CHEM 102 INNOTECH SHOP 4

Candidates' matriculation Number:.....

Page No:.....

Question Number:.....

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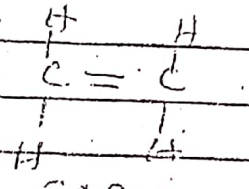
Saturated & Unsaturated

Do not write on either margin

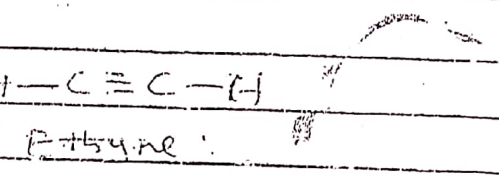
SATURATED AND UNSATURATED

Organic compounds are either described as saturated or unsaturated, depending upon whether the compound contain one or more double or triple covalent bonds among its bonds. Eg alkanes are saturated because they have single bond ⇒ CH_4, C_2H_6, C_3H_8 etc.

The alkene and alkynes are said to be unsaturated because the contain one or more multiple bond(s).



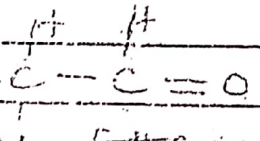
Ethene



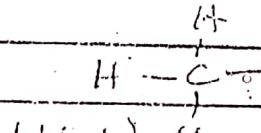
Ethyne

The carbon - carbon double or triple covalent bonds represents the functional groups in the series. $C=C$ or $C\equiv C$ functional group.

Compounds containing double or triple bonds between a carbon atom and an atom of another element can also be said to be unsaturated.



Ethanal (an aldehyde)



Ethanonitrile (a nitrile)

ALKANES = Paraffins

The alkanes (Paraffins) form a homologous series of saturated hydrocarbons and corresponded to a general formula C_nH_{2n+2}. Successive members of the series differ in composition by the increment $-CH_2-$.

Carbon atoms of alkanes = sp^3 hybridized.

The carbon atoms of the members are sp^3 hybridized. They are normally very stable compounds and are relatively unreactive in comparison with their unsaturated counterparts. Paraffin means little affinity.

Nomenclature

CH_4 H_3C-CH_3 or C_2H_6 $H_3C-CH_2-CH_2-CH_2-CH_3$

methane Ethane or C_5H_{12} or $CH_3(CH_2)_3$

Pentane

$CH_3-C(CH_3)_2-CH_3$

2,2-Dimethylpropane

Natural sources of alkane

The major sources of alkanes are natural gas and petroleum. Natural gas contain mainly methane (90%) with small amount of ethane, propane and butane.

Petroleum: Fractional distillation of crude petroleum yields several fractions in the neighbourhood of 150 different components. eg Methane etc.

The anaerobic (absence of air) decomposition of the large, complicated organic molecules of vegetable matter ultimately produces methane as an end-product.

Coal mines provide a natural source of methane where it is known as fire damp.

Natural sources of alkane

→ Natural gas (90% CH_4 & little C_2H_6, C_3H_8 & C_4H_{10})

→ petroleum

Fractional distillation yields about 150 compounds

→ Anaerobic decomposition of large complicated organic molecules of vegetable matter yields CH_4

→ Coal mines provide natural source of CH_4.

It is known as coal damp

Question Number:.....

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Chemical Properties of Methane

Unreactivity towards inorganic reagents: Methane does not react with acids, alkali or oxidizing agents in solution

Oxidation: It burns in air with a hot, non-luminous flame to form carbon(IV) oxide and water

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$$

Halogenation

A mixture of methane and chlorine does not react in the dark, but forms a mixture of halogenated products when heated or exposed to ultraviolet (UV) light. Such light catalysed reactions are called photochemical reactions

Mechanism of halogenation

Mech: $Cl_2 \xrightarrow{UV\ light} Cl^\bullet + Cl^\bullet$

$Cl_2 \xrightarrow{UV} Cl^\bullet + Cl^\bullet$ ... Initiation ... (i)

$CH_4 + Cl^\bullet \longrightarrow {}^\bullet CH_3 + HCl$ ... (2)

$CH_3^\bullet + Cl_2 \longrightarrow CH_3Cl + Cl^\bullet$ ... (3)

$CH_3Cl + Cl^\bullet \longrightarrow {}^\bullet CH_2Cl + HCl$ ... (4)

$^\bullet CH_2Cl + Cl_2 \longrightarrow CH_2Cl_2 + Cl^\bullet$ ... (5)

$CH_2Cl_2 + Cl^\bullet \longrightarrow {}^\bullet CHCl_2 + HCl$ ... (6)

$^\bullet CHCl_2 + Cl_2 \longrightarrow CHCl_3 + Cl^\bullet$ ... (7)

$CHCl_3 + Cl^\bullet \longrightarrow {}^\bullet CCl_3 + HCl$ ... (8)

$^\bullet CCl_3 + Cl_2 \longrightarrow CCl_4 + Cl^\bullet$ ... (9)

Propagation

Carbon tetrachloride

$Cl^\bullet + Cl^\bullet \longrightarrow Cl_2$

$CH_3^\bullet + {}^\bullet CH_3 \longrightarrow CH_3-CH_3$

$Cl^\bullet + {}^\bullet CH_3 \longrightarrow CH_3Cl$

... (10) Termination

Chemical properties of CH_4:

(1) Unreactivity towards inorganic reagents.

CH_4 does not react with acids, bases, oxidizing agents in solution

(2) CH_4 burns in air with a hot, non-luminous flame to form CO_2 & H_2O

$C_xH_y + \frac{y}{4}O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$

$CH_4 + 2O_2 \longrightarrow CO_2 + H_2O$

(3) Halogenation.

CH_4 and Cl_2 don't react in the dark

→ forms mixture of halogenated pdts when heated or exposed to UV light

→ Light catalysed rxns = photochemical rxns

Alkenes (Olefins)

The alkenes (olefins) form a homologous series of unsaturated hydrocarbon containing carbon – carbon double bond and corresponding to a general formula C_nH_{2n}. Like the alkanes successive members of the series differ in composition by the increment $-CH_2-$. (SP^2 hybridized)

Nomenclature.

The compounds are named as for the alkanes, but with the suffix -ene. The chain is numbered from the end nearer to the double bond.

$CH_3CH_2CH=CH_2$ — But-1-ene

$CH_3CH=CHCH_2CH_3$ — Pent-2-ene

$CH_3-CH(CH_3)-CH=CH-CH_2-CH_3$ — 3-Methylhex-3-ene

$CH_3CH_2CH(C_6H_5)-CH=CH_2$ — 3-Phenylpent-1-ene

$CH_3CH=CHCH_3 \Rightarrow$ But-2-ene

Natural Sources of Alkene

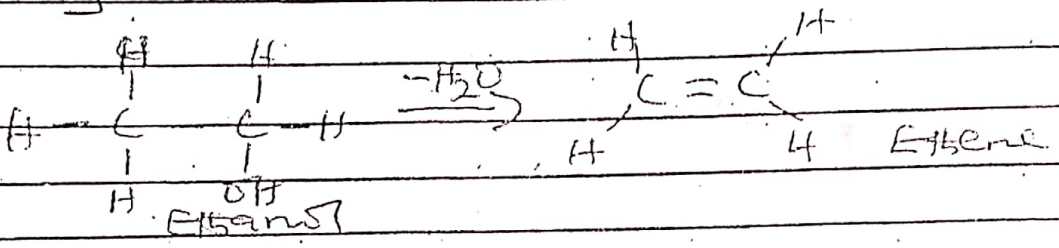
The commercial source of alkene is natural gas or naphtha fraction from the distillation of petroleum. Alkenes can be cracked either thermally or catalytically to obtain alkenes.

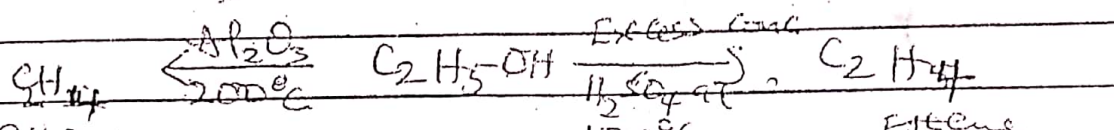
→ Alkenes are also known as olefins.
→ Homologous series of Unsaturated HC with C=C
→ CnH2n (General formula).
→ Named with the suffix -ene.

Natural sources of olefins
→ Commercial source of alkene = Natural gas or
→ Naphtha fraction of fractional distillation of Petroleum.
Types of cracking
→ Thermal cracking → Catalytic cracking

Synthesis of Alkenes

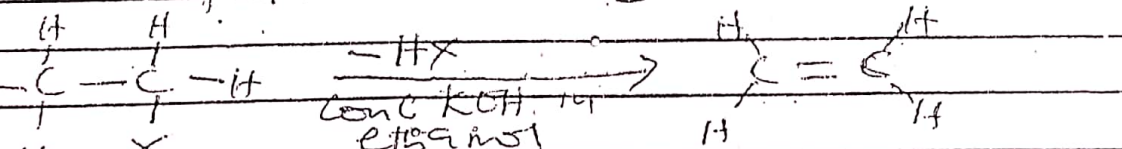
1) Dehydration of an alcohol: Alcohols with $-OH$ and $-H$ groups on adjacent carbon atoms can be dehydrated to alkenes





b) Dehydrohalogenation of halogenoalkanes

The hydrogen halide HX can be removed from halogenoalkane molecule by refluxing with a conc. solution of potassium hydroxide in ethanol.



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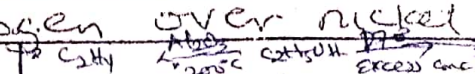
CHEMICAL PROPERTIES.

1) ADDITION REACTIONS

Ethene and all other alkenes are characterised by their addition reactions in which the double bond is converted into a single bond and atoms or groups are added to each of the two carbon atoms

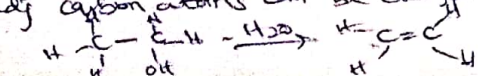
a) With Hydrogen.

Ethene reacts with hydrogen over nickel catalyst at 150°C to form ethane.



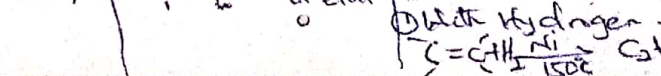
Synthesis of Ethene

1) Dehydration of an alcohol: Alcohols with $-H$ & $-OH$ groups on adj carbon atoms can be dehydrated.



2) Dehydrohalogenation of Halogenoalkane.
Remove hydrogen halide (HX) by refluxing with Conc KOH in EtOH.

Chem Pplus
Addition rxn. to convert C=C to C-C
1) With Hydrogen.



$CH_2=CH_2 + H_2 \xrightarrow[150°C]{Ni \text{ as catalyst}} CH_3-CH_3$

Finely divided platinum or palladium are more active catalysts and the reaction takes place at room temperature.

2) With Halogens

Ethene reacts with Chlorine to form 1,2-dibromoethane or 1,2-dichloroethane

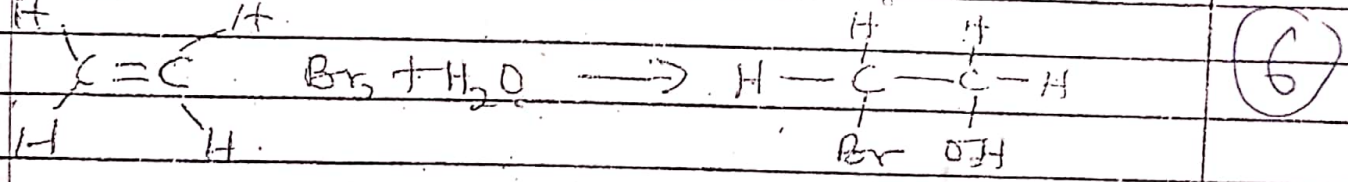
$CH_2=CH_2 \longrightarrow ClCH_2-CH_2Cl$

Flourine tends to react explosively and the reaction with Iodine is very slow.

The decolorisation of a solution of bromine in tetrachloromethane serves as a good test for the presence of C=C (double) bonds, and the amount of bromine used up measures the number of such bonds in a molecule.

3) With bromine or Chlorine water

Ethene reacts on bubbling through bromine or chlorine water at room temperature to form, mainly bromo- or chloroethanols.



2-Bromoethanol

The product is colourless, therefore the reaction with bromine or chlorine water can be used as a test for C=C bonds.

4) With Hydrogen Halides

Hydrogen halides (HBr, HCl, HF, HI) add on to ethene to form halogenoethanes.

(6)

Addition reaction with Halogens:

Ethene + Cl_2 = 1,2-dichloroethane
+ Br_2 = 1,2-dibromoethane

$CH_2=CH_2 + Cl_2 \longrightarrow CH_2Cl-CH_2Cl$

$CH_2=CH_2 + Br_2 \longrightarrow BrCH_2-CH_2Br$

→ Reaction with F_2 is too explosive
→ Reaction with I_2 is too slow

Test for olefins

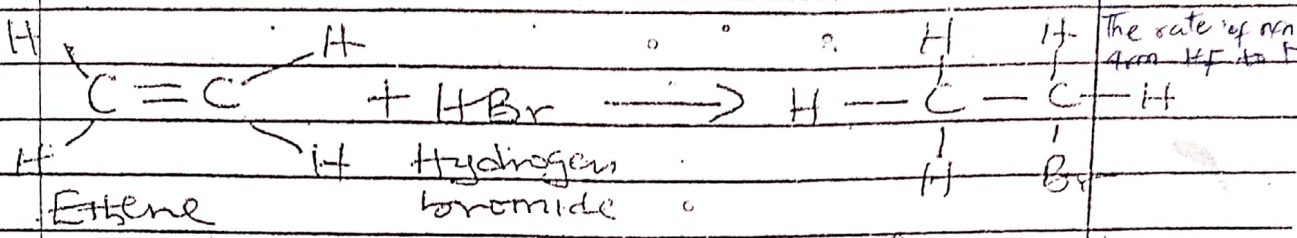
(A) Decolourization of Bromine in CCl_4 soln. Amt of Br used up, signifies no of such bonds in a molecule.

(B) With Bromine or Chlorine H_2O

$C_2H_4 + Br_2 + H_2O \xrightarrow{\text{room temp}}$ bromo or chloroethanol (colourless solution).

Markownikoff rule states that the negative part of the addendum adds to the carbon atom that is join to the least number of hydrogen atoms

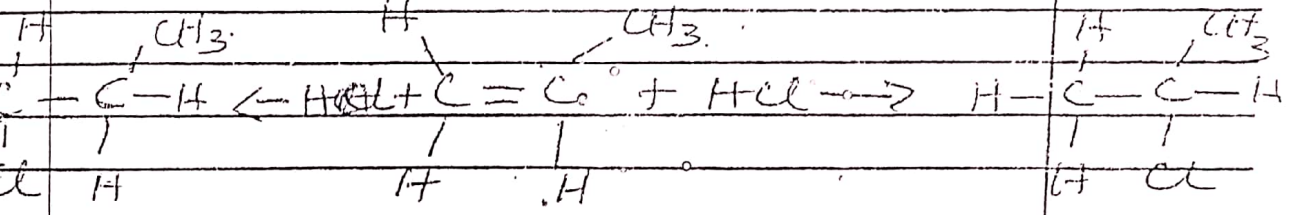
3) With Halogen Halides
$C_2H_4 + HX \rightarrow$ alkylhalogenether



The rate of rxn increase from HF to HI.

The rate of reaction increases in passing from HF to HI (in order of increasing acid strength) and the rate is only satisfactory for HBr and HI.

MARKOWNIKOV'S RULE :- Addition of hydrogen halide e.g HCl to an unsymmetrical alkene such as propene could yield two possible products



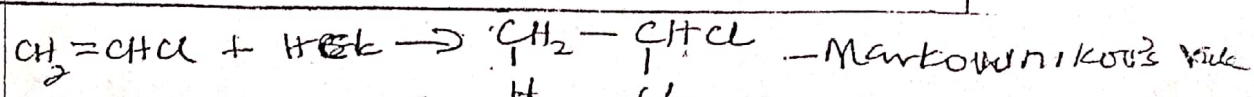
1-Chloropropane Propene 2-Chloropropane

Under normal conditions 2-Chloropropane is the major product in obeyance to the Markownikoff's rule, which states that in the addition of HX (HCl, HBr) to a C=C, double bond in an unsymmetrical alkene, the H atom attaches itself to the carbon atom linked to the largest number of hydrogen atoms

Markownikoff's rule states that in addition of HX to a C=C in an unsymmetrical alkene, the H-atom attaches itself to a C-atom linked to the largest no of hydrogen atoms

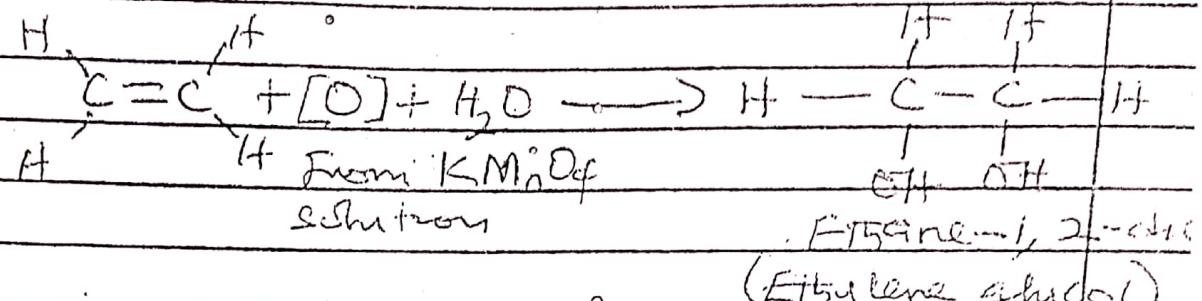
POLYMERISATION → Ethene polymerizes to form Polythene

Ethene polymerises by adding unto itself to form addition polymer (polythene) which finds wide application in usage



(6) Addition of Hydroxyl groups

This is known as Hydroxylation, It is done using dilute aqueous solution of potassium manganate (VII) adds two hydroxyl groups onto ethene

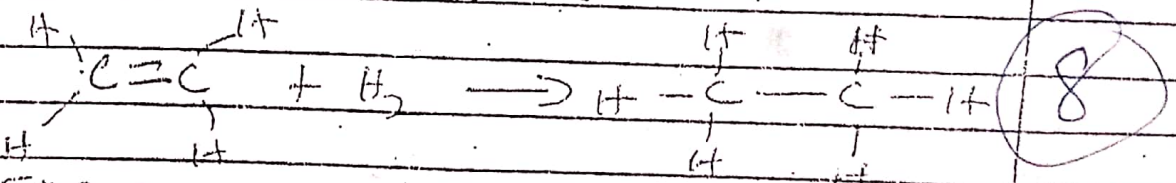


This is another test for the C=C bond as the manganate (VII) solution is decolourised if it is acidified. A very dilute manganate (VII) solution at a low temperature is necessary to avoid oxidation of the diol.

Hydrogen peroxide (H_2O_2) in the presence of a little osmium tetroxide (O_2O_4) can be used instead of potassium manganate (VII)

(7) Hydrogenation

A mixture of ethene and hydrogen passed over platinum black or palladium without heating or over finely divide nickel at 140°C, produces ethane



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The number of C=C bond present in a molecule can be determined by the amount of hydrogen used up. Catalytic hydrogenation is important industrially for it

(6) Hydroxylation rxn.
Ethene + 1% KMnO4 + H2O adds 2 OH groups to ethene
C=C + [O] + H2O → C(OH)–C(OH) (ethane-1,2-diol)
It is also a test for C=C as the KMnO4 soln is decolorized if it is acidified.

H2O2 in the presence of Osmium tetroxide (O2O4) can be used in place of KMnO4

(7) Hydrogenation:
C=C + H2 —Pt black/Palladium→ C–C or
C=C + H2 —Ni, 140°C→ C–C

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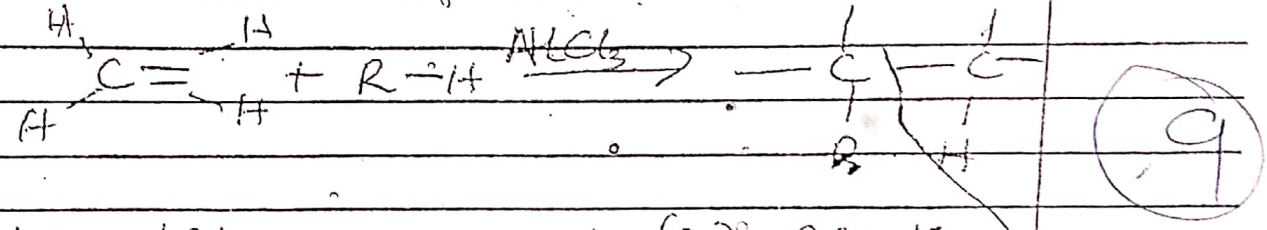
Question No. ...

Catalytic hydrogenation is impt industrially to enable a mixture of inedible unsaturated oils to be converted into saturated edible fats is margarine is prduced by mixing fish oils and H_2 with milk and vitamins

enable a mixture of inedible unsaturated oils to be converted into saturated, edible fats. For example margarine is made by mixing fats and oils and hydrogenated oils with milk and vitamins.

(8) ALKYLATION

An alkyl group R from a saturated hydrocarbon R—H, can be added onto an alkene in the presence of Lewis acid as a catalyst.



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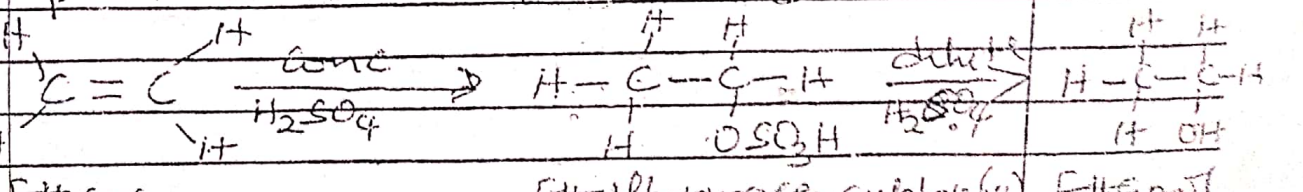
(9) With tetraoxosulphate (VI) acid

This is also known as the hydration of ethene. Concentrated tetraoxosulphate (VI) acid reacts with ethene to form ethylhydrogen sulphate (VI). The reaction takes place at room temperature and can be used to remove alkenes from gas mixtures. The ethylhydrogensulphate (VI) is an oily liquid which is hydrolysed on warming with dilute acids to give ethanol.

The hydration can also be brought about directly by passing ethene and steam over a phosphoric (V) acid catalyst at 300°C and 70 atmospheres. The reaction provides an important method for making ethanol.



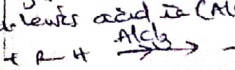
Ethene — Ethylhydrogensulphate (VI) — Ethanol

(9) With H_2SO_4 / Hydration of Ethene

$C_2H_4 + Conc\ H_2SO_4 \rightarrow$ Ethoxyhydrogen sulphate (VI)

8. Alkylation

An alkyl grp R can be added to C=C in the presence of a lewis acid ie ($AlCl_3$) as a catalyst



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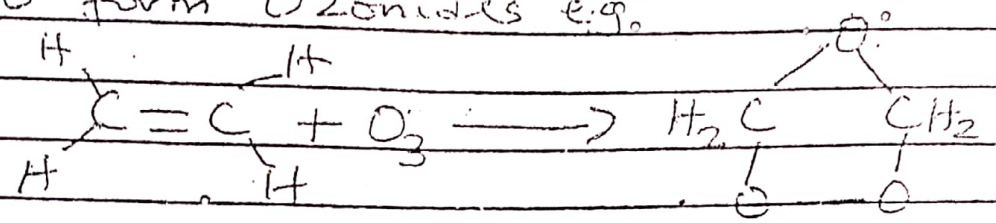
(10) Ozonolysis

When alkenes are dissolved in organic solvents, they can react with Ozone (O_3) to form Ozonides e.g.



Ethene Ozonide

Ozonides are unstable and may explode hence a low temperature is required for Ozonolysis. The peroxide bond is unstable, hence compounds containing it are now generally isolated.

Ethene Ozonide is readily hydrolysed with water to a mixture of methanal and hydrogen peroxide, half of methanal is then oxidized to methanoic acid by the hydrogen peroxide.

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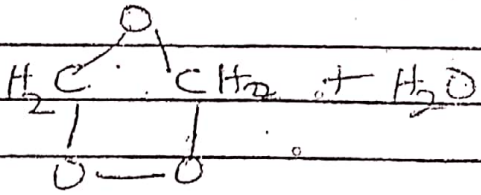


Methanal

$$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O$$

Methanoic acid

(11) With Oxygen

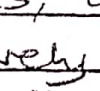
Alkenes, like other hydrocarbons burn explosively in air or oxygen

$$2C_nH_{2n} + 3nO_2 \longrightarrow 2nCO_2 + 2nH_2O$$

In the presence of silver as catalyst, ethene undergoes oxidation with oxygen to form epoxyethane (ethene oxide).

10. Ozonolysis

When you dissolve alkenes in org solvents, they can react with ozone (O_3) to form ozonides

$C_2H_4 + O_3 + O_3 \longrightarrow$  10

Ethene ozonide

Ethene ozonide is hydrolysed with H_2O to form a mixture of methanal & H_2O_2

Ethene ozonide $+ H_2O_2 \rightarrow 2HCHO + H_2O_2$

½ of methanal is then oxidised to methanoic acid by the H_2O_2

$HCHO + H_2O_2 \longrightarrow HCOOH + H_2O$

(11) Rxn with O_2

They burn explosively in air H_2O. $2nC_nH_{2n} + 3nO_2 \rightarrow 2nCO_2 + 2nH_2O$

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Epoxyethane is readily converted into ethan-1,2-diol by heating with water at 200°C under pressure.

$2CH_2 = CH_2 + O_2 \xrightarrow[300°C]{Ag\ cat} 2H_2C - CH_2 \xrightarrow[200°C]{H_2O}$

Epoxyethane

$2H_2C - CH_2$

HO OH

Ethan-1,2-diol.

Dienes

When two C=C bonds are present in a given hydrocarbon, such a hydrocarbon is known generally as a diene. The position of the bonds being differentiated by number. E.g

$CH_2 = CH = CH_2$ Propadiene

$CH_2 = CH - CH = CH_2$ Buta-1,3-diene

$CH_2 = CH - CH_2 - CH = CH_2$ Pent-1,4-diene

Cycloalkenes

Cycloalkenes are cyclic hydrocarbon which contains one or more double bonds. E.g

Cyclohexene

Cyclohexene

Diels-Alder Reaction

It is also called cyclo addition reactions because ring systems are formed without elimination of any compound. It involves the reaction of a diene (i.e a molecule with two

In the presence of a Silver Catalyst, Ethene undergoes oxidation with O_2 to form epoxyethane (ethene oxide)

$2CH_2 = CH_2 + O_2 \xrightarrow[200°C]{Ag\ cat} 2H_2C - CH_2$

$2H_2C - CH_2 \xleftarrow[200°C]{H_2O}$ O

OH OH

Dienes

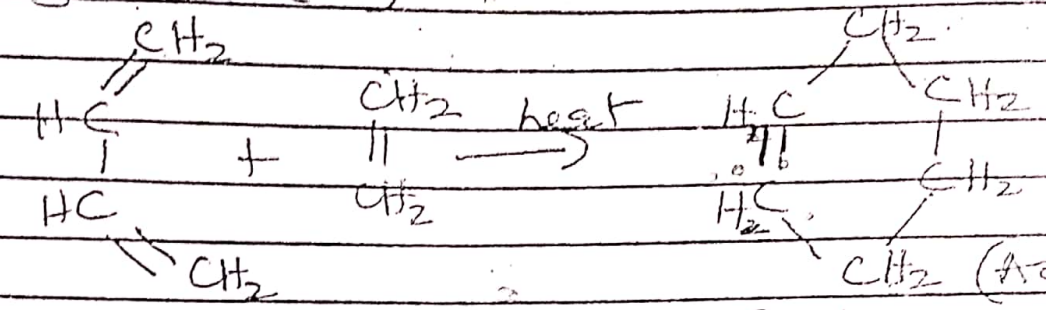
When 1,2 C=C are present in a HC, it is a diene.

Cyclo Alkenes.

Are acyclic HC which contain 1 or more C=C bond

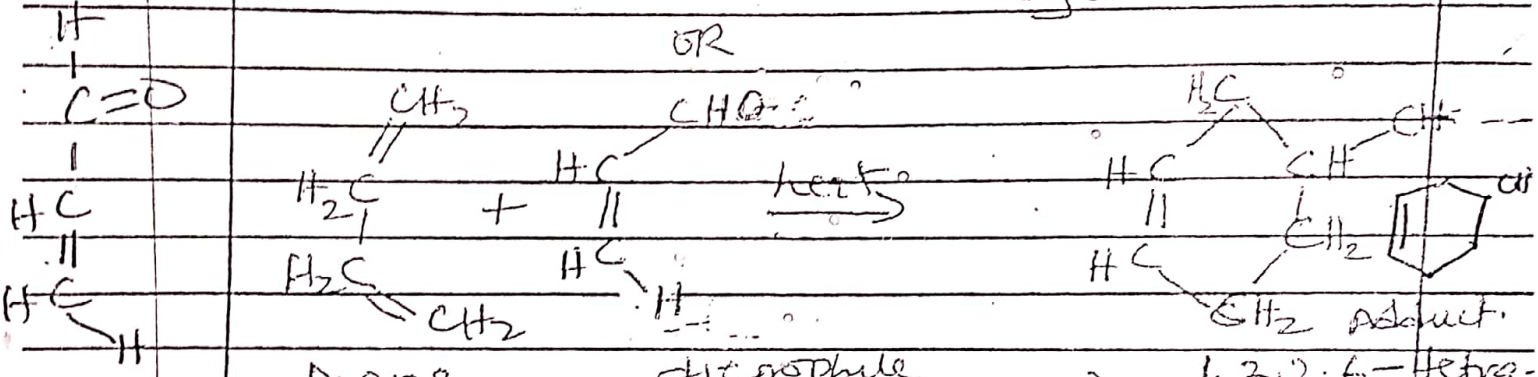
Cyclohexene.

double bonds) with a dienophile (a molecule highly reactive with a diene, e.g alkene.)



Cyclohexane

OR



Diene
1, 3 - Butadiene

dienophile
(Acrylic aminoacids)

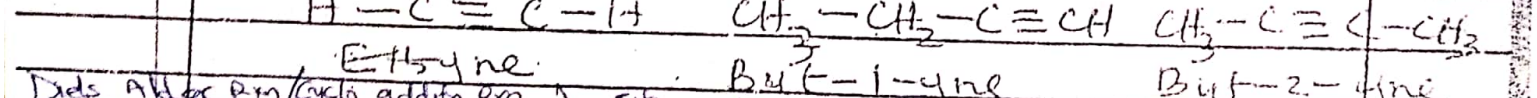
1, 2, 3, 6 - Tetrahydrobenzaldehyde

Alkynes

Alkyne are unsaturated hydrocarbons that contain the carbon-carbon triple bond (C≡C) and have its general formula C_nH_{2n-2}

Nomenclature

The compounds are named as for the alkanes with the same number of carbon atoms but replacing the suffix -ane with -yne.

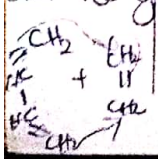


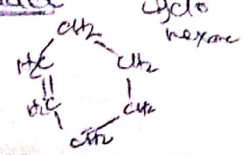
Ethyne

But-1-yne

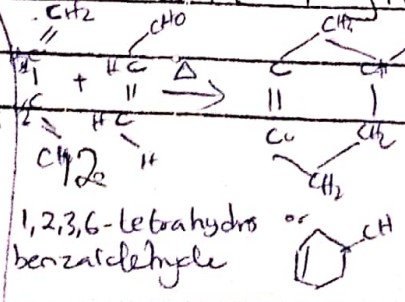
But-2-yne

Diels Alder Rxn/Cyclo addits Rxn
Prob btw a diene and a dienophile
diene: molecule with 2 C=C bond.
dienophile: molecule highly reactive with a diene to give Adduct





Cyclo hexane



1,2,3,6-tetrahydro benzaldehyde

Alkynes
Contain C≡C bond
General formula = C_nH_{2n-2}
Nomenclature
Have suffix -yne

Question No.

Chemical properties

With halogen halides

Ethyne reacts with halogen acids. Eg:

$$CH\equiv CH \xrightarrow[Hg\,Cl\ cat.]{HCl} CH_2=CHCl \xrightarrow{HCl} CH_3-CHCl_2$$

Ethyne — 200°C — Chloroethene (Vinylchloride) — 1,1-dichloroethane

The vinyl chloride is used for making (PVC).

Markownikov's rule takes effect in the second stage of the addition process.

With metals

Ethyne differs from ethene in forming salts with several metals; for example, if ethyne is passed through an ammoniacal solution of copper (I) chloride, a red precipitate of copper (I) dicarbide is formed

$$CH\equiv CH + Cu_2Cl_2 + 2NH_4 \longrightarrow \underset{\text{copper(I) dicarbide}}{Cu\,C\equiv C\,Cu} + 2NH_4Cl$$

Or if ethyne is passed through an ammoniacal solution of silver(I) trioxonitrate(V) solution of silver nitrate, a white precipitate of silver dicarbide Ag_2C_2 is produced.

$$RC\equiv CH + AgNO_3 \xrightarrow{NH_3\ soln} \underset{\text{greyish white ppt}}{Ag\,C\equiv C\,Ag} + HNO_3$$

This formation serves as a useful test for ethyne or for other alkynes with a terminal $C\equiv C$ bond.

$$HC\equiv CH + AgNO_3 \xrightarrow{NH_3\ soln} Ag-C\equiv C-Ag + HNO_3$$

This reaction is a precursor to terminal alkynes