Introduction to Organic Chemistry
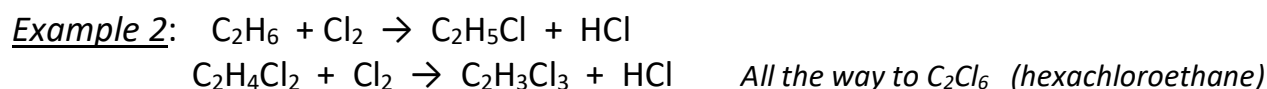## Part Two: Reactions of Organic Compounds

This part is composed of some reactions of hydrocarbons and some reactions of organic compounds that contain other functional groups as explained below.

I. Reactions of Hydrocarbons:

A. Substitution Reactions
Alkanes are the least reactive among all organic compounds. They do not usually react with strong acids or bases, or with most oxidizing or reducing agents. However, they undergo substitution reactions. Such reactions require highly reactive reagents, such as chlorine and fluorine. In the case of chlorination, one of the chlorine atoms replaces a hydrogen atom.

Example 1: $CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$
$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$ *All the way to CCl_4 (carbon tetrachloride)*

Example 2: $C_2H_6 + Cl_2 \rightarrow C_2H_5Cl + HCl$
$C_2H_4Cl_2 + Cl_2 \rightarrow C_2H_3Cl_3 + HCl$ *All the way to C_2Cl_6 (hexachloroethane)*

B. Combustion Reactions
Hydrocarbons burn very easily releasing great amounts of energy. They are the main source of all types of energy. Heat is produced upon their direct combustion. This heat would be used directly, or used to produce electricity, which is used in various ways in our life.
Hydrocarbons produce water, carbon dioxide and heat energy upon combustion. Oxygen is required for combustion to take place. The simplest hydrocarbon, methane (alkane), burns as follows:
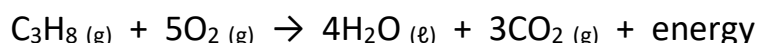
$$CH_{4\ (g)} + 2O_{2\ (g)} \rightarrow 2H_2O_{\ (\ell)} + CO_{2\ (g)} + energy$$
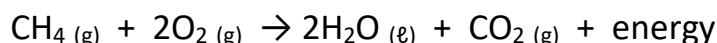
When oxygen is not sufficient, gaseous carbon monoxide and water are produced.

$$2CH_{4\ (g)} + 3O_{2\ (g)} \rightarrow 4H_2O_{\ (\ell)} + 2CO_{(g)} + energy$$
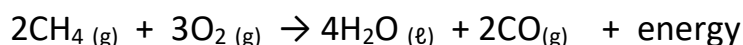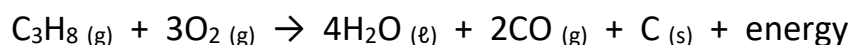
Sometimes carbon is produced upon combustion depending on the available amount of oxygen.
Another example is the combustion of propane:

$$C_3H_{8\ (g)} + 5O_{2\ (g)} \rightarrow 4H_2O_{\ (\ell)} + 3CO_{2\ (g)} + energy$$

When combustion reaction of alkanes happens with insufficient amount of oxygen, carbon monoxide and water are produced, also, elemental carbon may also produced.
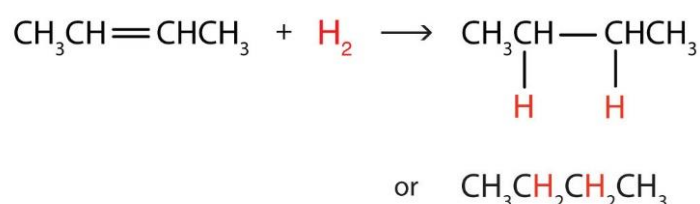
$$C_3H_{8\ (g)} + 3O_{2\ (g)} \rightarrow 4H_2O_{\ (\ell)} + 2CO_{\ (g)} + C_{\ (s)} + energy$$

Unsaturated hydrocarbons, burn to produce a yellow, soothy flame due to incomplete combustion in air. The flame is sooty because the percentage of carbon is comparatively higher than that in alkanes and so is not get completely oxidized in air.
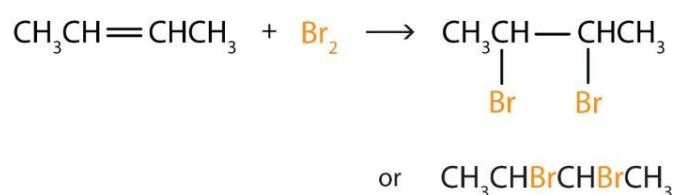
C. Addition Reactions

Addition reactions apply to <u>unsaturated</u> hydrocarbons, alkenes and alkynes. In this reaction, both parts of a reactant are added to the carbon-carbon double bond. A variety of reagents add to the double or triple bonds. Hydrogen (H_2), halogen (Br_2), water, hydrogen halides may add to unsaturated hydrocarbons. Examples in which alkanes, alkyl halides and alcohols are produced as shown below:
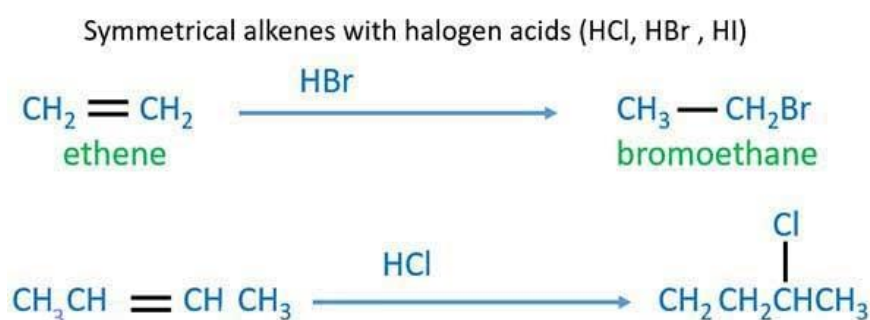
A. <u>Hydrogenation</u> to form <u>alkanes</u>: This reaction happens in presence of catalyst like platinum (Pt).
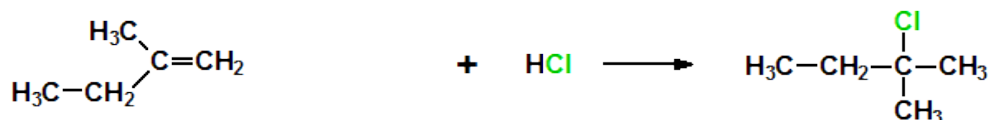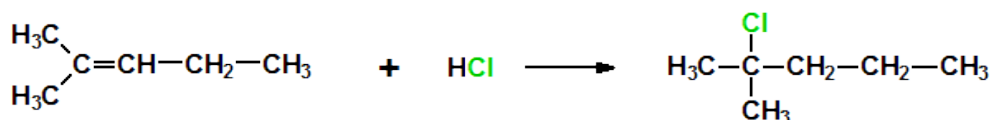
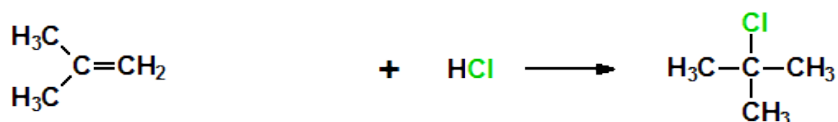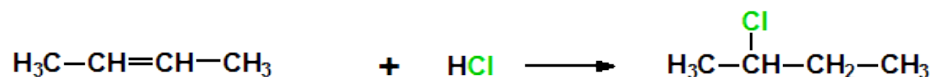$$CH_3CH=CHCH_3 \ + \ H_2 \ \longrightarrow \ CH_3CH\underset{H}{-}CH\underset{H}{-}CHCH_3$$

$$\text{or} \quad CH_3CH_2CH_2CH_3$$

B. <u>Halogenation</u> to form <u>alkyl halide</u>:

$$CH_3CH=CHCH_3 \ + \ Br_2 \ \longrightarrow \ CH_3CH\underset{Br}{-}CH\underset{Br}{-}CHCH_3$$

$$\text{or} \quad CH_3CHBrCHBrCH_3$$

C. <u>Addition of a halogen acid</u> (HF, HCl, HBr, HI) to produce <u>alkyl halide</u>:

Symmetrical alkenes with halogen acids (HCl, HBr , HI)

$$CH_2=CH_2 \ \xrightarrow{\ HBr\ } \ CH_3-CH_2Br$$
ethene ⟶ bromoethane

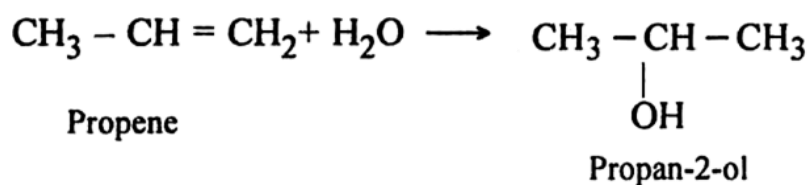$$CH_3CH=CH\,CH_3 \ \xrightarrow{\ HCl\ } \ CH_2\,CH_2\underset{Cl}{C}HCH_3$$

If the alkene is unsymmetrical there are two possible products. The major product is predicted according to Markonikov's rule (Markonikov's addition). <u>Hydrogen goes to the carbon that is richer in hydrogen.</u>

$$CH_3—CH{=}CH_2 \ + \ HCl \ \longrightarrow \ CH_3–\underset{\underset{Cl}{|}}{CH}–CH_2{-}H \qquad CH_3{-}\underset{\underset{H}{|}}{\overset{\overset{Cl}{|}}{C\!\!\!\!/H}}–CH_2$$

$$CH_2{=}\overset{\overset{Cl}{|}}{CH} \ + \ HBr \ \longrightarrow \ H–CH_2–\underset{\underset{Br}{|}}{CH} \qquad Br{-}\overset{\overset{Cl}{|}}{C\!\!\!\!/H_2}–\underset{\underset{H}{|}}{CH}$$

$$H_3C–CH{=}CH–CH_3 \qquad + \quad HCl \quad \longrightarrow \quad H_3C–\underset{\underset{Cl}{|}}{CH}–CH_2–CH_3$$

$$\underset{H_3C}{\overset{H_3C}{>}}C{=}CH_2 \qquad + \quad HCl \quad \longrightarrow \quad H_3C–\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}–CH_3$$

$$\underset{H_3C}{\overset{H_3C}{>}}C{=}CH–CH_2–CH_3 \qquad + \quad HCl \quad \longrightarrow \quad H_3C–\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}–CH_2–CH_2–CH_3$$

$$\underset{H_3C–CH_2}{\overset{H_3C}{>}}C{=}CH_2 \qquad + \quad HCl \quad \longrightarrow \quad H_3C–CH_2–\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}–CH_3$$
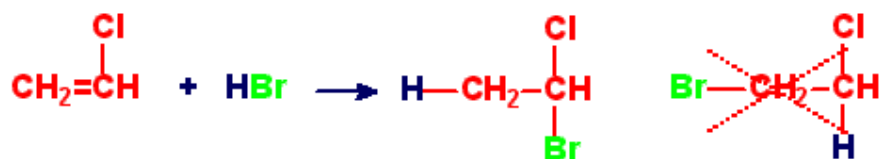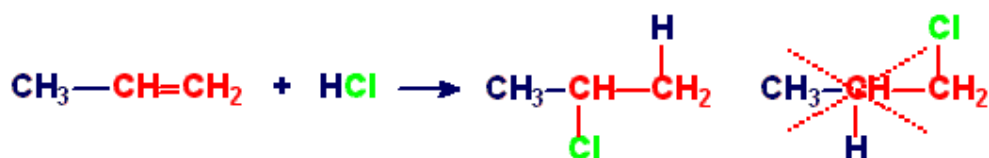
D. Hydration reaction (Addition of water) to produce alcohol. This reaction requires the presence of a strong acid catalyst (usually H_2SO_4). This reaction also follows Markonikov's Rule.

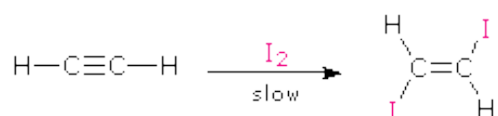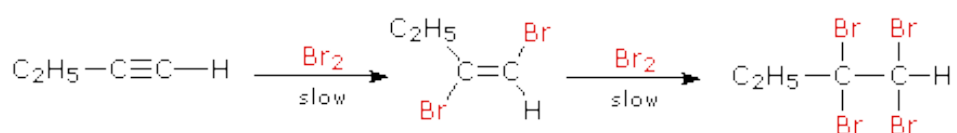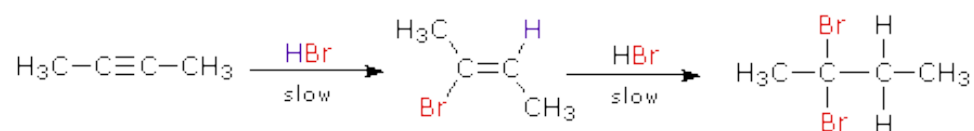$$CH_3CH{=}CHCH_3 \ + \ H_2O \ \longrightarrow \ CH_3CH\underset{\underset{H}{|}}{-}\underset{\underset{OH}{|}}{CH}CH_3$$
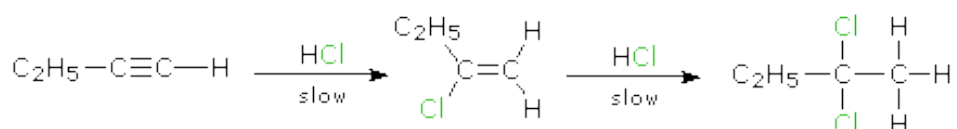
or $\quad CH_3CH_2CHOHCH_3$
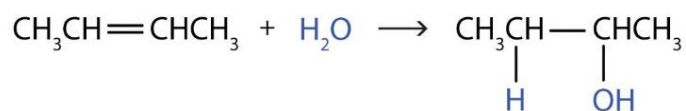
Unsymmetrical addition: (Markonikov's Rule)

$$CH_3 – CH = CH_2 + H_2O \ \longrightarrow \ CH_3 – \underset{\underset{OH}{|}}{CH} – CH_3$$

Propene $\qquad\qquad\qquad$ Propan-2-ol

Reactions of Alkynes

> ### Reactions of <u>Alkynes</u>:
> ### Anything an alkene does, an alkyne does twice

$$CH_3-CH_2-C\equiv CH + HCl \longrightarrow CH_3CH_2\underset{\underset{Cl}{|}}{C}=CH_2$$

HCl

$H_3C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-C\equiv CH$ + $2Cl_2$ ⟶ $H_3C-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{CH}}$

1-butyne

$H_3C-C\equiv C-CH_3$ + $2Cl_2$ ⟶ $H_3C-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-CH_3$

2-butyne
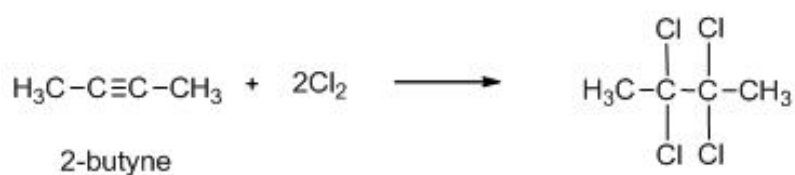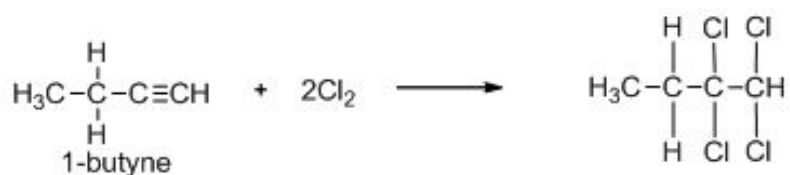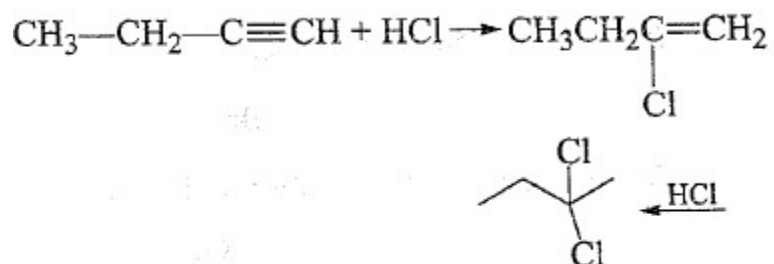
Reactions of Aromatic Hydrocarbons:

The major reaction of aromatic hydrocarbons is <u>substitution</u> reaction in which a hydrogen is replaced by another group. A famous example on that is the <u>nitration</u> of benzene in concentrated H_2SO_4 and HNO_3, where the nitro group replaces one of the hydrogens to give nitrobenzene. This is a very important reaction because there are many reactions in which nitrobenzene can be converted into many other aromatic functional groups.
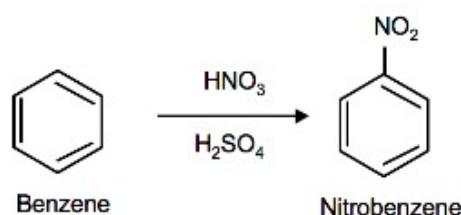
This is an industrially important reaction, because there are mechanisms for converting the nitro group to many other possible functional groups.

Hydrogenation can be used to create a fully saturated ring system. However, his reaction is much more difficult compared to hydration of unsaturated hydrocarbons due to the extra stability of the benzene ring.

II. Reactions of organic compounds that contain other functional groups:

1. <u>Reactions of Alcohols:</u>

Alcohols undergo oxidation, dehydration, substitution and esterification reactions.

A. <u>Oxidation:</u> (reaction with oxygen)

Oxidation reaction occurs when a molecule loses electrons. This appears as an increase in the number of oxygen atoms or a decrease in the number of hydrogen atoms in the oxidation products. Some common oxidizing agents include potassium permanganate ($KMnO_4$), chromic acid (H_2CrO_4), sodium dichromate ($Na_2Cr_2O_7$), and others. The oxidation products depend on the type of alcohol.

Primary alcohols are oxidized first with <u>weak</u> oxidizing agents to give aldehydes. Then usually oxidized further to give carboxylic acids. Also, primary alcohols oxidize to give carboxylic acid when strong oxidizing agents are used. Secondary alcohols are oxidized to ketones, which cannot be oxidized any further. Tertiary alcohols do <u>not</u> undergo oxidation. So, oxidation of alcohols is a way to prepare <u>aldehydes</u>, <u>ketones</u> and <u>carboxylic acids</u>. This is illustrated in the general reactions below:
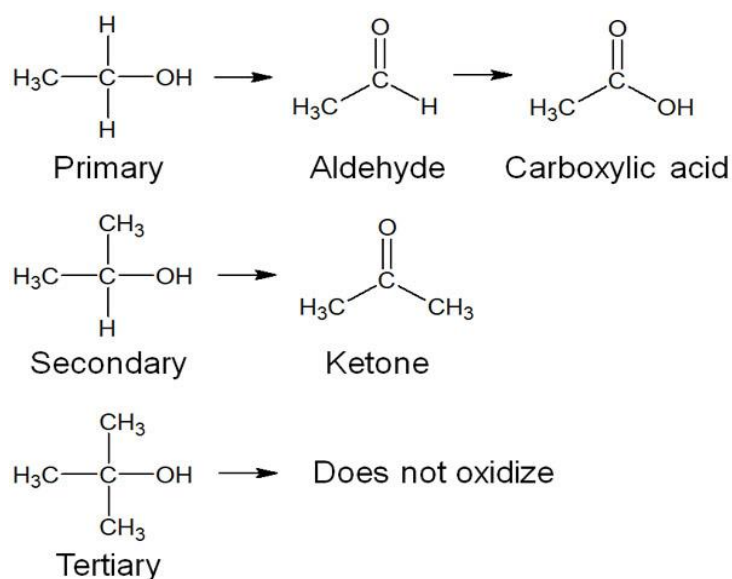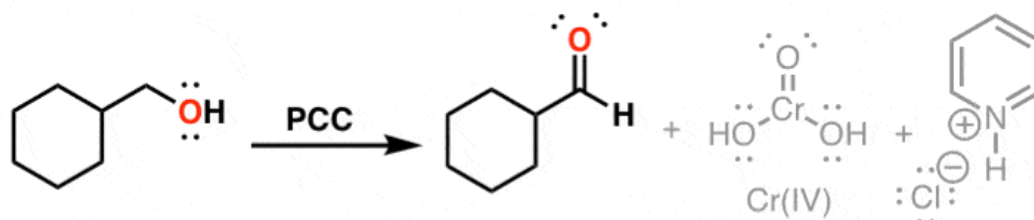

<u>Examples</u>:
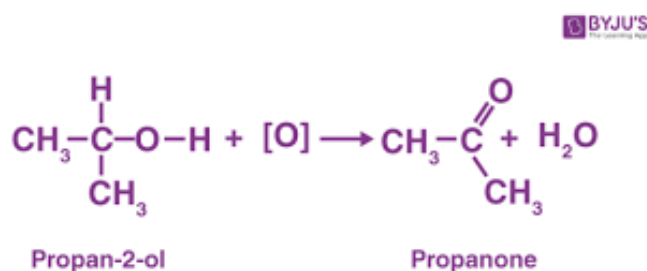
Oxidation of 2-propanol (2° alcohol)

$$CH_3CH_2OH \xrightarrow[\text{H}^+/\text{K}_2\text{Cr}_2\text{O}_7]{\text{H}^+/\text{KMnO}_4} CH_3COOH$$

Ethanol   Ethanoic acid

$$CH_3CH_2CH_2OH \xrightarrow[\text{H}^+/\text{K}_2\text{Cr}_2\text{O}_7]{\text{H}^+/\text{KMnO}_4} CH_3CH_2COOH$$

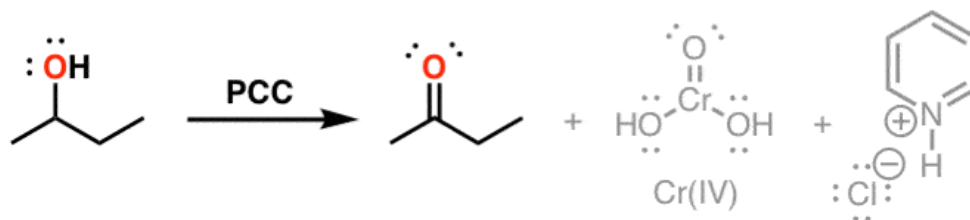Propanol   Propanoic acid

Benzyl alcohol   Benzoic acid
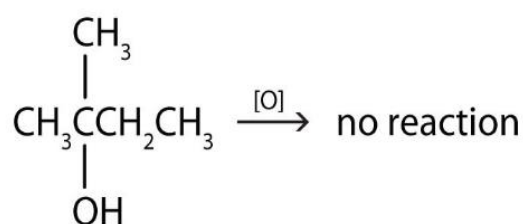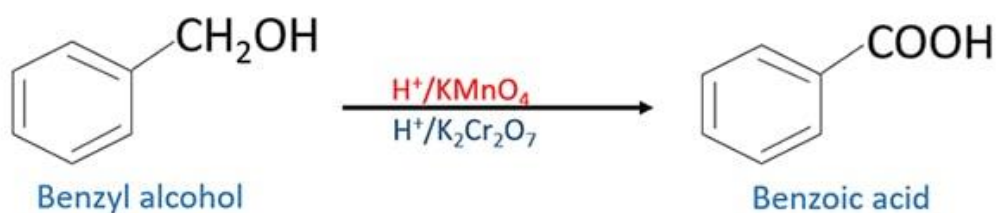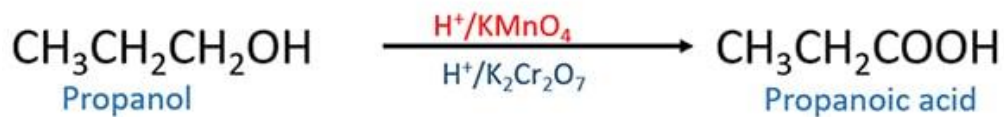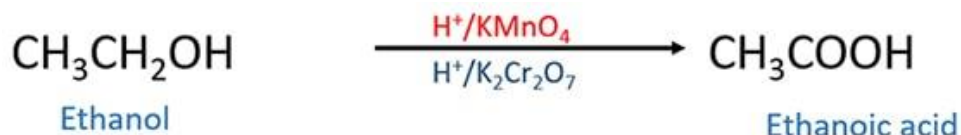
Oxidation of 1° alcohols

Pyridinium chlorochromate (PCC) is used to oxidize a primary alcohol to an aldehyde. Because the reaction is not run in water, the oxidation of the alcohol stops at the aldehyde.

**Example 1: Oxidation of primary alcohols to aldehydes**

Example 2: Oxidation of secondary alcohols to ketones

$$\underset{\text{secondary alcohol}}{R-\overset{\overset{\displaystyle OH}{|}}{\underset{}{CH}}-R'} \xrightarrow{Na_2Cr_2O_7/H_2SO_4} \underset{\text{ketone}}{R-\overset{\overset{\displaystyle O}{\|}}{\underset{}{C}}-R'}$$

cyclohexanol $\xrightarrow[H_2SO_4]{Na_2Cr_2O_7}$ cyclohexanone (90%)

Secondary alcohol $\xrightarrow[H_2SO_4, H_2O]{Na_2Cr_2O_7}$ Ketone

cyclohexyl methanol $\xrightarrow[H_2SO_4]{Na_2Cr_2O_7}$ cyclohexanecarboxylic acid (92%)
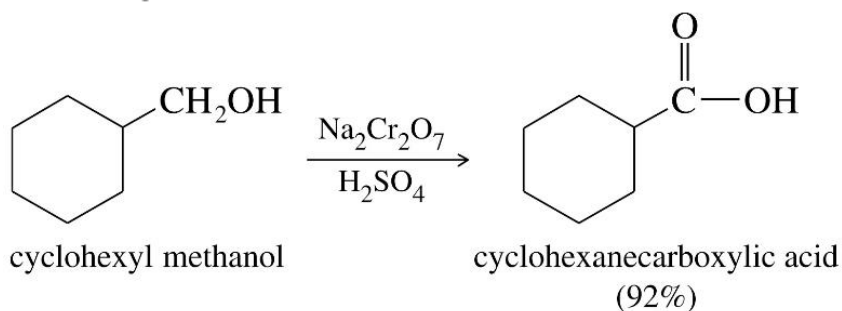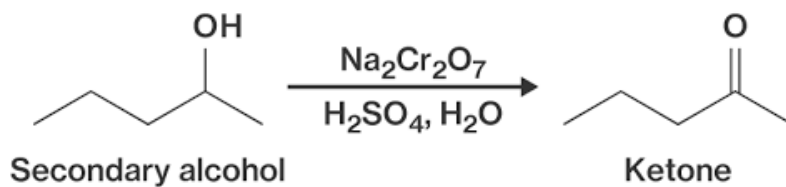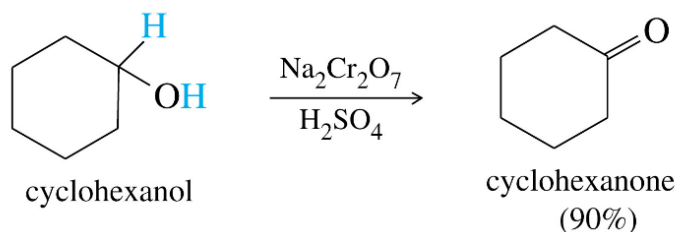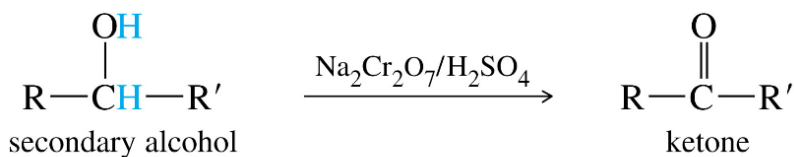
7. In Activity 2 (Volume 1), you explored the oxidation of primary alcohols. Using your new knowledge, explain why Reaction 1 below results in an aldehyde, and Reaction 2 results in a carboxylic acid.
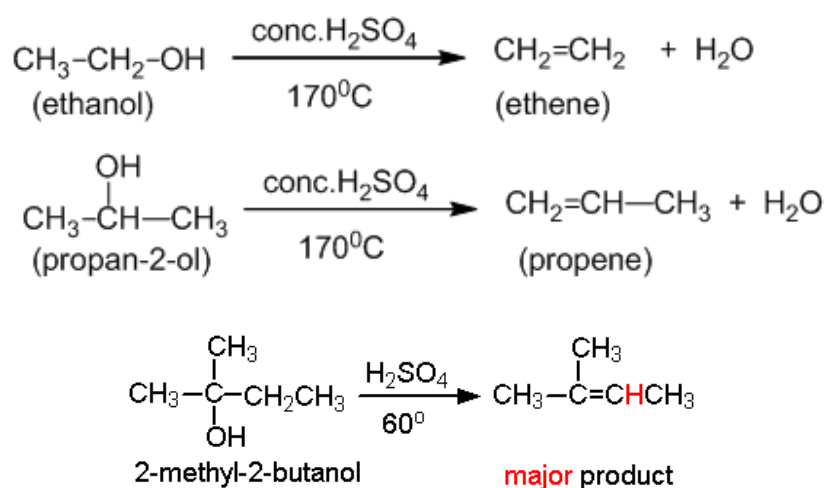
Reaction 1 OH $\xrightarrow[CH_2Cl_2]{PCC}$

Reaction 2 OH $\xrightarrow[H_2SO_4/H_2O]{Na_2Cr_2O_7}$
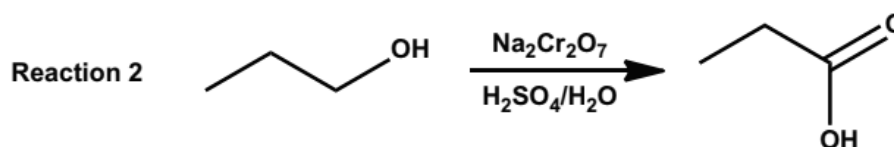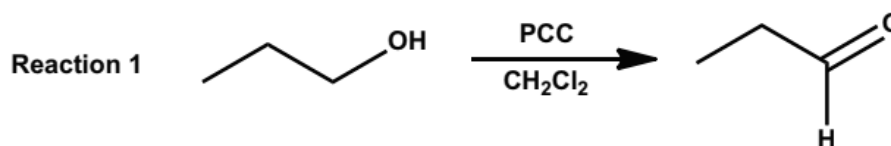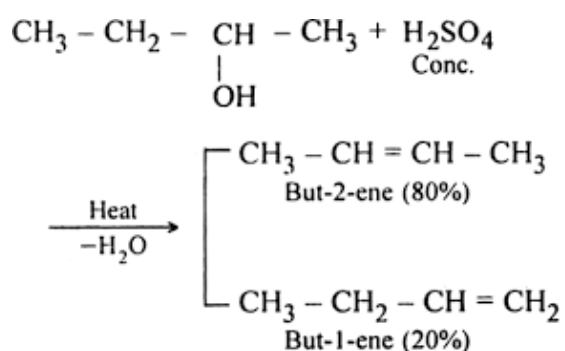
B. Dehydration:

Heating alcohols in concentrated sulfuric acid (H_2SO_4) at 180°C removes the OH group and a H from an adjacent carbon to produce an alkene, with water as a by-product. Since water is "removed" from the alcohol, this reaction is known as a dehydration reaction (or an elimination reaction)

Alcohols dehydrate (lose water) in presence of concentrated sulfuric acid at warm temperature to produce alkenes. Water is produced as a by-product. They also dehydrate at high temperature in presence of H_2SO_4 to give ethers as will be seen soon.

$$CH_3-CH_2-OH \xrightarrow[170^0C]{conc.H_2SO_4} CH_2=CH_2 + H_2O$$
(ethanol)   (ethene)

$$\underset{\text{(propan-2-ol)}}{CH_3-\underset{OH}{CH}-CH_3} \xrightarrow[170^0C]{conc.H_2SO_4} CH_2=CH-CH_3 + H_2O$$
(propene)

$$\underset{\text{2-methyl-2-butanol}}{CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2CH_3} \xrightarrow[60^0]{H_2SO_4} \underset{\text{major product}}{CH_3-\overset{CH_3}{C}=CHCH_3}$$

If there is more than one possible product of a dehydration reaction, the major product can be predicted from Zaitsev's Rule:

The Zaitsev's Rule: When an alkene is produced in an elimination reaction, the major product is the one with the more highly substituted double bond because it is more stable.

$$CH_3 - CH_2 - \underset{OH}{CH} - CH_3 + \underset{Conc.}{H_2SO_4}$$

$$\xrightarrow[-H_2O]{Heat} \begin{cases} CH_3 - CH = CH - CH_3 \\ \text{But-2-ene (80\%)} \\ \\ CH_3 - CH_2 - CH = CH_2 \\ \text{But-1-ene (20\%)} \end{cases}$$

Dehydration may happen at carbon 1 or carbon 2 to give two different products as seen in the second and third examples above.
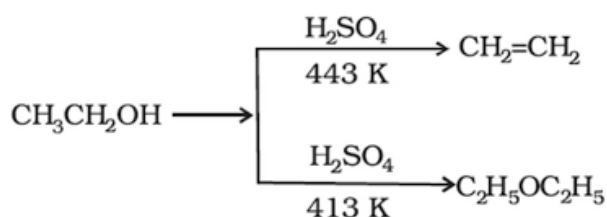
When alcohols dehydrate at high temperature (170 °C) and excess acid, an alkene is produced as shown in the above examples. This is called <u>unimolecular</u> dehydration. Alcohols may undergo <u>bimolecular</u> dehydration at low temperature (140 °C) where excess alcohol is used. The product under these conditions is an <u>ether</u>. Diethyl ether is produced upon oxidation of ethanol at 140 °C in excess ethanol as follows:

$$CH_3CH_2OH + HOCH_2CH_3 \xrightarrow[\text{140°C, excess ethanol}]{\text{concd } H_2SO_4} CH_3CH_2\text{—}O\text{—}CH_2CH_3 + H_2O$$
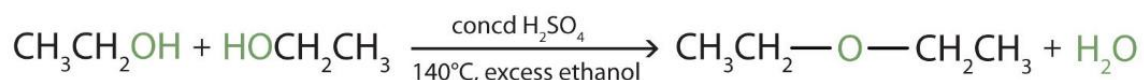
Two molecules of ethanol   Diethyl ether

Comparison:

$$CH_3CH_2OH \longrightarrow
\begin{cases}
\xrightarrow[\text{443 K}]{H_2SO_4} CH_2{=}CH_2 \\
\\
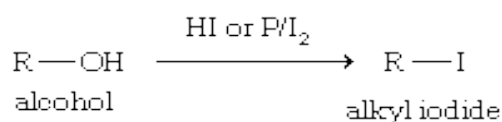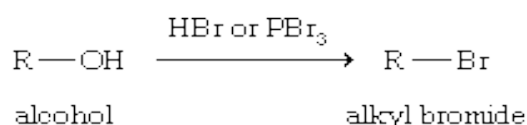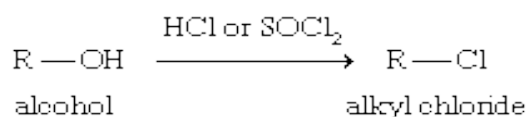\xrightarrow[\text{413 K}]{H_2SO_4} C_2H_5OC_2H_5
\end{cases}$$

C. <u>Substitution Reactions</u>:
The halogen atom replaces the hydroxyl group to give alkyl halides.
- The order of reactivity of alcohols is 3° > 2° > 1° methyl.
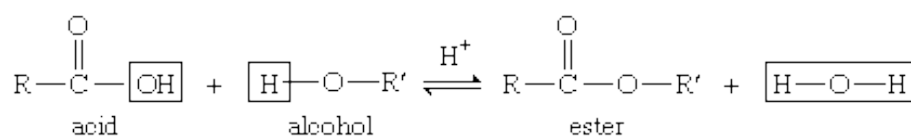- The order of reactivity of the hydrogen halides is HI > HBr > HCl (HF is generally unreactive).

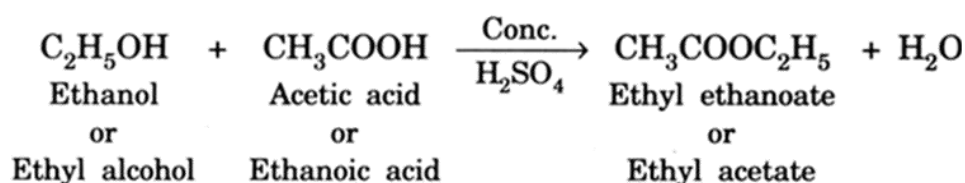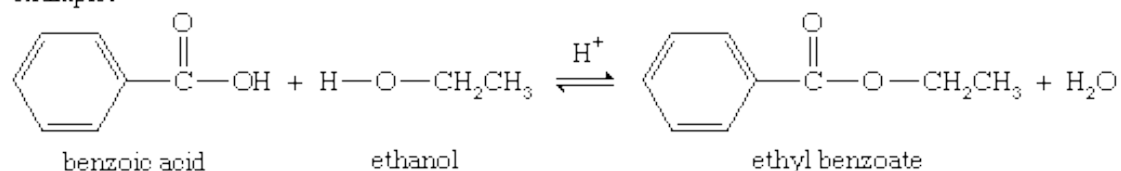**Alcohols can be converted to Alkyl Halides with HX acids**

$$R\!-\!OH \xrightarrow{\text{HCl or SOCl}_2} R\!-\!Cl$$

alcohol   alkyl chloride

$$R\!-\!OH \xrightarrow{\text{HBr or PBr}_3} R\!-\!Br$$

alcohol   alkyl bromide

$$R\!-\!OH \xrightarrow{\text{HI or P/I}_2} R\!-\!I$$

alcohol   alkyl iodide

examples: $(CH_3)_3 C\!-\!OH \xrightarrow{\text{HCl}} (CH_3)_3 C\!-\!Cl$

t-butyl alcohol   *t*-butyl chloride

cyclohexanol   bromocyclohexane

$$CH_3CH_2CH_2CH_2\!-\!OH \xrightarrow{\text{P/I}_2} CH_3CH_2CH_2CH_2\!-\!I$$

1-butanol   1-iodobutane
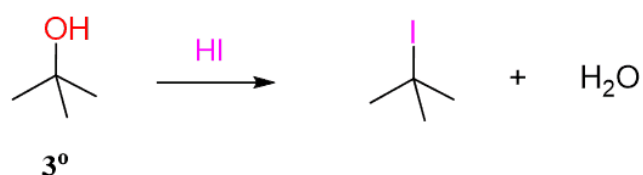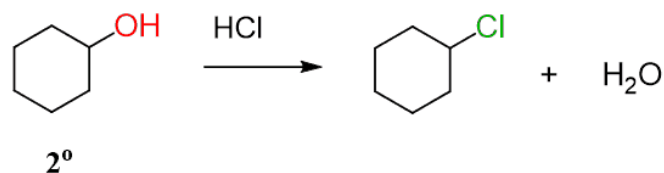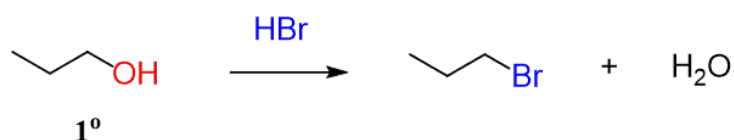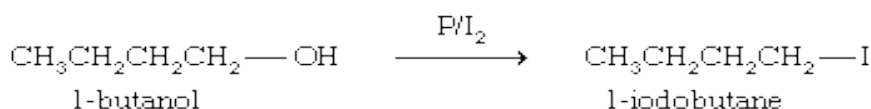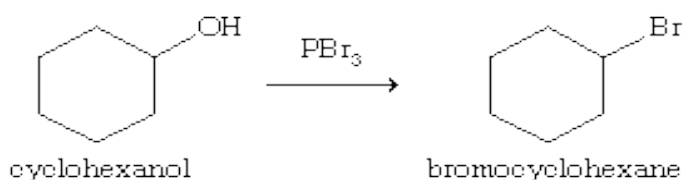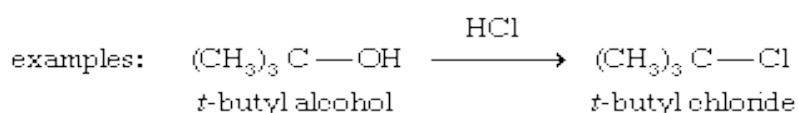
D. Esterification;

Alcohols react with carboxylic acids to give esters. The hydroxyl group of the acid combines with the hydrogen of the alcohol molecule to produce water molecule. This reaction is equilibrium reaction so it is difficult to get a good yield, however, there are some methods (applying acid derivatives) from which high yield can be obtained.

acid   alcohol   ester

example:

benzoic acid   ethanol   ethyl benzoate

$$C_2H_5OH + CH_3COOH \xrightarrow[\text{H}_2\text{SO}_4]{\text{Conc.}} CH_3COOC_2H_5 + H_2O$$

Ethanol   Acetic acid   Ethyl ethanoate

or   or   or

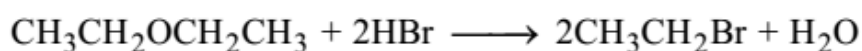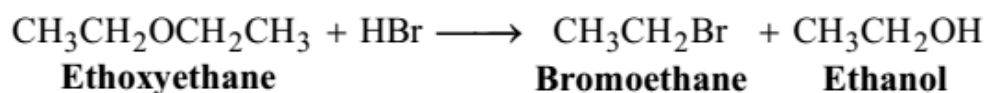Ethyl alcohol   Ethanoic acid   Ethyl acetate

2. <u>Reactions of Ethers</u>:

Ethers show good solvent properties for many nonpolar organic compounds. This makes them good medium to run reactions in.

Even though ethers are unreactive, and they are stable towards bases, oxidizing agents, and reducing agents, they actually undergo just one kind of reaction. It is acid cleavage reaction. Cleavage takes place only under extreme conditions like high temperatures and in concentrated acids (usually HI or HBr).

Cleavage by hydrobromic acid gives water, alkyl bromide and alcohol. If two moles of the acid are available per mole of ether all ether is converted into alkyl halide, where water is also produced. The cleavage reactions of ethers are used to prepare alkyl halides. Cleavage of diethyl ether (ethoxyethane) in hydrobromic acid is shown below:

$$CH_3CH_2OCH_2CH_3 + HBr \longrightarrow CH_3CH_2Br + CH_3CH_2OH$$
$$\textbf{Ethoxyethane} \qquad\qquad \textbf{Bromoethane} \quad \textbf{Ethanol}$$

$$CH_3CH_2OCH_2CH_3 + 2HBr \longrightarrow 2CH_3CH_2Br + H_2O$$

Cleavage of t-butyl methyl ether by hydroiodic acid HI gives alkyl iodide (t-butyl iodide) and methanol.
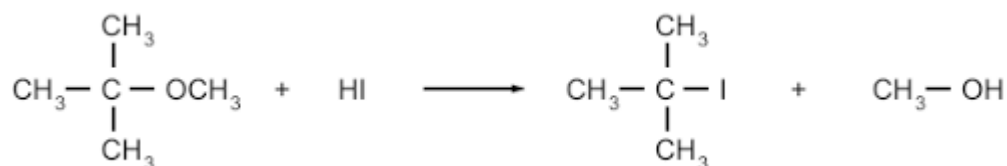
The acid reactivity follows the order:

$$\text{Reactivity of HX:} \quad HI > HBr > HCl$$

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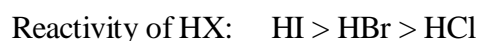
3. <u>Reactions of Aldehydes and Ketones</u>:
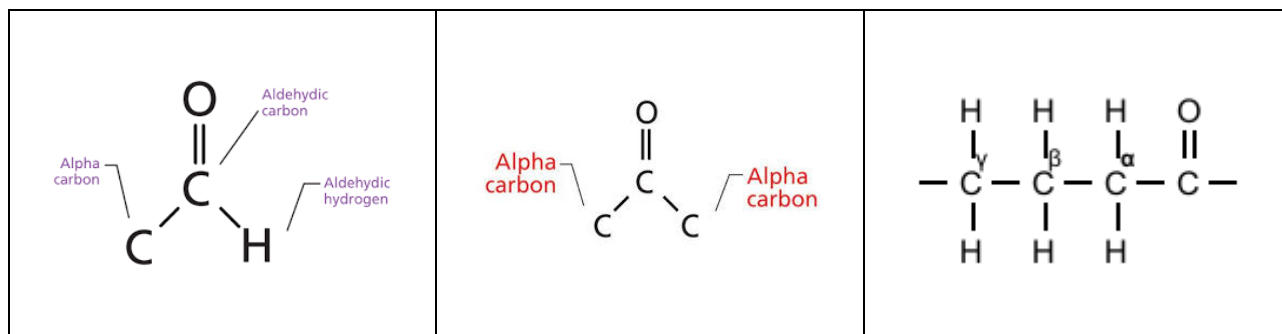
Reactions of aldehydes and ketones may be classified into two main groups:

Reactions on the carbonyl group:
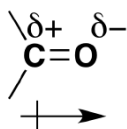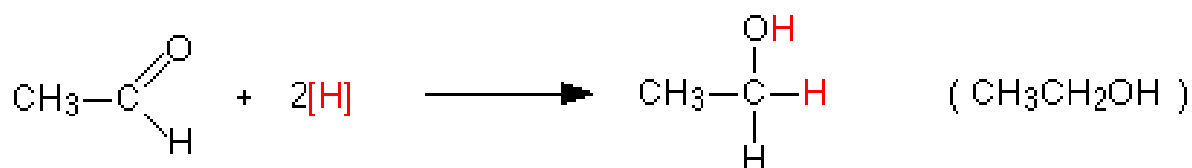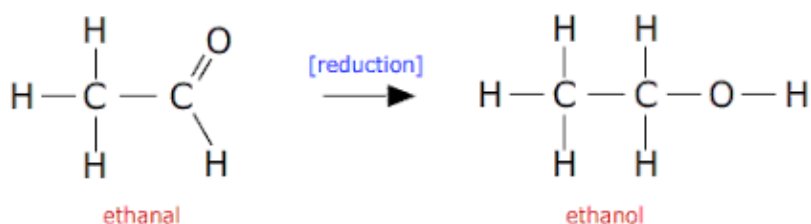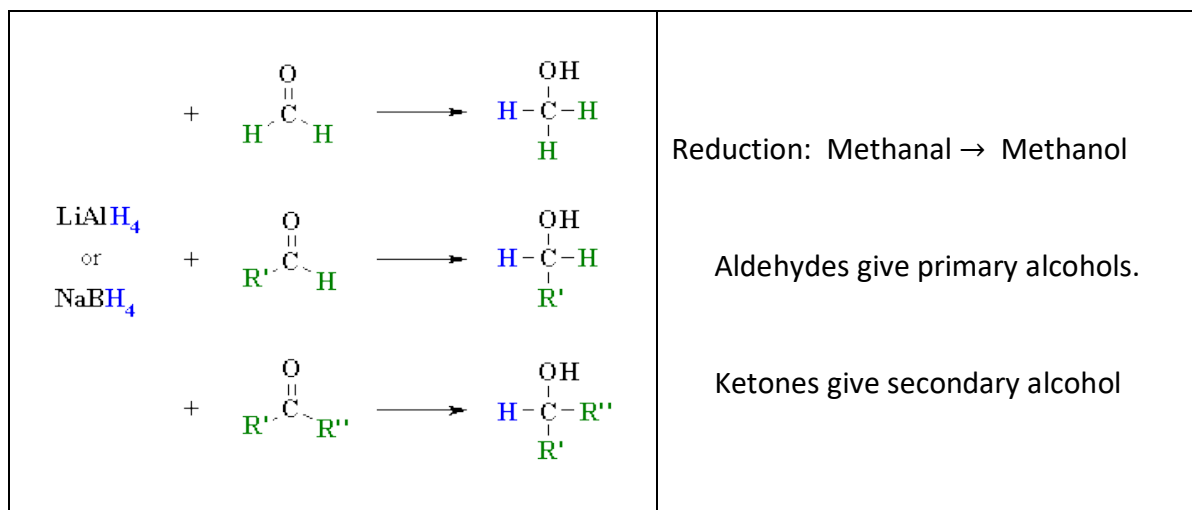

Reactions on the α-carbon:

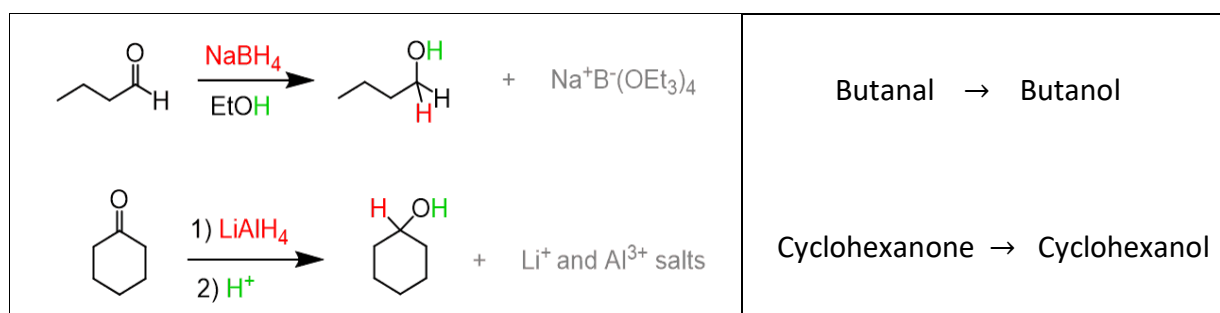Hydrogens attached to the alpha carbon are <u>acidic</u>. This enables them of making certain types of reaction.

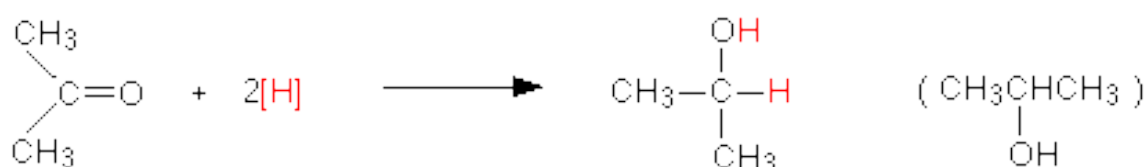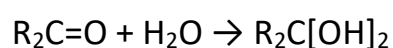*Some of the aldehyde and ketone compounds' reactions are shown below:*

A. Reduction Reactions:

Aldehydes can be reduced to primary alcohols (RCHO → RCH$_2$OH) by the use of reducing agents like lithium aluminum hydride (LiAlH$_4$), sodium borohydride (NaBH$_4$) and hydrogen (H$_2$) in the presence of a catalyst such as Ni, Pd, and Pt.

Reduction: Methanal → Methanol

Aldehydes give primary alcohols.

Ketones give secondary alcohol

ethanal   ethanol

(CH$_3$CH$_2$OH)

Butanal	→	Butanol
Cyclohexanone	→	Cyclohexanol

Ketones are reduced to secondary alcohols.   link2

$R_2C=O + H_2O \rightarrow R_2C[OH]_2$

B. Oxidation Reaction:

Aldehydes can be oxidized to carboxylic acids with both mild and strong oxidizing agents. However, ketones can be oxidized only by using extremely strong oxidizing agents. This type of oxidation happen with cleavage. Typical oxidizing agents for aldehydes include either potassium permanganate ($KMnO_4$) or potassium dichromate ($K_2Cr_2O_7$) in acidic medium.

$$CH_3CH \xrightarrow[\text{Ag}_2O,\ \text{or}\ H_2O_2]{\text{KMnO}_4,\ \text{CrO}_3,} CH_3C-OH$$
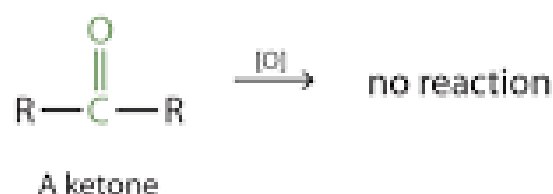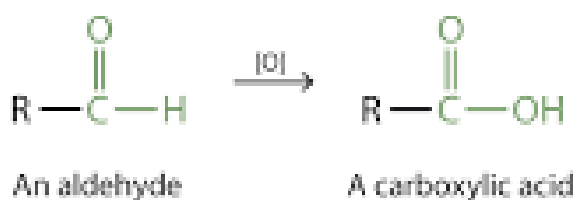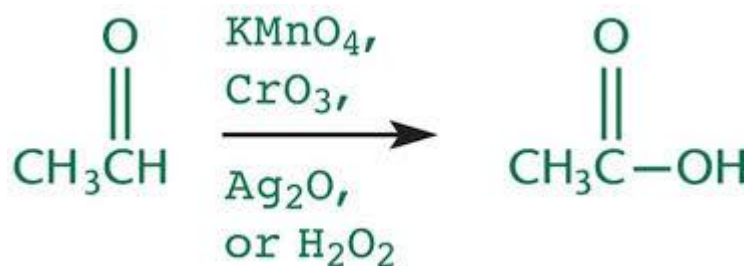
C. Nucleophilic Addition:

The most common reaction of aldehydes (and ketones) is the nucleophilic addition reactions.

This addition consists of <u>adding a nucleophile and a hydrogen across the carbon-oxygen double bond</u>.

The carbonyl group is polarized due to differences in electronegativities of the carbon and oxygen atoms. The carbon atom is partially positive, and the oxygen atom is partially negative.
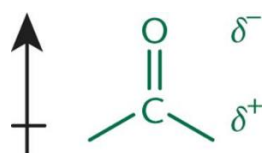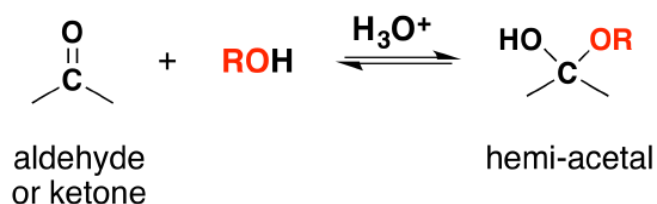

Aldehydes are usually more reactive toward nucleophilic substitutions than ketones because of both <u>steric and electronic effects</u>. Some of the reactions are shown below:

1. <u>Addition of Water to produce alcohols</u> (Hydration Reaction):
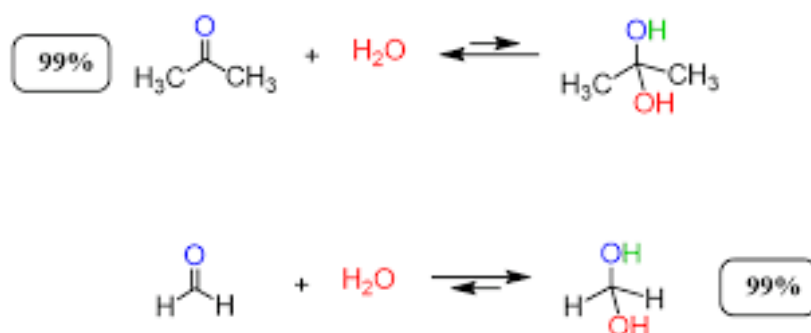
2. Addition of Alcohol to produce <u>Hemi-acetals</u>:
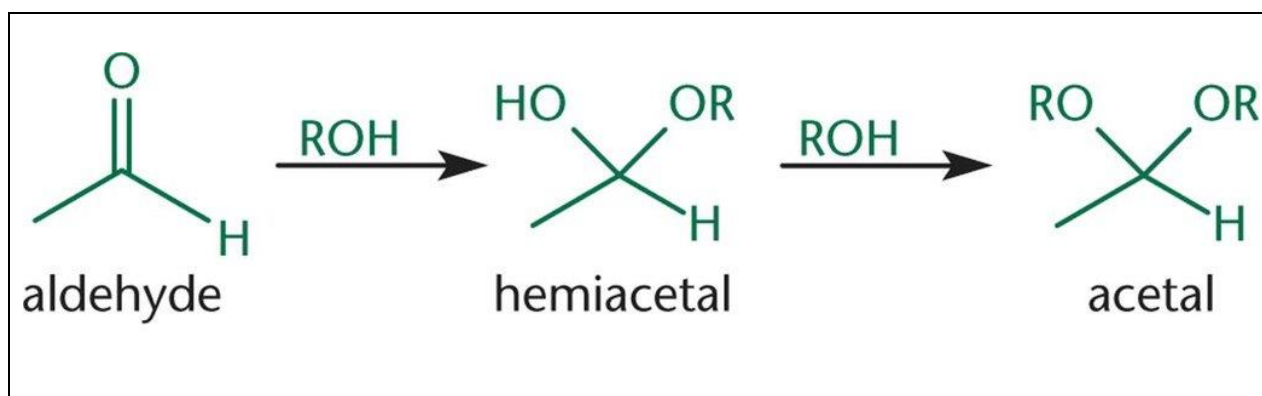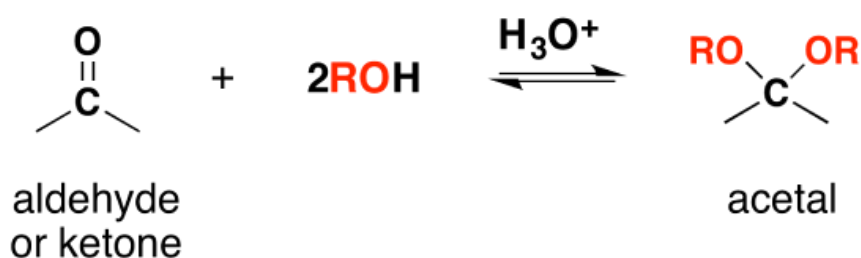
<u>Hemiacetals</u>: Structures that contain <u>alcohol and ether</u> groups on the same carbon.

3. Addition of Alcohol to produce <u>Acetals</u>:
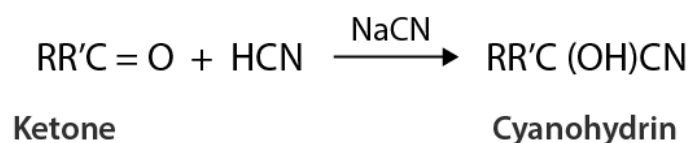
<u>Acetals</u>: Structures that contain <u>two ether groups</u> on the same carbon
   (<u>*Note*</u>: *you are not responsible for the naming of acetals and hemiacetals*)
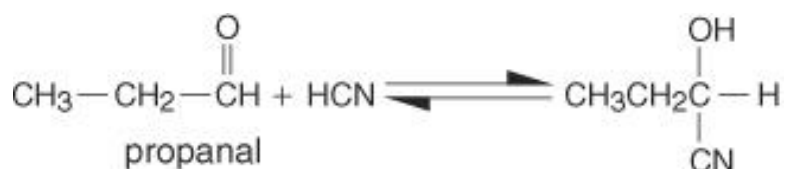

4. Addition of Hydrogen Cyanide to produce <u>cyanohydrin</u>:
Cyanohydrin is a structure with cyano (-CN) and hydroxyl (-OH) groups attached to the same carbon.   (<u>*Note*</u>: *you are not responsible for the naming of cyanohydrines*)

$$RR'C = O + HCN \xrightarrow{NaCN} RR'C\,(OH)CN$$

Ketone   Cyanohydrin

$$CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{CH} + HCN \rightleftharpoons CH_3CH_2\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}-H$$

propanal

$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + HCN \rightleftharpoons CH_5\overset{\overset{\displaystyle OH}{|}}{\underset{\underset{\displaystyle CN}{|}}{C}}-CH_3$$
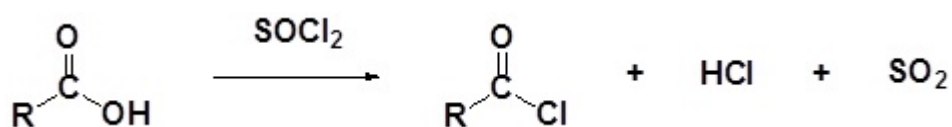
acetone

There are many other important reactions that aldehydes and ketones may undergo. These are like addition of ammonia and its derivative to imines, ... and many others.
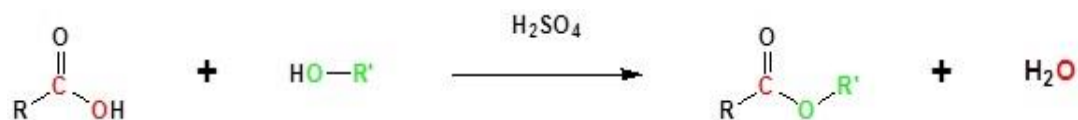
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5. Reactions of Carboxylic acids: Link
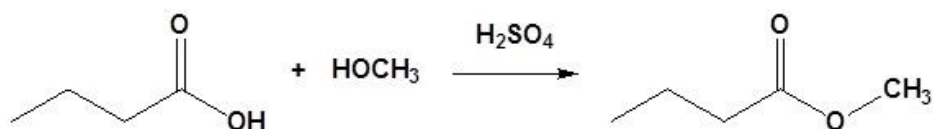
A. Reaction with thionyl chloride to give acid chloride:

$$R-COOH \xrightarrow{SOCl_2} R-COCl + HCl + SO_2$$
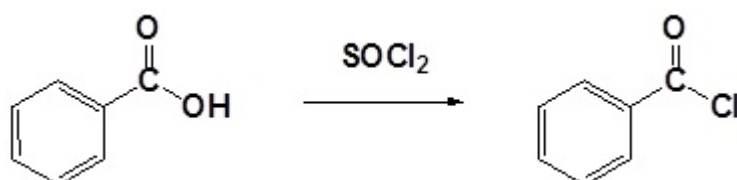
B. Reaction with acid Chloride to produce acid anhydride.:

Acid Chloride   Carboxylic Acid   Acid Anhydride
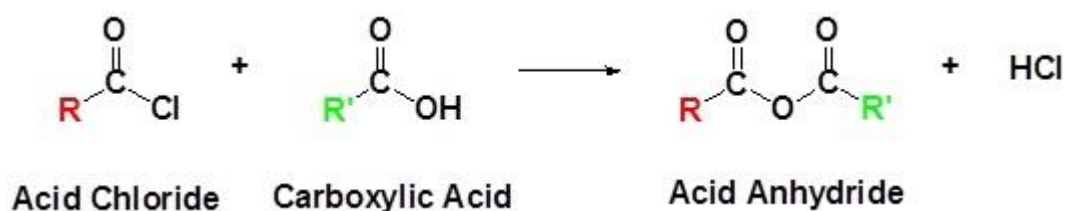
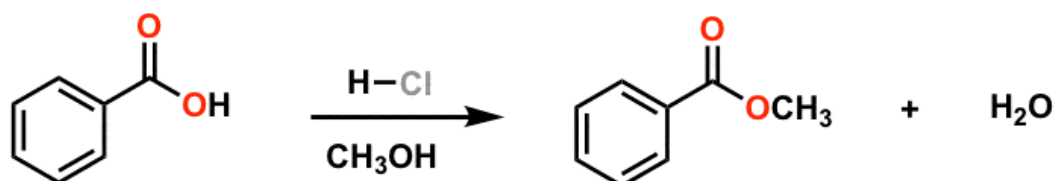C. Reaction with alcohols in acidic medium (H_2SO_4) gives ester and water.

Example: Reaction of butanoic acid with methanol to give methyl propyl ester,

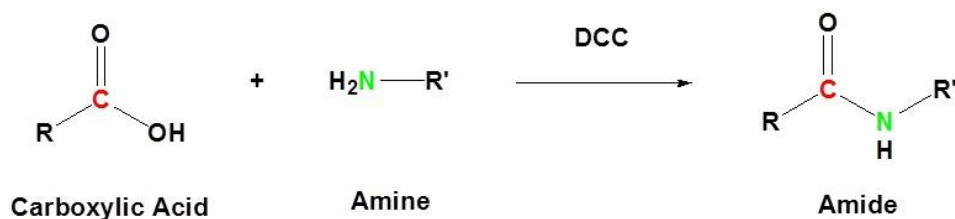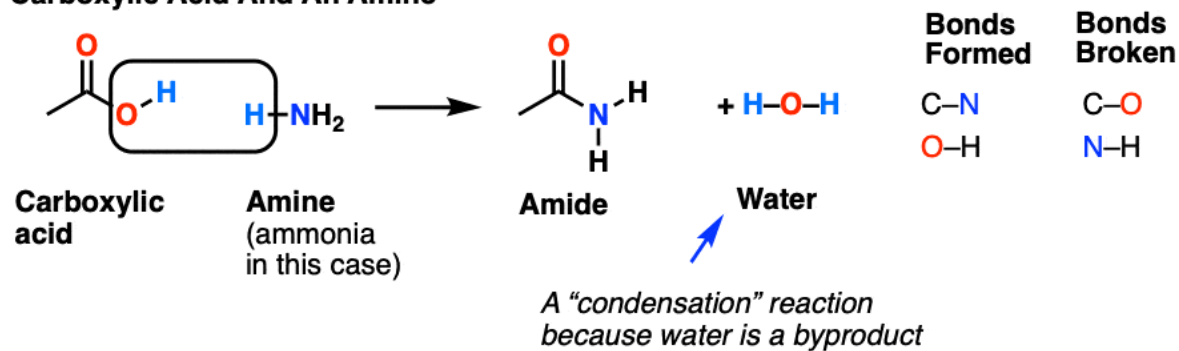Another example:

Fischer esterification example

D. Reaction with amine to produce an <u>amide</u>:
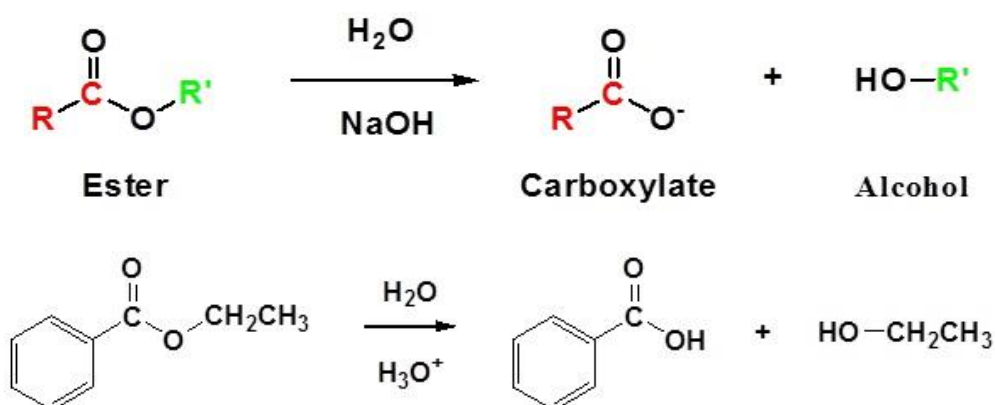
Amides Are The Product of A Net "Condensation" Reaction Between A Carboxylic Acid And An Amine

	Bonds Formed	Bonds Broken
	C–N	C–O
	O–H	N–H

A "condensation" reaction because water is a byproduct

6. Reactions of Esters:

Esters can be cleaved back into a carboxylic acid and an alcohol by reaction with water and a base. The reaction is called a saponification reaction. The name comes from the way by which soaps are used to be made. Soaps are prepared by an ester hydrolysis of fats.

Cleavage reaction to give carboxylic acid and alcohol.

THE END

Imine: Nitrogen is double bonded to carbon

Imide: Nitrogen is bonded to two carbonyl groups

Amide: Nitrogen is bonded to carbonyl

Cyanihydrine: cyanide and hydroxyl groups are bonded to the same carbon

Acid anhydride: Two acyl groups connected by an oxygen