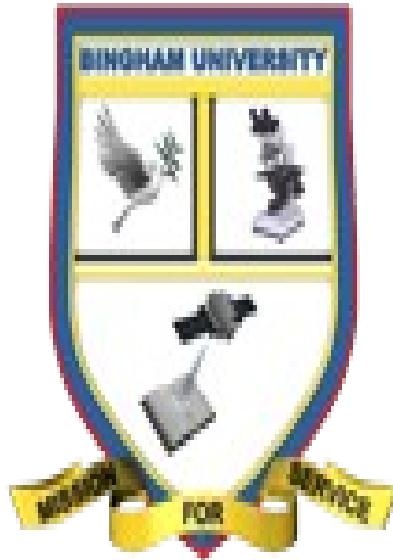




CHM 103: Organic Chemistry I

Presented by:

Assoc Prof Okoli BJ MRSC, MACS



Bingham University



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Department of Chemical Science,
Faculty of Science & Technology

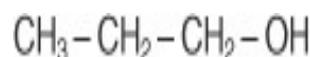


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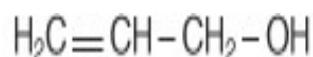


Alcohols

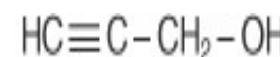
- Alcohols are hydroxy-substituted alkanes, alkenes, or alkynes in which the substitution occurs on a saturated carbon.
- The general formula for alcohols is $C_nH_{2n+1}OH$
E.g.



propanol



2-propenol



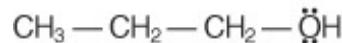
2-propynol

Nomenclature

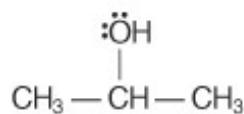
In the IUPAC system, use the following series of rules to name alcohols:

1. Pick out the longest continuous chain to which the hydroxyl group is directly attached. The parent name of the alcohol comes from the alkane name for the same chain length. Drop the -e ending and add -ol.
2. Number the parent chain so that the carbon bearing the hydroxyl group has the lowest possible number. Place the number in front of the parent name.
3. Locate and name substituents other than the hydroxyl group.

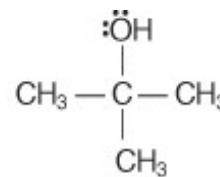
The following examples show how you apply these rules:



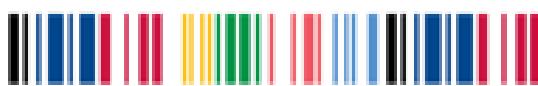
1-propanol



2-propanol



2-methyl-2-propanol

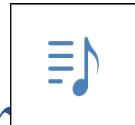
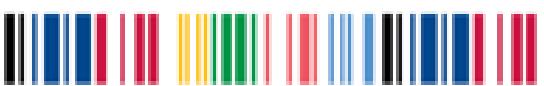


➤ Classification of alcohols

Depending on the location of the OH (hydroxyl or hydroxy) functional group, alkanols can be classified as one of the following:

- ❖ primary alcohols (1°)
- ❖ secondary alcohols (2°)
- ❖ tertiary alcohols (3°)

Classification	(${}^\circ$)	General Formula	Location of -OH group
Primary	1°	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	-OH on a terminal (end) carbon atom
Secondary	2°	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{R}' \end{array}$	-OH on a carbon atom is bonded to 2 other carbon atoms
Tertiary	3°	$\begin{array}{c} \text{R}'' \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{R}' \end{array}$	-OH on a carbon atom is bonded to 3 other carbon atoms



➤ The table below gives examples of primary, secondary and tertiary alkanols:

Classification	(°)	General Formula	Examples	
Primary	1°	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{H} \end{array}$	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\begin{array}{c} \text{H} \\ \\ \text{C}-\text{OH} \\ \\ \text{H} \end{array}$ butan-1-ol (or 1-butanol)	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\begin{array}{c} \text{H} \\ \\ \text{C}-\text{OH} \\ \\ \text{H} \end{array}$ pentan-1-ol (or 1-pentanol)
Secondary	2°	$\begin{array}{c} \text{H} \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{R}' \end{array}$	$\text{CH}_3-\text{CH}_2-\begin{array}{c} \text{H} \\ \\ \text{C} \\ \\ \text{CH}_3 \end{array}-\text{OH}$ butan-2-ol (or 2-butanol)	$\text{CH}_3-\text{CH}_2-\begin{array}{c} \text{HO} \\ \\ \text{C} \\ \\ \text{H} \end{array}-\text{CH}_2-\text{CH}_3$ pentan-3-ol (or 3-pentanol)
Tertiary	3°	$\begin{array}{c} \text{R}'' \\ \\ \text{R}-\text{C}-\text{OH} \\ \\ \text{R}' \end{array}$	$\text{CH}_3-\begin{array}{c} \text{CH}_3 \\ \\ \text{C} \\ \\ \text{CH}_3 \end{array}-\text{OH}$ 2-methylpropan-2-ol (or 2-methyl-2-propanol)	$\text{CH}_3-\text{CH}_2-\begin{array}{c} \text{OH} \\ \\ \text{C} \\ \\ \text{CH}_3 \end{array}-\text{CH}_2-\text{CH}_3$ 3-methylpentan-3-ol (or 3-methyl-3-pentanol)



Physical Properties of Alkanols

Alkanols are polar molecules. This effects their physical properties.

Boiling Point

Alkanols are polar molecules: $R-O^{\delta-}-H^{\delta+}$

where the carbon chain is represented by R and δ^- represents a partial negative charge on the oxygen atom and δ^+ represents a partial positive charge on the hydrogen atom attached to the oxygen atom of the alkanol.

Hydrogen bonding can therefore occur between the alkanol molecules as shown below:

$R-O^{\delta-}-H^{\delta+}$ where - represents a covalent bond between atoms within the molecule
and .. represents the hydrogen bond between molecules

.

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In order to boil an alkanol, enough energy must be supplied to break both

.

.

1. the stronger hydrogen bonds between the polar parts of the molecules and

.

2. the weaker intermolecular forces (london or dispersion forces) between the non-polar carbon (alkyl) chains (R).

$H^{\delta+}-O^{\delta-}-R$

The boiling points of some primary alkanols are given in the table below. Can you see a trend in the boiling points of these primary alkanols?

As the carbon chain gets longer (molecular mass increases) the boiling point increases.

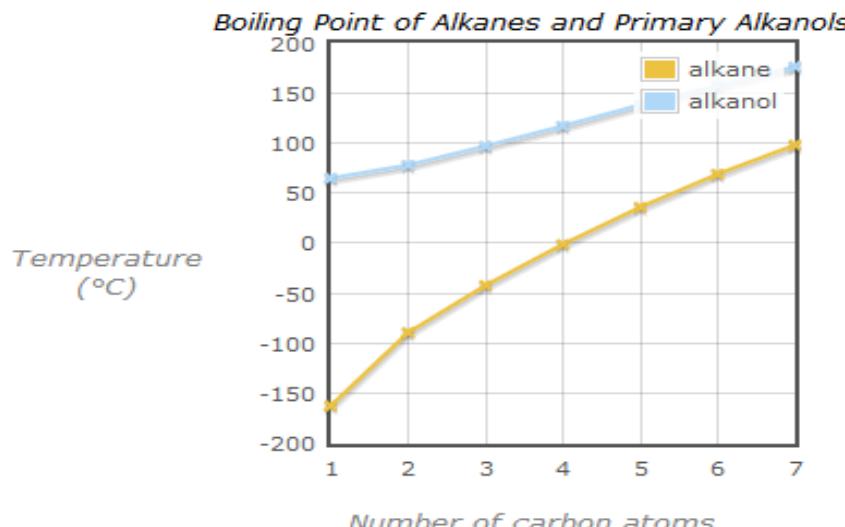
As the non-polar carbon chain length increases, the weak intermolecular forces (dispersion or london forces) holding the chains together weakly becomes increasingly significant so more energy is required to separate the molecules.

Compare the boiling point of each alkanol with the boiling point of its parent alkane as shown in the table below. Can you see a pattern, or trend, in the data?

number of carbon atoms in carbon chain	boiling point (°C)	
	alkane	alkan-1-ol
1	<i>meth</i>	-162 65
2	<i>eth</i>	-88.6 78
3	<i>prop</i>	-42.1 97
4	<i>but</i>	-0.5 117
5	<i>pent</i>	36.1 138



You can see the trend clearly if you graph the data as shown below:



The boiling point of an alkanol is higher than the boiling point of the corresponding alkane because the energy required to break the hydrogen bonds between alkanol molecules is greater than the energy required to break the weak intermolecular forces between alkane molecules.

Increasing the number of polar OH (hydroxyl or hydroxy) functional groups on alkanol molecules increases the boiling point of the alkanol as shown in the table below:

name	formula	boiling point ($^{\circ}\text{C}$)	name	formula	boiling point ($^{\circ}\text{C}$)
ethanol (ethyl alcohol)	$\text{CH}_3\text{-CH}_2\text{-OH}$	78	propan-1-ol (1-propanol)	$\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-OH}$	97
ethane-1,2-diol (1,2-ethanediol) (ethylene glycol)	$\text{HO-CH}_2\text{-CH}_2\text{-OH}$	197	propane-1,2,3-triol (1,2,3-propanetriol) (glycerol)	$\begin{matrix} \text{H} & \text{H} & \text{H} \\ & & \\ \text{HO-} & \text{C} - & \text{C} - & \text{C} - \text{OH} \\ & & \\ \text{H} & \text{OH} & \text{H} \end{matrix}$	290

Ethane-1,2-diol (1,2-ethanediol or ethylene glycol) has more OH (hydroxyl or hydroxy) functional groups than ethanol. More OH functional groups means that more hydrogen bonds can form between the molecules. Since hydrogen bonds are a stronger intermolecular force than the dispersion (london) forces that act between the non-chains, more energy will be required to separate molecules of ethane-1,2-diol than needed to separate molecules of ethanol. Ethane-1,2-diol has a higher boiling point than ethanol.



Similarly, propane-1,2,3-triol (1,2,3-propanetriol or glycerol) has 3 OH functional groups while propan-1-ol (1-propanol) has only 1 OH functional group.

More OH functional groups means that more hydrogen bonds can form between molecules of propane-1,2,3-triol than can form between molecules of propan-1-ol.
More energy will be required to separate molecules of propane-1,2,3-triol.
Propane-1,2,3-triol has a higher boiling point than propan-1-ol.

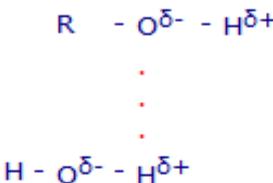
Solubility

The table below gives the solubility of some primary alkanols in water. Can you see a pattern, or trend, in the data?

Preferred IUPAC name (alternative IUPAC name)	formula	Solubility (g/100g water)	Trend
methanol	CH ₃ -OH	miscible	
ethanol	CH ₃ -CH ₂ -OH	miscible	
propan-1-ol (1-propanol)	CH ₃ -CH ₂ -CH ₂ -OH	miscible	
butan-1-ol (1-butanol)	CH ₃ -CH ₂ -CH ₂ -CH ₂ -OH	8	more soluble
pentan-1-ol (1-pentanol)	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -OH	2.3	↓
hexan-1-ol (1-hexanol)	CH ₃ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -CH ₂ -OH	0.6	less soluble

For short chain alkanols, the ability of these alkanols to form hydrogen bonds with the polar water molecules is responsible for them being soluble in water (miscible with water), as shown in the diagram below:

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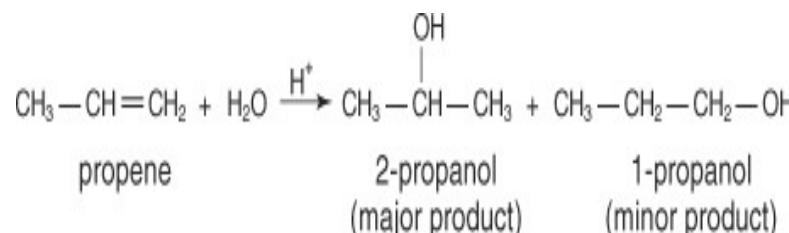
As the number of carbon atoms in the carbon (alkyl) chain increases however, the weak intermolecular forces (London or dispersion forces) acting between the non-polar alkyl chains become increasingly important.
Long non-polar alkyl chains are more attracted to each other than they are to the polar water molecules, so that the solubility of the alkanol molecules in water decreases.



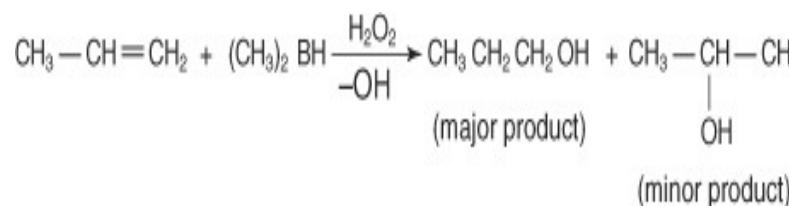
➤ Synthesis of Alcohols

1. *Hydration of alkenes*

The elements of water can be added to the double-bonded carbons of an alkene in either a Markovnikov's or an anti-Markovnikov's manner. As shown below, a hydrogen ion catalyzes the Markovnikov's addition.



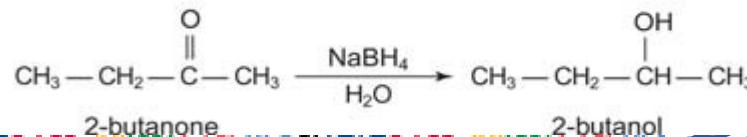
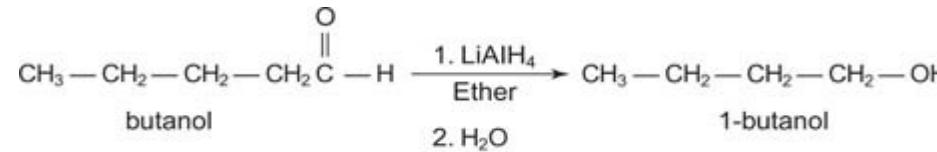
The anti-Markovnikov's addition results from a hydroboration-oxidation reaction



2. Reduction of aldehydes and ketones

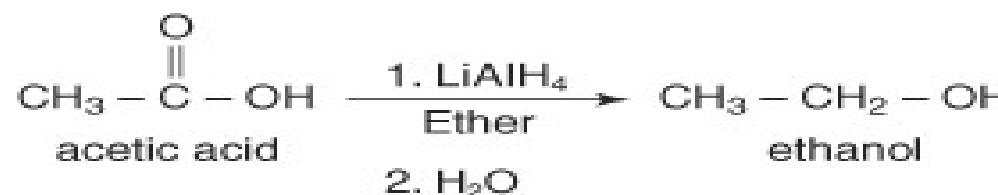
These types of compounds are best reduced by complex metal hydrides, such as lithium aluminum hydride (LiAlH_4) or sodium borohydride (NaBH_4).

Following are two examples of complex metal reductions:

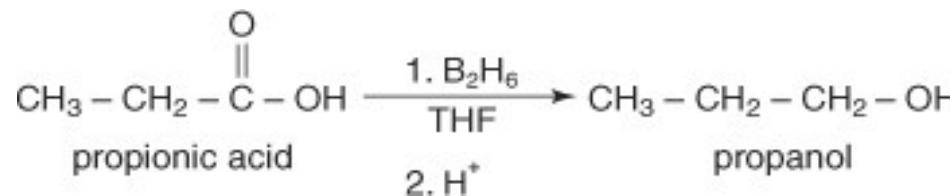


3. Reduction of carboxylic acids

The reduction of a carboxylic acid leads to the formation of a primary alcohol. This reduction requires a very strong reducing agent, and lithium aluminum hydride is the standard choice.

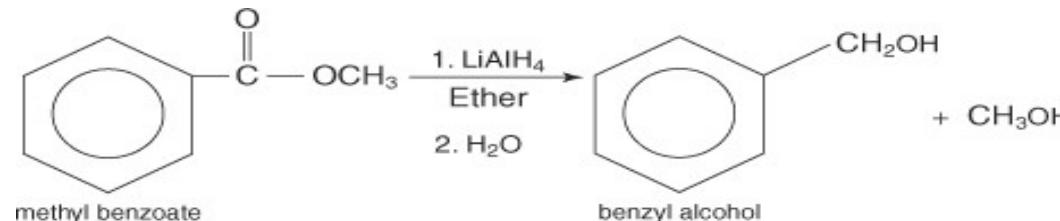


Diborane, B₂H₆, also reduces carboxylic acids to alcohols.



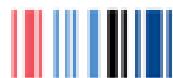
4. Reduction of esters

Esters, like carboxylic acids, are normally reduced with lithium aluminum hydride. In these reactions, two alcohols are formed. An example is the reduction of methyl benzoate to benzyl alcohol and methanol.

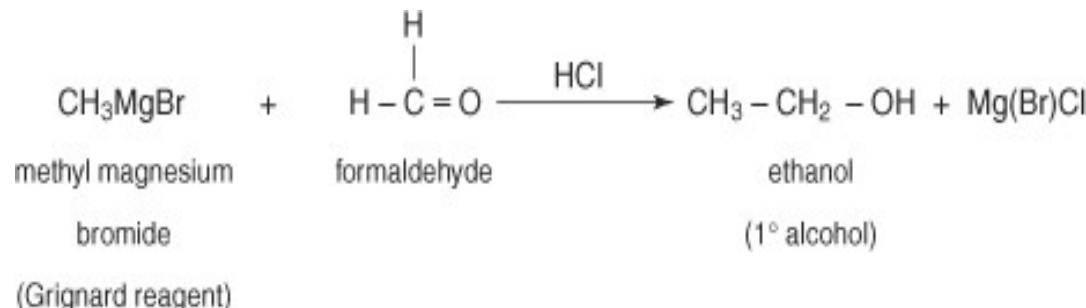


5. Grignard reaction with aldehydes and ketones

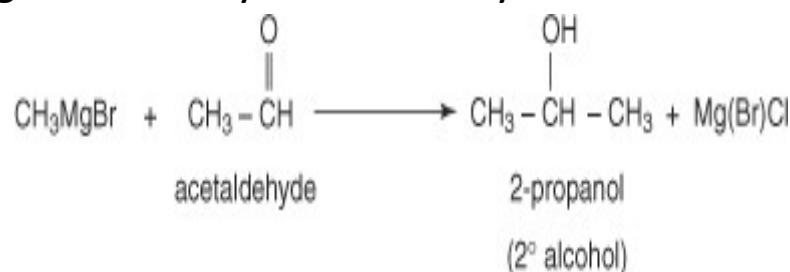
The Grignard reaction is the only simple method available that is capable of producing primary, secondary, and tertiary alcohols.



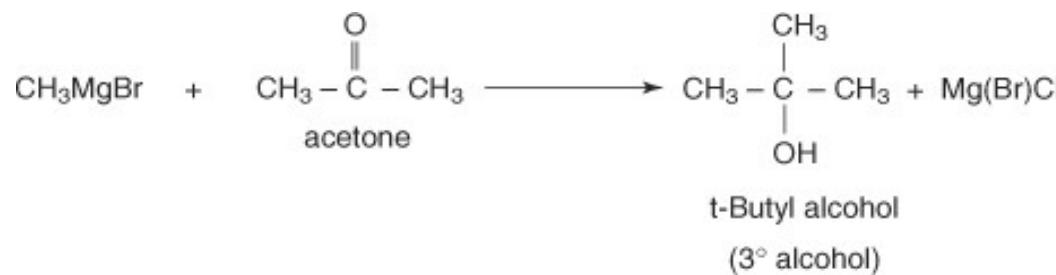
To produce a primary alcohol, the Grignard reagent is reacted with formaldehyde.



Reacting a Grignard reagent with any other aldehyde will lead to a secondary alcohol.



Finally, reacting a Grignard reagent with a ketone will generate a tertiary alcohol.



➤ Reactions of Alcohols

1. Metal salt formation

Alcohols are only slightly weaker acids than water, with a K_a value of approximately 1×10^{-16} . The reaction of ethanol with sodium metal (a base) produces sodium ethoxide and hydrogen gas.



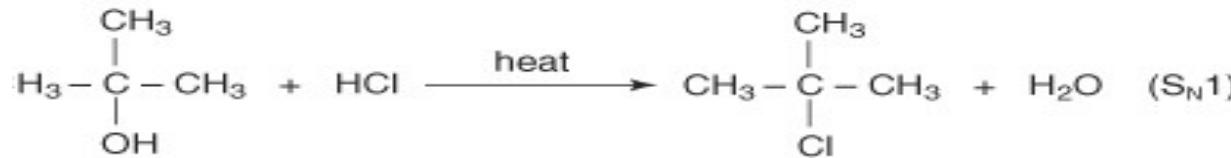
The acidity of alcohols decreases while going from primary to secondary to tertiary. This decrease in acidity is due to two factors:

- an increase of electron density on the oxygen atom of the more highly-substituted alcohol, and
- steric hindrance (because of the alkyl groups, which inhibit solvation of the resulting alkoxide ion).

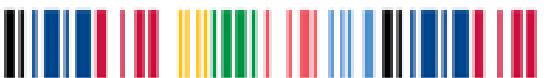
Both of these situations increase the activation energy for proton removal.

2. Alkyl halide formation

Alcohols are converted to alkyl halides by S N1 and S N2 reactions with halogen acids.



Primary alcohols favour S N2 substitutions while S N1 substitutions occur mainly with tertiary alcohols.



A more efficient method of preparing alkyl halides from alcohols involves reactions with thionyl chloride (SOCl_2).

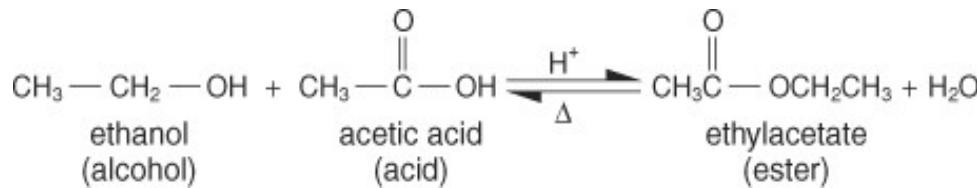


Because thionyl bromide is relatively unstable, alkyl bromides are normally prepared by reacting the alcohol with phosphorous tribromide (PBr_3).

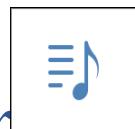
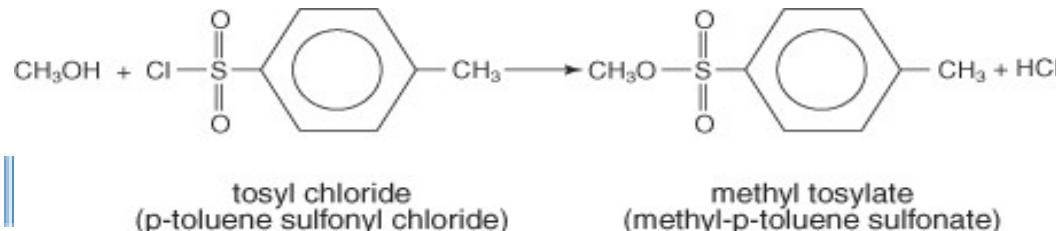


3. *Ester formation*

Esters are compounds that are commonly formed by the reaction of oxygen-containing acids with alcohols. Alcohols can be converted to esters by means of **the Fischer Esterification Process.**

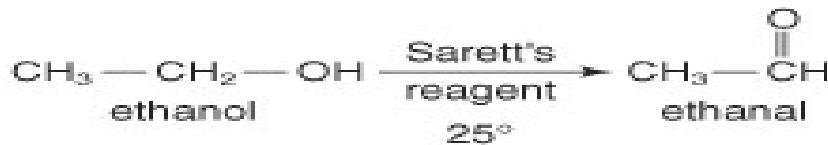


4. **Alkyl sulfonate formation.** Alcohols may be converted to alkyl sulfonates, which are sulfonic acid esters. These esters are formed by reacting an alcohol with an appropriate sulfonic acid. For example, methyl tosylate, a typical sulfonate, is formed by reacting methyl alcohol with tosyl chloride.

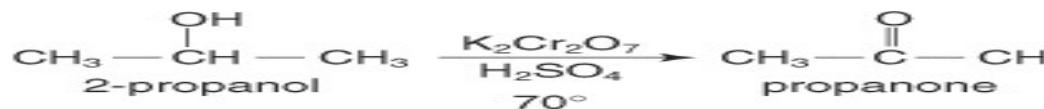


5. Formation of aldehydes and ketones: The oxidation of alcohols can lead to the formation of aldehydes and ketones. Aldehydes are formed from primary alcohols, while ketones are formed from secondary alcohols.

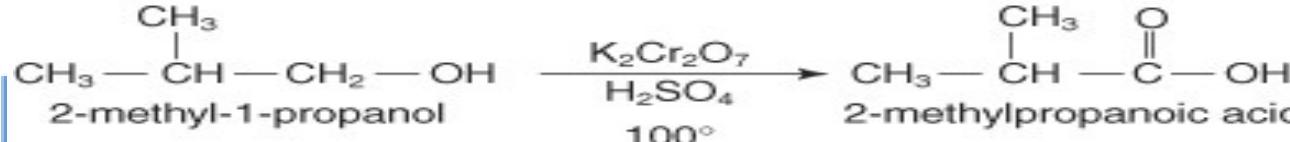
Because you can easily further oxidize aldehydes to carboxylic acids, you can only employ mild oxidizing agents and conditions in the formation of aldehydes. Typical mild oxidizing agents include manganese dioxide (MnO_2), Sarett-Collins reagent ($\text{CrO}_3 - (\text{C}_5\text{H}_5\text{N}_2)$), and pyridinium chlorochromate (PCC).



Because ketones are more resistant to further oxidation than aldehydes, we may employ stronger oxidizing agents and higher temperatures. Secondary alcohols are normally converted to ketones by reaction with potassium dichromate ($K_2Cr_2O_7$), potassium permanganate ($KMnO_4$), or chromium trioxide in acetic acid (CrO_3/CH_3COOH).



6. Carboxylic acid formation: Upon oxidation with strong oxidizing agents and high temperatures, primary alcohols completely oxidize to form carboxylic acids. The common oxidizing agents used for these conversions are concentrated potassium permanganate or concentrated potassium dichromate.





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