Alcohals and Epoxides

Unsaturated Alcohal :→ In unsaturated alcohals unsaturation & alcohal grp both are present. Unsaturation found as double & triple bond.

Three types of unsaturated alcohals :→

(i) When -OH grp. present on that carbon which attached to another carbon by double or triple bond

e.g. $CH_2=CH-OH \longrightarrow CH_3-CH=O$

vinyl al. shaw isomerism with ethylene oxide & al. acetaldehyde.

CH_2-CH_2 (O)

These alcohal are unstable.

(ii) When -OH grp isolated from multiple bond by single carbon atom.

e.g $CH_2=CH-CH_2-OH$ Propene-1-ol (Allyl alcohal)

$CH\equiv C-CH_2OH$ 2-propyne-1-ol (Proporgyl alcohal

(iii) When -OH grp & multiple bond are isolated by more than one carbon atom.

$CH_3-CH=CH-CH_2-CH_2OH$ 3-pentene-1-ol

$CH_2=CH-CH_2-CH_2-OH$ 3-butene-1-ol.

⇒(a) first type (i) of alcohals are not found because due to tautomerism they will convert into carbonyl compounds, but derivative of these compound are stable for example vinyl chloride, vinyl acetate etc.

⇒ Second & third (ii) & (iii) type of alcohals have properties of unsaturate bond & -OH grp

⇒ II type of alcohal have more active -OH gp because they possess double bond adjacent to carbon of -OH grp. which makes it more active.

e.g. $CH_2=CH-CH_2-OH$

Vinyl alcohal

Method of preparation :→

① Hydrolysis of Vinyl bromide with silver oxide in hot water

$$CH_2=CH-Br + AgOH \longrightarrow AgBr + CH_2=CH-OH$$

$$\downarrow$$

$$CH_3CHO$$

② Ethyne $\xrightarrow[HgSO_4]{H_2O, H_2SO_4}$ $H-C\equiv C-H$ $\longrightarrow$ $H-\underset{H}{\overset{H}{C}}-C(=O)-H$

In these rxns vinyl alcohal is an intermediate and actual product is acetaldehyde.

$$CH\equiv CH + HCl \xrightarrow{Hg^{2+}} CH_2=CH-Cl$$

$$CH_2Cl-CH_2Cl \xrightarrow{600-650^\circ C} CH_2=CH-Cl + HCl$$

Tautomerism (टॉटोमेरिज्म):→ When two structural isomers are present in dynamic equilibrium (गतिक संतुलन) and convert into each others (interchange), so these are called Tautomers and this process called tautomerism.

Example of Tautomerism is keto-enol tautomerism.

Enol :- OH grp attached to double bonded carbon.

Keto → oxygen atom attached to single bond atom.

$$-C=C-OH \rightleftharpoons -\underset{H}{\overset{|}{C}}-C=O$$

Enol Keto

Both of these there is a tautomeric equilibrium but equilibrium shifted more toward Keto form. Keto form is more stable & enol is found as a intermediate.

Mechanism:→

$$-C=C-O-H \rightleftharpoons \left[-C-C-O\right]^{\ominus} + H^{\oplus} \rightleftharpoons -\underset{H}{\overset{|}{C}}-C=O$$

Enol form Hybrid anion Keto form.

Allyl alcohal $CH_2=CH-CH_2-OH$

Method of preparation :→

(1) From propene :→

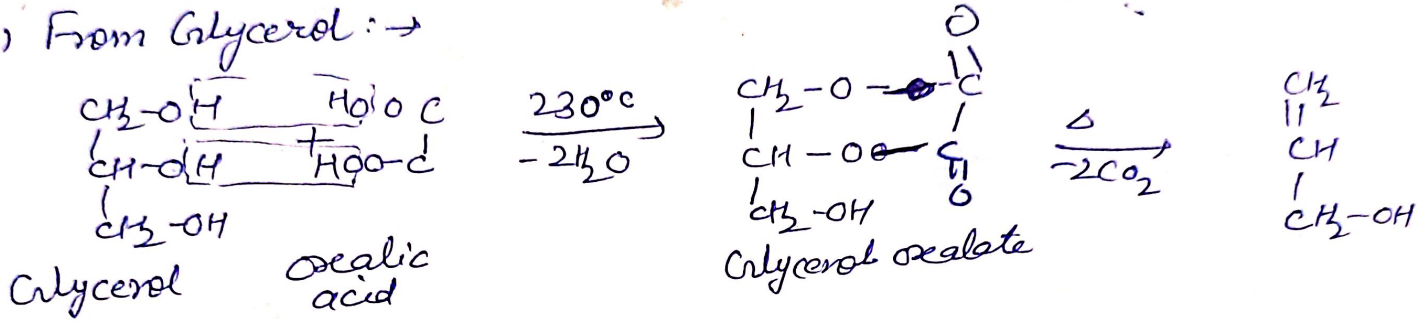
$$CH_2=CH-CH_3 + Cl_2 \xrightarrow{500^\circ C} CH_2=CH-CH_2-Cl + HCl$$

Allyl chloride

$\xrightarrow[150^\circ C]{H_2O}$ NaOH (aq.)

$$CH_2=CH-CH_2-OH + NaCl$$

(2) From Glycerol :→



Glycerol — oxalic acid — Glycerol oxalate

(3) From propargyl alcohal :→

$$\underset{\underset{CH}{\|}}{CH} + HCHO \rightarrow CH\equiv C-CH_2-OH \xrightarrow[Ni,\Delta]{H_2} CH_2=CH-CH_2-OH$$

Propargyl alcohal — reduction

Physical properties :–

⇒ It is colourless liquid (B.P – 97°C)

⇒ It is dissolved in water, ethanol & ether

Chemical Properties :→ Allyl alc. double bond & –OH grp की rxn दोनो देता है due to –I effect of –OH grp addition rxn of double bond according to antimarknoff's rule.

Reaction of double bond :→

(1) Reduction :→

$$CH_2=CH-CH_2-OH \xrightarrow{H_2, Pt/\Delta} CH_3-CH_2-CH_2OH$$

(2) Addⁿ with Halogen :→

$CH_2=CH-CH_2-OH + Br_2 \longrightarrow CH_2(Br)-CH(Br)-CH_2-OH$

2,3-dibromopropanol

(3) With Halogen acid :→

$CH_2=CH-CH_2-OH \xrightarrow{H-Br} CH_2(Br)-CH(H)-CH_2-OH$

3-bromopropanol (according antimarkonikoff's)

$CH_2=CH-CH_2-OH + HO-Cl \longrightarrow CH_2(OH)-CH(Cl)-CH_2-OH$

Hypochlorous acid

2-chloro-1,3-propan-diol

(4) Hydroxylation :→

$CH_2=CH-CH_2-OH + H_2O + [O] \xrightarrow[KMnO_4]{\text{Alkaline}} CH_2(OH)-CH(OH)-CH_2(OH)$

Glycerol

(5) Ozonolysis :→

$CH_2=CH(CH_2-OH) + O_3 \longrightarrow$ Ozonide $\xrightarrow[-H_2O_2]{H_2O} HCHO + CHO-CH_2-OH$

Glycolic aldehyde

Reaction of Primary -OH grp :→

(1) $2\,CH_2=CH(CH_2-OH) + 2Na \longrightarrow 2\,CH_2=CH(CH_2-ONa) + H_2$

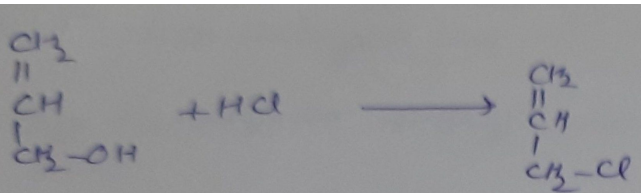
Sodium allylate

(2) Rxⁿ with fatty acid :→

$CH_2=CH(CH_2OH) + HOOC-CH_3 \xrightarrow{H^+} CH_2=CH(CH_2OOCCH_3) + H_2O$

Allylacetate

(3)

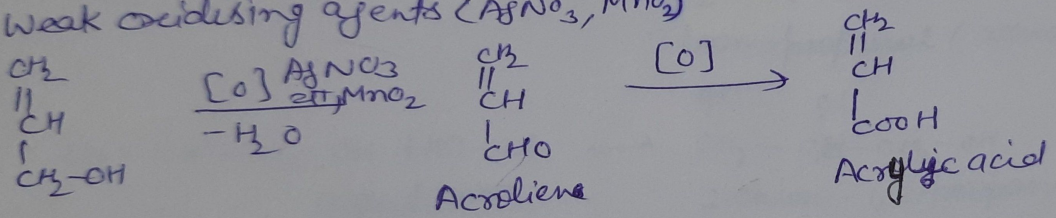


Allyl chloride.

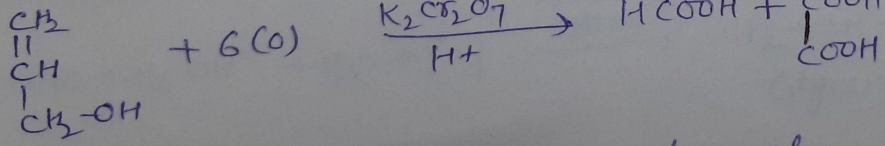
(4) Rxn with acid chloride :→

$$CH_2=CH-CH_2-OH + ClOC\cdot CH_3 \longrightarrow CH_2=CH-CH_2OOCCH_3 + HCl$$

(5) Weak oxidising agents ($AgNO_3$, MnO_2)



Strong oxidising agents → ($K_2Cr_2O_7$ or $KMnO_4$)



Uses :- (i) In the formation of glycerol.