I B. pharmacy (II sem)
BP 202T. Pharm. organic chemistry-I
(Theory) DR. T. SIVAKKUMAR

UNIT- II :- Alkenes

Functional group of alkenes is C=C. They are unsaturated hydrocarbons.

sp^2 Hybridization in alkenes

The carbon-hydrogen bonds of ethylene are sigma bonds, formed by overlap of sp^2 orbitals of carbon, instead of sp^3 orbitals as in ethane.

Nomenclature of alkenes:-

common names are used for three simple alkenes: ethylene, propylene and Isobutylene.

The rules of IUPAC system are

1. Select as the parent structure the longest continuous chain that contains the carbon-carbon double bond. Each name is derived by changing the ending -ane of the corresponding alkane name to -ene.

$H_2C=CH_2$ Ethene.

$CH_3-CH=CH_2$ propene.

$H_3C-CH_2-CH=CH_2$ 1-Butene.

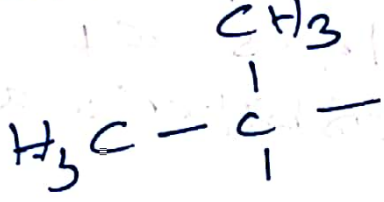
2)

2, Indicate by a number of the double bond in the Parent chain.

$H_3C - CH_2 - CH = CH_2$ (1-Butene)

$CH_3 CH = CH CH_3$ (2-Butene (Cis- or trans))

3) Indicate by numbers the position of alkyl groups attached to parent chain.



3,3-Dimethyl-1-butene.

Physical Properties

They are Insoluble in water. Soluble in non-polar solvents like benzene, ether, chloroform or ligroin. Less dense than water. Boiling point rises with increasing carbon number. Alkenes are weakly polar.

Industrial source:-

Petroleum and natural gas are the chief primary source.

(3) Preparation of alkenes.

Alkenes upto four carbon atoms can be obtained from Petroleum Industry in pure form.

1. Dehydrohalogenation of alkyl halides.

General

$$-\overset{|}{C}-\overset{|}{C}- + KOH \xrightarrow{\text{alcohol}} -C=C- + KX + H_2O$$

H, X

Specific example :-

$$H_3C-CH_2-CH_2-Cl \xrightarrow{KOH(alc)} CH_3-CH_2-CH=CH_2$$

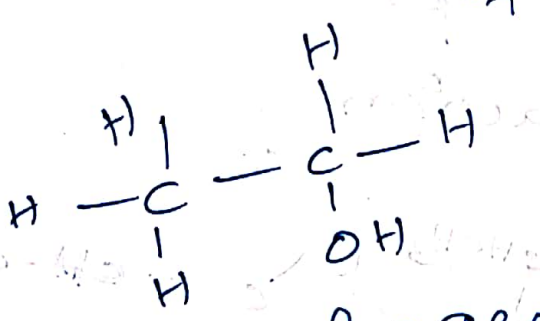
(1-Butene)

2. Dehydration of alcohols

$$-\overset{|}{C}-\overset{|}{C}- \xrightarrow{acid} -C=C- + H_2O$$

H, OH

Ease of dehydration of alcohols $3^0 > 2^0 > 1^0$



$$\xrightarrow{acid} H-C=C-H + H_2O.$$

(3) Dehalogenation of vicinal dihalides

$$-\overset{|}{C}-\overset{|}{C}- + Zn \longrightarrow -C=C- + ZnX_2$$

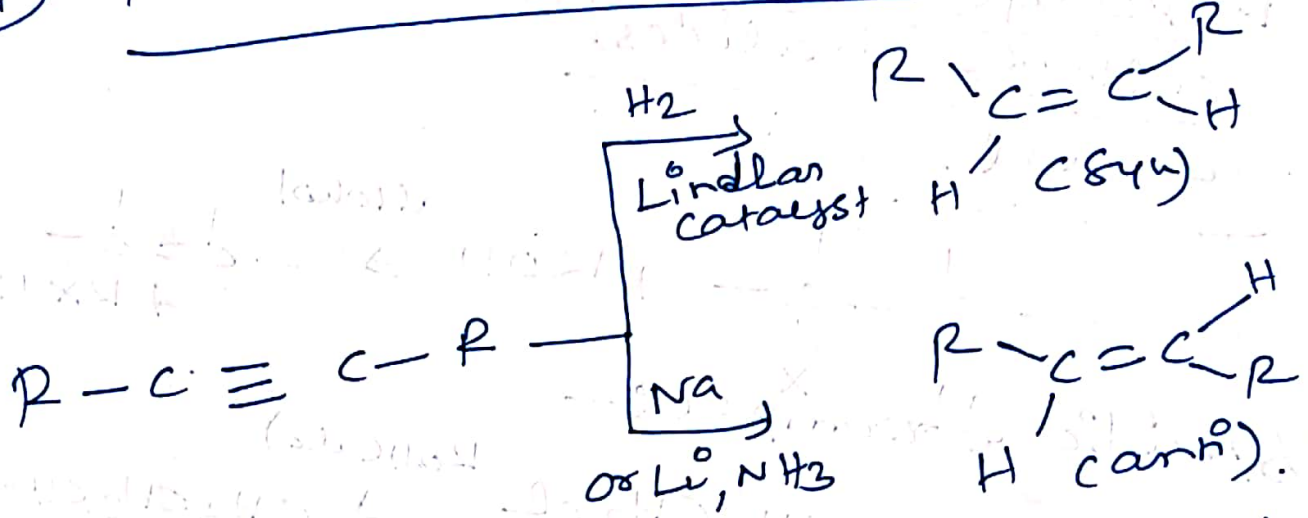
X, X

(4)

$CH_3CHBrCHBrCH_3 \xrightarrow{Zn} CH_3CH=CHCH_3$

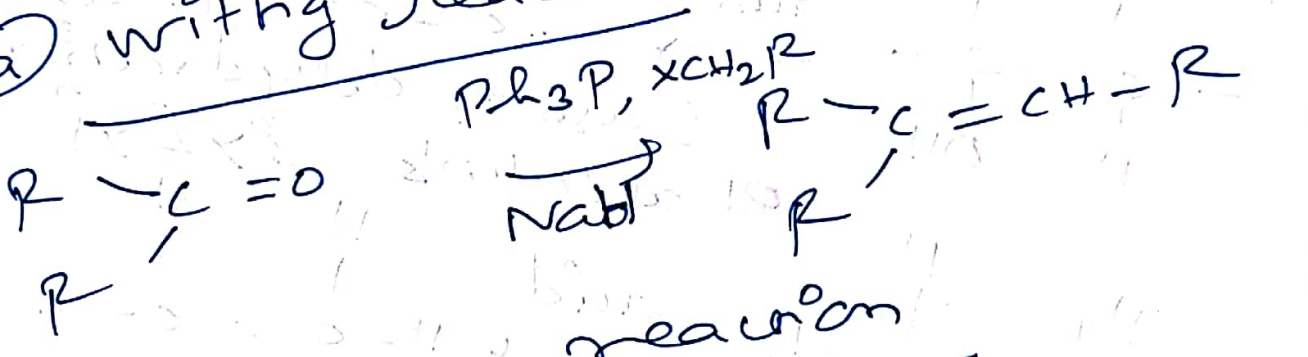
2 Butene.

(4) Reduction of alkynes

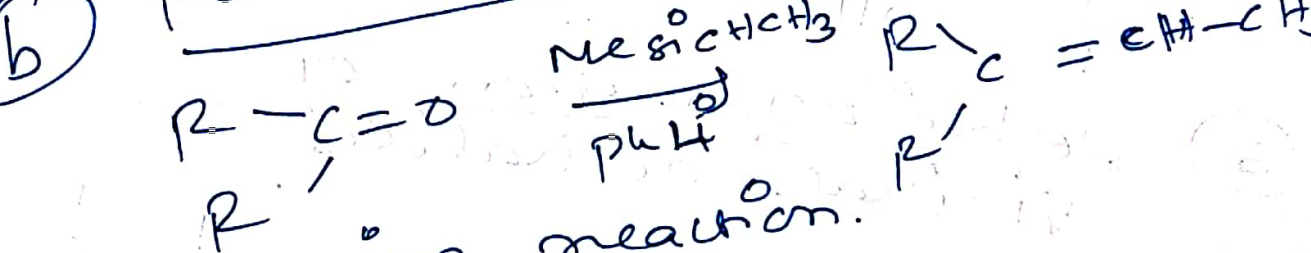


(5) Conversion of aldehydes and ketones to alkenes.

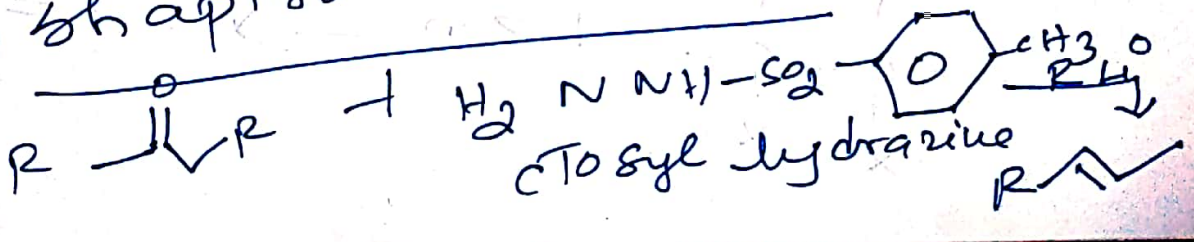
(a) Wittig reaction.



(b) Peterson reaction



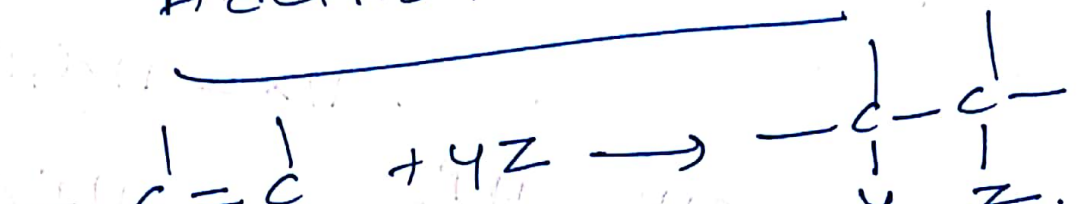
(c) Shapiro reaction.



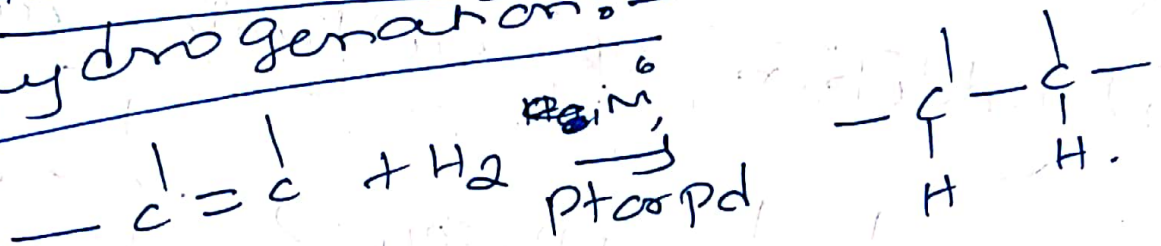
⑤ E_1 and E_2 Elimination reactions were already completed!

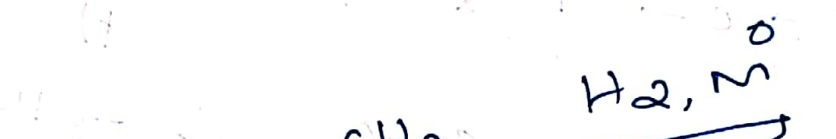
Reaction of alkenes

Addition reactions.

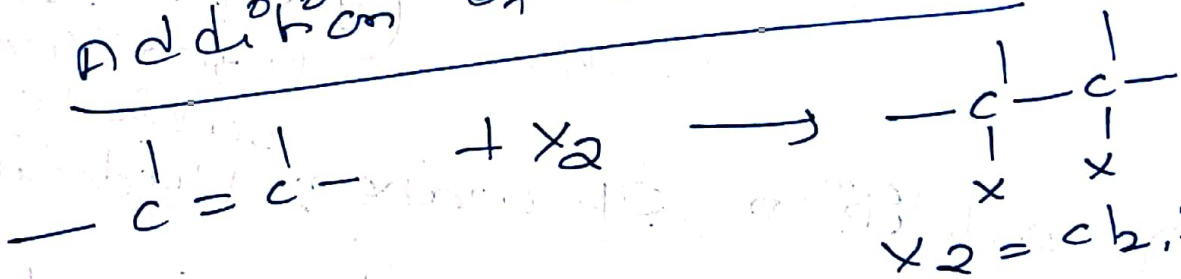


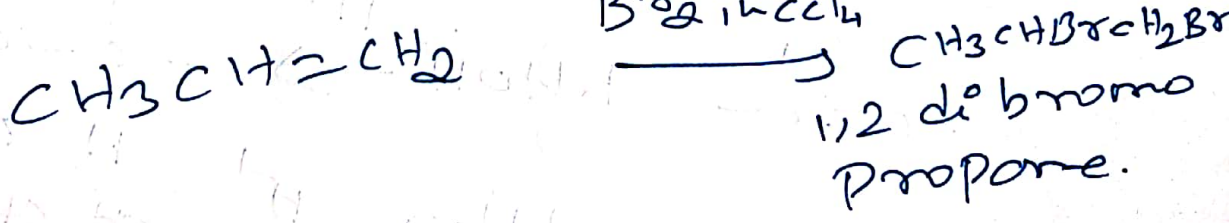
1. Addition of hydrogen: catalytic hydrogenation:-





2. Addition of halogens:-





(6)

(3) Addⁿ of hydrogen halides:-

$$-\overset{|}{C}=\overset{|}{C} + HX \longrightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{X}{C}}-$$

HX = HCl, HBr, HI.

$H_3C-CH=CH_2 \xrightarrow{HI} CH_3CHICH_3$
(2Iodo propane)

(4) Addition of sulfuric acid:

$$-\overset{|}{C}=\overset{|}{C}- + H_2SO_4 \rightarrow -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OSO_3H}{C}}-$$

$H_3C-CH=CH_2 \xrightarrow[H_2SO_4]{conc.} H_3C-\underset{\underset{OSO_3H}{|}}{CH}-CH_3$

(Isopropyl hydrogen sulfate)

(5) Addition of water: Hydration.

$$-\overset{|}{C}=\overset{|}{C}- + HOH \xrightarrow{H^+} -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}-$$

$H_3C-CH=CH_2 + H_2O \xrightarrow{H^+} CH_3CH(OH)-CH_3$

Isopropyl alcohol
(2-Propanol)

⑥ Halohydrin formation:-

$$-\overset{|}{C}=\overset{|}{C}- + X_2 + H_2O \rightarrow -\overset{|}{C}(X)-\overset{|}{C}(OH)- + HX$$

$$H_3C-CH=CH_2 \xrightarrow[H_2O]{Cl_2} H_3C-\underset{OH}{CH}-\underset{Cl}{CH_2}$$

(1-chloro-2-propanol)

⑦ Dimerization

$$H_3C-\underset{CH_3}{C}=CH_2 + CH_3-\underset{CH_3}{C}=CH_2 \xrightarrow{\text{acid.}}$$

$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}-CH=\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}-CH_3$$

2,4,4 Trimethyl 2-pentene.

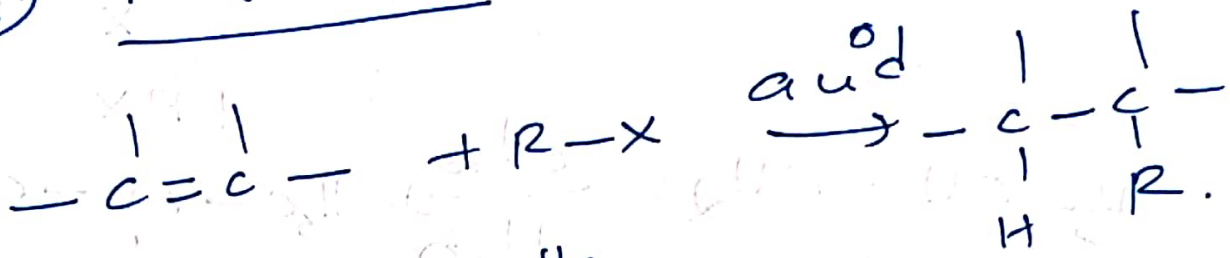
$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}-CH_2-\underset{CH_3}{\overset{CH_3}{\overset{|}{C}}}=CH_2$$

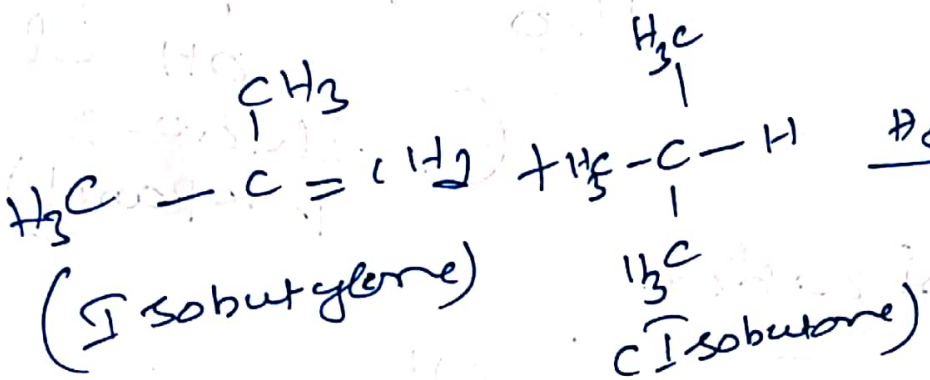
2,4,4, Trimethyl-1-pentene

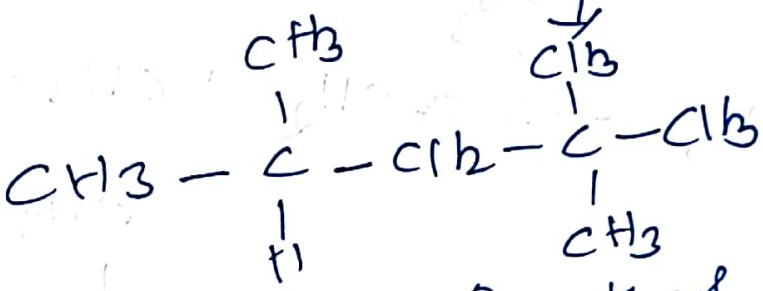
—

(8)

(8) Alkylation :-

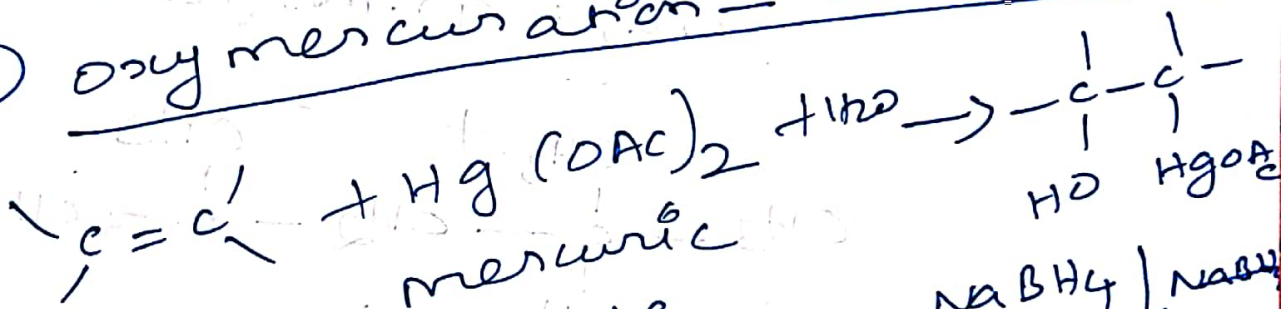






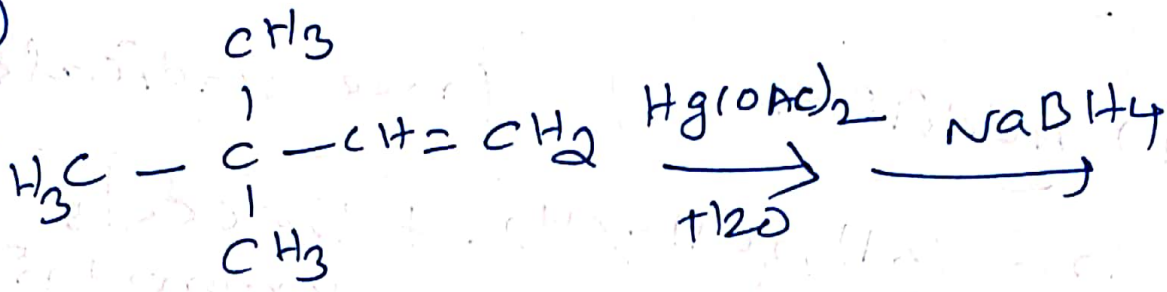
(2,2,4 Trimethyl pentane)

(9) Oxymercuration – demercuration

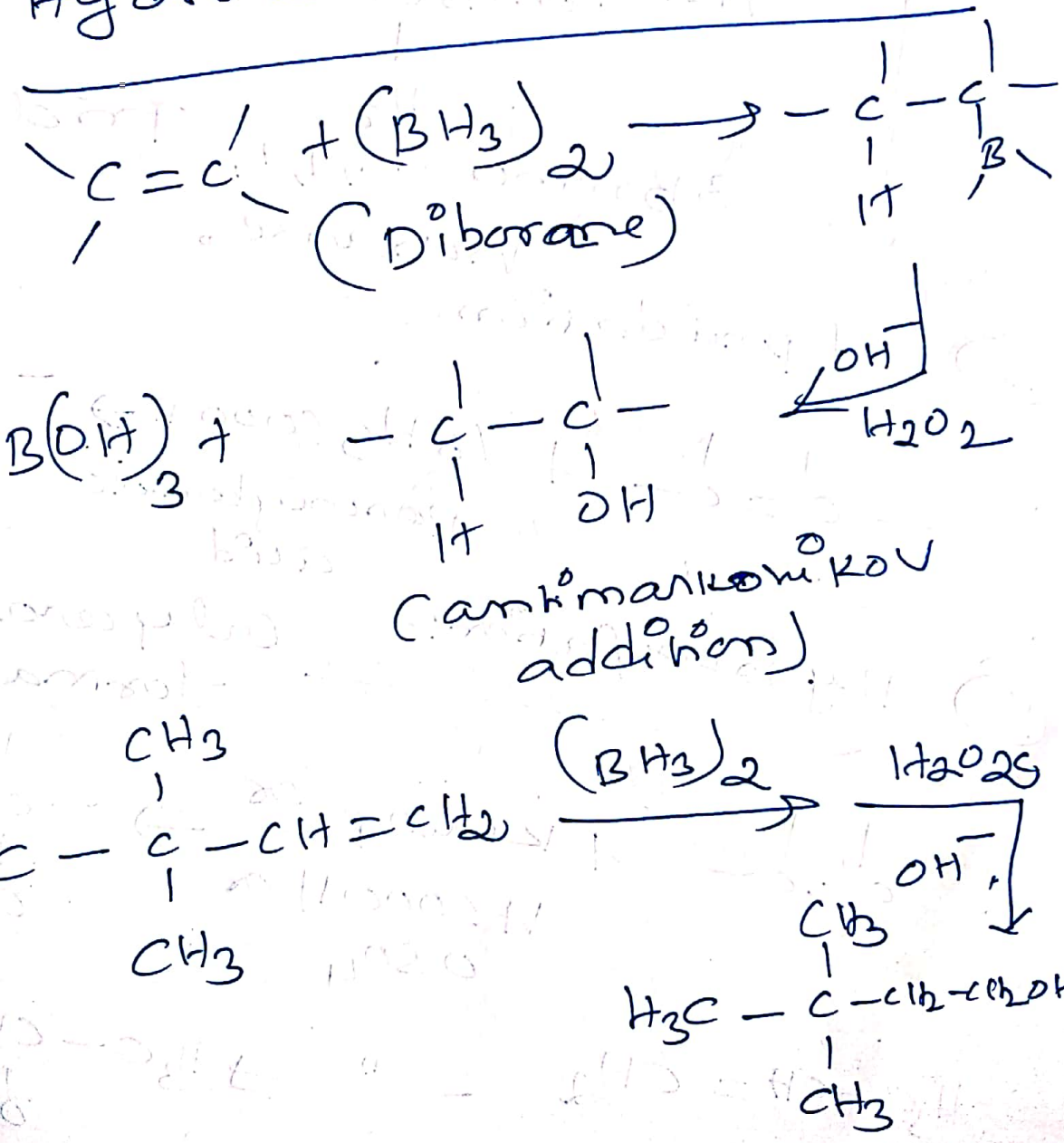


(Markonikov addition)

(9)



(10) Hydroboration – oxidation.



(10)

(11) Addition of free radicals.

$n-C_6H_{13}CH=CH_2$ + $BrCCCl_3$

1-octene

Bromotri chloromethane

↓ peroxides

$n-C_6H_{13}CH(Br)-CH_2-CCl_3$

3 Bromo-1,1,1, Trichloro nonane.

(12) Epoxidation.

$-C=C-$ + C_6H_5COOH → $-C(O)-C-$

peroxybenzoic acid

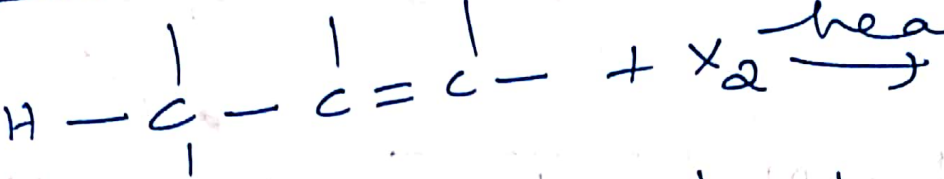
(13) Hydroxylation:- Glycerol formation.

$-C=C-$ + $KMnO_4$ or $HCOOH$ or OSO_4 → $-C(OH)-C(OH)-$

$H_3C-CH=CH_2$ → $H_3C-CH(OH)-CH_2(OH)$

(1,2 Propane diol)

(14) Halogenation:- Allylic substitution.

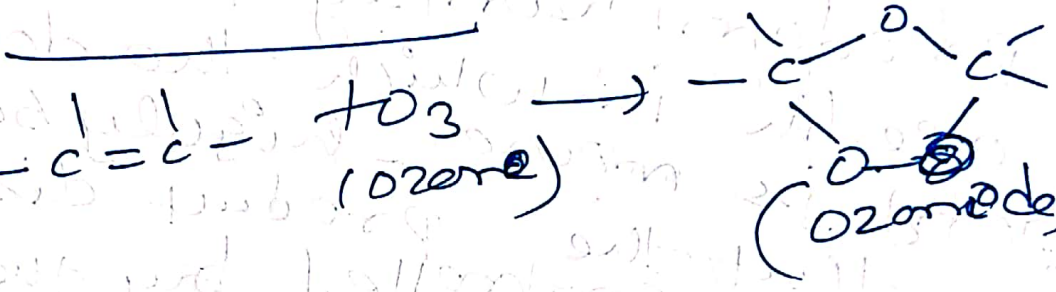


$X_2 = Cl_2, Br_2$

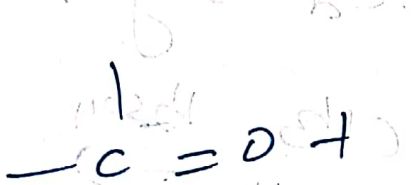
$H_3C-CH=CH_2 \xrightarrow[600^\circ C]{Cl_2} Cl-CH_2-CH=CH_2$

Allyl chloride (3-chloro-1-propene)

(15) Ozonolysis

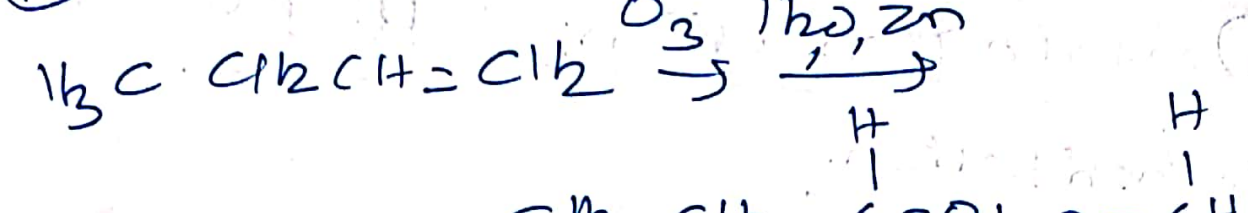


(ozonide)



(aldehydes and ketones)

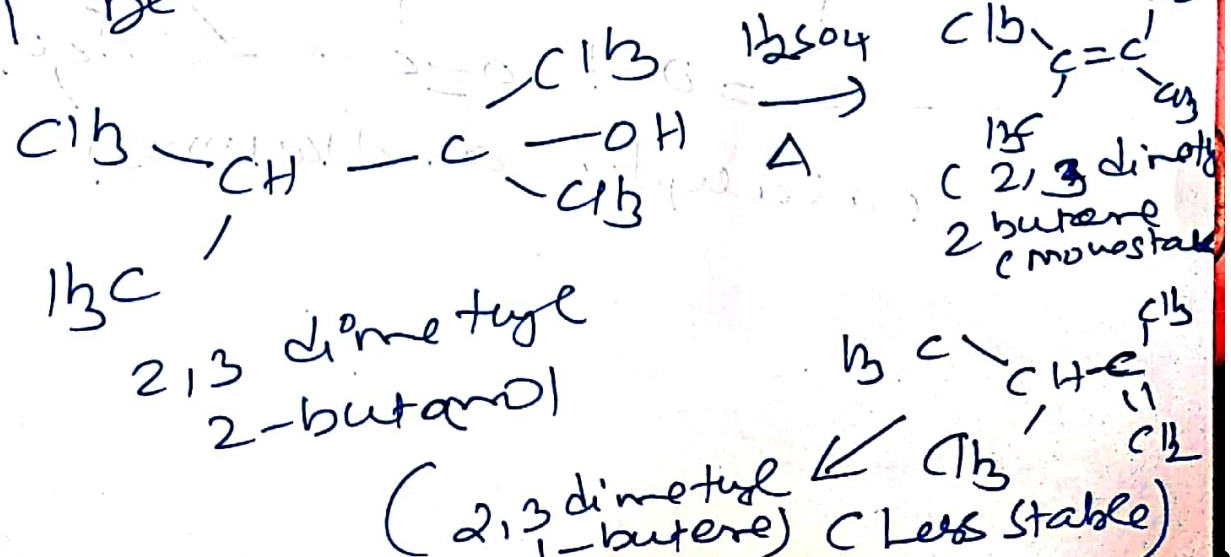
(12)



Saytzeff rule also called as Zaitsev's rule.

It is an empirical rule for predicting the favored alkene product in elimination reactions.

It implies base-induced eliminations (E2) will lead predominantly to the alkene in which the double bond is more highly substituted i.e that the product distribution will be controlled by thermodynamics.



(13)

Stability of conjugated dienes.

Heats of hydrogenation for mono substituted alkenes ($RCH=CH_2$) are close to 30 kcal/mol. for disubstituted alkenes ($R_2C=CH_2$) 28 kcal/mol and for trisubstituted alkenes ($R_2C='CHR$) are 27 kcal/mol. Hence for a compound containing more than one double bond, the heat of hydrogenation is the sum of heats of hydrogenation of individual double bonds.

For conjugated dienes, the measured values are slightly lower than expected. For 1,3 butadiene, we expect 2×30 or 60 kcal. The actual value is 57 kcal. In 1,3 penta diene, the actual value is 54.1 kcal/mol. conjugated dienes ie 1,3 — penta diene is more stable than the non conjugated 1,4 pentadiene.

14

$CH_2 = CH - CH = CH_2$

Expected : 30+30 = 60 Kcal

observed = 54 Kcal

$CH_3 - CH = CH - CH = CH_2$

Expected: 28+30 = 58 Kcal

observed : 54.

Dienes are divided in to three classes according to the arrangement of double bonds.

$-C=C-C=C-$

conjugated double bonds

$-C=C-C-C=C-$

Isolated double bonds

$-C=C=C-$

cumulated double bonds.

(15)

Free radical addition reactions of conjugated dienes

$CH_2=CH-CH=CH_2 + BrCCl_3$

↓ Peroxide

$CH_2=CH-\underset{\underset{Br}{|}}{CH}-\underset{\underset{CCl_3}{|}}{CH_2}$ + $\overset{\overset{Br}{|}}{CH_2}-CH=CH-\underset{\underset{CCl_3}{|}}{CH_2}$

(1,2) (1,4)

mechanism :-

peroxide → radical

radical + $BrCCl_3$ → Rad–Br + $\dot{C}Cl_3$

$CH_2=CH-CH=CH_2$ + $\dot{C}Cl_3$

$CH_2=CH-\underset{\underset{CCl_3}{|}}{CH}-CH_2$ ↔ $CH_2-CH=CH-\underset{\underset{CCl_3}{|}}{CH_2}$

$CH_2\cdots CH\cdots CH-CH_2$ (Br, CCl_3)

↓ $BrCCl_3$

$CH_2=CH-\underset{\underset{Br}{|}}{CH}-\underset{\underset{CCl_3}{|}}{CH_2}$

(1,2 addn)

$H_2C-\underset{\underset{Br}{|}}{CH}=CH-\underset{\underset{CCl_3}{|}}{CH_2}$

(1,4 addn)

References:-

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Robert Neilson Boyd
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