Practice of alcohols: ch#18.

Prep of Alcohols:

(1) Electrophillic addition of water in alkene: (Hydration of alkenes)

Reagent: H_3PO_4

Temp: 300°C

Pressure: 60°-70° Atm.

Rxns:

$CH_2=CH_2 + H_2O \xrightarrow[300^\circ C]{H_3PO_4,\ 60\text{-}70\ atm} CH_3-CH_2-OH$

ethene — ethanol

$CH_3-CH=CH_2 + H_2O \xrightarrow[300^\circ C]{H_3PO_4,\ 60\text{-}70\ atm} CH_3-\underset{OH}{CH}-CH_3$

prop-1-ene — propan-2-ol.

$CH_3-CH=CH-CH_3 + H_2O \xrightarrow[300^\circ C]{H_3PO_4,\ 60\text{-}70\ atm} CH_3-\underset{OH}{CH}-CH_2-CH_3$

but-2-ene — butan-2-ol.

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alkene + water ⟶ alcohol

Temp: 300°C ; Pressure: 60-70 atm.

Reagent: H_3PO_4, H_2SO_4

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(2) By reaction of alkenes with $KMnO_4$:

Reagent: cold, dil, acidified sol. of $KMnO_4$ ($KMnO_4 + H_2SO_4$).

$CH_2=CH_2 + 2H_2O + 2MnO_4^{-1} + 6H^+ \longrightarrow \underset{OH}{CH_2}-\underset{OH}{CH_2} + Mn^{+4}$

ethene — ethane 1,2-diol

$CH_3-CH=CH_2 + 2H_2O + MnO_4 + H^+ \longrightarrow CH_3-\underset{OH}{CH}-\underset{OH}{CH_2} + Mn^{+4}$

prop-1-ene — propane 1,2-diol

$CH_3-CH=CH-CH_3 + H_2O + MnO_4 + H^+ \longrightarrow CH_3-\underset{OH}{CH}-\underset{OH}{CH}-CH_3 + Mn^{+4}$

but-2-ene — butane 2,3-diol.

Reagent: $KMnO_4 + H_2SO_4$
Temp: cold

alkene + water + MnO_4^- + H^+ ⟶ diol + Mn^{+4}

(3) Substitution of Haloalkanes:

Reagent: NaOH

Temp: heat

$R-X + NaOH \xrightarrow{heat} R-OH + NaX.$

E.g

$CH_3-CH_2-Cl + NaOH \xrightarrow{heat} CH_3-CH_2-OH + NaCl$

chloroethane — ethanol.

$CH_3-\underset{Cl}{CH}-CH_3 + NaOH \xrightarrow{heat} CH_3-\underset{OH}{CH}-CH_3 + NaCl$

2 chloropropane — propan-2-ol.

$CH_3-CH_2-\underset{Cl}{CH}-CH_3 + NaOH \xrightarrow{heat} CH_3-CH_2-\underset{OH}{CH}-CH_3 + NaCl.$

2 chlorobutane — butan-2-ol.

Reagent: NaOH

Temp: heating

Alkyl halides + NaOH ⟶ alcohols + NaX.

(4) Reduction of carbonyl compounds:

Reagent: Reducing reagents: $LiBH_4$, $LiAlH_4$

aldehyde → 1°ROH
Ketone → 2°ROH

• Aldehydes:

$CH_3-\underset{\underset{O}{\|}}{C}-H + 2[H^+] \xrightarrow{LiAlH_4} CH_3-\underset{OH}{CH}-H$

ethanal — ethanol

$H-\underset{\underset{O}{\|}}{C}-H + 2[H^+] \xrightarrow{LiAlH_4} H-\underset{OH}{CH}-H \ (CH_3-OH).$

methanal — methanol

$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-H + 2[H^+] \xrightarrow{LiAlH_4} CH_3-CH_2-\underset{OH}{CH}-H$

propanal — propan-1-ol.

• Ketones:

$$R-\underset{\underset{O}{\|}}{C}-R' + 2[H^+] \xrightarrow{LiAlH_4} R-\underset{\underset{OH}{|}}{CH}-R'$$

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + 2[H^+] \xrightarrow{LiAlH_4} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

Propanone → propan-2-ol

$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-CH_3 + 2[H^+] \xrightarrow{LiAlH_4} CH_3-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3$$

butan-2-one → butan-2-ol.

Reagent: $LiAlH_4$.

Ald $\xrightarrow{[H^+]}$ 1° ROH

Ket $\xrightarrow{[H^+]}$ 2° ROH

$$R-\underset{\underset{O}{\|}}{C}-H + 2[H^+] \xrightarrow{LiAlH_4} R-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-H$$

$$R-\underset{\underset{O}{\|}}{C}-R' + 2[H^+] \xrightarrow{LiAlH_4} R-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-R'$$

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(5) Hydrolysis of Esters: (→ alkyl alkanoate)

catalyst/reagents: dil. Acid or dil Base.

• Reversible rxns:

• Esterification rxn.

• Acidic: (alkanoate. / alkyl)

$$CH_3-\underset{\underset{O}{\|}}{C}-O-C_2H_5 + H_2O \overset{[H^+]}{\rightleftharpoons} CH_3-\underset{\underset{O}{\|}}{C}-OH + C_2H_5OH$$

ethyl ethanoate → ethanoic acid + ethanol

$$CH_3-CH_2-\underset{\underset{O}{\|}}{C}-O-CH_2-CH_3 + H_2O \overset{[H^+]}{\rightleftharpoons} CH_3-CH_2-\underset{\underset{O}{\|}}{C}-OH + CH_3-CH_2-OH$$

ethyl propanoate → propanoic acid + ethanol

• Basic catalysed: (saponification rxns).

$$CH_3-\underset{\underset{O}{\|}}{C}-OC_2H_5 + NaOH \overset{H_2O}{\rightleftharpoons} CH_3-\underset{\underset{O}{\|}}{C}-ONa + C_2H_5OH$$

ethyl ethanoate → Sodium acetate

$$C_2H_5-\underset{\underset{O}{\|}}{C}-OC_2H_5 + NaOH \overset{H_2O}{\rightleftharpoons} C_2H_5-\underset{\underset{O}{\|}}{C}-ONa + C_2H_5OH$$

ethyl propanoate → Sodium propanoate

- Rxn name: Esterification rxn.
- Reagents: $[H^+]$, NaOH.
- Esters + water $\xrightarrow{H^+}$ carboxylic acid + alcohol.
- Esters + NaOH $\underset{H_2O}{\rightleftharpoons}$ carboxylic acid + alcohol.
  carboxylic acid sodium salt

- base catalysed → saponification rxn: soap formation.

(6) Reduction of carboxylic acid:

Carboxylic acid $\xrightarrow{[H]}$ alcohols.

$-COOH \xrightarrow{2[H]} R-\overset{O}{\overset{\|}{C}}-H \xrightarrow{2[H]}$ alcohols $\xrightarrow{2[H]}$ HCs.

$\xrightarrow{4[H]^+}$

$R-COOH + 4[H^+] \xrightarrow{LiAlH_4} R-CH_2-OH + H_2O.$

$CH_3-COOH + 4[H^+] \xrightarrow{LiAlH_4} CH_3-CH_2-OH + H_2O$

$CH_3-CH_2-COOH + 4[H^+] \xrightarrow{LiAlH_4} CH_3-CH_2-CH_2-OH + H_2O$

$HCOOH + 4[H^+] \xrightarrow{LiAlH_4} H-CH_2-OH + H_2O.$

- Reagent: $LiAlH_4$
- $-COOH + 4[H^+] \xrightarrow{LiAlH_4} -OH + H_2O.$

18.5 Reactions of Alcohols:

(a) COMBUSTION:

React with O_2. $\quad C + O_2 \longrightarrow CO_2 + H_2O + heat$.

Form CO_2 & Water, heat $\quad$. used as octane fuel for racing cars.

$CH_3-OH + 2O_2 \longrightarrow CO_2 + 2H_2O + heat$.
methanol

$CH_3-CH_2-OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O + heat$.
ethanol

$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + 5O_2 \longrightarrow 3CO_2 + 4H_2O + heat$.
propan-2-ol

Alcohol $\longrightarrow$ CO_2, H_2O

(b) Reactions with $SOCl_2$, PX_3, to give Alkyl Halide:

halogenating agents.

- Rxn with $SOCl_2$:

Alcohols + thionyl chloride $\longrightarrow$ alkyl chlorides. + SO_2 + HCl

$CH_3OH + SOCl_2 \xrightarrow{pyridine} CH_3Cl + SO_2 + HCl$.
methanol, thionyl chloride, chloromethane

$CH_3CH_2OH + SOCl_2 \longrightarrow CH_3CH_2Cl + SO_2 + HCl$.
ethanol, thionyl chlorid, chloroethan

$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + SOCl_2 \xrightarrow{pyridine} CH_3CH(Cl)CH_3 + SO_2 + HCl$.
propan-2-ol, 2 chloropropane.

Alcohols $\longrightarrow$ alkyl chlorides.

- Rxn with PX_3:

Alcohols + $PX_3 \longrightarrow RX + H_3PO_3$.

$CH_3OH + PCl_3 \longrightarrow CH_3Cl + H_3PO_3$ (phosphorous acid)

$CH_3CH_2-OH + PBr_3 \longrightarrow CH_3CH_2Br + H_3PO_3$.

$CH_3-CH_2-CH_2-OH + PCl_3 \longrightarrow CH_3CH_2CH_2Cl + H_3PO_3$

Alcohols $\longrightarrow$ alkyl halides.

• Rxns with PCl_5:

Alcohols + PX_3 ⟶ $RX + POCl_3 + HCl$.

Alcohols + PX_5 ⟶ $RX + H_3PO_4 + H_2O$.

$CH_3OH + PCl_5 \longrightarrow CH_3Cl + H_3PO_4 + H_2O$.

$CH_3CH_2OH + PBr_5 \longrightarrow CH_3CH_2Br + H_3PO_4 + H_2O$

OR

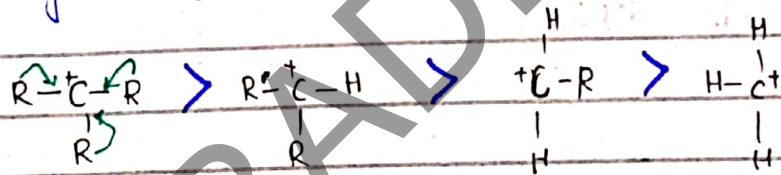
$POCl_3 + HCl$.

(c) Reaction with HX:

Why 3° ROH give reaction with HX immediately?

3° ROH give reaction immediately due to the stability of carbocations. Tertiary carbocations are most stable due to the presence of 3 R groups that have an electron donating nature.

• Stability order of carbocations:



Tertiary Carbocation > Sec 2° > 1° Prim > Methyl. (CH_3^+).

$R\text{-}OH + H\text{-}Br \xrightarrow{H^+} R\text{-}Br + H_2O$.

E.g:

$CH_3OH + HBr \xrightarrow{H^+} CH_3Br + H_2O$

$CH_3\text{-}CH_2OH + HBr \xrightarrow{H^+} CH_3CH_2Br + H_2O$.

$CH_3\text{-}CH(OH)\text{-}CH_3 + HBr \xrightarrow{H^+} CH_3\text{-}CH(Br)CH_3 + H_2O$.

Alcohols ⟶ Alkyl Halides.

LUCAS TEST:

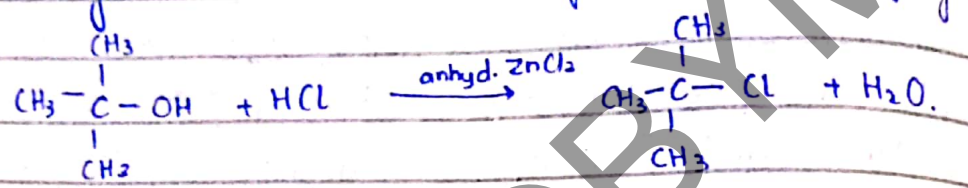
distinguishes b/w 1°, 2°, 3° ROH.

Lucas' reagent: $ZnCl_2 + HCl$ (anhydrous, concentrated) ⟶ gives an oily layer of haloalkanes.

$$R\text{-}OH + HCl \xrightarrow[HCl]{ZnCl_2} RCl + H_2O.$$

both are polar — non polar + polar → will form an oily layer.

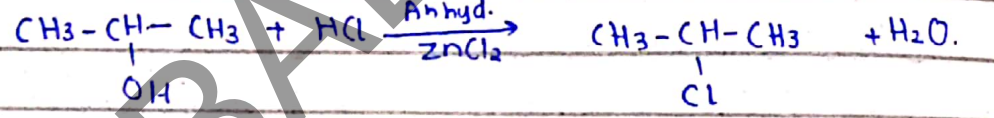
(a) Tertiary alcohol (3°ROH): immediatly forms an oily layer.



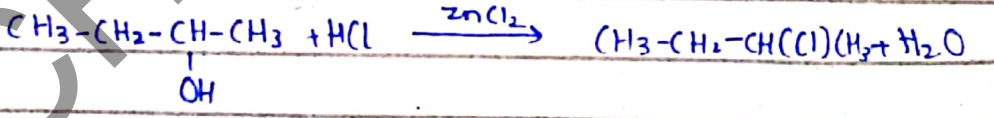
2 methyl propan-2-ol → 2 methyl 2 chloropropane.

[Oily layer: Immediatly.]

(b) Secondary alcohol (2°ROH): oily layer in 5-10 mins.



propan-2-ol → 2 chloropropane.



butan-2-ol → 2 chlorobutane.

[Oily layer in 5-10 min].

(c) Primary alcohols: oily layer formation on heating.

$$CH_3OH + HCl \xrightarrow{ZnCl_2} CH_3Cl + H_2O$$

$$CH_2CH_2OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2Cl + H_2O$$

(Oily layer formed after heating)

Q: How will you distinguish b/w propan-2-ol & 2 methyl propan-2-ol.

Propan-2-ol: $CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$ (2° ROH)

2 methylpropan-2-ol: $H_3C-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$ (3° ROH)

→ We can distinguish b/w 2° ROH & 3° ROH by using lucas test. Reacting both with $HCl/ZnCl_2$:

$CH_3-CH(OH)CH_3 + HCl \xrightarrow{ZnCl_2} CH_3CH(Cl)CH_3 + H_2O$.

↳ gives an oily layer after 5-10 mins.

$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 + HCl \xrightarrow{ZnCl_2} CH_3-\underset{\underset{Cl}{|}}{C}(CH_3)-CH_3 + H_2O$

↳ gives an oily layer immediatly.

• These experiments/test confirm that propan-2-ol is a 2° ROH & 2 methyl propan-2-ol is a 3° ROH.

Exercise: Qno: 6 (ii)

.How will you distinguish between propan-1-ol & propan-2-ol?

$CH_3-CH_2-CH_2-OH$: propan-1-ol.

$CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$: propan-2-ol.

By doing/performing Lucas test: i.e reacting both the alcohols with $HCl/ZnCl_2$ we can find out which type of R-OH these are:

$CH_3-CH_2-CH_2-OH + HCl \xrightarrow{ZnCl_2} CH_3CH_2CH_2(Cl) + H_2O$. (1° ROH)

Gives an oily layer on heating.

→ only 1° ROH give oily layer on heating.

$CH_3-CH(OH)-CH_3 + HCl \xrightarrow{ZnCl_2} CH_3-CH(OH)-CH_3 + H_2O$. (2° ROH)

Gives oily layer after 5-10 minutes.

→ Only 2° ROH give oily layer after 5-10 mins.

Exercise Qno: 11 (i):

How will you distinguish between the following:

(i) An alcohol & an alkyl halide:

An alcohol will give Lucas test while an alkyl halide won't; i.e:

$CH_3\text{-}OH + HCl \xrightarrow{ZnCl_2} CH_3Cl + H_2O$.

(form an oily layer)

$CH_3Cl + HCl \xrightarrow{ZnCl_2}$ No reaction.

(d) Reaction with KBr:

$$\text{alcohol} + KBr \xrightarrow[\text{Heat}]{H_2SO_4} R\text{-}Br + KHSO_4 + H_2O.$$

E.g:

$$CH_3OH + KBr + H_2SO_4 \xrightarrow{heat} CH_3Br + KHSO_4 + H_2O.$$

$$CH_3\text{-}CH(OH)CH_3 + KBr + H_2SO_4 \xrightarrow{heat} CH_3\text{-}CH(Br)CH_3 + KHSO_4 + H_2O.$$

Alcohol ⟶ Alkyl bromide.

(e) Dehydration of alcohols:

dehydrating agents: Al_2O_3, H_2SO_4.

- low Temp, high conc. of ROH ⟶ ether.
- high Temp, low conc. of ROH ⟶ alkene.

→ At 140°C: alcohol ⟶ ether.

$$C_2H_5OH + C_2H_5OH \xrightarrow[140^\circ C]{H_2SO_4} C_2H_5\text{-}O\text{-}C_2H_5 + H_2O$$

ethoxyethane.

Intermolecular elimination

H_2O is removed b/w 2 molecules of -ROH.

$$CH_3OH + C_2H_5OH \xrightarrow[140^\circ C]{H_2SO_4} CH_3\text{-}O\text{-}C_2H_5 + H_2O.$$

$$CH_3\boxed{OH + OH}CH_3 \xrightarrow[140^\circ C]{H_2SO_4} CH_3\text{-}O\text{-}CH_3 + H_2O$$

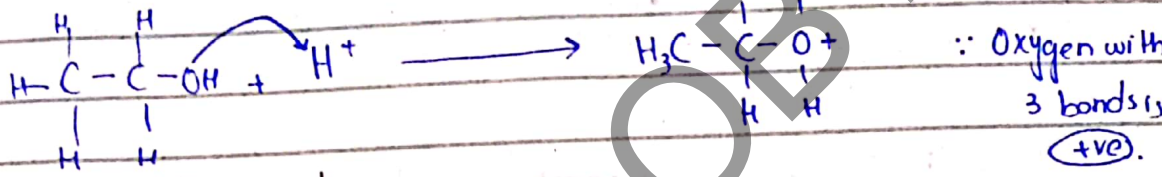
• At 180°C: alcohol → alkene.

$C_2H_5-OH \xrightarrow[180^\circ C]{H_2SO_4} H_2C=CH_2 + H_2O$ — Intermolecular elimination. ↓ water removed from within an ROH molecule.

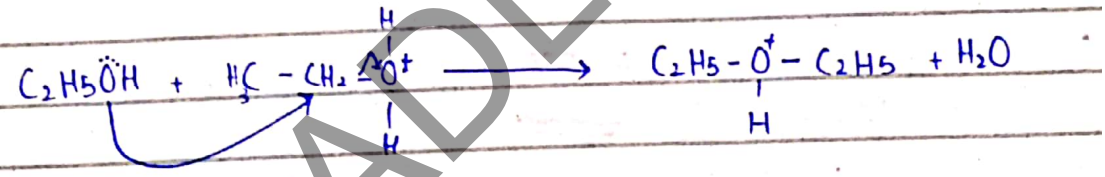
$CH_3-CH(OH)-CH_3 \xrightarrow[180^\circ C]{H_2SO_4} CH_3-CH=CH_2 + H_2O.$

→ Mechanism of "Dehydration of Alcohol" at 140°C:

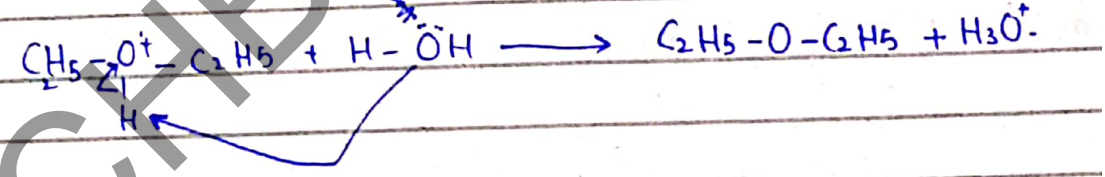
(i) Protonation: addition of H^+:



(ii) Nucleophillic attack:



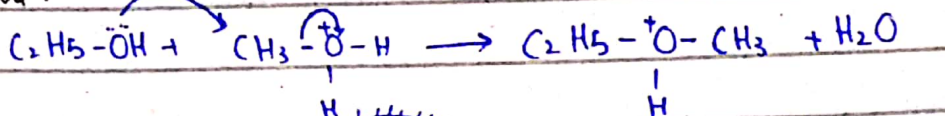
(iii) Regeneration of catalyst:



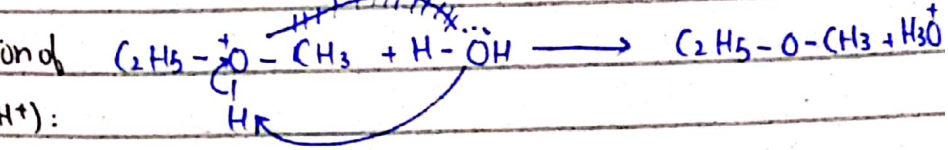
→ Mechanism of $CH_3-OH + C_2H_5-OH \xrightarrow[180^\circ C]{H_2SO_4}$

(i) Protonation: $CH_3OH + H^+ \longrightarrow CH_3-\overset{+}{O}(H)-H$

(ii) Attack of Nu^-:



(iii) Regeneration of catalyst (H^+):



→ Mechanism of dehydration of Alcohol at 180°C:

$$CH_3OH + CH_3OH \xrightarrow[180^\circ C]{H_2SO_4} CH_3-O-CH_3 + H_2O.$$

(i) Protonation: $CH_3OH + H^+ \longrightarrow CH_3-\overset{+}{O}H$ (H)

(ii) Nu attack: $CH_3-\ddot{O}-H + CH_3-\overset{+}{O}H \longrightarrow CH_3-\overset{+}{O}-CH_3 + H_2O$ (H)

(iii) Regeneration of H+ (catalyst): $CH_3-\overset{+}{O}(H)-CH_3 + H_2\ddot{O}: \longrightarrow CH_3-O-CH_3 + H_3O^+$

(f) Formation of Esters: Reaction with carboxylic acid:

$$\text{Alcohols} + -COOH \xrightarrow{H_2SO_4/Al_2O_3} \text{Ester} + H_2O.$$

$$CH_3OH + CH_3COOH \rightleftharpoons CH_3-COO-CH_3 + H_2O.$$

$$CH_3OH + C_2H_5COOH \rightleftharpoons C_2H_5COOCH_3 + H_2O.$$

$$C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O.$$

$$RCOOH + ROH \longrightarrow RCOOR' + H_2O.$$

(g) Oxidation of Alcohols:

↳ Alcohols $\xrightarrow{[O]}$ ——.

↳ Oxidizing agents: $KMnO_4 + H_2SO_4$

$K_2Cr_2O_7 + H_2SO_4$

↳ $Cr_2O_7^{-2} \longrightarrow Cr^{+3}$

(orange) (green)

↳ Detection Test

MCQ: When $1K_2Cr_2O_7$ reacts with $4H_2SO_4$, how many [O] are produced?

Ans: 3[O].

Question: Why do we add a few drops of H_2SO_4 in oxidizing agents? To make the oxygen available, for the process of oxidation. H_2SO_4 will make the oxygen available from the oxidizing agent ($KMnO_4$, $K_2Cr_2O_7$).

1° ROH $\xrightarrow{[O]}$ Aldehyde $\xrightarrow{[O]}$ carboxylic acid

2° ROH $\xrightarrow{[O]}$ Ketone

3° ROH $\xrightarrow{[O]}$ No reaction.

↳ Instead, it undergoes elimination rxn (dehydration) & produces Alkenes.

(a) Oxidation of 1°ROH:

$$1°ROH \xrightarrow{[O]} RCHO \xrightarrow{[O]} RCOOH.$$

e.g:

$$CH_3OH + [O] \xrightarrow[50°C]{K_2Cr_2O_7 + H_2SO_4} HCHO + H_2O.$$

methanal

$$CH_3CH_2OH + [O] \xrightarrow[50°C]{K_2Cr_2O_7 + H_2SO_4} CH_3CHO + H_2O.$$

propanal

(b) Oxidation of 2°ROH:

$$2°ROH \xrightarrow{[O]} \text{Ketones } (RCOR').$$

$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 + [O] \xrightarrow[50°C]{K_2Cr_2O_7 + H_2SO_4} CH_3\overset{O}{\overset{||}{C}}-CH_3 + H_2O.$$

propanone

$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_2-CH_3 + [O] \xrightarrow[50°C]{K_2Cr_2O_7 + H_2SO_4} CH_3-\overset{O}{\overset{||}{C}}-CH_2-CH_3 + H_2O.$$

butanone.

(c) ~~Oxidation~~ of 3°ROH: (dehydration of ROH)

- not oxidized by $KMnO_4$ or $K_2Cr_2O_7$ (in the presence of H_2SO_4)
- On heating ⟶ alkene.

$$CH_3-CH_2-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-OH \xrightarrow{H_2SO_4} CH_3-CH=\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}} + H_2O.$$

2 methyl butan-2-ol

2 methyl butan-2-ene.

Q: What is saytzeff's rule?

Ans: Internal alkenes/ alkynes are more stable than terminal alkenes/ alkynes.

↳ This is why we can not make alkene (double bond) on the upper & lower methyl groups in the above given example, because, in it, we have ability to make an internal alkene i.e inside the chain.

Exercise: Q no: 5 (ii)

(ii) Imp S.q: Why do tertiary alcohols donot oxidize?

Ans: Oxidizing agents ($KMnO_4$ & $K_2Cr_2O_7$) oxidizid a C to hydrogen bond $-\overset{|}{C}-H$ but in 3°ROH; there is not $-\overset{|}{C}-H$ bond at α C arbon. So these oxidizing agents donot oxidize 3° ROH.

Furthermore; There is hinderness on the 3° carbons these are crowded & this why oxidation does not occur. Rather they show Elimination rxns (dehydration

$$CH_3-CH_2-\overset{CH_3}{\underset{CH_3}{C}}-OH + [O] \xrightarrow{H_2SO_4} CH_3-CH=\overset{CH_3}{\underset{CH_3}{C}} + H_2O.$$

(h) Iodoform reactions:

Confirmatory test:

(i) Ethanal vs acetaldehyde

(ii) Methyl ketones vs other ketones

(iii) Ethanol vs all 1°ROH

(iv) Methyl containing vs all 2°ROH.
2°ROH

Reagent: $I_2 + NaOH$ (base catalysed rxns).

→ pale yellow ppt of tri-iodomethane: detection

(i) Ethanol vs 1°ROH:

$$CH_3-CH_2-OH + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + HCOONa + 5NaI + 5H_2O.$$

(ii) Methyl containing vs 2°ROH.
2°ROH

$$R-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3 + 4I_2 + 6NaOH \xrightarrow{\Delta} CHI_3 + RCOONa + 5NaI + 5H_2O.$$