

AL- MUSTAQBAL UNIVERSITY
College Of Health And Medical Techniques
Prosthetic Dental Techniques Department
Second Grade
Second Semester



Advanced chemistry
Lecture 14 (The theoretical part)
(Alcohols, Classification, properties, and their reactions)

By:

Assist.Prof.Dr.Ahmed A. AL-Khafagi

- **Objectives of the Semester:**
- **General goal:**

Informing the student of all the structural and chemical properties of most dental materials and how to deal with them.

- **Own goal:**

Enabling the student of the Department of Prosthetic Dental Techniques to know the molecular structure of dental materials.

- **Reference text:**

1- Organic Chemistry by Robert T. Morrison and Robert N. Boyd. (Latest edition).

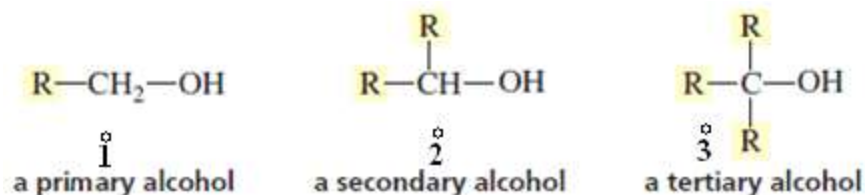
2- Organic Chemistry by McCurry; Thomason learning; CA, USA; Latest edition.

Alcohols

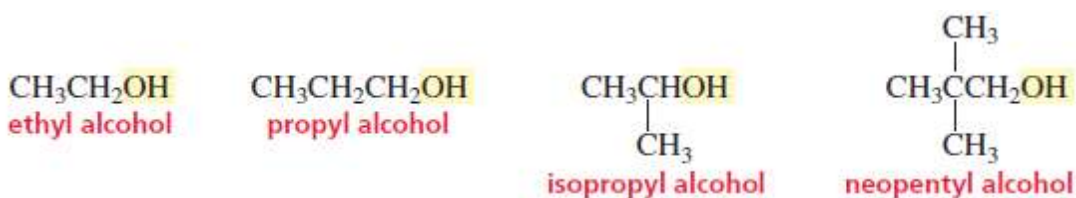
Alcohols are organic compounds with general formula, R-OH.

Nomenclature of Alcohols

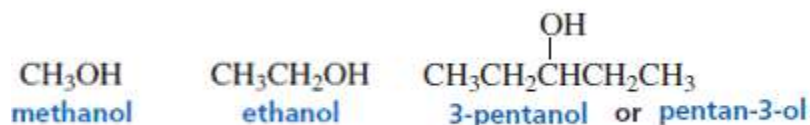
Alcohols are compounds in which a hydrogen of an alkane has been replaced by an OH group. Alcohols are classified as primary, secondary, or tertiary, depending on whether the OH group is bonded to a primary, secondary, or tertiary carbon—the same way alkyl halides are classified.



The common name of an alcohol consists of the name of the alkyl group to which the OH group is attached, followed by the word "alcohol."

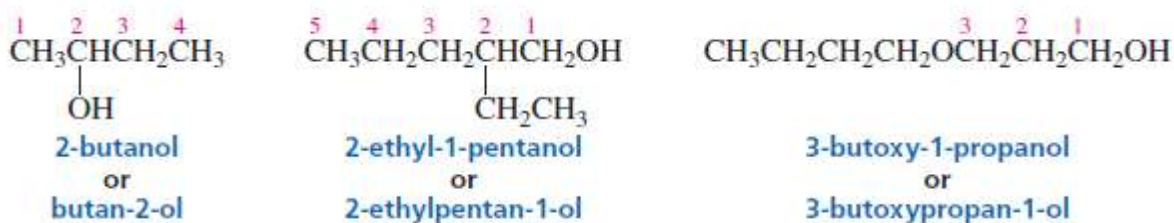


The functional group is the center of reactivity in a molecule. In an alcohol, the OH is the functional group. The IUPAC system uses a suffix to denote certain functional groups. The systematic name of an alcohol, for example, is obtained by replacing the "e" at the end of the name of the parent hydrocarbon with the suffix "ol."

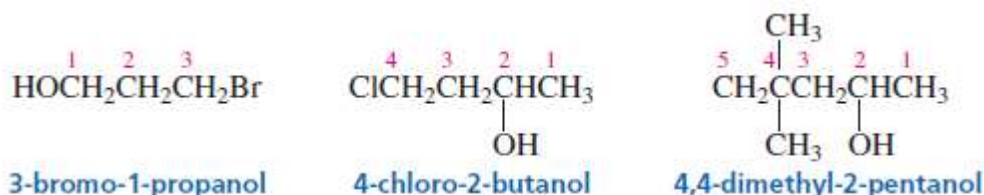


The following rules are used to name a compound that has a functional groupsuffix:

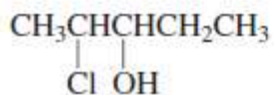
1. The parent hydrocarbon is the longest continuous chain *containing the functionalgroup*.
2. The parent hydrocarbon is numbered in the direction that gives the *functionalgroup suffix the lowest possible number*.



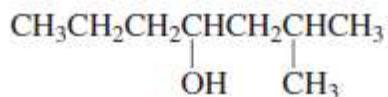
3. If there is a functional group suffix and a substituent, the functional group suffix gets the lowest possible number.



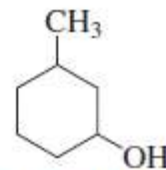
4. If the same number for the functional group suffix is obtained in both directions, the chain is numbered in the direction that gives a substituent the lowest possible number. Notice that a number is not needed to designate the position of a functional group suffix in a cyclic compound, because it is assumed to be at the 1-position.



2-chloro-3-pentanol
not
4-chloro-3-pentanol

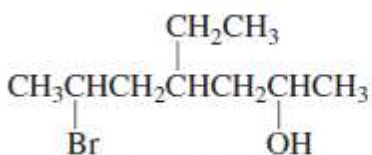


2-methyl-4-heptanol
not
6-methyl-4-heptanol

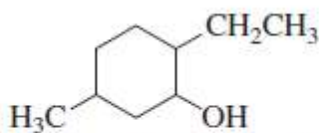


3-methylcyclohexanol
not
5-methylcyclohexanol

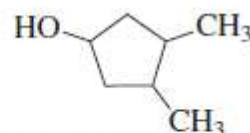
5. If there is more than one substituent, the substituents are cited in alphabetical order.



6-bromo-4-ethyl-2-heptanol



2-ethyl-5-methylcyclohexanol



3,4-dimethylcyclopentanol

Physical properties

Alcohols, in contrast, contain the very polar -OH group. In particular, this group contains hydrogen attached to the very electronegative element, oxygen, and therefore permits hydrogen bonding. The physical properties (Table 15.1) show the effects of this hydrogen bonding.

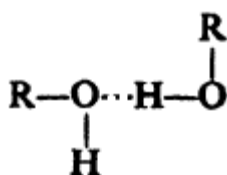


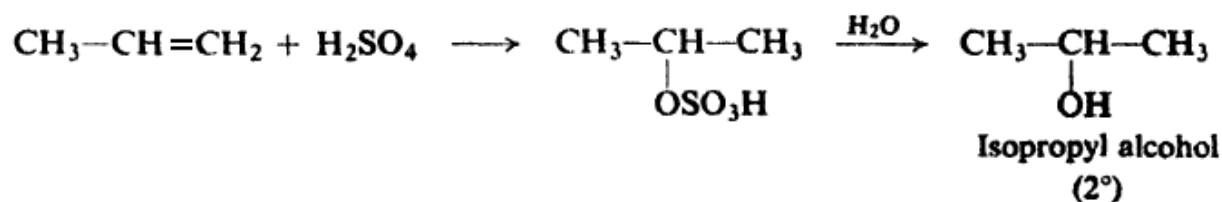
Table 15.1 ALCOHOLS

Name	Formula	M.p., °C	B.p., °C	Density at 20°C	Solub., g/100 g H ₂ O
Methyl	CH ₃ OH	- 97	64.5	0.793	∞
Ethyl	CH ₃ CH ₂ OH	-115	78.3	.789	∞
<i>n</i> -Propyl	CH ₃ CH ₂ CH ₂ OH	-126	97	.804	∞
<i>n</i> -Butyl	CH ₃ (CH ₂) ₂ CH ₂ OH	- 90	118	.810	7.9
<i>n</i> -Pentyl	CH ₃ (CH ₂) ₃ CH ₂ OH	- 78.5	138	.817	2.3
<i>n</i> -Hexyl	CH ₃ (CH ₂) ₄ CH ₂ OH	- 52	156.5	.819	0.6
<i>n</i> -Heptyl	CH ₃ (CH ₂) ₅ CH ₂ OH	- 34	176	.822	0.2
<i>n</i> -Octyl	CH ₃ (CH ₂) ₆ CH ₂ OH	- 15	195	.825	0.05
<i>n</i> -Decyl	CH ₃ (CH ₂) ₈ CH ₂ OH	6	228	.829	
<i>n</i> -Dodecyl	CH ₃ (CH ₂) ₁₀ CH ₂ OH	24			
<i>n</i> -Tetradecyl	CH ₃ (CH ₂) ₁₂ CH ₂ OH	38			
<i>n</i> -Hexadecyl	CH ₃ (CH ₂) ₁₄ CH ₂ OH	49			
<i>n</i> -Octadecyl	CH ₃ (CH ₂) ₁₆ CH ₂ OH	58.5			
Isopropyl	CH ₃ CHOHCH ₃	- 86	82.5	.789	∞
Isobutyl	(CH ₃) ₂ CHCH ₂ OH	-108	108	.802	10.0
<i>sec</i> -Butyl	CH ₃ CH ₂ CHOHCH ₃	-114	99.5	.806	12.5
<i>tert</i> -Butyl	(CH ₃) ₃ COH	25.5	83	.789	∞
Isopentyl	(CH ₃) ₂ CHCH ₂ CH ₂ OH	-117	132	.813	2
<i>active</i> -Amyl	(-)-CH ₃ CH ₂ CH(CH ₃)CH ₂ OH		128	.816	3.6
<i>tert</i> -Pentyl	CH ₃ CH ₂ C(OH)(CH ₃) ₂	- 12	102	.809	12.5
Cyclopentanol	<i>cyclo</i> -C ₅ H ₉ OH		140	.949	
Cyclohexanol	<i>cyclo</i> -C ₆ H ₁₁ OH	24	161.5	.962	
Allyl	CH ₂ =CHCH ₂ OH	-129	97	.855	∞
Crotyl	CH ₃ CH=CHCH ₂ OH		118	.853	16.6
Methylvinyl- carbinol	CH ₂ =CHCHOHCH ₃		97		
Benzyl	C ₆ H ₅ CH ₂ OH	- 15	205	1.046	4
<i>α</i> -Phenylethyl	C ₆ H ₅ CHOHCH ₃		205	1.013	
<i>β</i> -Phenylethyl	C ₆ H ₅ CH ₂ CH ₂ OH	- 27	221	1.02	1.6
Diphenylcarbinol (Benzhydrol)	(C ₆ H ₅) ₂ CHOH	69	298		0.05
Triphenylcarbinol	(C ₆ H ₅) ₃ COH	162.5			
Cinnamyl	C ₆ H ₅ CH=CHCH ₂ OH	33	257.5		
Ethylene glycol	CH ₂ OHCH ₂ OH	- 16	197	1.113	
Propylene glycol	CH ₃ CHOHCH ₂ OH		187	1.040	
1,3-Propanediol	HOCH ₂ CH ₂ CH ₂ OH		215	1.060	
Glycerol	HOCH ₂ CHOHCH ₂ OH	18	290	1.261	
Pentaerythritol	C(CH ₂ OH) ₄	260			6

Alcohols show increase in boiling point with increasing carbon number, and decrease in boiling point with branching that because the hydrogen bonds that hold the molecules together. The solubility behavior of alcohols also reflects their ability to form hydrogen bonds. In sharp contrast to hydrocarbons, the lower alcohols are miscible with water and solubility changes with increase the number of carbons.

Industrial source

(a) Hydration of alkenes. Alkenes containing four or five carbon atoms can be separated from the mixture obtained from the cracking of petroleum. Alkenes are readily converted into alcohols either by direct addition of water, or by addition of sulfuric acid followed by hydrolysis.



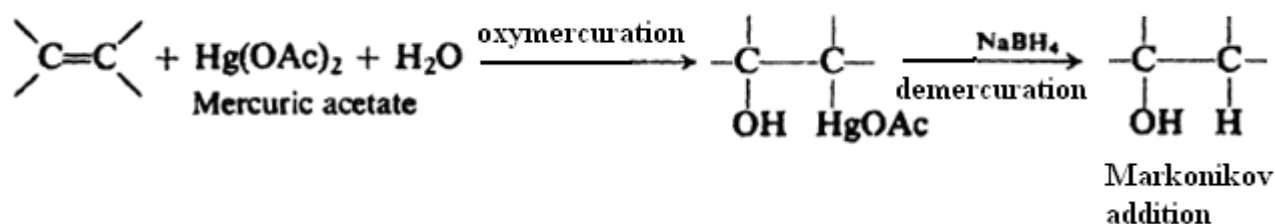
(b) Fermentation of carbohydrates. Fermentation of sugars by yeast, the oldest synthetic chemical process used by man, is still of enormous importance for the preparation of ethyl alcohol and certain other alcohols.

Preparation of alcohols

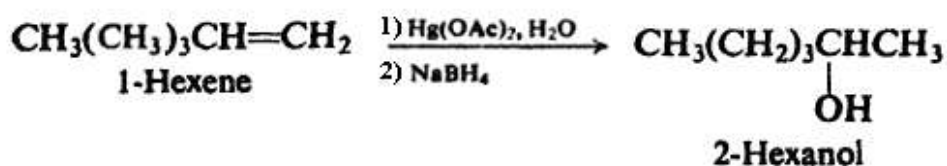
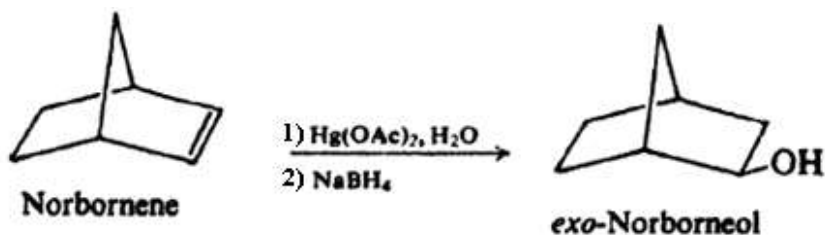
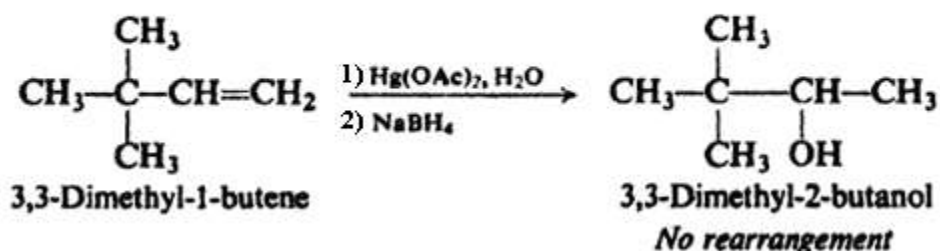
Most of the simple alcohols and a few of the complicated ones are available from the industrial sources. Other alcohols must be prepared by one of the methods outlined below.

1. Oxymercuration-demercuration.

The first stage, oxymercuration, involves addition to the carbon-carbon double bond of OH and HgOAc. Then, in demercuration, the HgOAc (CH₃COOHg) is replaced by H via sodium borohydride, NaBH₄. The reaction sequence amounts to hydration of the alkene, but is much more widely applicable than direct hydration.

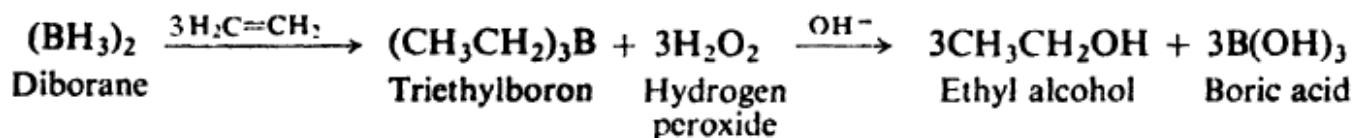


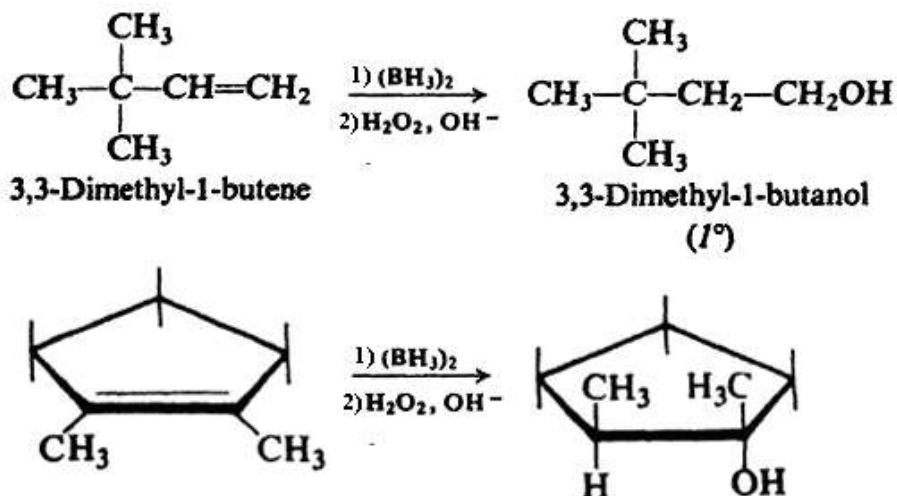
Examples:



2- Hydroboration-oxidation

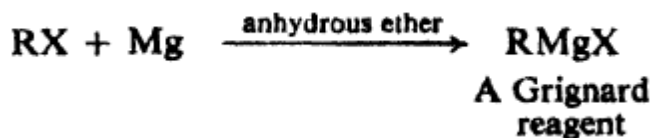
With the reagent diborane, $(\text{BH}_3)_2$, alkenes undergo hydroboration to yield alkylboranes, R_3B , which on oxidation give alcohols. For example:



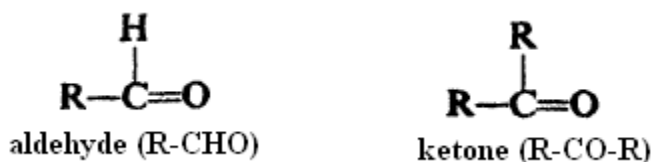


3- Grignard synthesis of alcohols.

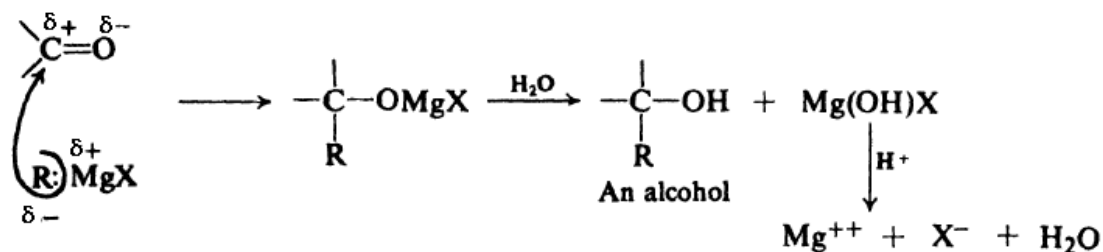
The Grignard reagent, we recall, has the formula RMgX , and is prepared by the reaction of metallic magnesium with the appropriate organic halide. This halide can be alkyl (1, 2, 3), allylic, aralkyl (e.g., benzyl), or aryl (phenyl or substituted phenyl). The halogen may be $-\text{Cl}$, $-\text{Br}$ or $-\text{I}$. (Arylmagnesium chlorides must be made in the cyclic ether tetrahydrofuran instead of ethyl ether.)



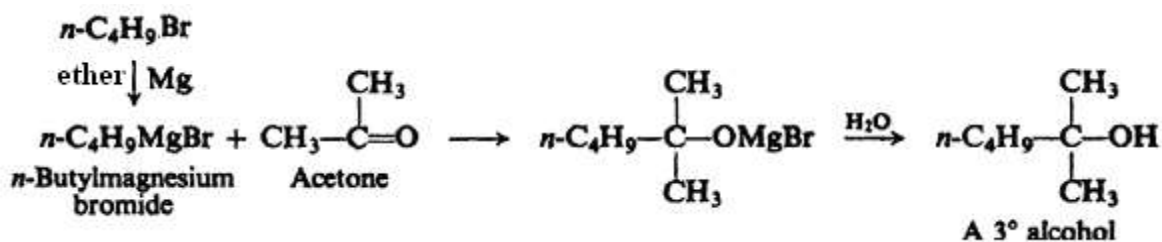
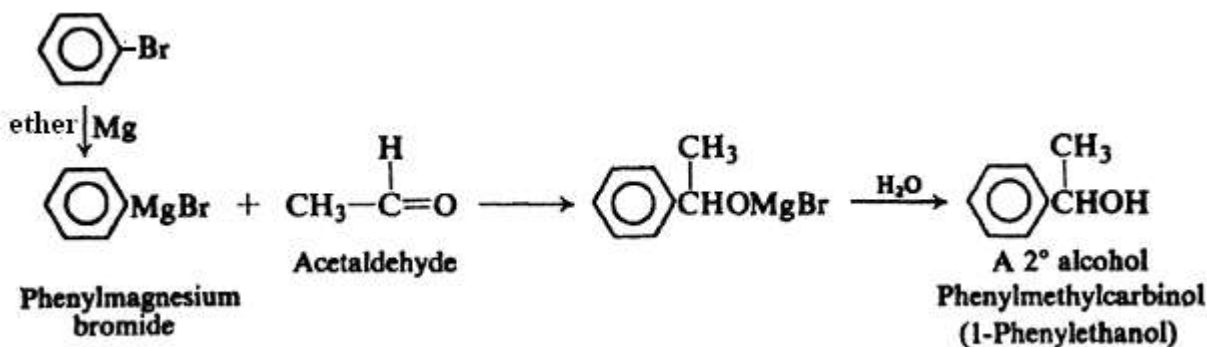
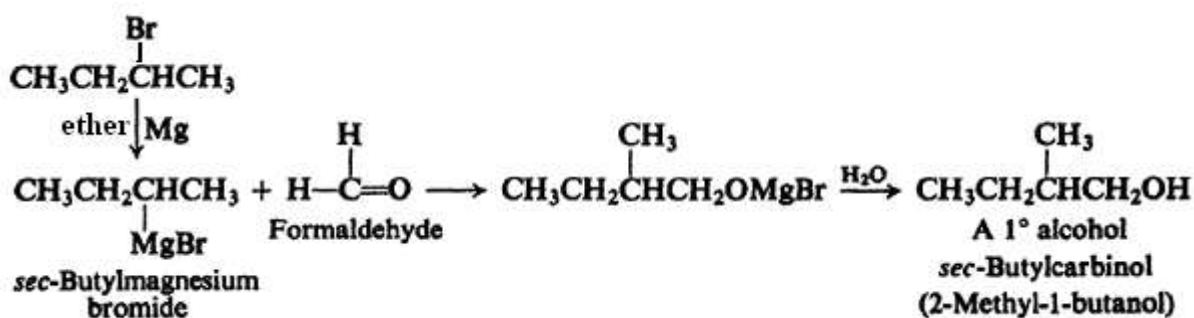
One of the most important uses of the Grignard reagent is its reaction with aldehydes and ketones to yield alcohols. Aldehydes and ketones have the general formulas:



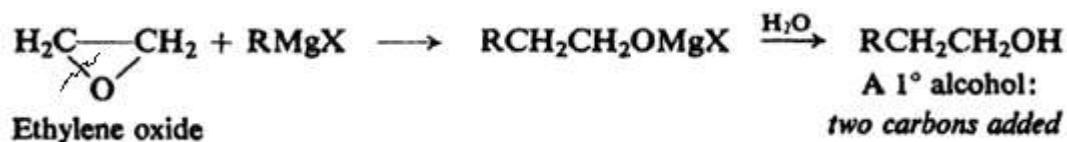
The carbon-magnesium bond of the Grignard reagent is a highly polar bond, carbon being negative relative to electropositive magnesium. It is not surprising, then, that in the addition to carbonyl compounds, the organic group becomes attached to carbon and magnesium to oxygen.



Examples:



A related synthesis utilizes ethylene oxide to make primary alcohols containing two more carbons than the Grignard reagent.

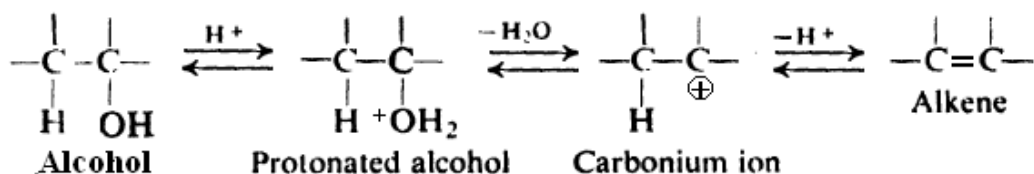


Reactions of alcohols

We can see that alcohols undergo many kinds of reactions, to yield many kinds of products.

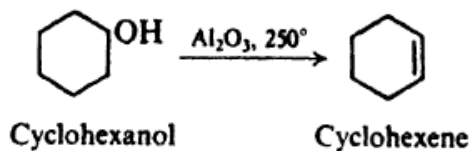
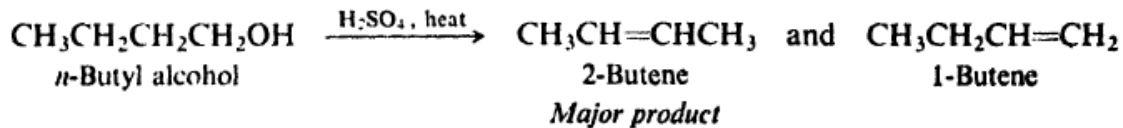
1- Dehydration to yield alkenes

The mechanism of dehydration involves (1) formation of the protonated alcohol, ROH_2^+ , (2) its slow dissociation into a carbonium ion, and (3) fast expulsion of a hydrogen ion from the carbonium ion to form an alkene.



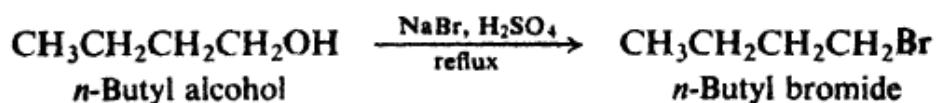
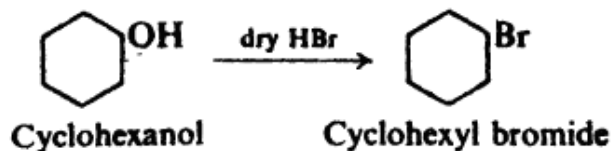
**The stability and hence rate of formation of the simple alkylcations follows the sequence $3^\circ > 2^\circ > 1^\circ$ and also a carbonium ion can rearrange, and that this rearrangement seems to occur whenever a 1,2-shift of hydrogen or alkyl group can form a more stable carbonium ion.

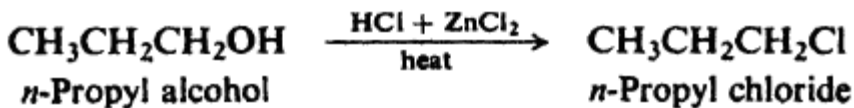
Examples:



2- Reaction with hydrogen halides

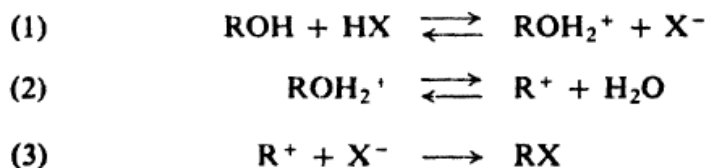
Alcohols react readily with hydrogen halides to yield alkyl halides. The least reactive of the hydrogen halides, HCl, requires the presence of zinc chloride for reaction with primary and secondary alcohols; on the other hand, the very reactive tert-butyl alcohol is converted to the chloride by simply being shaken with concentrated hydrochloric acid at room temperature. For example:





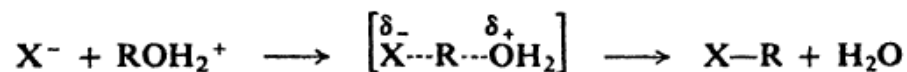
Alcohols react with hydrogen halides to follow the mechanism of nucleophilic substitution reaction (SN1 or SN2):

Mechanism SN1:



SN1:
all except methanol and most 1° alcohols

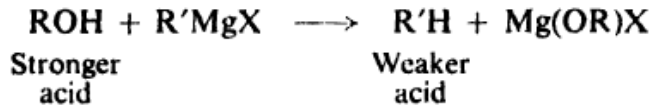
Mechanism SN2:



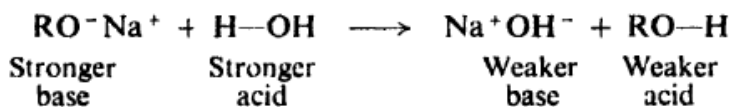
SN2:
most 1° alcohols and methanol

3- Alcohols as acids

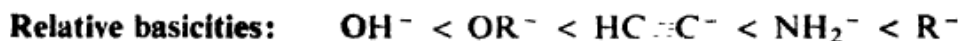
The acidity of alcohols is shown by their reaction with active metals to form hydrogen gas, and by their ability to displace the weakly acidic hydrocarbons from their salts (e.g., Grignard reagents):



With the possible exception of methanol, they are weaker acids than water, but stronger acids than acetylene or ammonia:

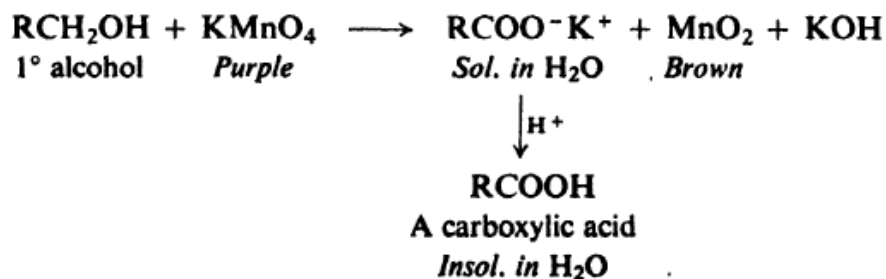


As before, these relative acidities are determined by displacement. We may expand our series of acidities and basicities, then, to the following:

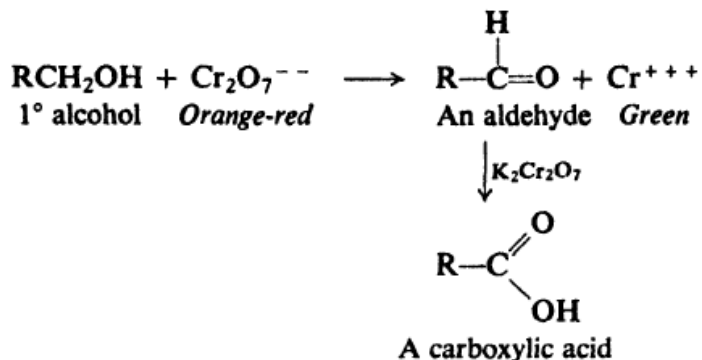


4- Oxidation of alcohols

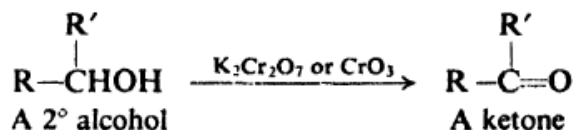
Primary alcohols can be oxidized to carboxylic acids, RCOOH, usually by heating with aqueous KMnO_4 .



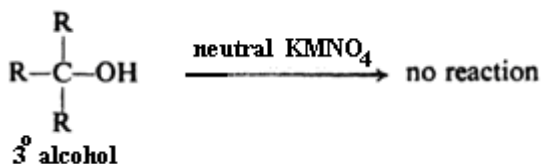
Primary alcohols can be oxidized to aldehydes, RCHO, by the use of $K_2Cr_2O_7$. Aldehydes are themselves readily oxidized to acids, the aldehyde must be removed from the reaction mixture by special techniques before it is oxidized further.



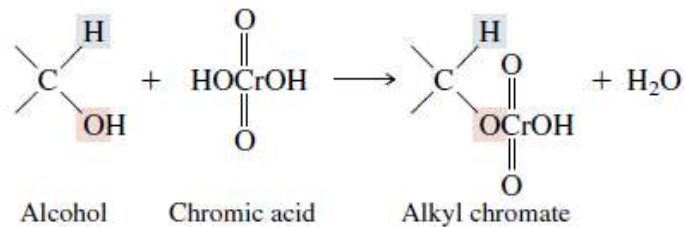
Secondary alcohols are oxidized to ketones, R_2CO , by chromic acid in a form selected for the job at hand: aqueous $K_2Cr_2O_7$, CrO_3 in glacial acetic acid, CrO_3 in pyridine, etc. Hot permanganate also oxidizes secondary alcohols.



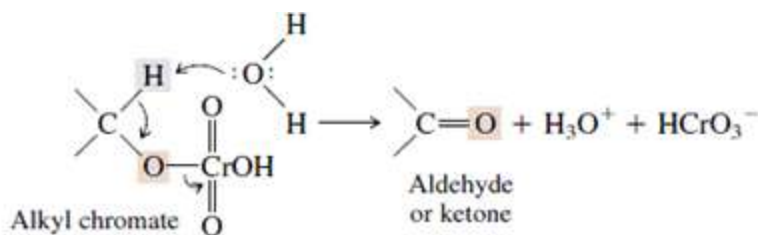
*With no hydrogen attached to the carbinol carbon, tertiary alcohols are not oxidized at all under alkaline conditions.



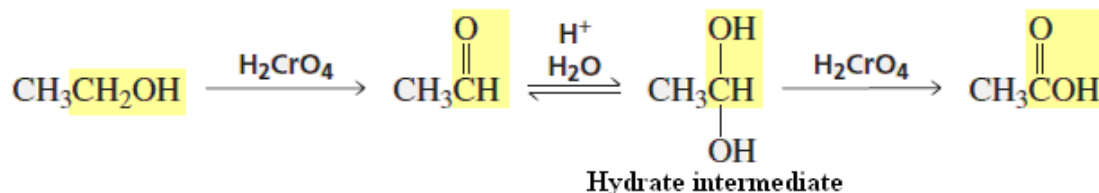
The oxidation mechanism of alcohol and the effect of hydrogen attached to the carbinol carbon, chromic acid oxidation involves initial formation of an alkyl chromate:



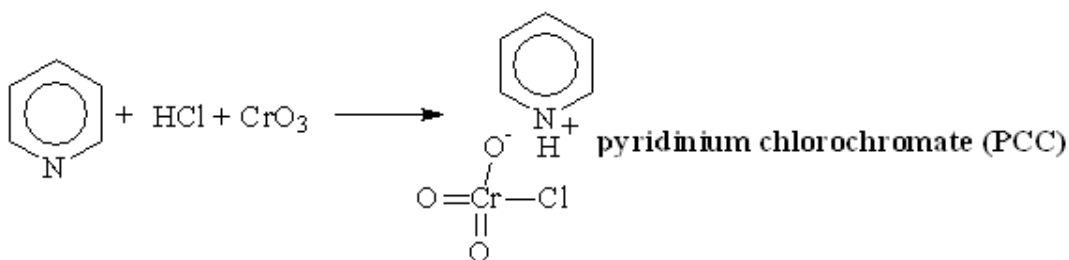
This alkyl chromate then undergoes an elimination reaction to form the carbon–oxygen double bond.



When a primary alcohol is oxidized to a carboxylic acid, the alcohol is initially oxidized to an aldehyde, which is in equilibrium with its hydrate. It is the hydrate that is subsequently oxidized to a carboxylic acid.



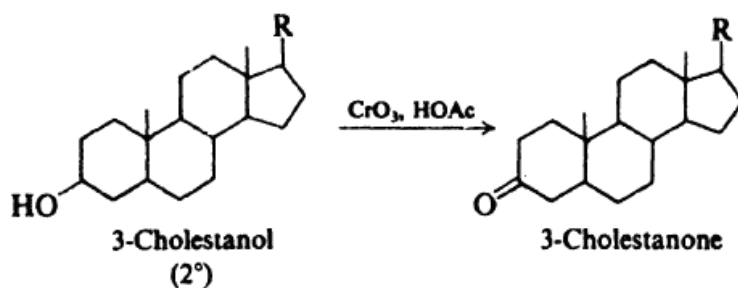
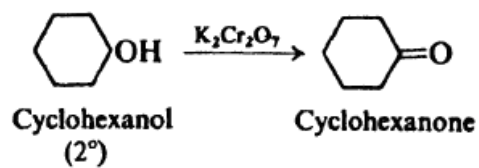
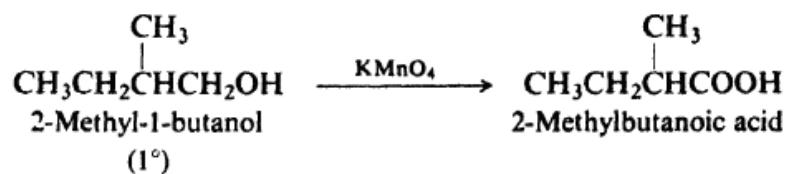
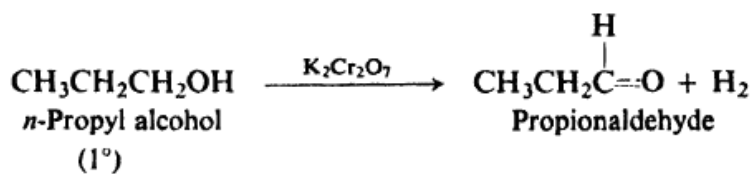
The oxidation reaction can be stopped at the aldehyde if the reaction is carried out with pyridinium chlorochromate (PCC), because PCC is used in an anhydrous solvent. If water is not present, the hydrate cannot be formed.



- Primary alcohol + PCC → aldehyde

- Sec. alcohol + PCC → ketone

Examples:



Thank You For Your Attention