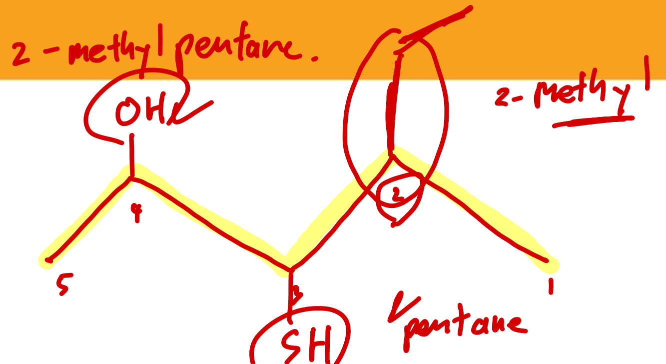
Chapter 12

Alcohols, Thiols, Ethers, Aldehydes, and Ketones

Functional Groups



A **functional group** is a specific atom or group of atoms within a molecule that determines the molecule's **chemical behavior** and **reactivity pattern**.

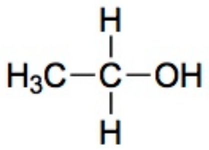
It is the **reactive site** of an organic compound where chemical reactions typically occur.

Functional groups define:

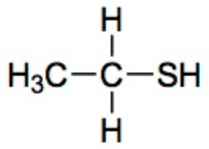
- The **class** of the compound (e.g., alcohol, aldehyde, ketone).
- The **types of reactions** the compound undergoes (e.g., oxidation, reduction, substitution).
- The **physical properties** such as solubility, boiling point, and polarity.

Functional Group	Structure	Class Name
–OH	Hydroxyl group	Alcohol
–SH	Thiol (sulfhydryl) group	Thiol
C–O–C	Ether linkage	Ether
–CHO	Carbonyl (formyl) group	Aldehyde
C=O (within chain)	Carbonyl group	Ketone

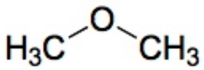
alcohol



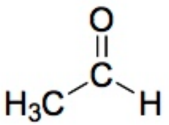
thiol



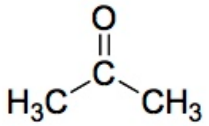
ether



aldehyde

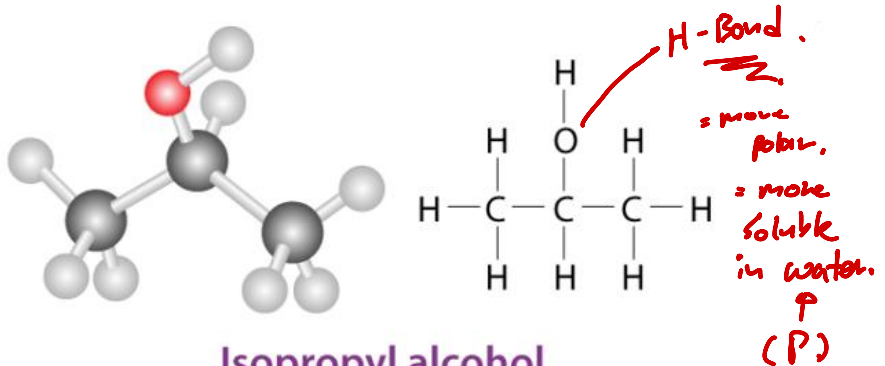


ketone



Alcohols

- contain **oxygen**
- contain a **hydroxyl group (—OH)** attached to a carbon atom
- are named by replacing the *–e* ending of the corresponding alkane with *–ol*
- form **hydrogen bonds**, leading to higher boiling points than alkanes or ethers
- are **soluble in water** when they have one to three carbon atoms
- are found in beverages, disinfectants, and fuels



Isopropyl alcohol

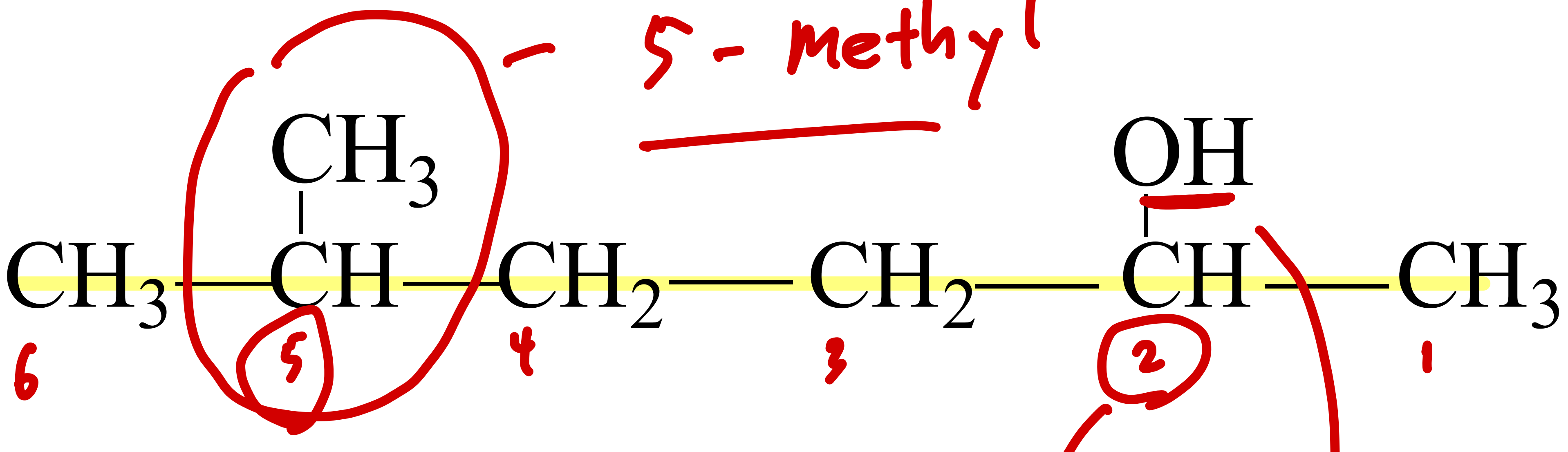
Naming Alcohols

The names of alcohols

- in the IUPAC system replace the ***e*** with ***ol***
- with common names use the name of the alkyl group followed by ***alcohol***

Formula	IUPAC	Common Name
CH_4	methane	
$CH_3{-}OH$	methanol	methyl alcohol
$CH_3{-}CH_3$	ethane	
$CH_3{-}CH_2{-}OH$	ethanol	ethyl alcohol

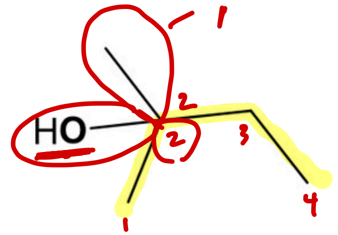
Give the IUPAC name for the following compound:



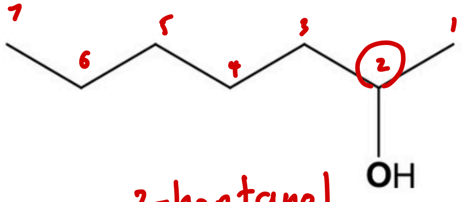
5 - methyl - 2 -Hexanol

5 - methyl hexan -2- ol

Give the IUPAC name for the following compounds:

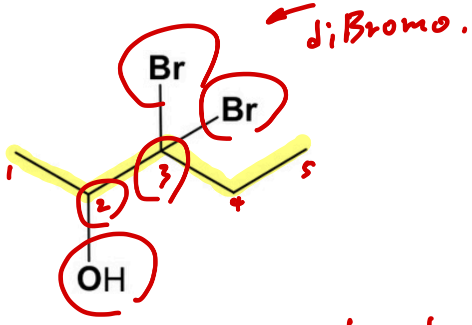
1) 

2- methyl - 2- Butanol

2) 

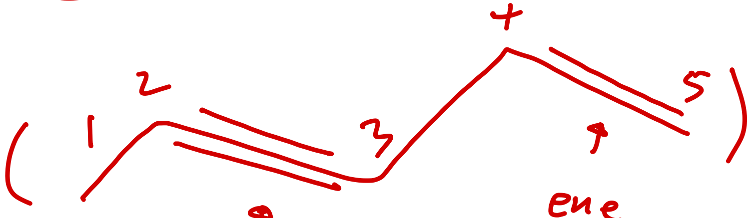
2-heptanol.

hepta-2-ol

3) 

3,3-dibromo - 2-pentanol

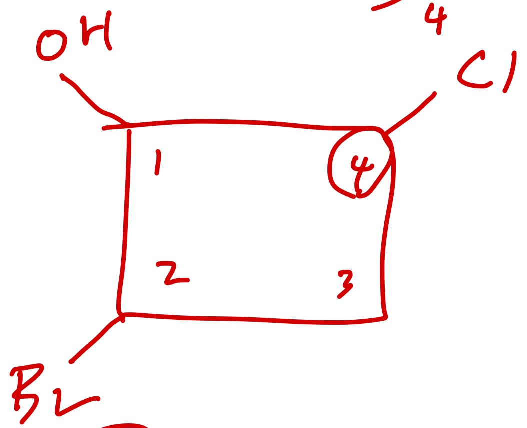
3,3, dibromopentan-2-ol

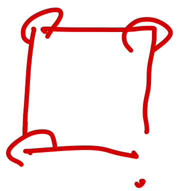


pent-2-yne-4-ene.

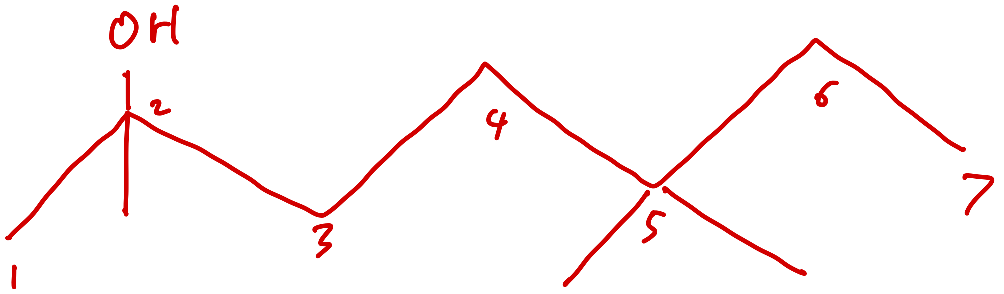
Draw the structural formula of the following

- 2-Bromo-4-chlorocyclobutanol



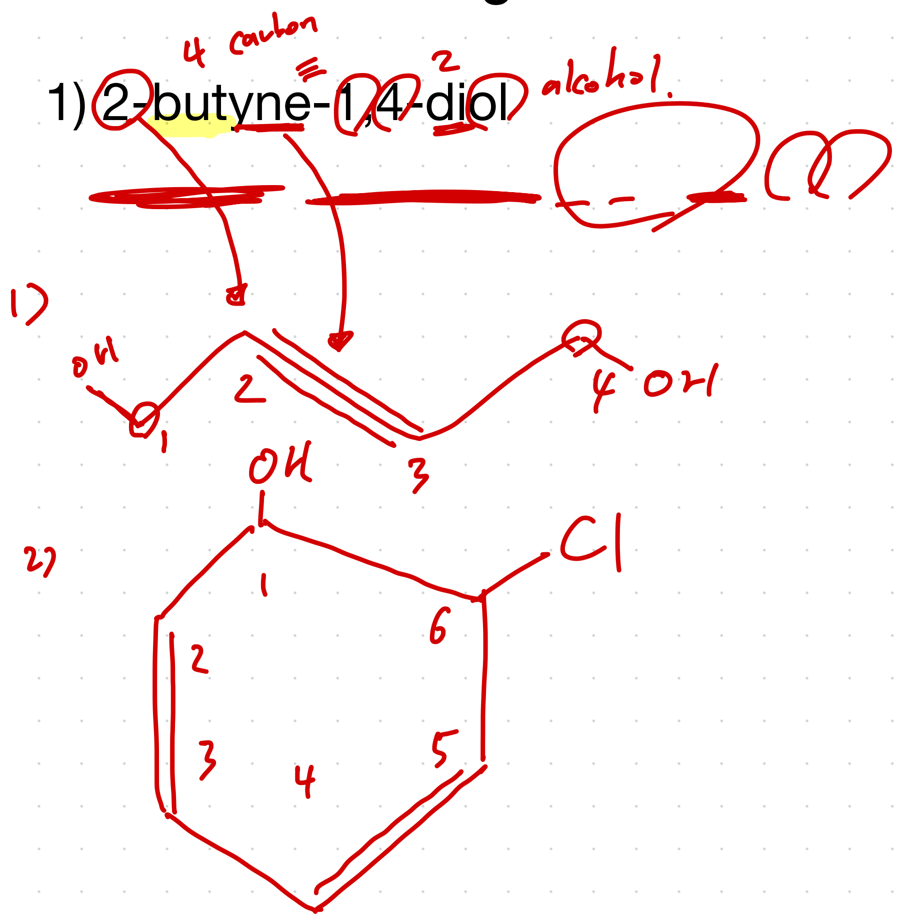


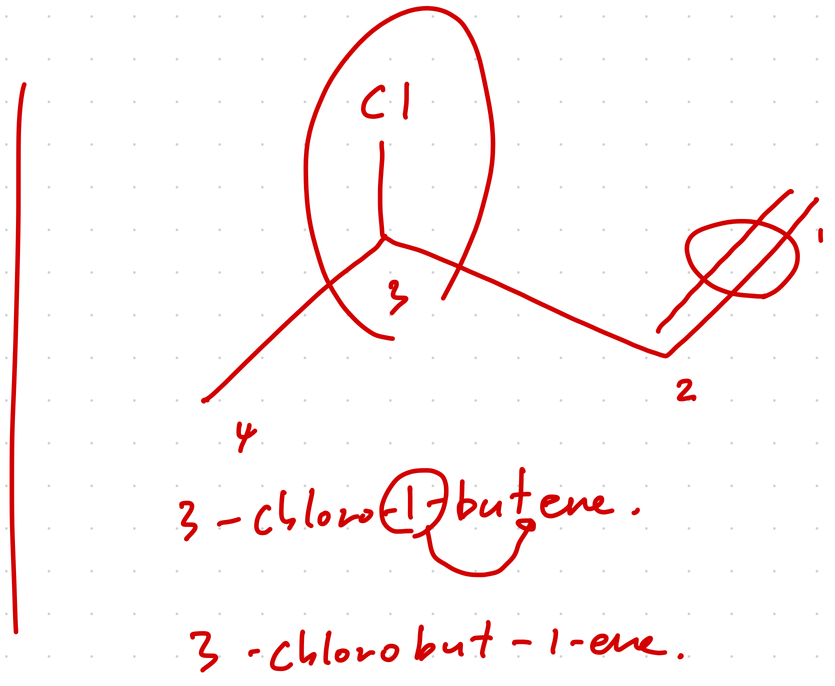
- 2,5,5-trimethyl-2-heptanol



Draw the following molecules:

1) 2-butyne-1,4-diol

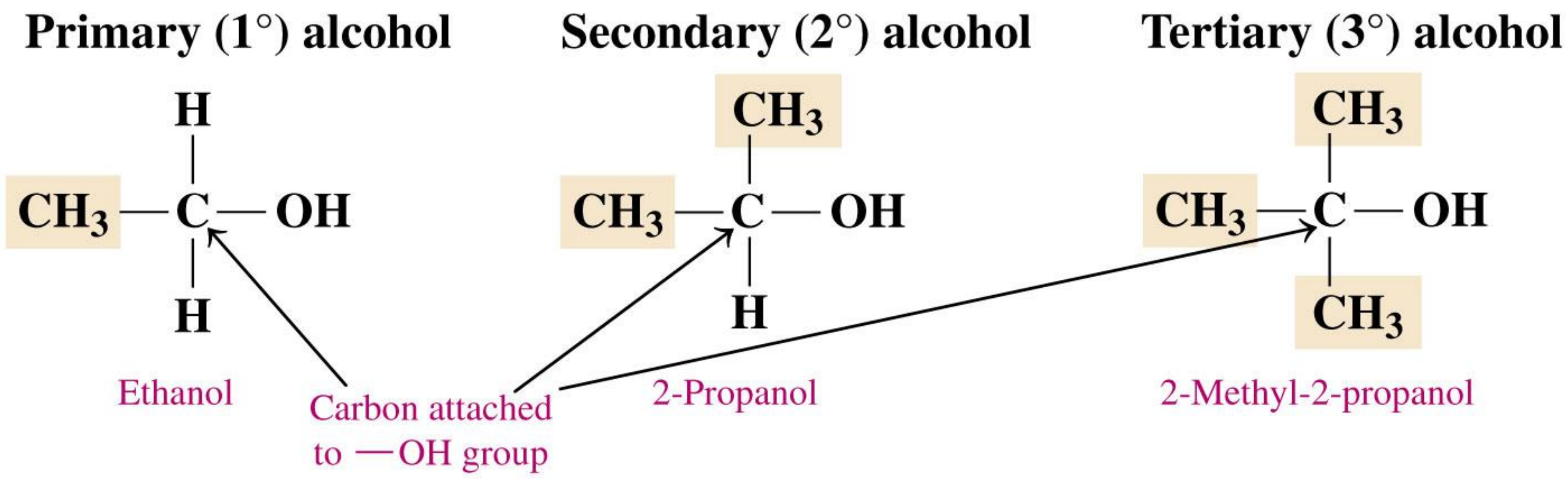




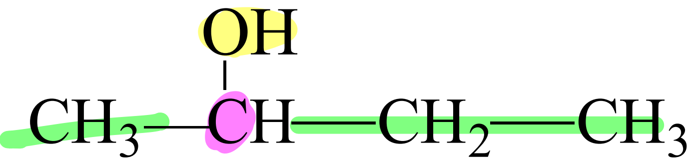
Classification of Alcohols

Alcohols are classified

- by the number of alkyl groups attached to the carbon bonded to the hydroxyl
- as primary (1°), secondary (2°), or tertiary (3°)



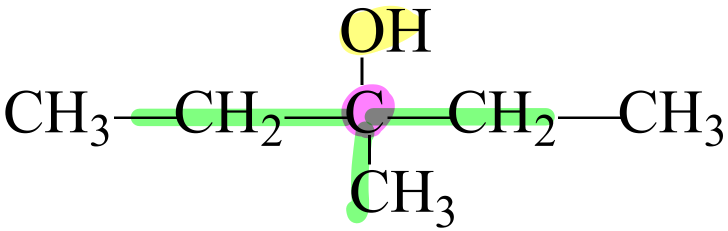
Classify each alcohol as primary, secondary, or tertiary.

A. 

2

B. $CH_3-CH_2-CH_2-OH$

1

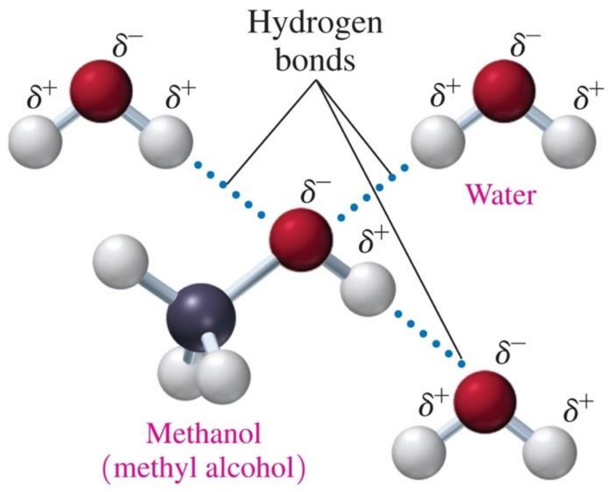
C. 

3

Solubility of Alcohols in Water

Alcohols

- contain polar —OH groups and form hydrogen bonds with other alcohol molecules and with water
- that have one to three carbons are soluble in water; the solubility of alcohols in water decreases with increasing number of carbons



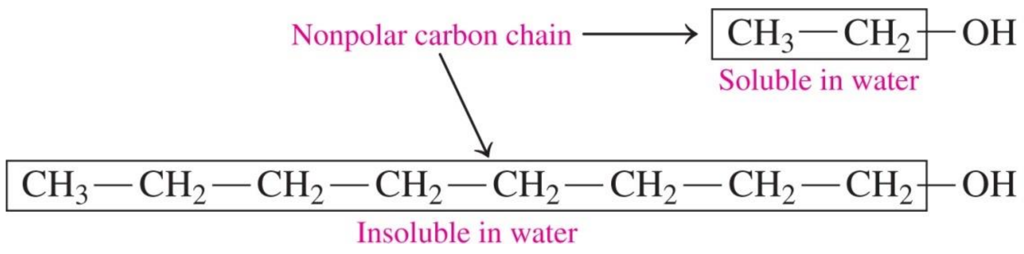


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TABLE 12.1 Solubility of Some Alcohols

Compound	Condensed Structural Formula	Number of Carbon Atoms	Solubility in Water
Methanol	CH_3-OH	1	Soluble
Ethanol	CH_3-CH_2-OH	2	Soluble
1-Propanol	$CH_3-CH_2-CH_2-OH$	3	Soluble
1-Butanol	$CH_3-CH_2-CH_2-CH_2-OH$	4	Slightly soluble
1-Pentanol	$CH_3-CH_2-CH_2-CH_2-CH_2-OH$	5	Insoluble

Alcohols in Reactions

Alcohols can undergo several types of reactions that change their structure or oxidation state.

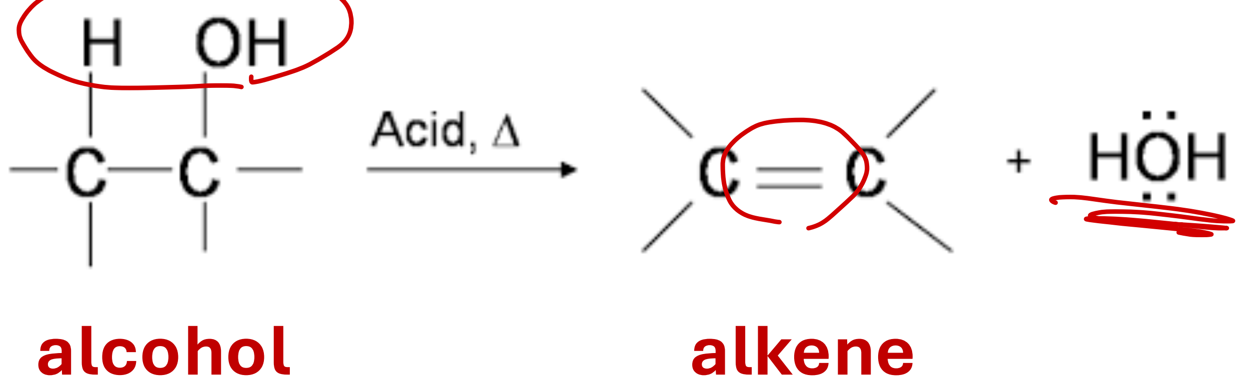
Reaction Type	Description	Product Example
Dehydration	Removal of H_2O → formation of alkene	$CH_3CH_2OH \rightarrow CH_2{=}CH_2 + H_2O$
Oxidation	↑ C–O bonds, ↓ C–H bonds	1° alcohol → aldehyde/acid, 2° → ketone
Combustion	Complete oxidation → $CO_2 + H_2O$	$CH_3CH_2OH + 3O_2 \rightarrow 2CO_2 + 3H_2O$
Esterification	Reaction with acid → ester + water	$CH_3CH_2OH + CH_3COOH \rightarrow CH_3COOCH_2CH_3 + H_2O$

Dehydration of Alcohols

$H_2 + O_2 \rightarrow H_2O$

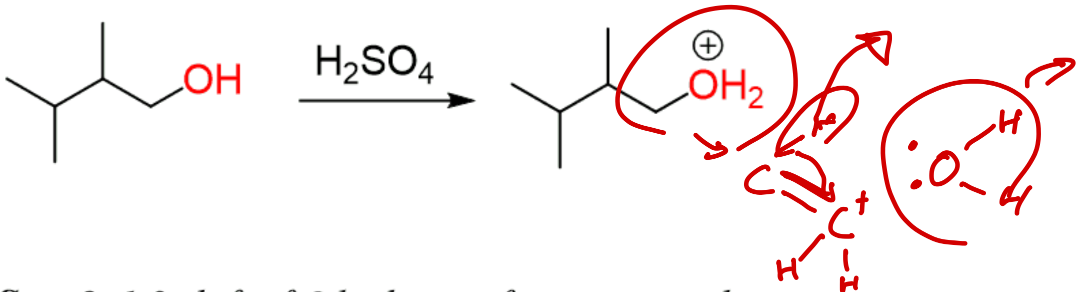
Alcohols undergo

- **dehydration** when heated with an acid catalyst
- the loss of —H and —OH from **adjacent** carbon atoms, producing an alkene and water

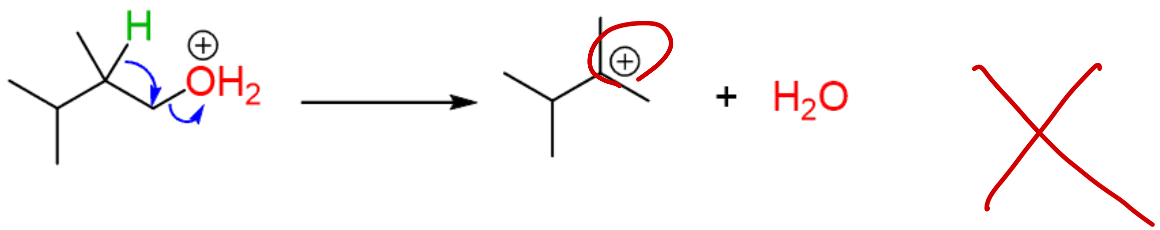


Rearrangements in Dehydration of Primary Alcohols

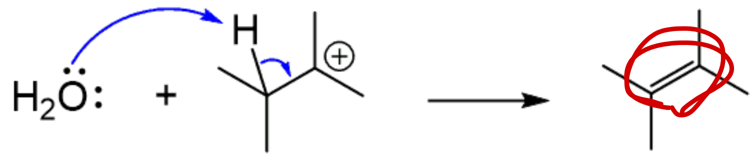
Step 1. *Protonation of the hydroxyl group*



Step 2. *1,2 shift of β-hydrogen forming a carbocation*



Step 3. *Removing β-hydrogen to form a π bond*

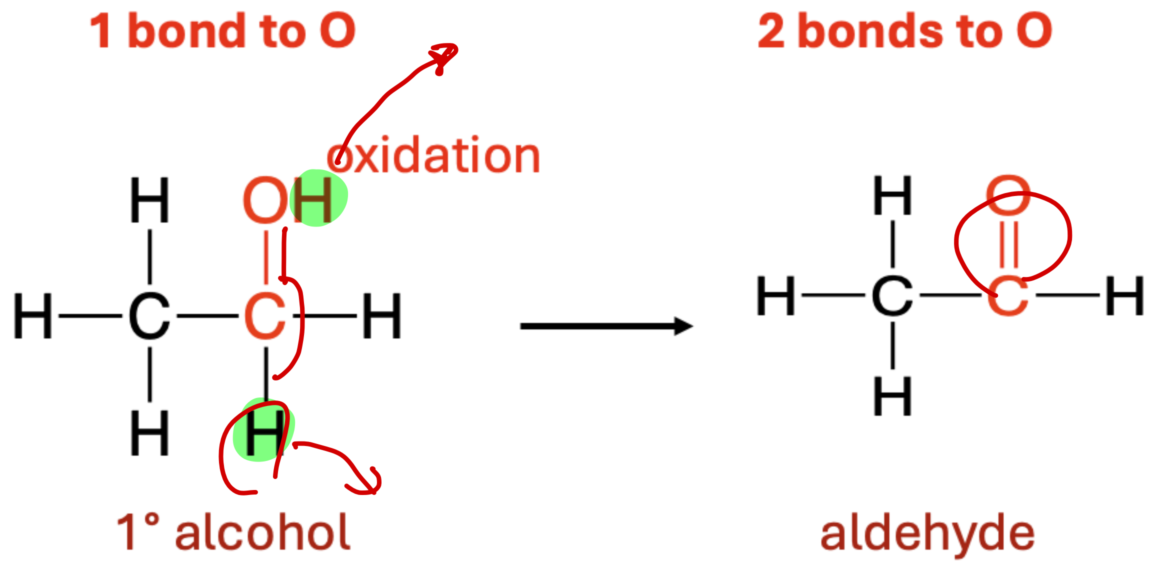


tetrasubstituted alkene

Oxidation of Primary (1°) Alcohols

Alcohols undergo **oxidation**, which increases the number of carbon and oxygen bonds.

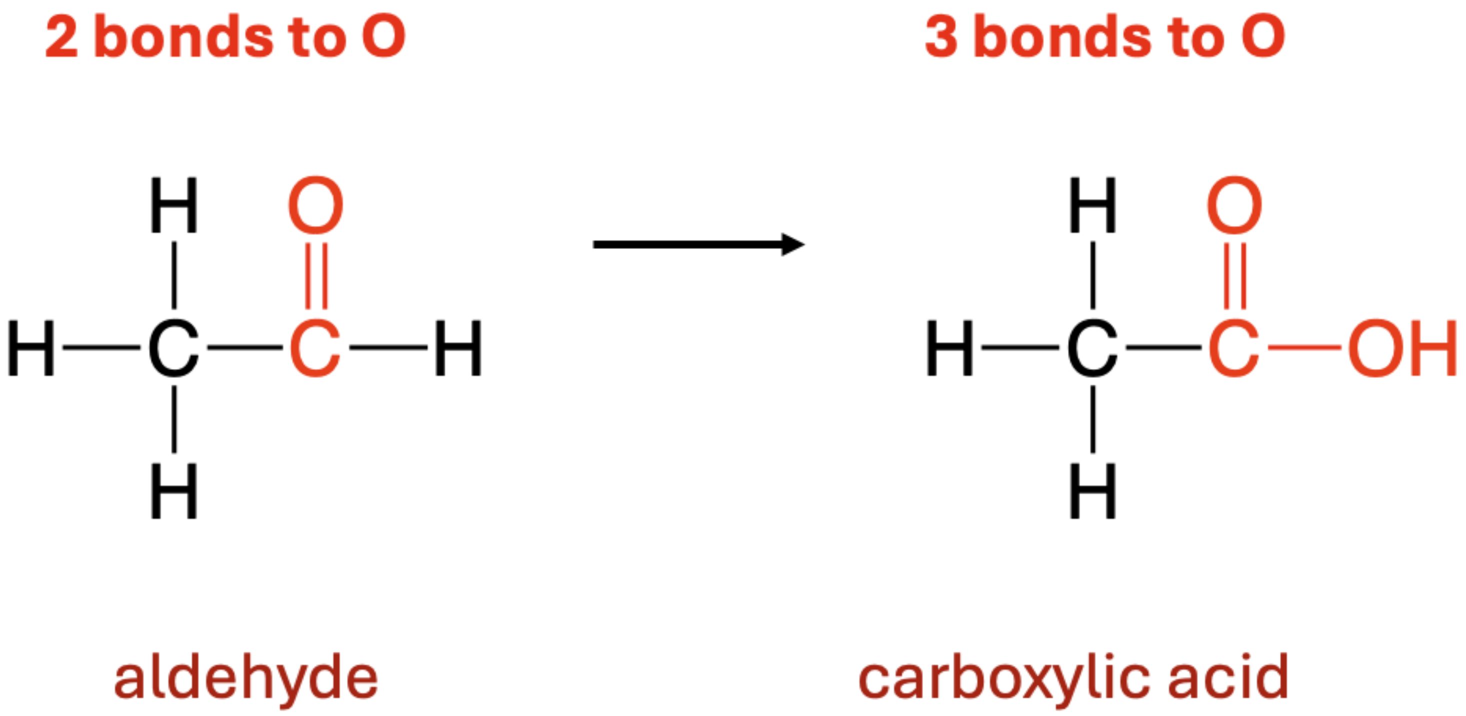
Primary alcohols are oxidized to produce an aldehyde.



Oxidation : losing e⁻

Reduction : gain e⁻

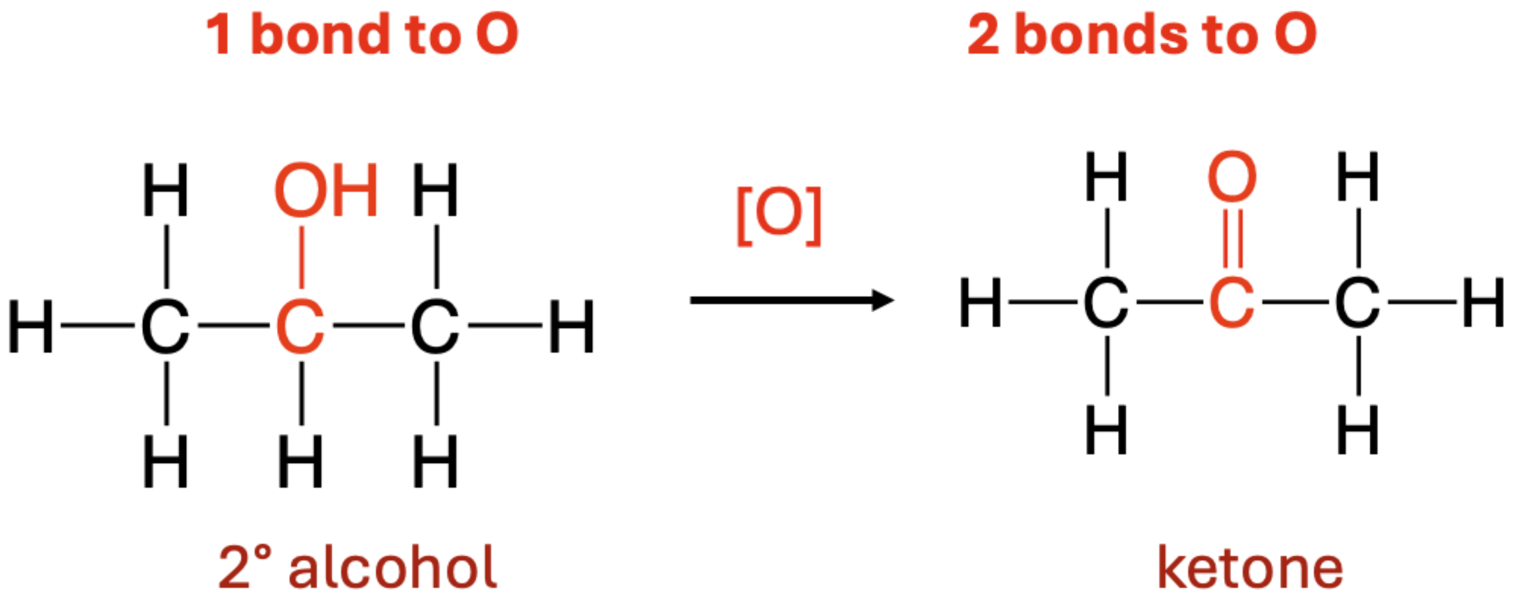
Aldehydes can further oxidize to produce a carboxylic acid.



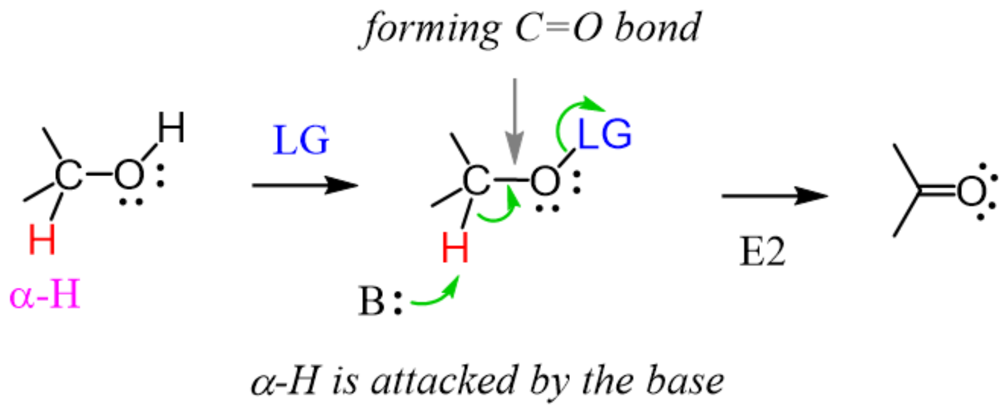
Oxidation of Secondary (2°) Alcohols

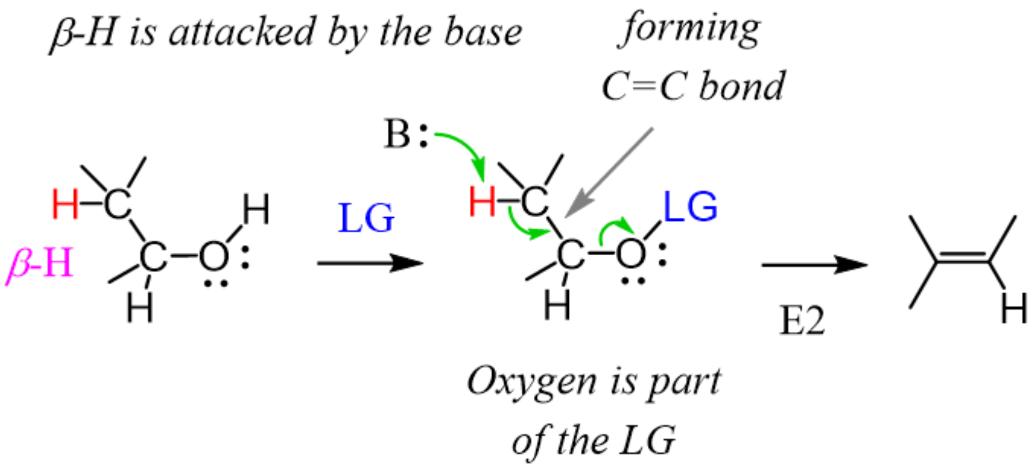
Secondary alcohols are oxidized to produce a ketone.

To indicate the process of oxidation, [O] is placed over the reaction arrow.



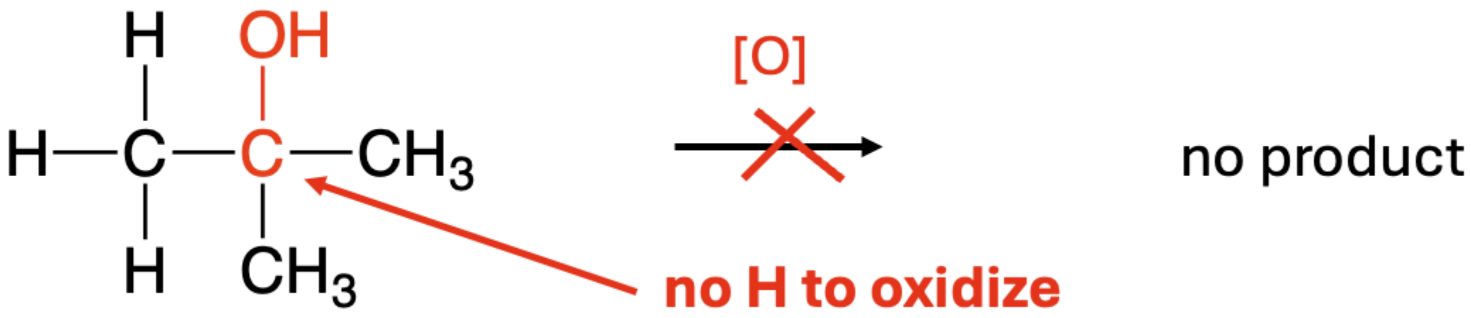
General Mechanism for the Oxidation of Alcohols





Oxidation of Tertiary (3°) Alcohols

Tertiary alcohols do not readily oxidize because there is no hydrogen atom on the carbon bonded to the —OH group.

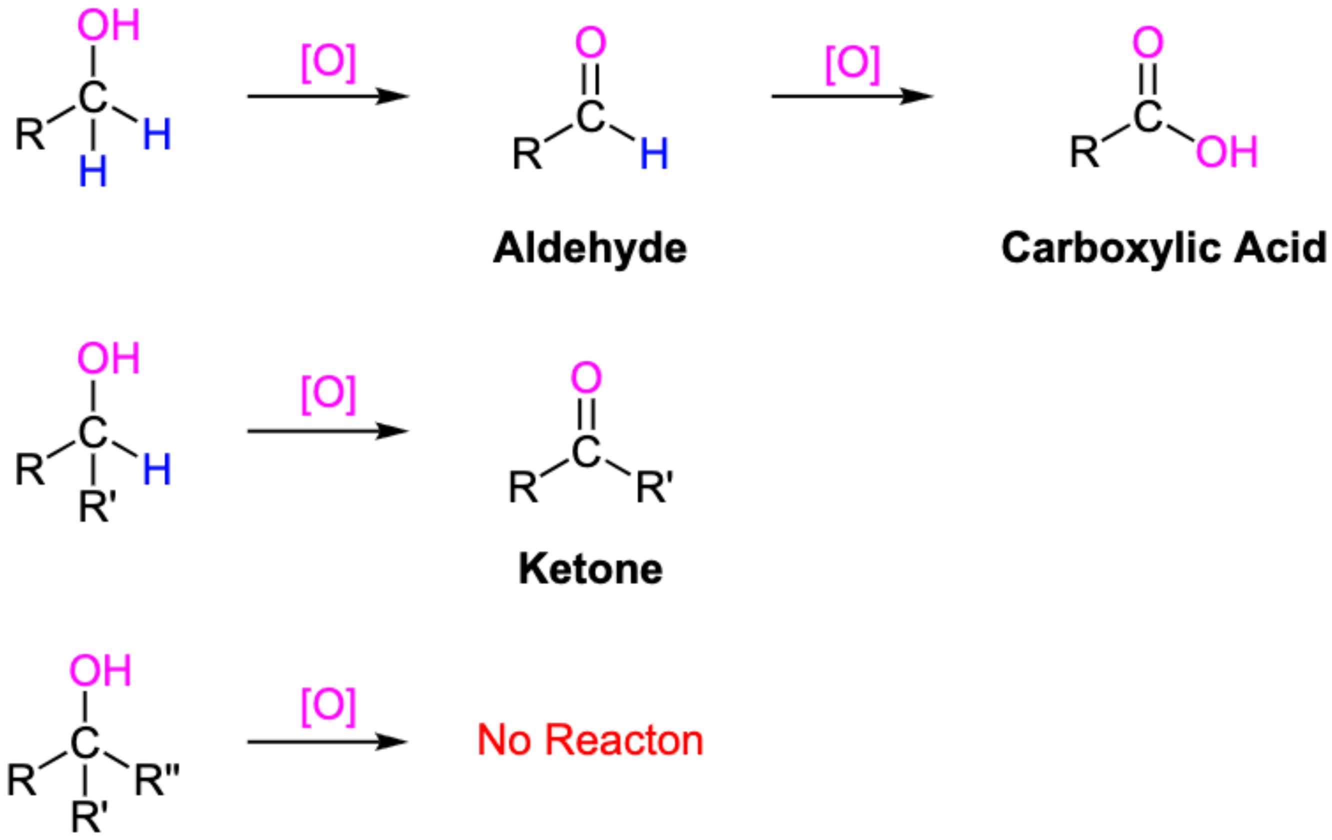


3° alcohol

Primary Alcohol

Secondary Alcohol

Teritary Alcohol

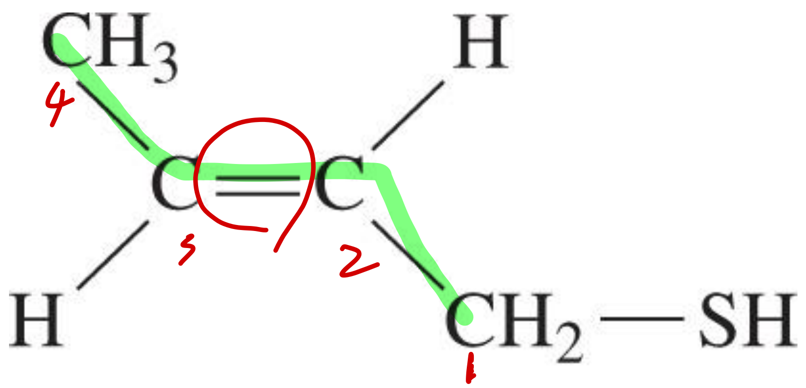


Thiols

Thiols

- contain sulfur
- contain a thiol (—SH) group
- often have strong and sometimes disagreeable odors
- are found in cheese, onions, garlic, and oysters
- are used to detect gas leaks

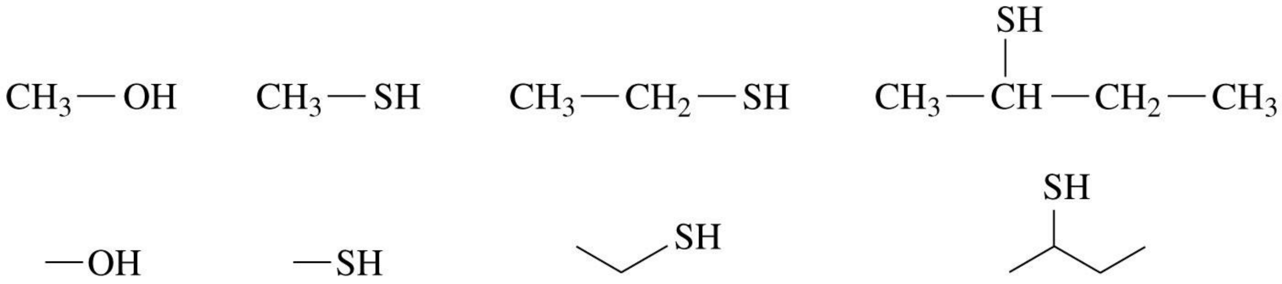
The spray of a skunk contains a mixture of thiols.



trans-2-Butene-1-thiol
(in skunk spray)

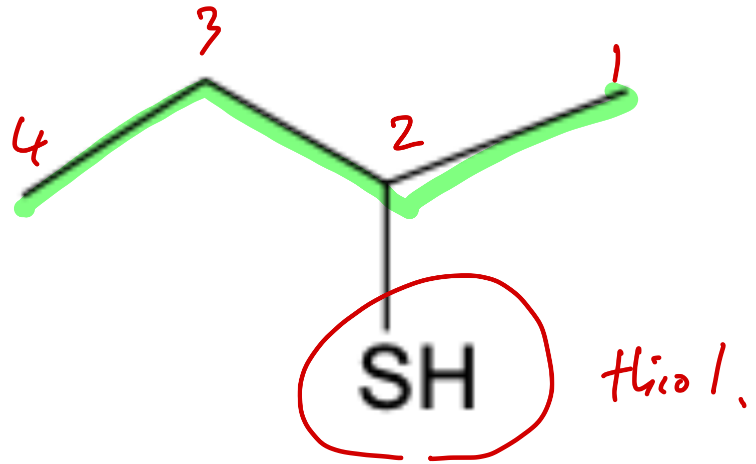
Naming Thiols

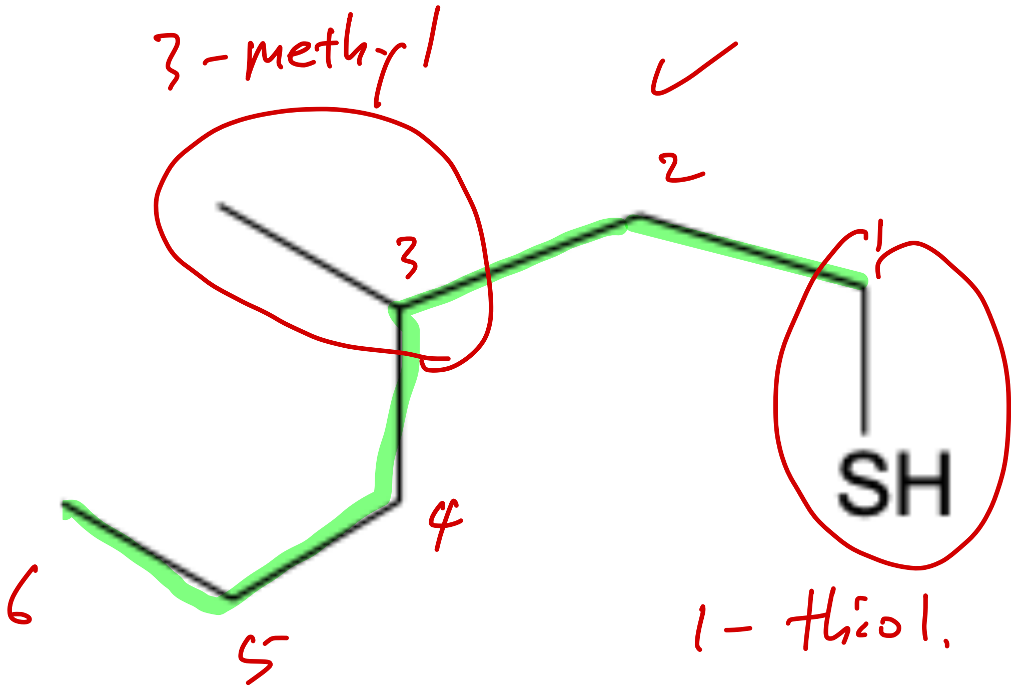
- In the IUPAC system, thiols are named by adding ***thiol*** to the alkane name of the longest carbon chain and numbering the carbon chain from the end nearer to the —SH group.
- Thiols are a family of sulfur-containing organic compounds that have a thiol group (—SH).



Methanol | Methanethiol | Ethanethiol | 2-Butanethiol

Give the IUPAC name for the following compounds:





2- butanethiol

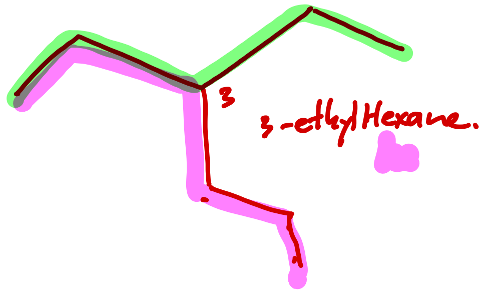
butane-2-thiol.

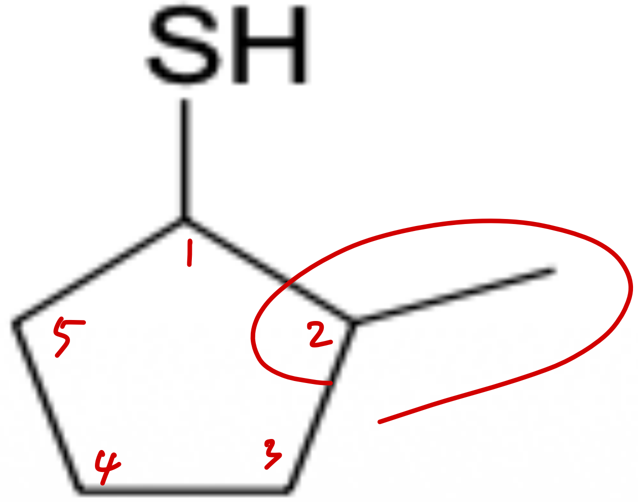
→ 3-methyl hexane-1-thiol

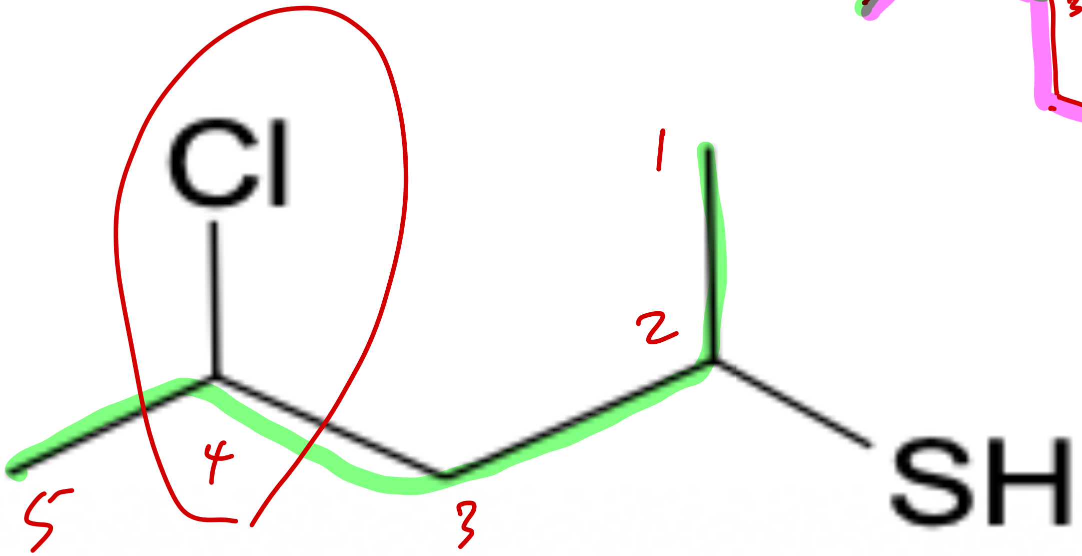
3-methyl-1-hexanethiol

Give the IUPAC name for the following compounds:

3-propyl- pentane.







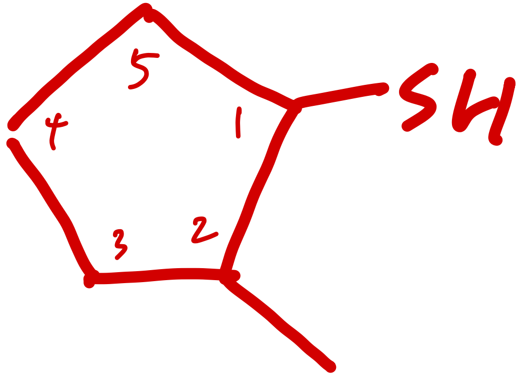
2- methyl Cyclopentane -1- thiol.

4-Chloro pentane -2- thiol

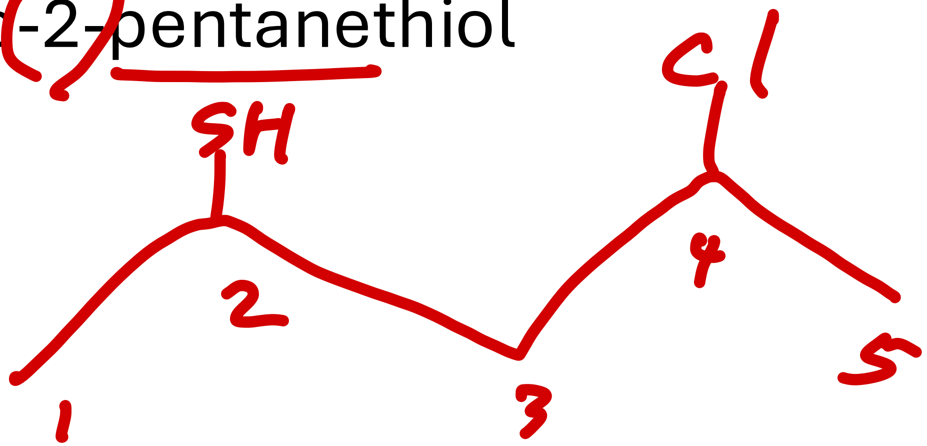
2-

Draw the structural formula of the following

- 2-Methylcyclopentanethiol



- 4-Chloro-2-pentanethiol



Oxidation of Thiols

losing H

When thiols undergo oxidation,

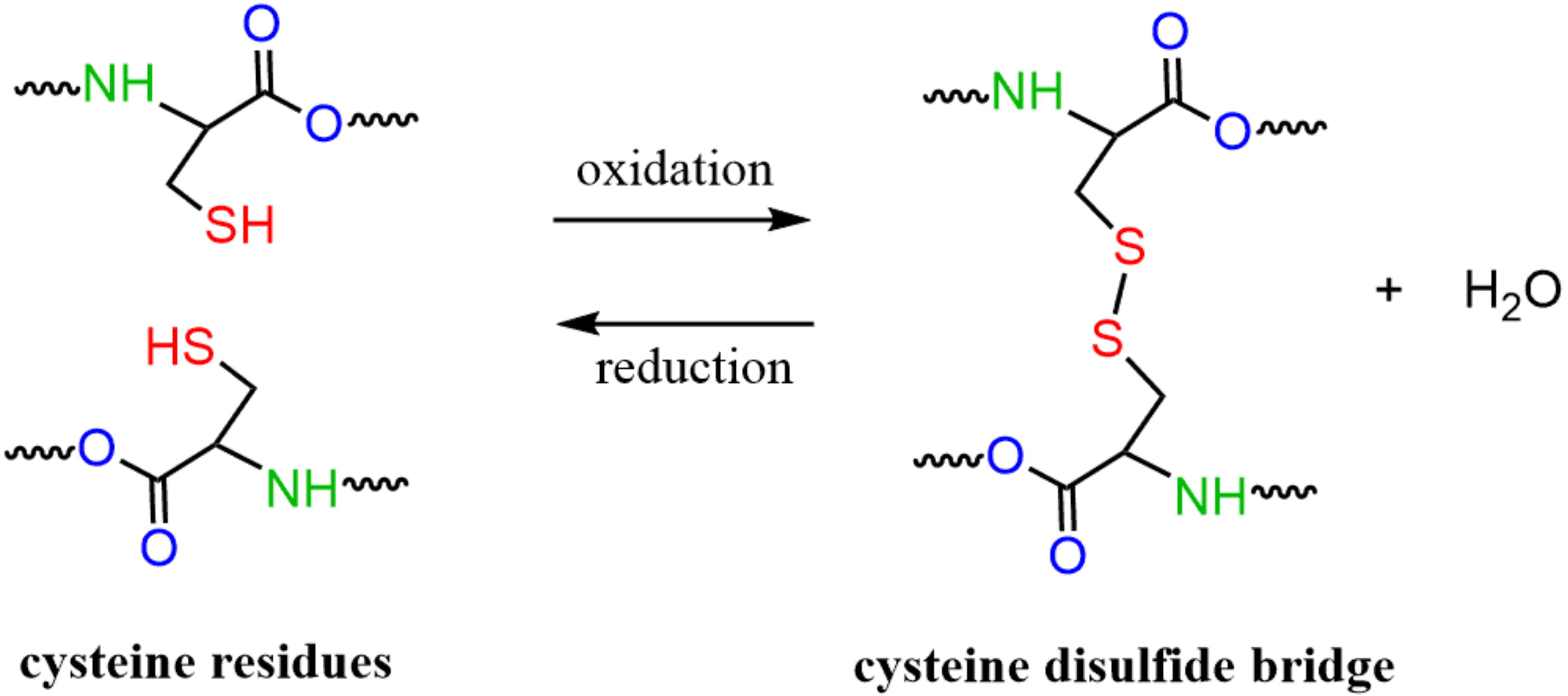
- an H atom is lost from each of two —SH groups
- the product is a **disulfide**
- protein in hair is cross-linked by disulfide bonds found in the amino acid cysteine

$$\text{Protein chain}-CH_2-\mathbf{SH} + \mathbf{HS}-CH_2-\text{Protein chain} \xrightarrow{[O]}$$

Cysteine side groups

$$\text{Protein chain}-CH_2-\mathbf{S}-\mathbf{S}-CH_2-\text{Protein chain} + \mathbf{H_2O}$$

Disulfide bond

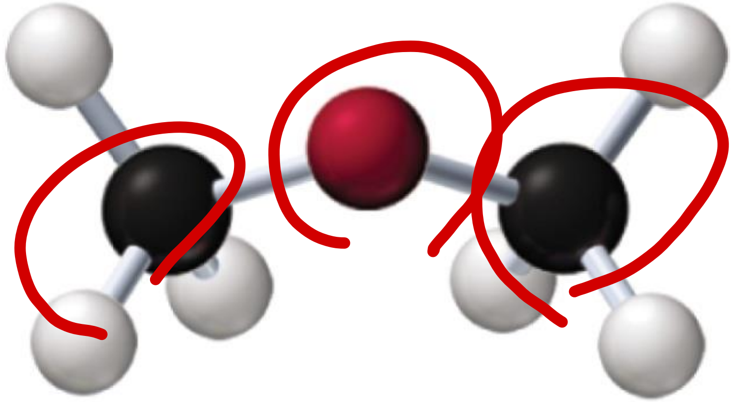


NH
O
O
SH
HS
O
NH
O
oxidation
reduction
NH
O
O
S
S
O
NH
O
+ H2O
cysteine residues
cysteine disulfide bridge

Ethers

An **ether**

- contains an —O— between two carbon groups that are alkyls or aromatic rings
- has a bent structure, like water and alcohols do
- has a common name that gives the alkyl names of the attached groups, followed by ***ether***



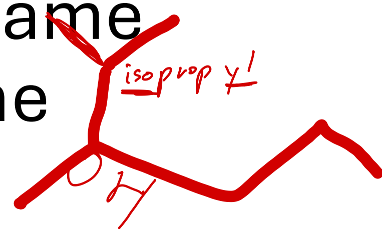
Dimethyl ether

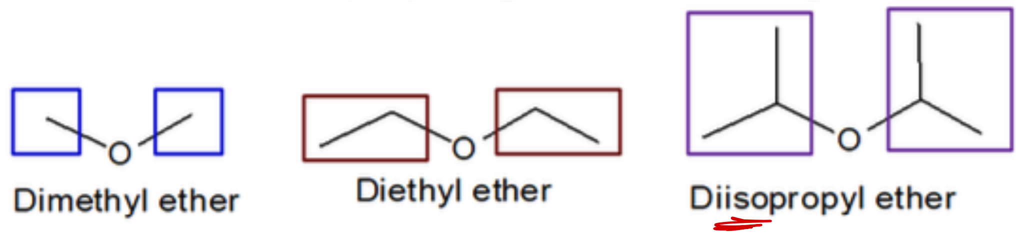
Naming Ethers

Most ethers have common names.

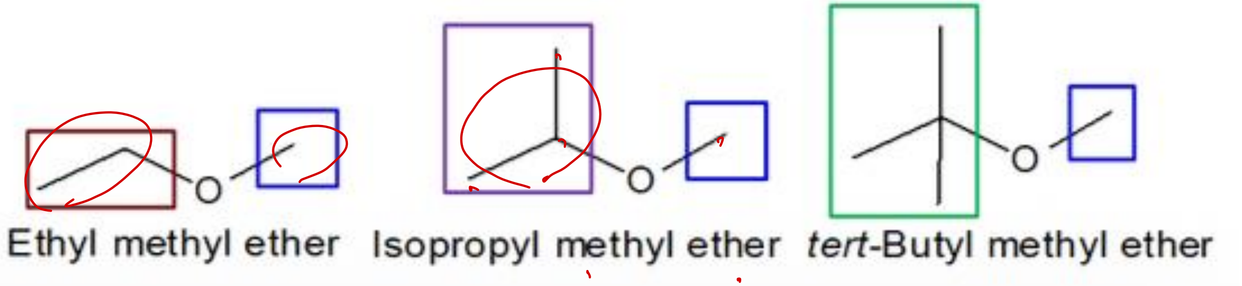
- The names
  - of each alkyl or aromatic group attached to the oxygen atom are written in alphabetical order
  - of the alkyl groups are followed by the word ***ether***

- For symmetrical ethers, name the alkyl group and add the prefix di.





- For unsymmetrical ethers,



More complex ethers are named using the IUPAC system

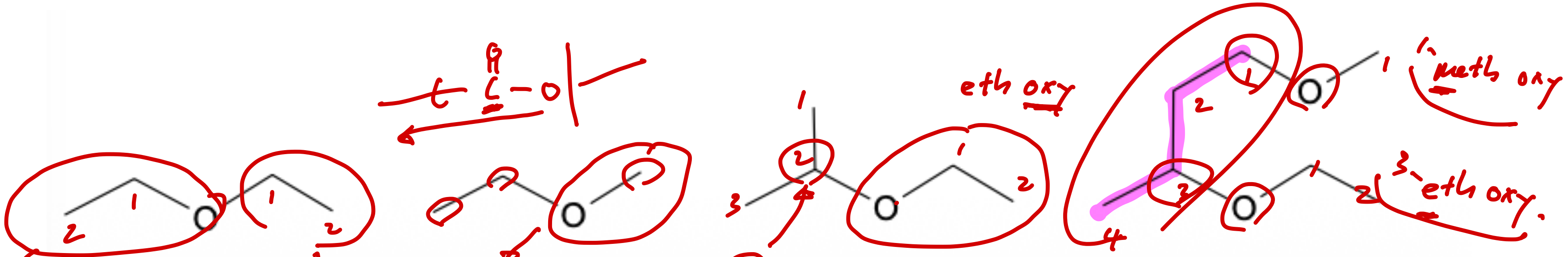
1. Find the two **alkyl groups** bonded to the ether oxygen.
2. The **smaller chain group** becomes the **substituent**, named as an **alkoxy group.**

CH_3O- **methoxy**

CH_3CH_2O- **ethoxy**

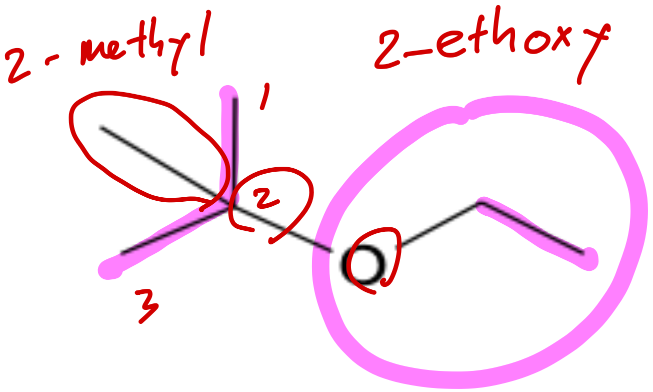
$CH_3CH_2CH_2O-$ **propoxy**

3. Number the other chain to give the **lower number** to the first substituent.

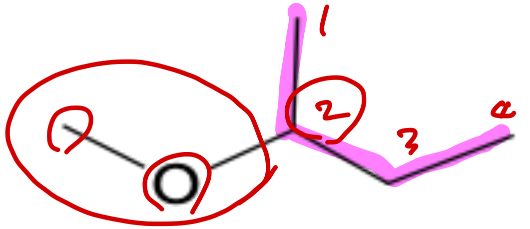


Ethoxyethane   Methoxyethane   2-Ethoxypropane   3-Ethoxy-1-methoxybutane

What is the IUPAC name for the following compound?



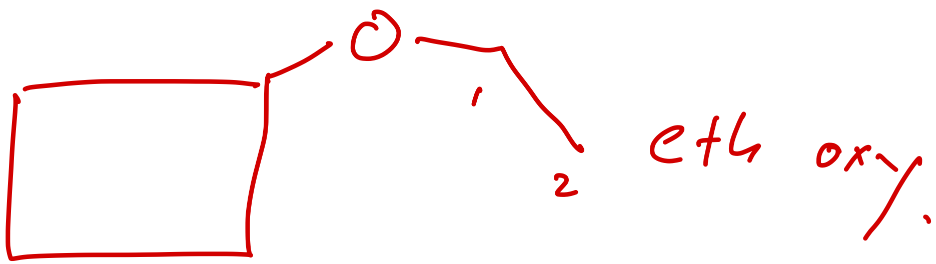
2 - ethoxy -2- methylpropane



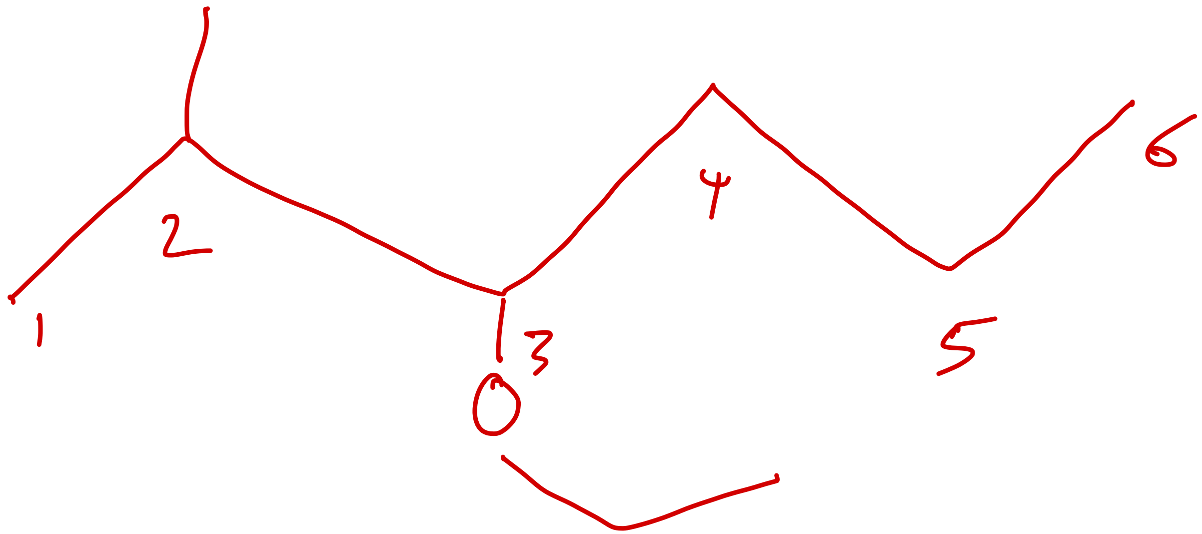
2- methoxy Butane

Draw the structural formula of the following

- Ethoxycyclobutane



- 3-Ethoxy-2-methylhexane



Stop Here

Aldehydes and Ketones: Carbonyl Group

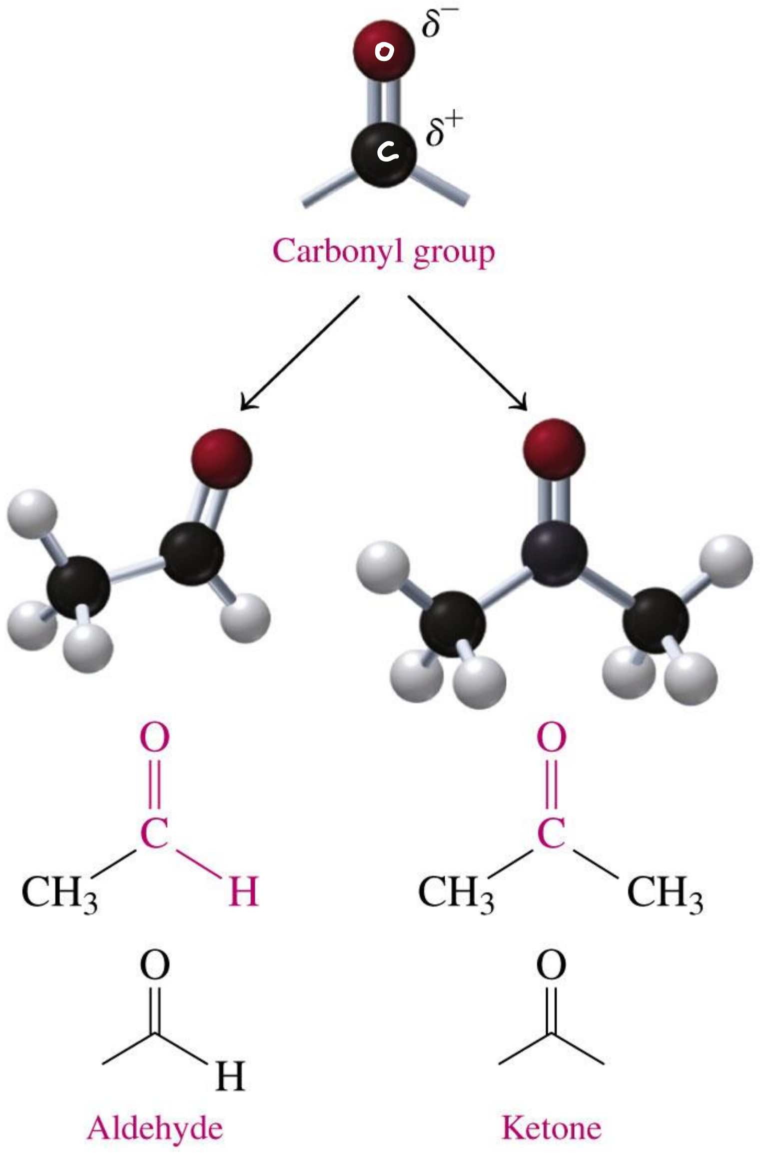
A carbonyl group

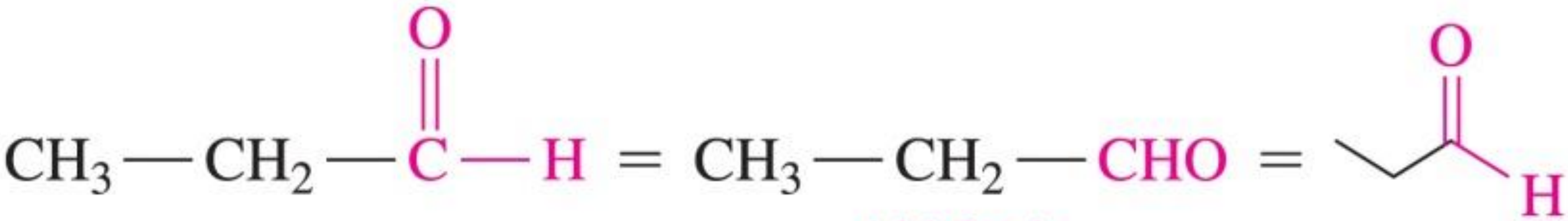
- consists of a carbon–oxygen polar double bond with two groups of atoms attached to the carbon
- has a very electronegative oxygen atom
- has two lone pair electrons on the O atom
- has a strong dipole with a partial positive charge on C and a partial negative charge on O

A carbonyl group in

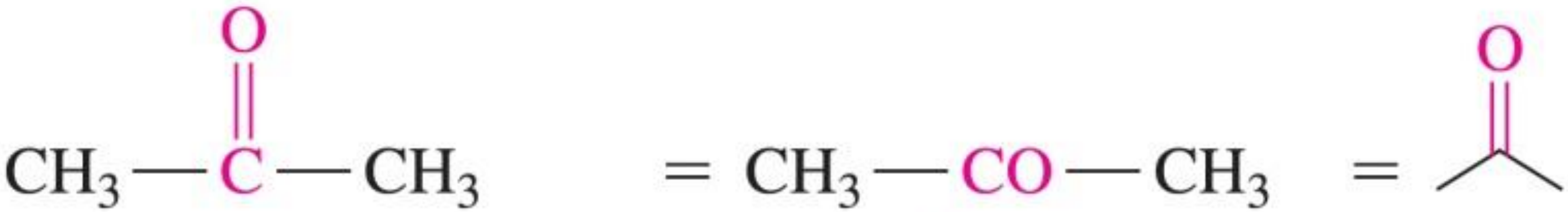
- an **aldehyde** is attached to a carbon atom and at least one H atom
  - An aldehyde group may be written as —CHO, with the double bond understood.

- a **ketone** is attached to two alkyl groups
  - In a ketone, the carbonyl group is bonded to two alkyl groups or aromatic rings. The keto group (C = O) can sometimes be written as CO.





Aldehyde



Ketone

Naming Aldehydes

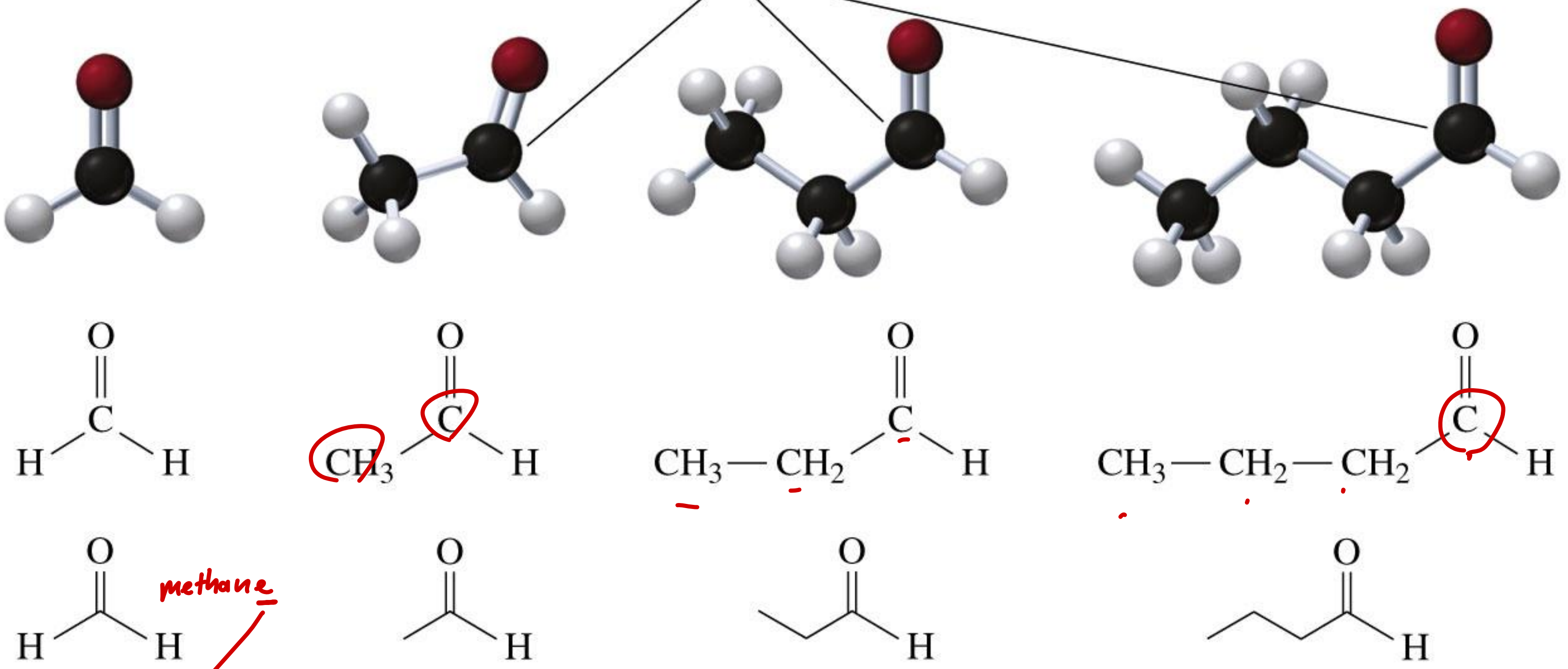
An aldehyde

- has an IUPAC name in which the ***e*** in the alkane name is changed to ***al***
- has a common name for the first four aldehydes that use their common names, which end in ***aldehyde***

one carbon, *form*	formaldehyde
two carbons, *acet*	acetaldehyde
three carbons, *propion*	propionaldehyde
four carbons, *butyr*	butyraldehyde

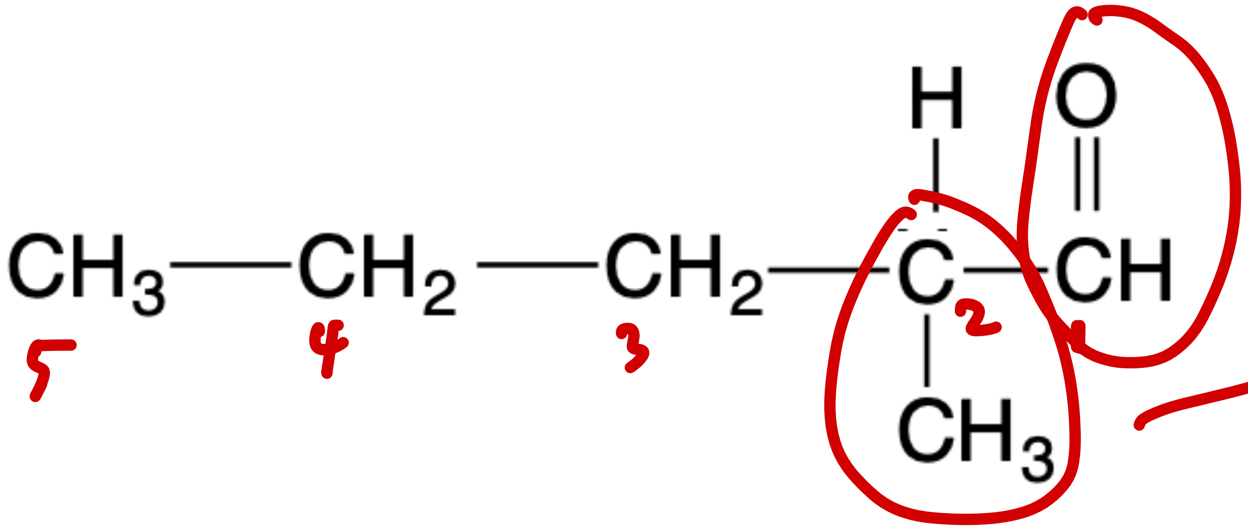
followed by *aldehyde*

The carbonyl carbon is at the end of the chain



IUPAC	Methanal	Ethanal	Propanal	Butanal
Common	(**form**aldehyde)	(**acet**aldehyde)	(**propion**aldehyde)	(**butyr**aldehyde)

Give the IUPAC name for the following aldehyde:

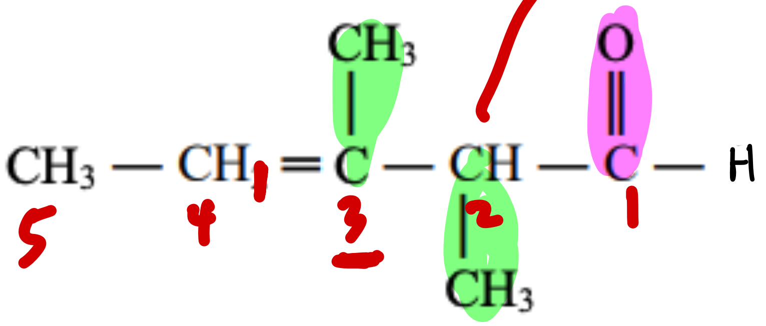


2- methyl

2-methyl pentanal

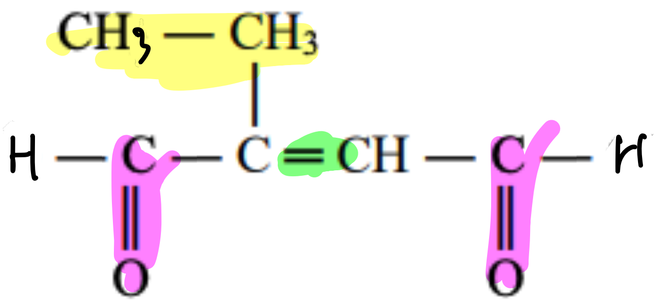
- Give the IUPAC name for the following aldehydes:

methyl



2,3 - dimethyl

3- pentenal



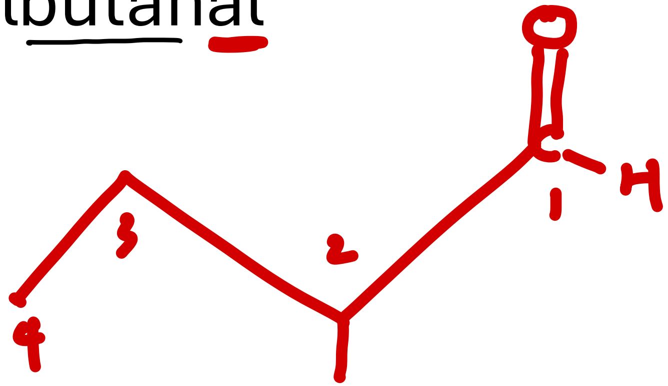
(1,4- buten di al)

2- buten -1,4 -dial

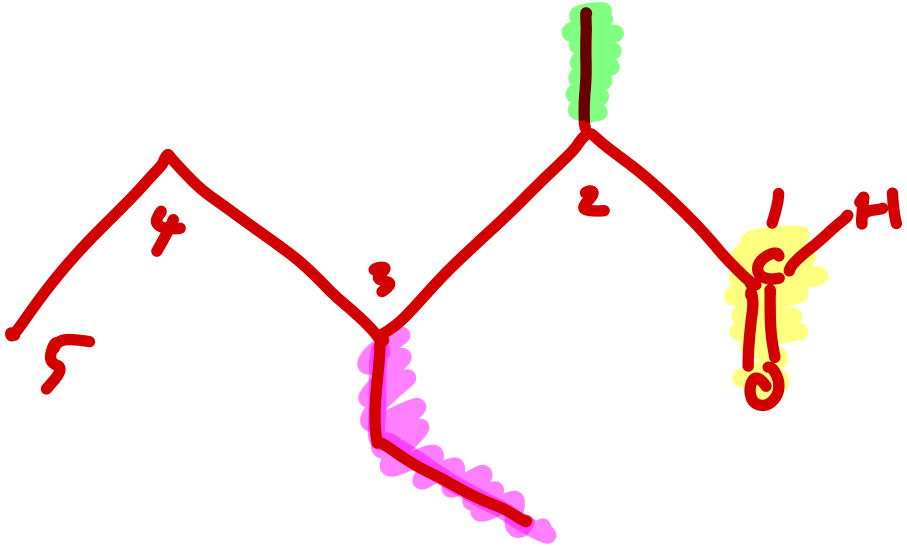
2 - ethyl - 2 - buten -1,4-dial.

Draw the following compounds.

- 2-Methylbutanal



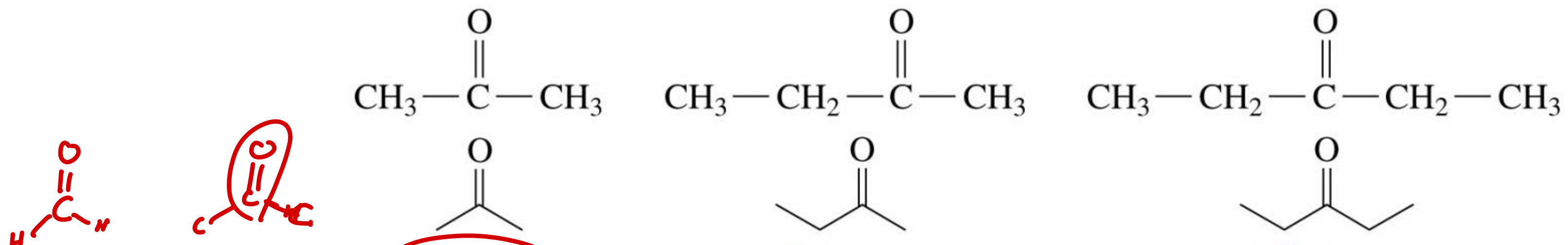
- 3-Ethyl-2-methylpentanal



Naming Ketones

When naming the following ketones

- in the IUPAC system, the ***e*** in the alkane name is replaced with ***one***
- with a common name, the alkyl groups attached to the carbonyl group are named alphabetically, followed by ***ketone***

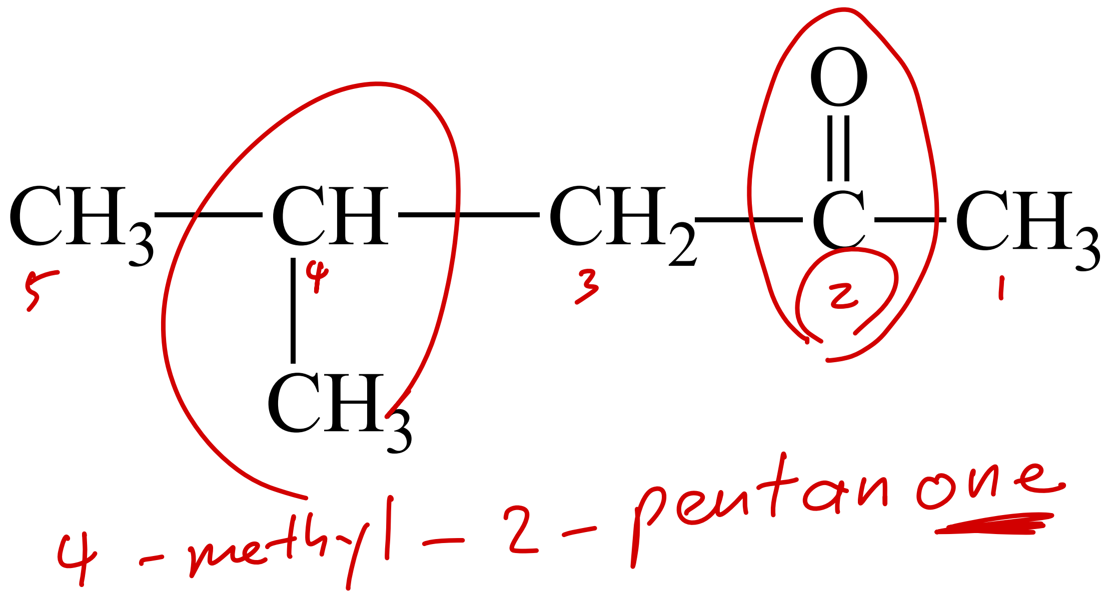


Propanone (dimethyl ketone; acetone)

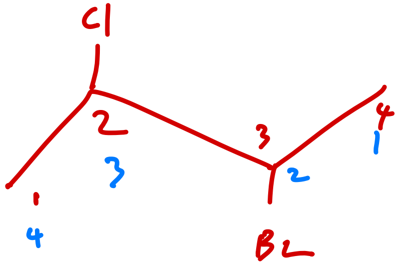
Butanone (ethyl methyl ketone)

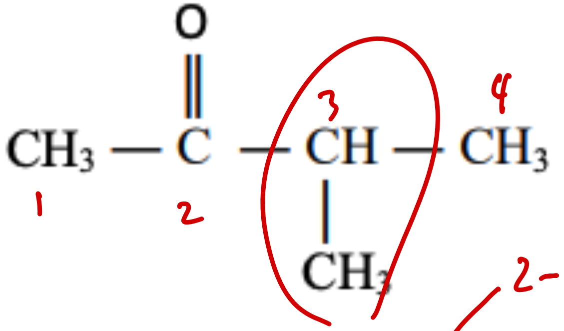
3-Pentanone (diethyl ketone)

Name the following ketone using the IUPAC system:

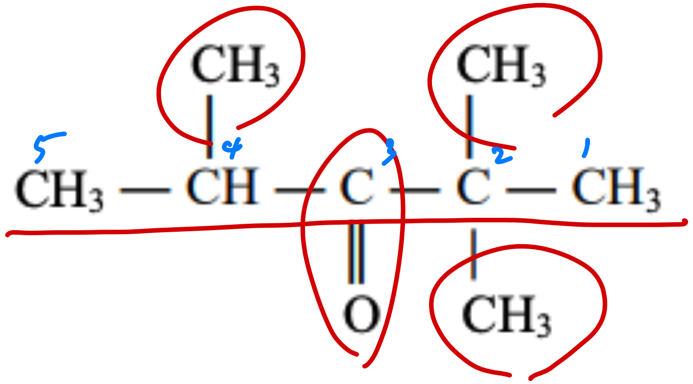


Name the following ketones using the IUPAC system:



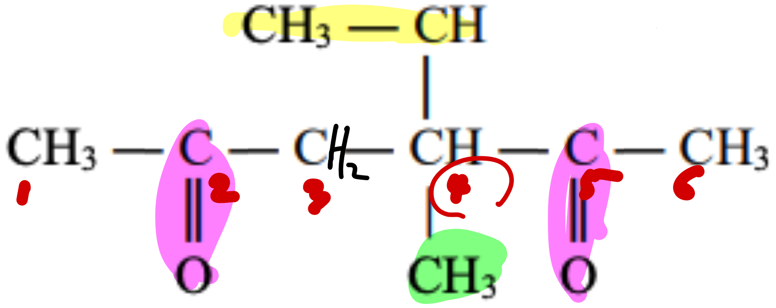


3-methyl 2-butanone



2,2,4-trimethyl-3-pentanone

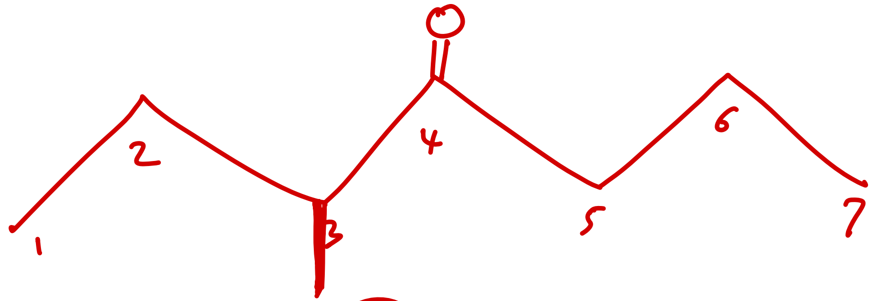
pentane-3-one.



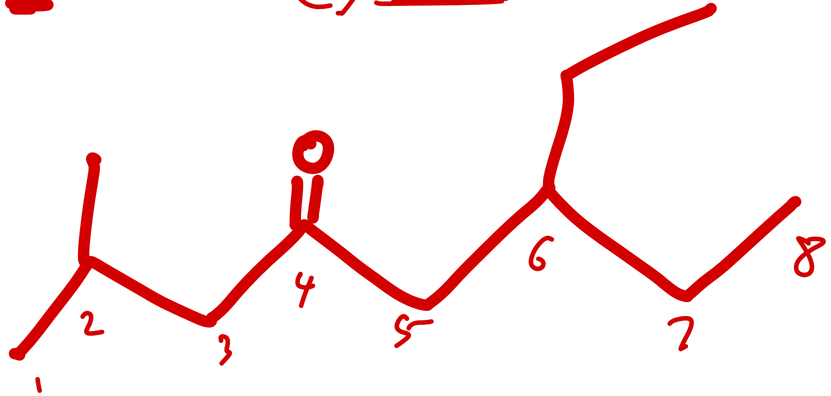
4-ethyl-4-methyl-Hexan-2,5-dione.

Draw the following compounds.

- 3-methyl-4-heptanone



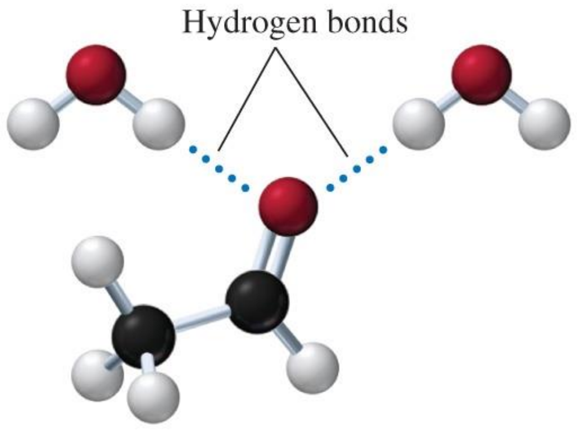
- 6-ethyl-2-methyl-4-octanone



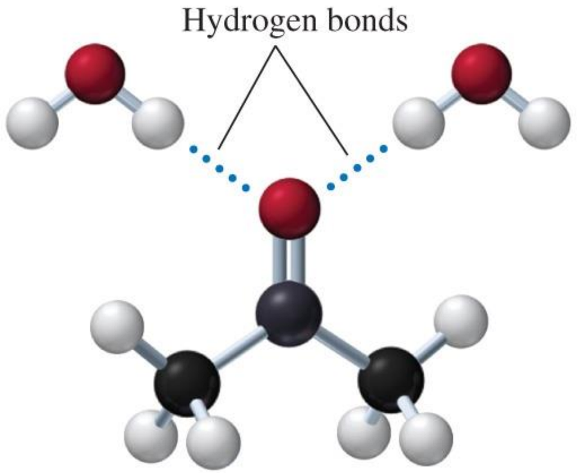
Aldehydes and Ketones in Water

Aldehydes and ketones

- form hydrogen bonds with water molecules between the carbonyl oxygen and hydrogen atoms on water molecules
- are **very soluble** when they have **four or fewer carbons** but not soluble when they have longer hydrocarbon chains, which are nonpolar, that diminish the solubility effect of the polar carbonyl group



Ethanal (acetaldehyde) in water



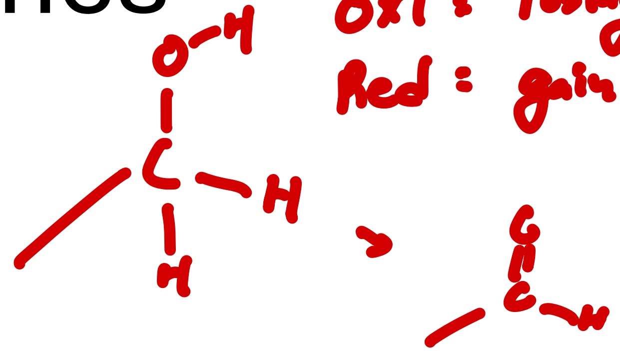
Propanone (acetone) in water

TABLE 12.2 Solubility of Selected Aldehydes and Ketones

Compound	Number of Carbon Atoms	Solubility in Water
Methanal (formaldehyde)	1	Soluble
Ethanal (acetaldehyde)	2	Soluble
Propanal (propionaldehyde)	3	Soluble
Propanone (acetone)	3	Soluble
Butanal (butyraldehyde)	4	Soluble
Butanone	4	Soluble
Pentanal	5	Slightly soluble
2-Pentanone	5	Slightly soluble
Hexanal	6	Insoluble
2-Hexanone	6	Insoluble

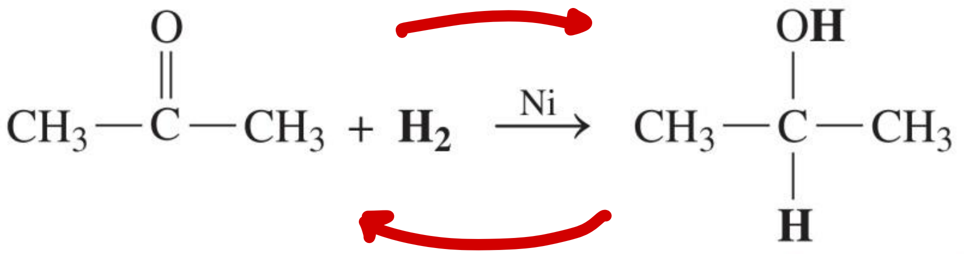
Reduction of Aldehydes and Ketones

oxi : losing e⁻
Red : gain e⁻



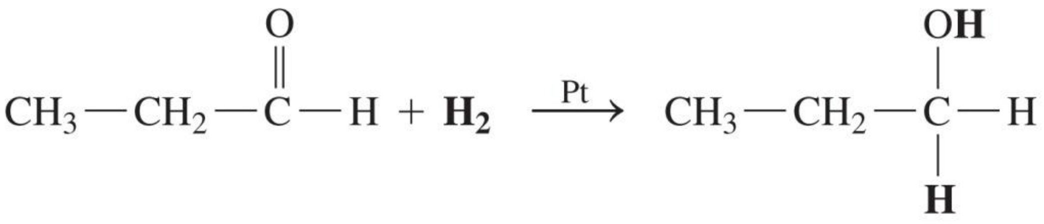
- Aldehydes reduce to form primary alcohols
- Ketones reduce to form secondary alcohols.
- A catalyst such as nickel, platinum, or palladium is needed for the addition of hydrogen to the carbonyl group.

Reduction



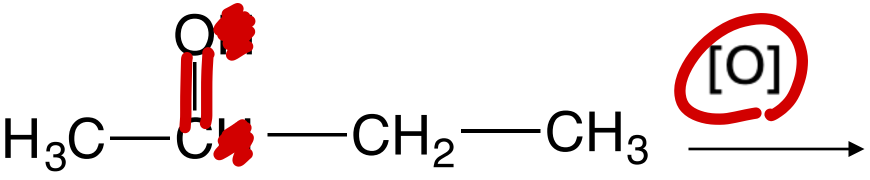
oxidation

Propanone (dimethyl ketone) → 2-Propanol (2° alcohol) (isopropyl alcohol)



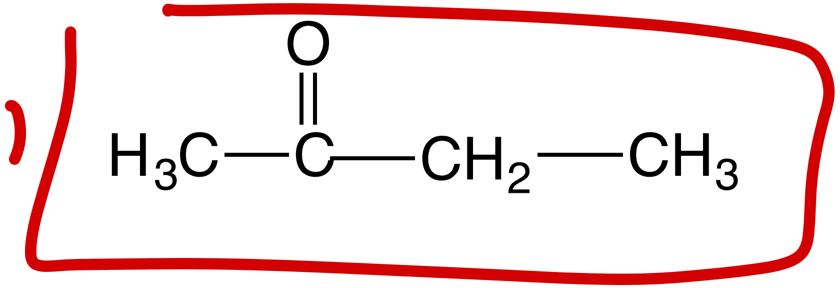
Propanal (propionaldehyde) → 1-Propanol (1° alcohol) (propyl alcohol)

Select the product for the oxidation of the following:

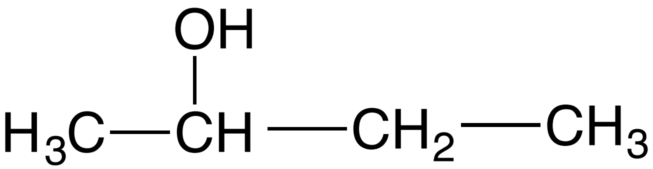


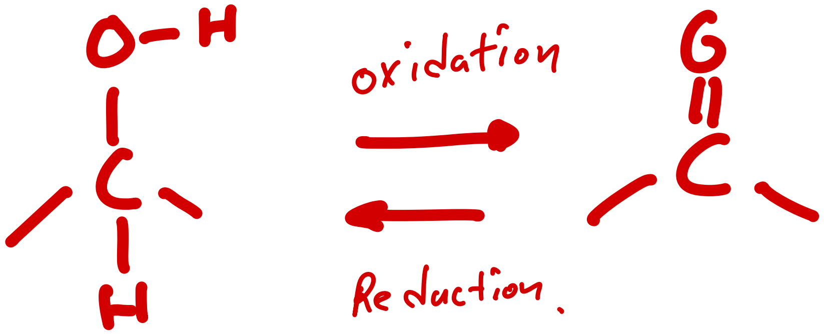
a) $H_3C-CH=CH-CH_3$

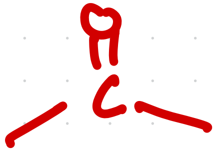
b)



c)





Alcohol	– OH	– ol
Thiol	– SH	– thiol
Ether	– O –	– oxy
Aldehyde		– al
Ketone		– one

butane - 1,4 - diol

butane diol.

(thiol) * don't drop "e" — ✓ butanethiol; ✗ butanthiol

we drop "e" to avoid double vowel.

like mono - oxide = monoxide

butane - ol (double vowel)

butane - thiol (not vowel)

pentanal