes linear polymerization. Divinyl acetylene and higher polymers are obtained



IMPORTANCE Vinyl acetylene is quite important.

It combines with HCl to form Chloroprene (2-Chloro-1,3-butadiene).



OR

Synthetic rubber is made by polymerization of Chloroprene.

2. USES OF ACETYLENE:-

- (1) Acetylene is used to cut and weld the metals. When acetylene is burnt in oxygen, oxyacetylene flame has a temp. of about 3000°C. For welding the proportion of oxygen and acetylene are so controlled that carbon monoxide and water is produced. Thus oxidation of metal is avoided. For cutting purposes an excess of oxygen is used. Thus oxyacetylene flame is able to cut Nickel Chrome plates.
- (2) Acetylene is used to prepare acetaldehyde and acetic acid.
- (3) It is used to prepare, ethanal, rubber, plastics, fabrics.
- (4) It is used to prepare acetylene tetrachloride which is a good solvent for varnishes, resins and rubber.
- (5) It is used for artificial ripening of fruit.

SOME IMPORTANT CONVERSIONS FOR PRACTICE (TRY YOURSELF)

- | | | |
|--------|---|--------------------|
| ETHENE | → | ETHANOL |
| " | → | ETHANE |
| " | → | ETHYNE |
| " | → | FORMALDEHYDE |
| " | → | GLYCOL |
| " | → | VICINAL DIBROMIDE |
| " | → | MUSTARD GAS |
| " | → | DUTCH LIQUID |
| ETHYNE | → | PROPYNE |
| " | → | ETHENE |
| " | → | ACETALDEHYDE |
| " | → | 1,1-DIBROMO ETHANE |
| " | → | METHYL CYANIDE |
| " | → | H.CN. |

- | | | |
|--------|---|-------------|
| ETHYNE | → | BENZENE |
| " | → | CHLOROPRENE |
- HOW WILL YOU DISTINGUISH BETWEEN
- ETHANE & ETHENE
- ETHENE & ETHYNE
- HOW WILL YOU PREPARE ETHENE FROM
- ETHYL BROMIDE
- ETHANOL
- SODIUM SUCCONATE
- ETHYNE

- 75 -

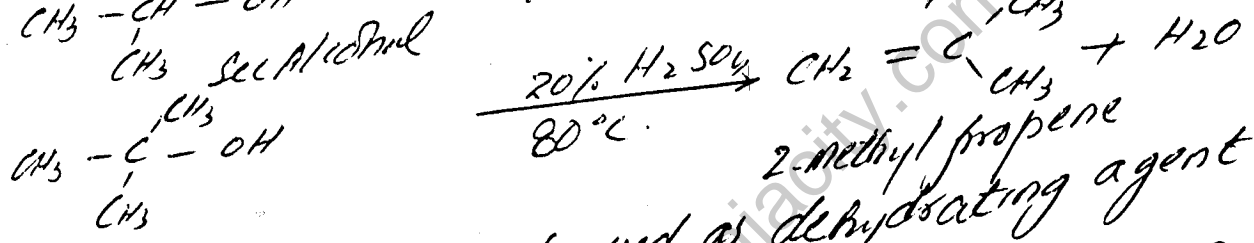
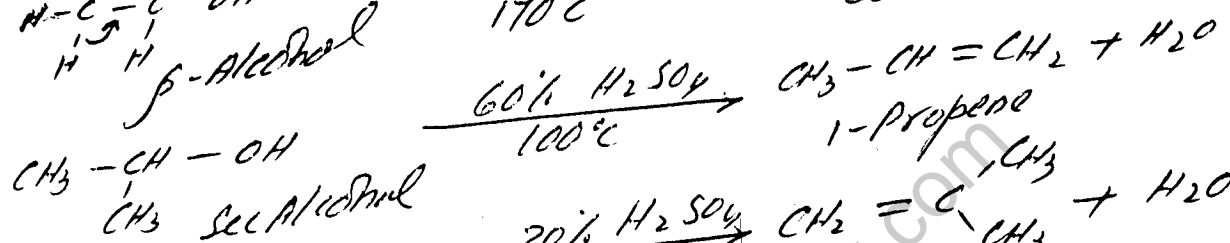
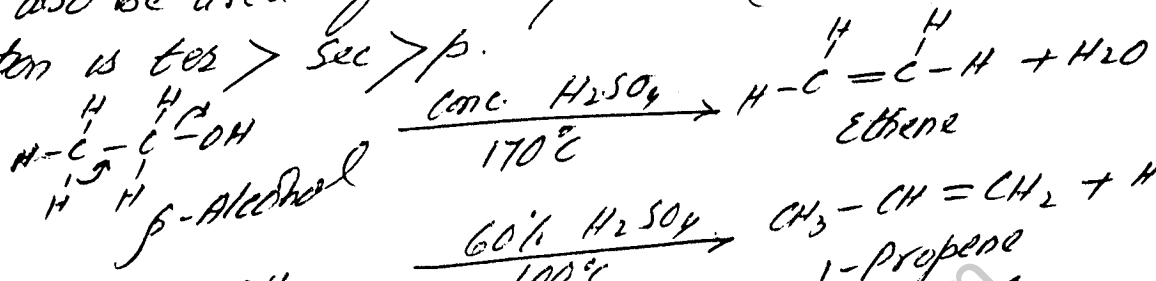
"ALKENES" (B.Sc. Organic)

APPROVED BY THE
HEAD OF CHEMISTRY
GOVT. DEGREE COLLEGE
R. N. SARGODHA

These are unsaturated hydrocarbons with at least one C=C double bond. These are converted into corresponding alkane by addition of one or more moles of H₂.

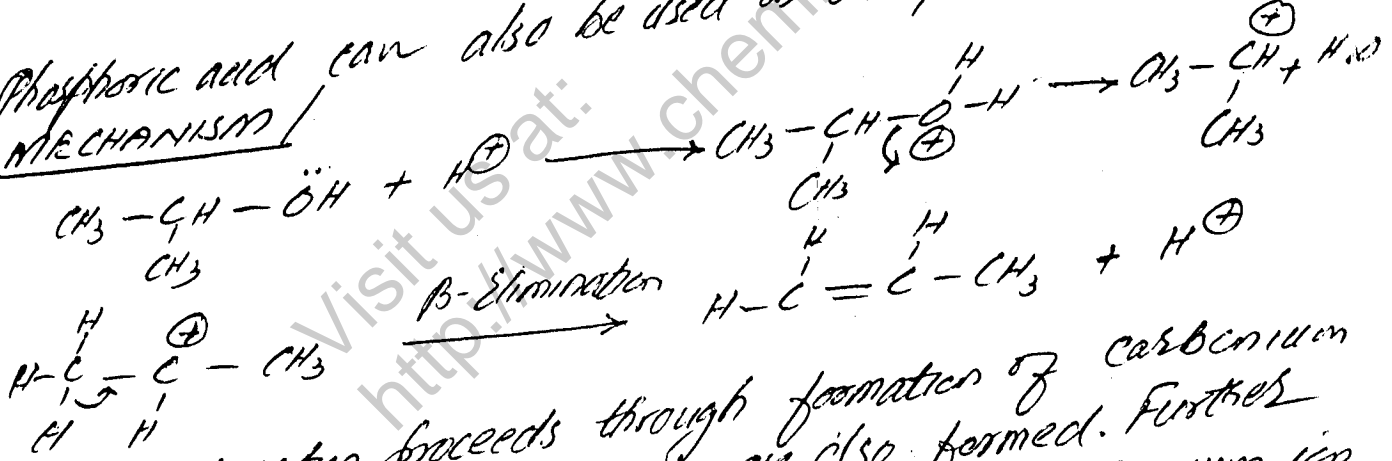
METHODS OF PREPARATION.

(i) DEHYDRATION OF ALCOHOL: The removal of water from an alcohol is called DEHYDRATION. Alcohols when passed over heated alumina undergo dehydration. Sulphuric acid can also be used for dehydration. The ease of dehydration is $ter > sec > p$.

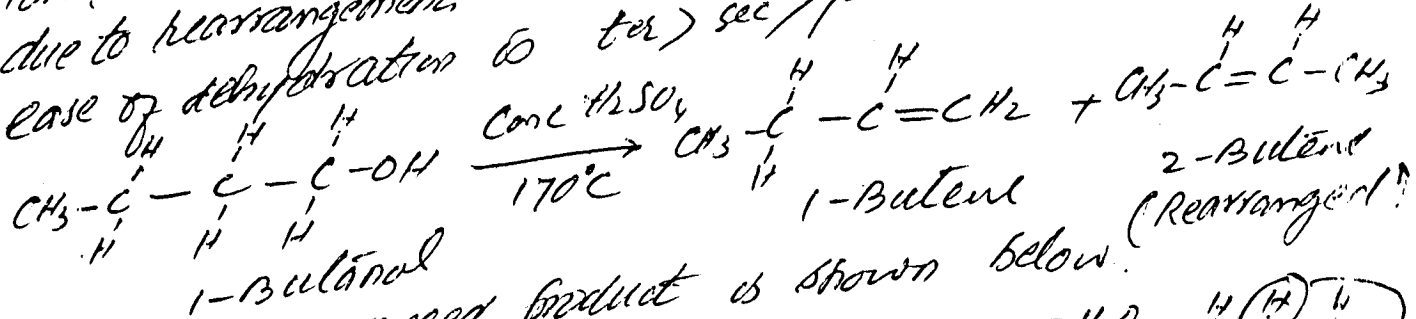


Phosphoric acid can also be used as dehydrating agent.

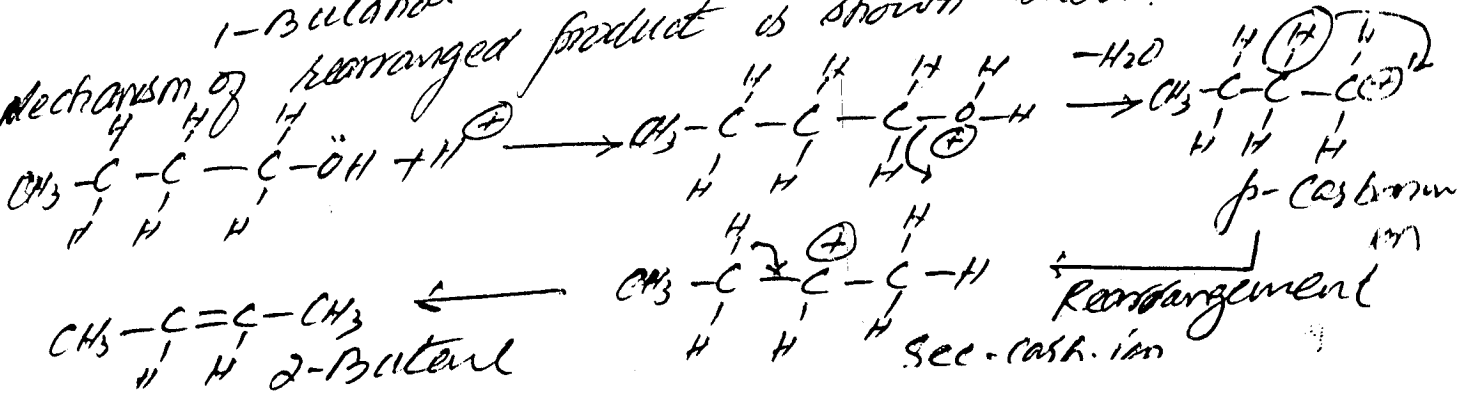
MECHANISM



Since reaction proceeds through formation of carbocation ion so rearranged products are also formed. Further due to rearrangement and stability of $ter.$ carbocation ease of dehydration is $ter > sec > p$.

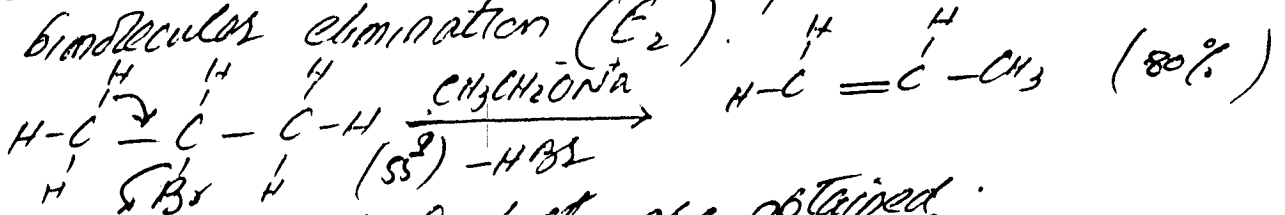


Mechanism of rearranged product is shown below.

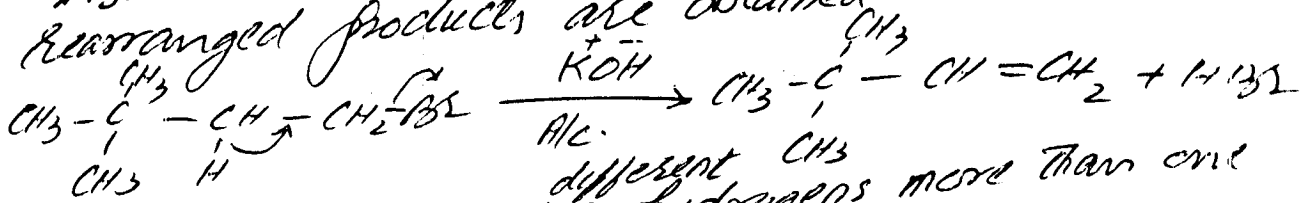


DEHYDROHALOGENATION OF ALKYL HALIDES.

Removal of ~~interior~~ hydrogen and halogen from two adjacent carbons is called dehydrohalogenation. The base used is Alcoholic KOH or ethanolic solution of NaOC_2H_5 . The reaction does not involve any carbocation. It is a bimolecular elimination (E_2).

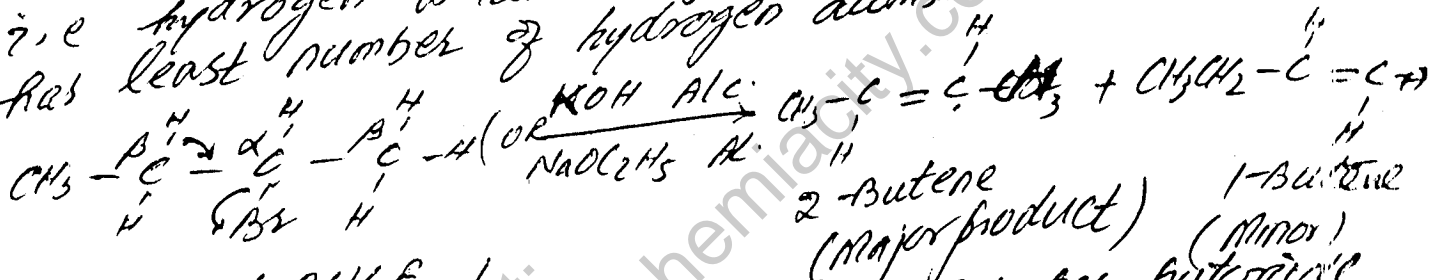


No rearranged products are obtained.

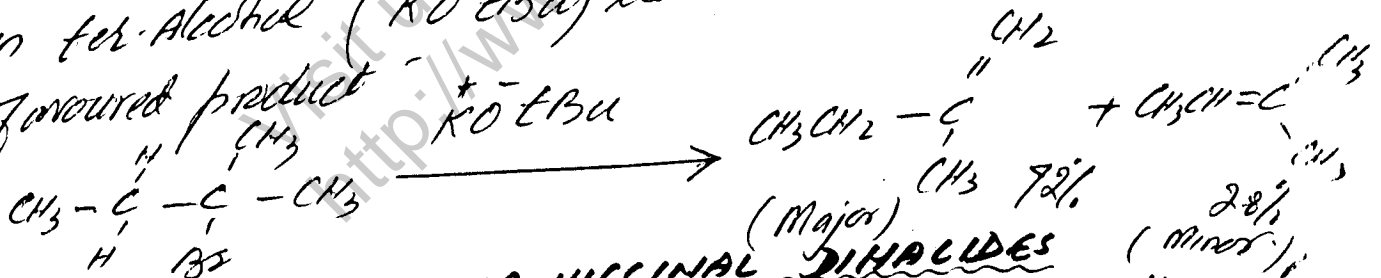


If there are more than one β -hydrogens more than one products are obtained.

SAYTZEFF RULE When KOH or alcoholic NaOC_2H_5 base is used more substituted alkene is major product i.e. hydrogen is removed from that β -carbon which has least number of hydrogen atoms.

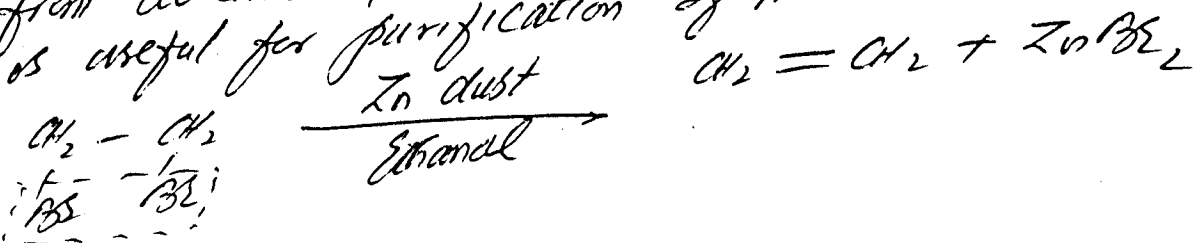


HOFMANN RULE When base used is Pot. ter. butoxide in ter. Alcohol (KO^tBu) least substituted alkene is favoured product.



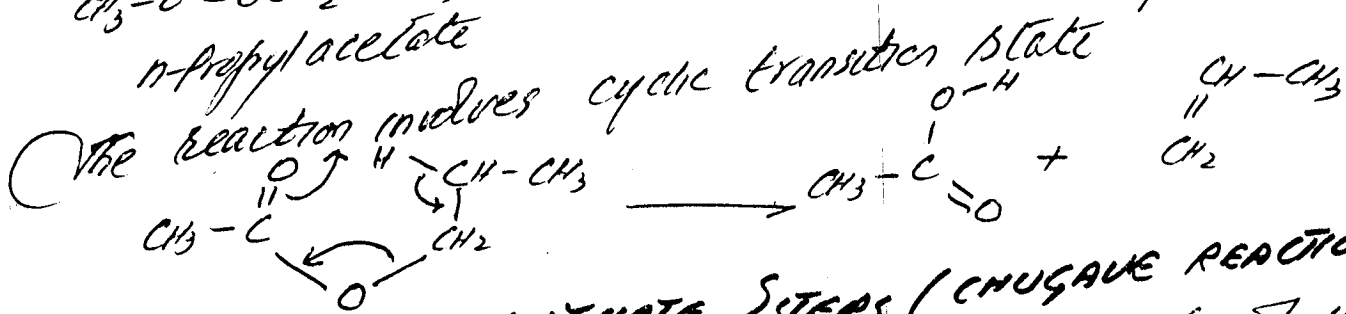
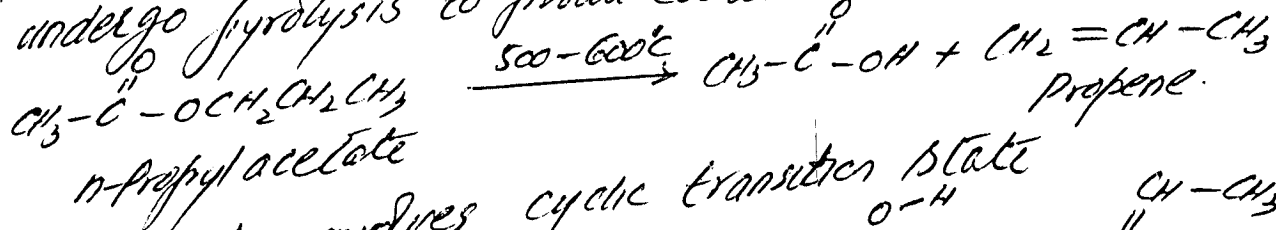
DEHALOGENATION OF VICINAL DIHALIDES

Vicinal dihalides on treatment with Zinc dust in ethanolic etc application because vic dihalides are themselves produced from alkenes. However bromination followed by dehalogenation is useful for purification of Alkenes.



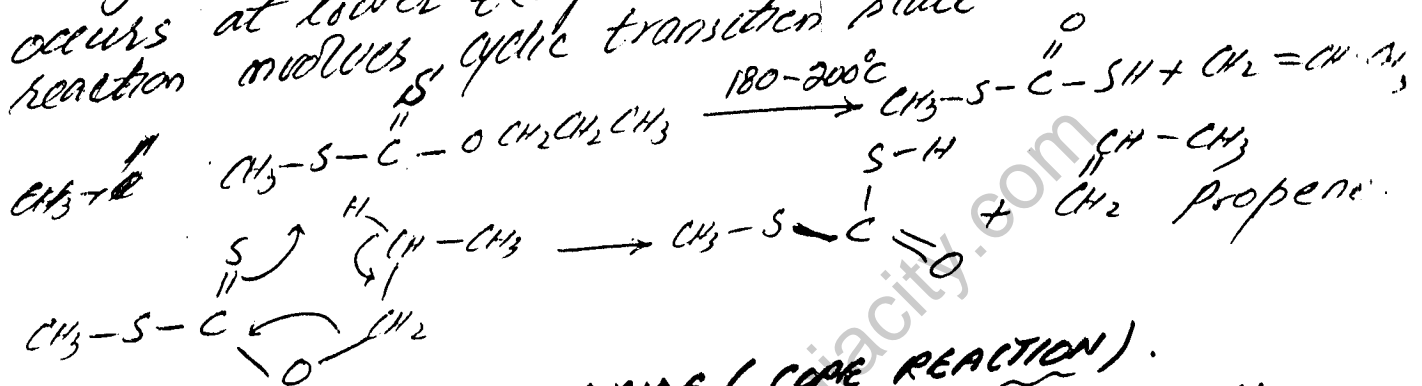
THERMAL ELIMINATION REACTION:-

(ii) PYROLYSIS OF ESTER:- Esters on heating to 500-600°C undergo pyrolysis to produce alkenes



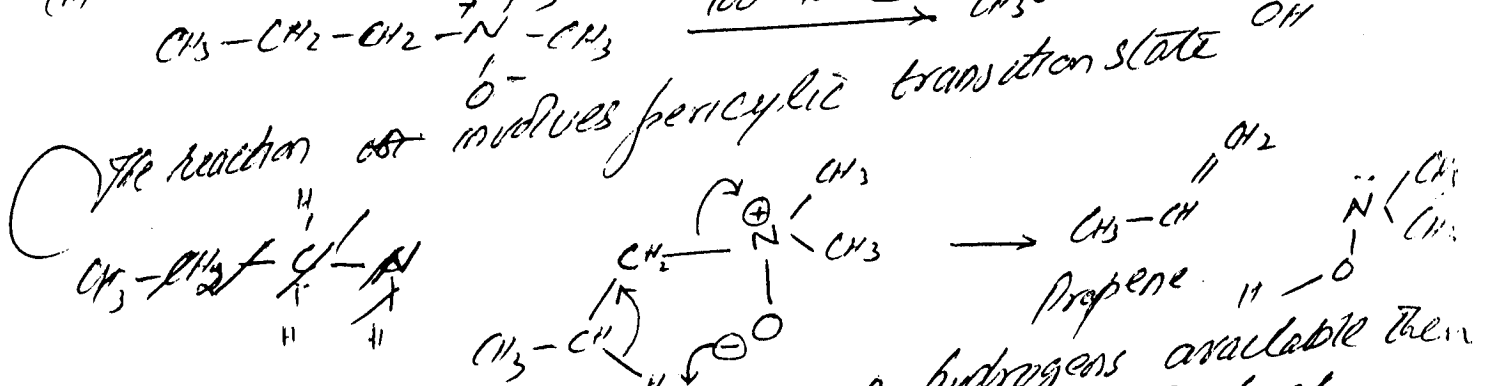
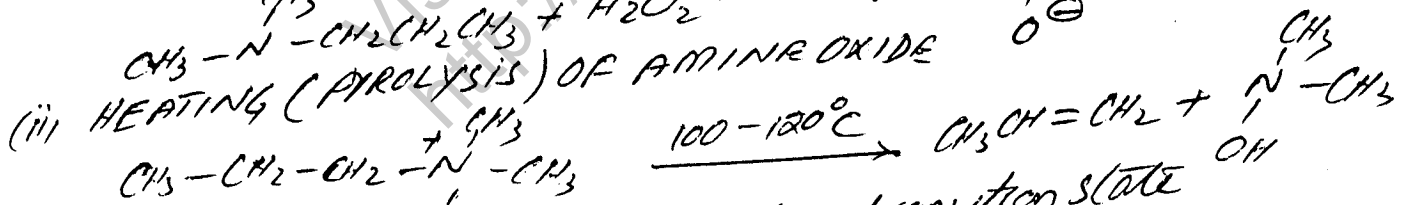
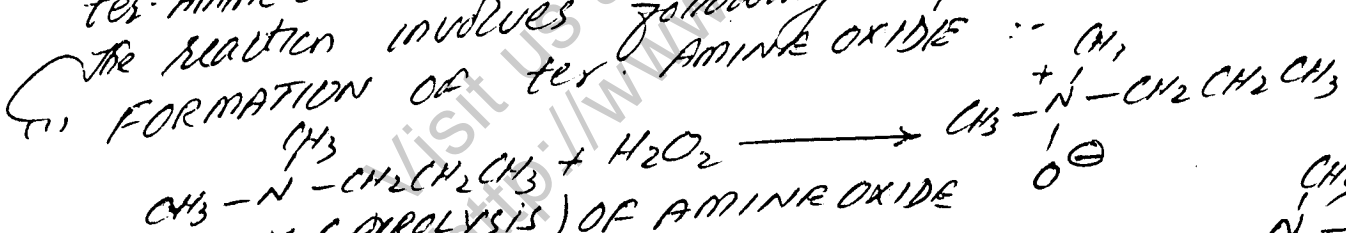
PYROLYSIS OF XANTHATE ESTERS (CHUGAUE REACTION).

A major advantage of this reaction is that pyrolysis occurs at lower temp as compared to esters. The reaction involves cyclic transition state.

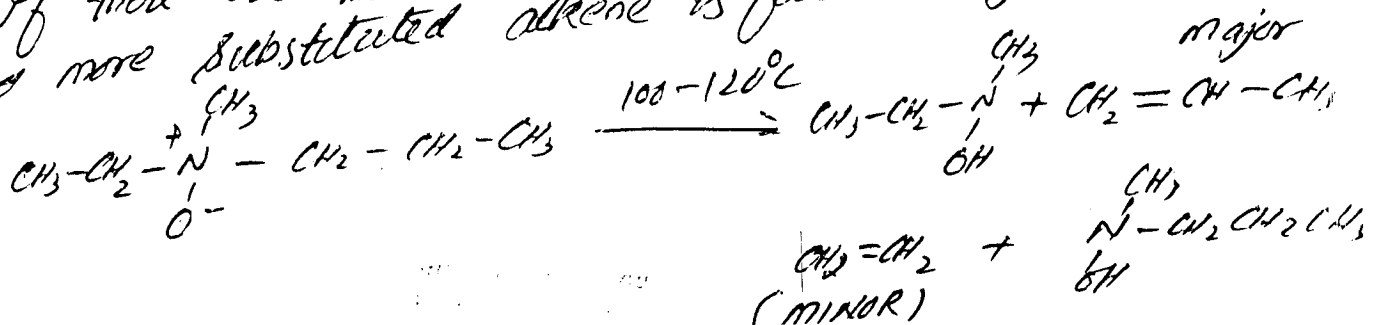


PYROLYSIS OF AMINE OXIDE (COPE REACTION).

ter. Amine oxide on heating to 100-120°C produce alkene. The reaction involves following steps:



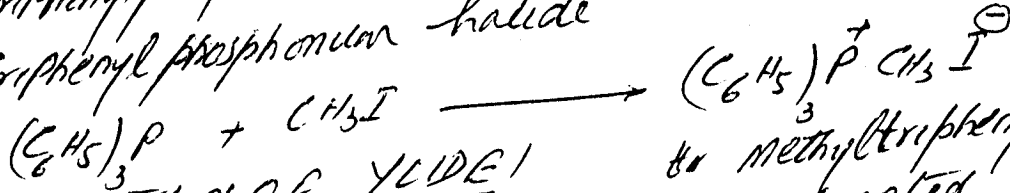
- If there are more than one beta-hydrogens available then the more substituted alkene is favoured product



Imp. WITIG REACTION

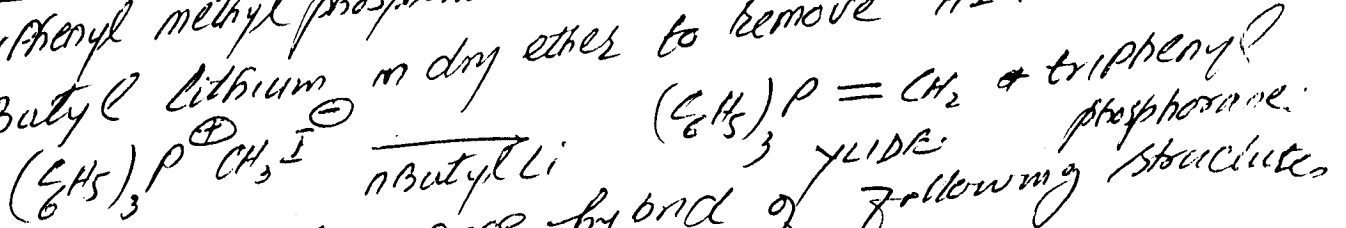
It involves formation of phosphonium ylide called Wittig Reagent. This ylide on treatment with Aldehyde or ketone produces alkene. The reaction involves following steps.

1) FORMATION OF tri HALIDE PHOSPHONIUM HALIDE
 triphenyl phosphine is mixed with p-alkyl halide to form triphenyl phosphonium halide

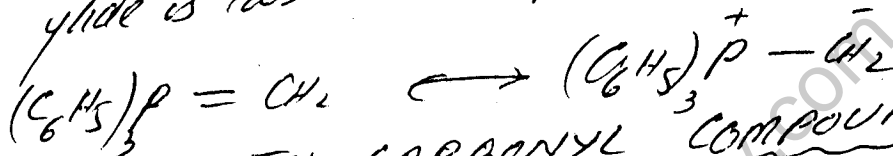


2) FORMATION OF YLIDE

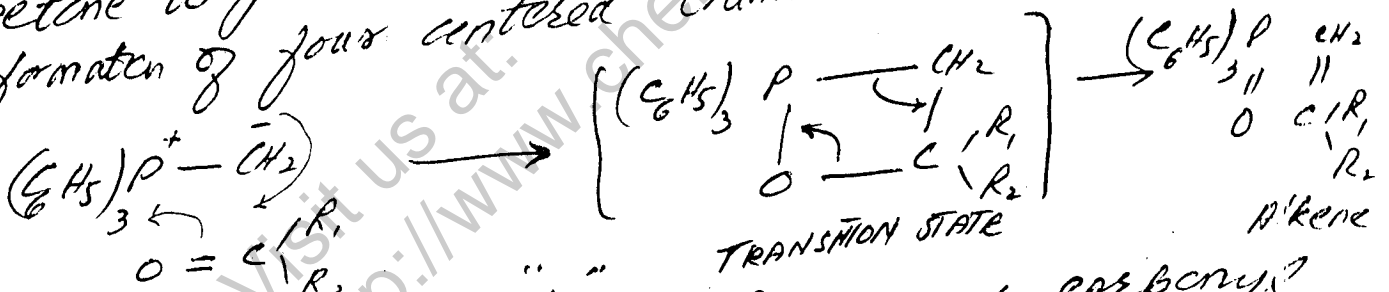
triphenyl methyl phosphonium iodide is treated with iodide n-butyl lithium in dry ether to remove HI.



This ylide is resonance hybrid of following structures

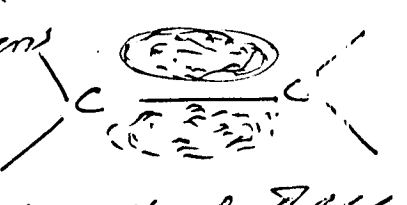


3) REACTION WITH CARBONYL COMPOUND
 The ylide is not isolated and it is treated with an aldehyde or ketone to give alkene. The reaction proceeds through formation of four centered transition state.

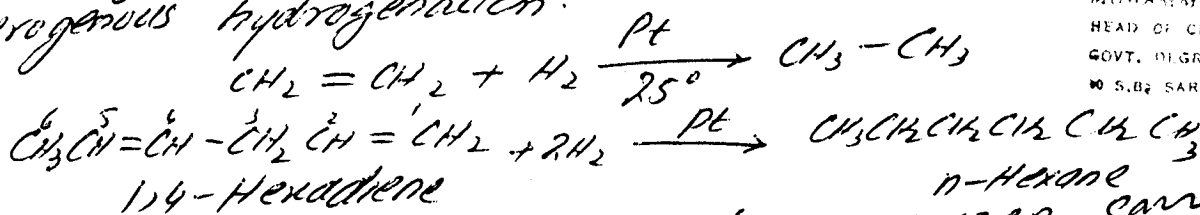


By suitable selection of p-alkyl halide and carbonyl compound different alkenes can be obtained.

REACTIONS OF ALKENES: - In Alkenes there is a sigma bond and a pi-bond present between double bonded carbons. pi-bonds is relatively weaker bond and lies above and below the plane of atoms. These pi-electrons are less involved in holding carbon atoms. Thus these electrons act as nucleophile and electrophile can easily attack these pi-electrons. Therefore alkenes can undergo electrophilic addition reactions. However alkenes can also undergo free radical addition reaction and also allylic substitution reactions.



HYDROGENATION / The addition of hydrogen to an unsaturated compound in presence of Ni, Pt or Pd to form a saturated compound is called hydrogenation. A solution of alkene is shaken under some pressure of H₂ gas in presence of catalyst. This is called heterogeneous hydrogenation.



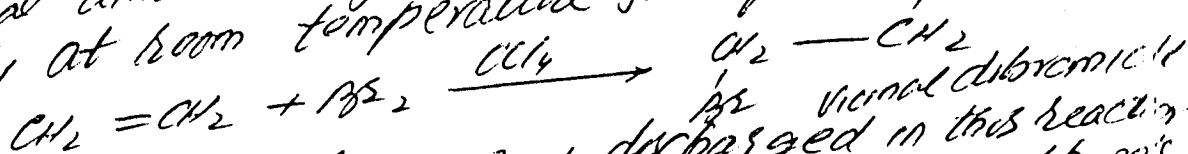
MURASIM
HEAD OF CHEMISTRY
GOVT. DEGREE COLLEGE
S.B. SARGODHA

The reaction is quantitative and volume of oxygen can be measured easily. Thus this reaction is used to determine number of double bonds in a compound. Hydrogenation reaction is used to convert vegetable oil to Banaspati Ghee.

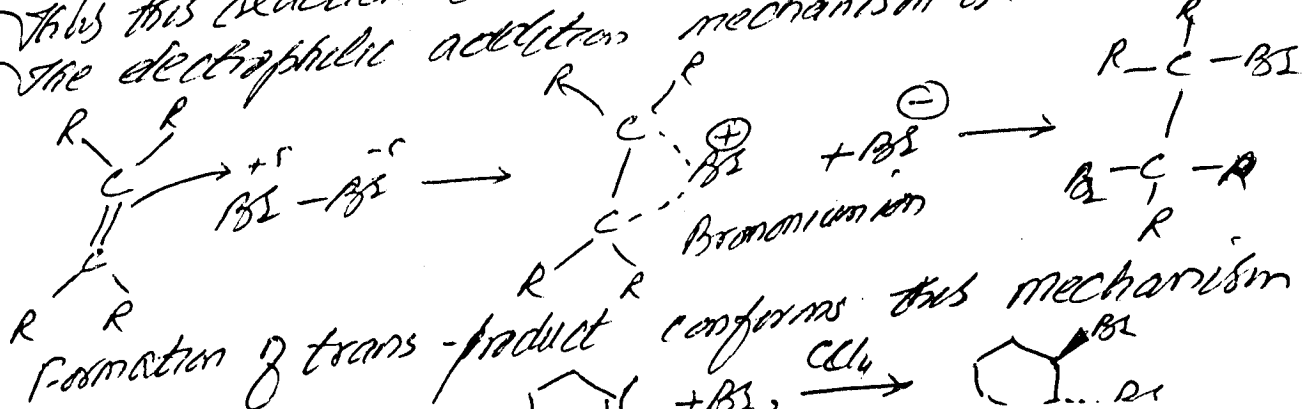
Hydrogenation is an exothermic reaction. The amount of heat evolved when 1 mole of unsaturated compound is converted into saturated compound is called heat of hydrogenation.

The heat of hydrogenation is almost 126 kJ per double bond. Heat of hydrogenation is used to calculate relative stabilities of organic compound. For example cis-2-pentene has heat of hydrogenation 120 kJ while trans isomer has 115 kJ/mole. It means trans isomer is 5 kJ/mole more stable than cis isomer. Similarly it can be shown that isobutylene is more stable than n-Butylene.

2 ADDITION OF HALOGENS / When alkene is treated with chlorine or bromine in presence of inert solvent like CCl₄ a vicinal dihalide is produced. The addition proceeds rapidly at room temperature. Iodine fails to react.



The yellow colour of bromine is discharged in this reaction. This reaction can be used to determine double bond. The electrophilic addition mechanism is shown below.

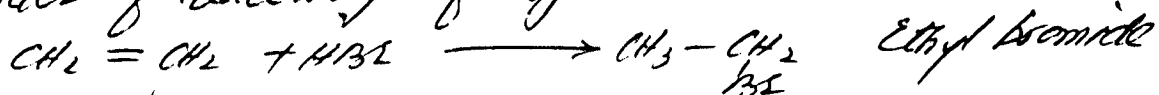


Formation of trans-product confirms this mechanism.

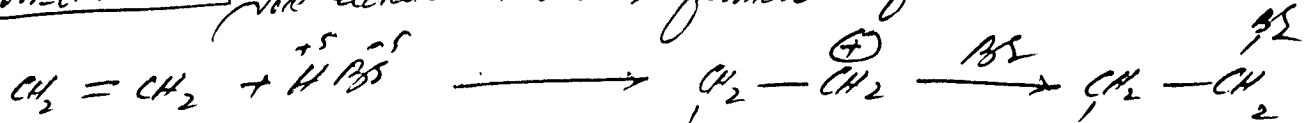
$$\text{Cyclohexene} + Br_2 \xrightarrow{CCl_4} \text{trans-1,2-dibromocyclohexane}$$

ADDITION OF HALOGEN ACIDS.

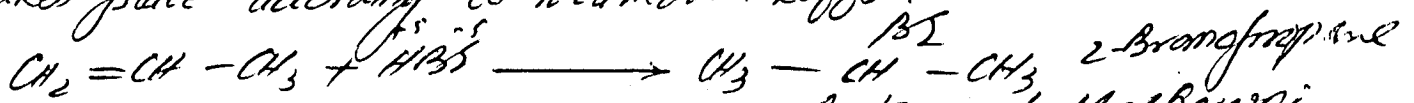
The addition of halogen acids to alkenes produces alkyl halide.
The order of reactivity of halogen acids is $\text{HI} > \text{HBr} > \text{HCl}$



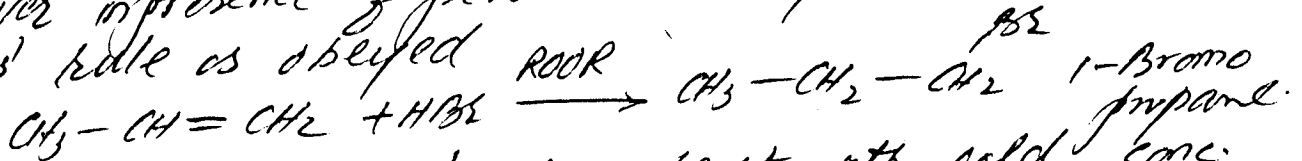
MECHANISM | The reaction involves formation of carbocation ion.



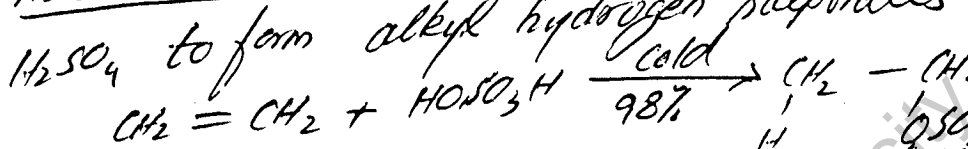
The addition of halogen acid to an unsymmetrical alkene takes place according to Markownikoff's rule.



However in presence of peroxide catalyst anti-Markownikoff's rule is obeyed



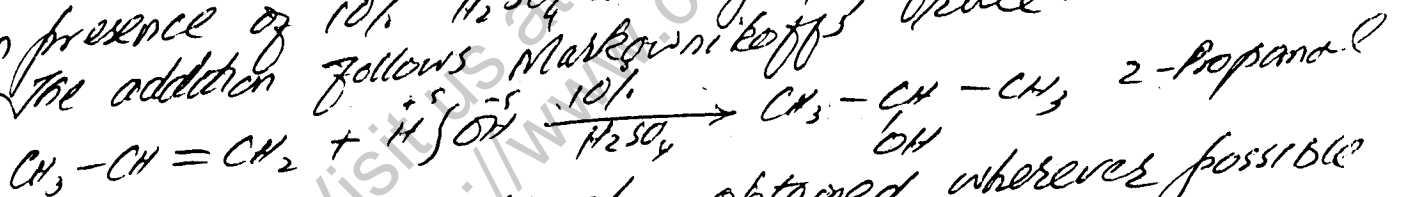
ADDITION OF H_2SO_4 | Alkenes react with cold conc. H_2SO_4 to form alkyl hydrogen sulphates.



For unsymmetrical alkenes Markownikoff's rule is obeyed

ADDITION OF WATER | Alkenes add a molecule of water in presence of 10% H_2SO_4 and HgSO_4 to form alcohols.

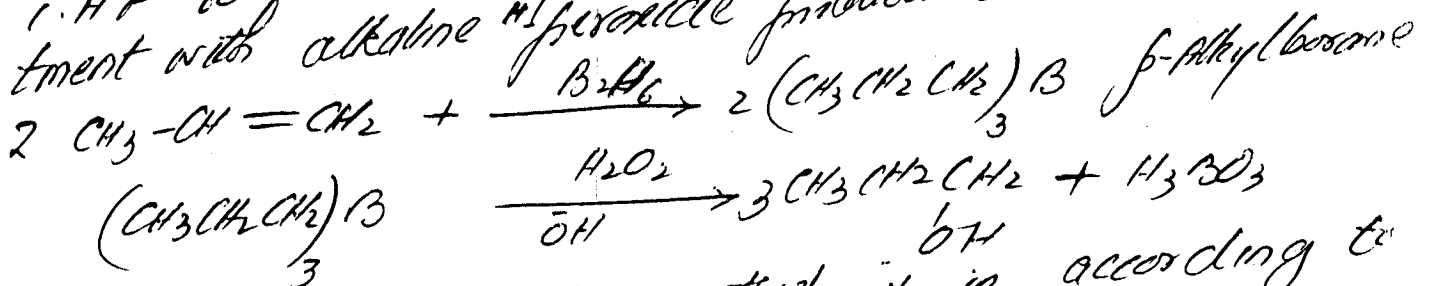
The addition follows Markownikoff's rule.



Rearranged products are also obtained wherever possible due to formation of intermediate carbocation ion.

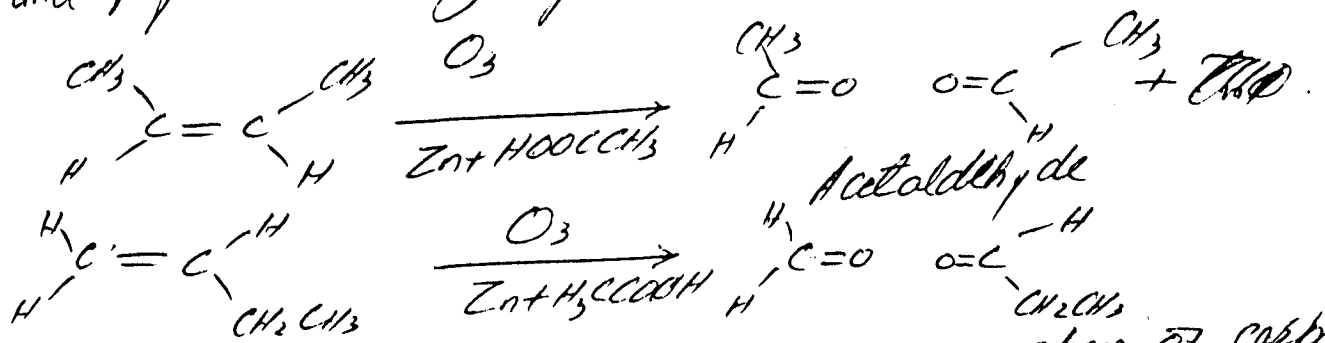
HYDROBORATION | Alkenes react with diborane or in T.H.F to form trialkyl boranes.

Trialkyl borane on treatment with alkaline H_2O_2 produces alk alcohol.

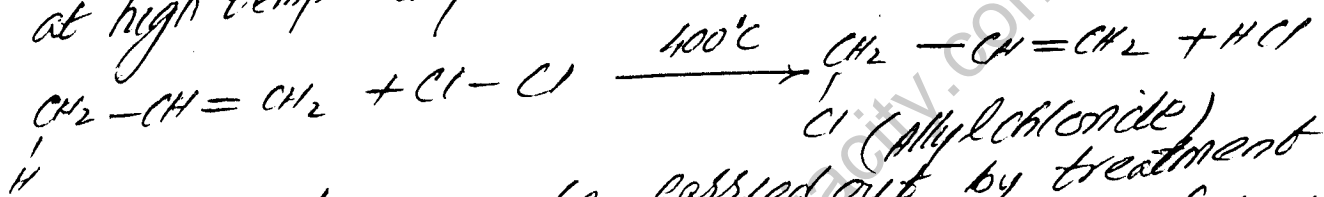


Alcohol produced by this method is in accordance to Anti-Markownikoff addition

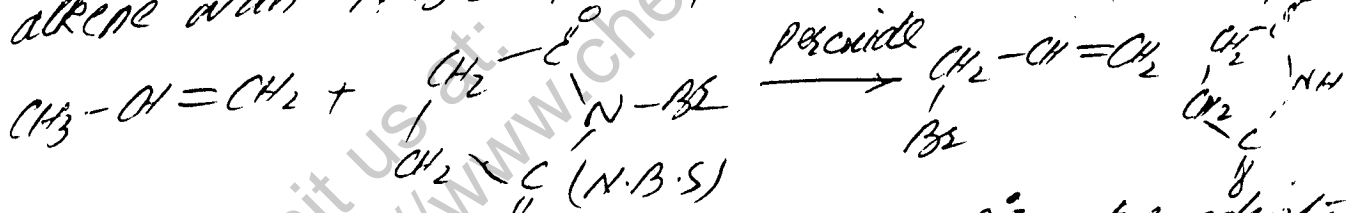
2-Butene will produce two molecules of acetaldehyde while 1-Butene will produce Formaldehyde and Propanal on ozonolysis



ALLYLIC SUBSTITUTION / The hydrogen atom of carbon adjacent to double bonded carbon is called allylic hydrogen. The replacement of this allylic hydrogen a substituent is called allylic substitution. For example when propene is treated with Cl_2 or Br_2 at high temp. allylic substitution occurs.

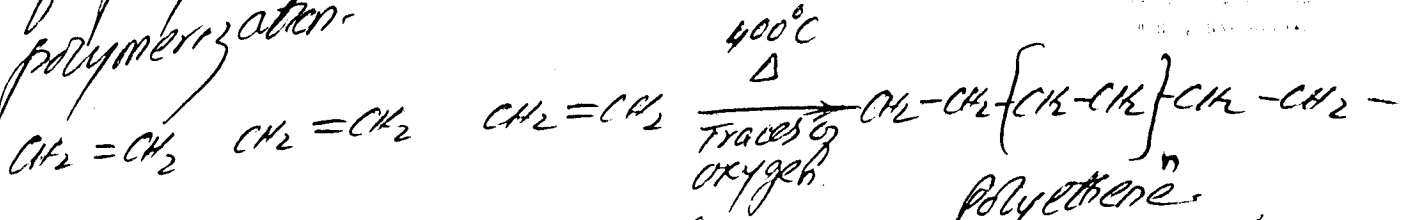


Allylic bromination can be carried out by treatment of alkene with N.B.S. in CCl_4 solvent and peroxide catalyst



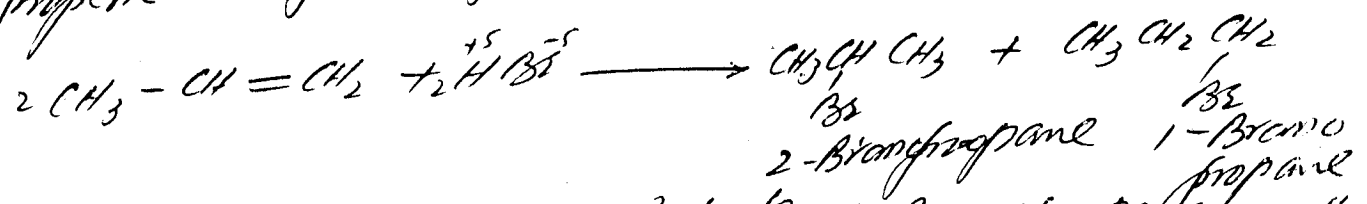
The reaction proceeds through formation of Br^\cdot intermediate

POLYMERIZATION / Alkenes under suitable conditions produce a large molecule of high molecular wt. This large molecule is called polymer. The repeating unit of polymer is called monomer. This process is called polymerization.



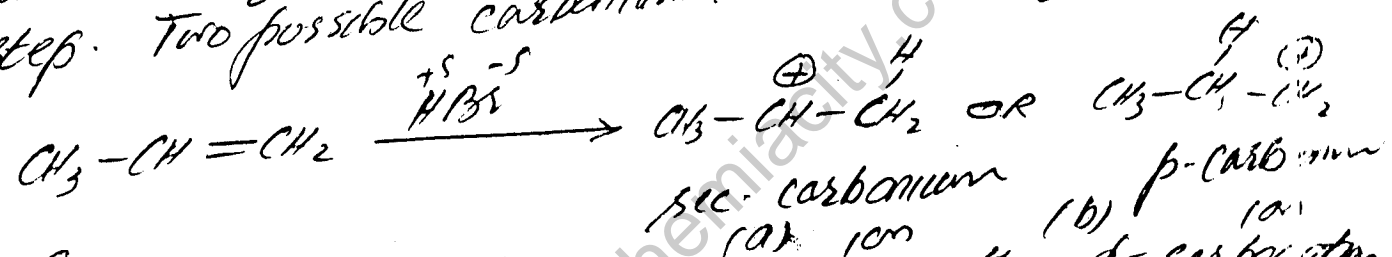
This is called addition polymerization. The most common polymers are polyethylene, polyvinyl chloride, polyvinyl cyanide, polyvinyl acetate etc.

Q.1 WHAT IS MARKOVNIKOFF'S RULE EXPLAIN?
 When an unsymmetrical reagent is added to an unsymmetrical alkene, the negative part of reagent will add to that carbon atom which has least number of hydrogen atoms. For example consider addition of HBr to propene. Two possible products are expected to form

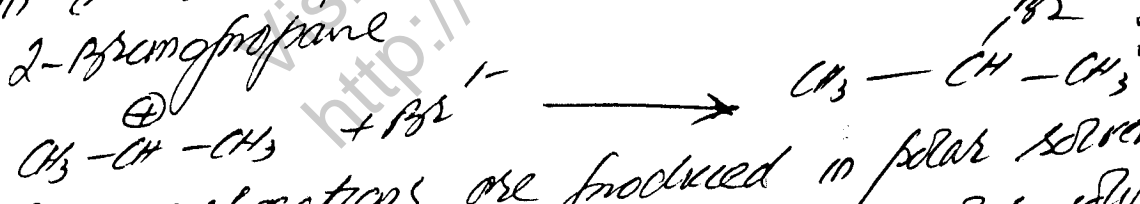


According to Markownikoff's rule 2-Bromopropane will be formed.

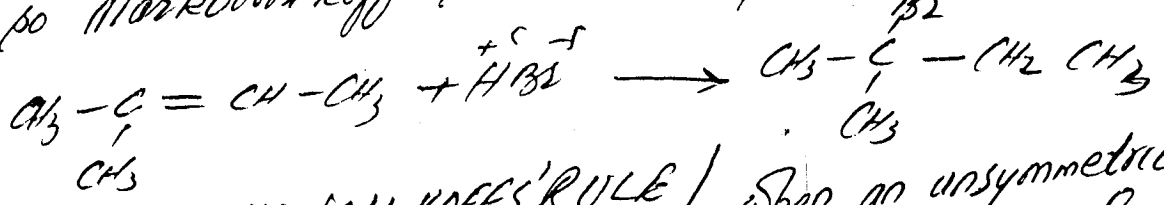
EXPLANATION The reaction proceeds through formation of carbonium ion. This electrophilic addition of HBr will proceed carbonium ion in first step. Two possible carbonium ions can be formed



Since sec. carbonium ion is more stable than p. carbonium ion so (a) will be formed in first step. In second step Br⁻ ion will attack (a) to form 2-Bromopropane



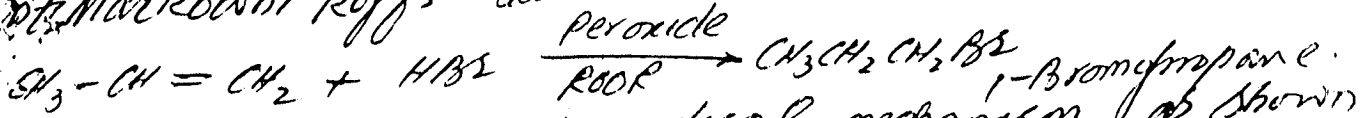
Since carbocations are produced in polar solvent only, so Markownikoff's rule is obeyed in polar solvent only.



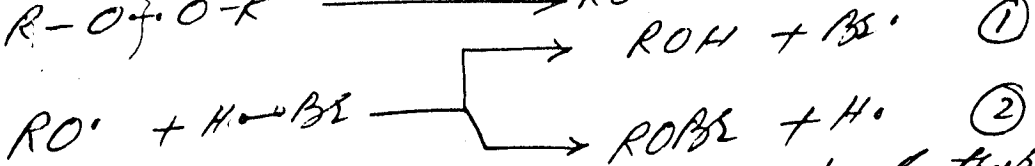
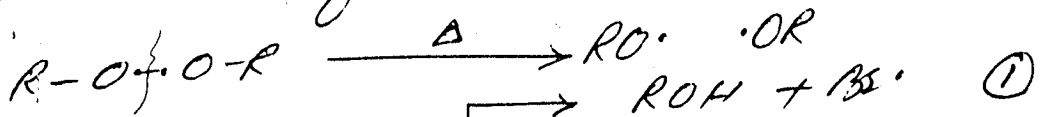
ANTI-MARKOVNIKOFF'S RULE When an unsymmetrical reagent (Halogen acid) is added to an unsymmetrical alkene in presence of an organic peroxide (ROOR), halogen will attach to that carbon atom which has maximum number of hydrogen atoms. This is just opposite to Markownikoff's rule. That is why it is called

MUHAMMAD ALI
 HEAD OF CHEMISTRY
 GOVT. DEGREE COLLEGE
 S.B. SARGODHA

Anti-Markovnikov's addition.

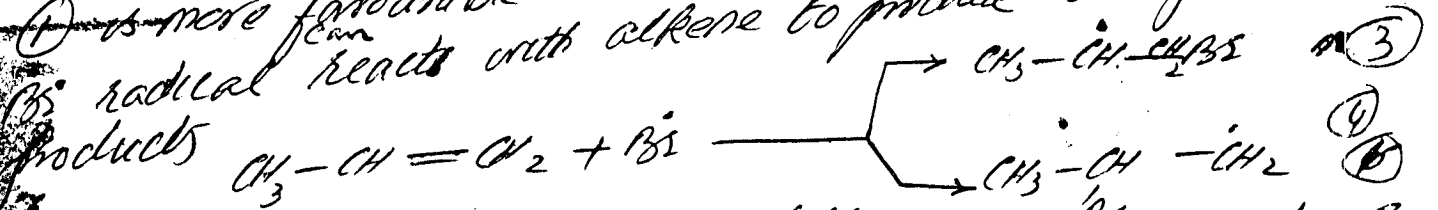


The reaction involves free radical mechanism as shown below.



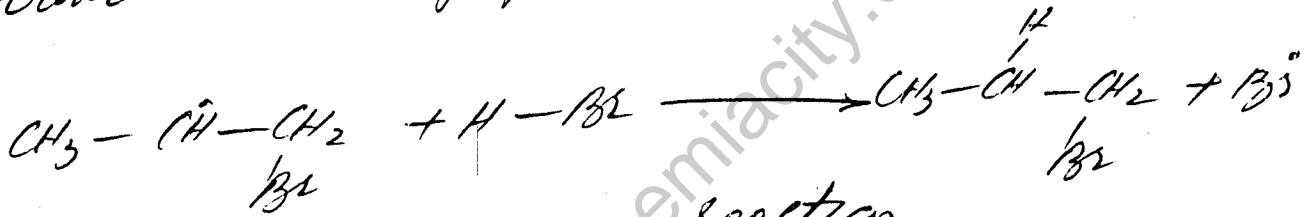
Since $\text{Br}\cdot$ is more stable than $\text{H}\cdot$ radical thus step (2) is more favourable.

$\text{Br}\cdot$ radical reacts with alkene to produce two possible products



Since sec. radical is more stable than $\text{Br}\cdot$ radical thus step (3) is favoured.

The sec. radical once again reacts with HBr to produce 1-Bromopropane and $\text{Br}\cdot$ radical again.



$\text{Br}\cdot$ radical continues this reaction.

COMPLETE FOLLOWING EQ. EXERCISE FOR STUDENTS
HELP YOURSELF

