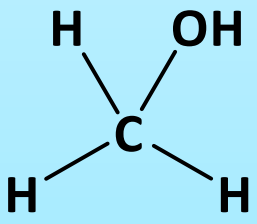
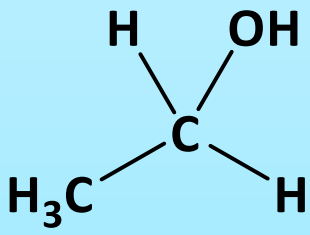
Alcohols

Alcohol

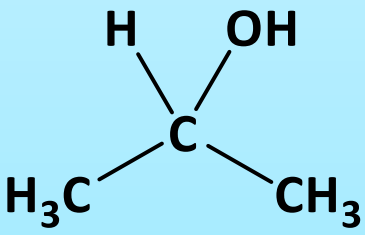
- An alcohol is a molecule that has a hydroxyl group (–OH) bonded to a saturated or sp^3 hybridized carbon atom
- The saturated carbon may be a simple alkyl or cycloalkyl group
- Examples of such compounds include:



methanol

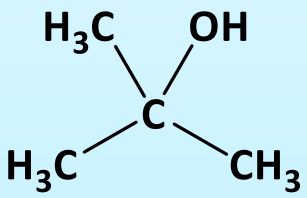


ethanol

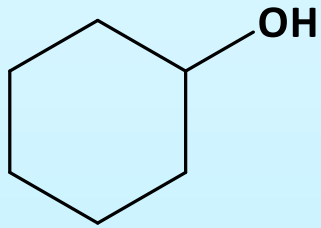


propanol

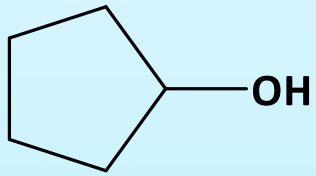
Alcohol



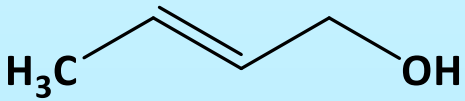
2-methyl-2-propanol



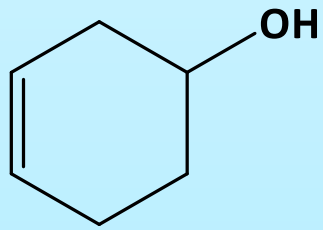
Cyclohexanol



Cyclopentanol



But-2-en-1-ol

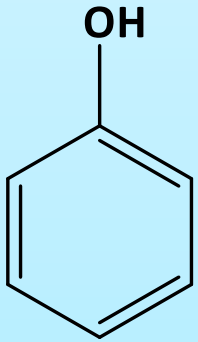


Cyclohex-3-en-1-ol

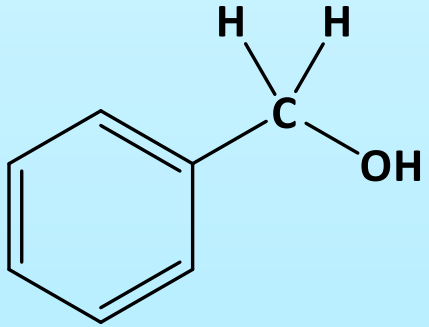
- **Note that when a hydroxyl group is directly bonded to a benzene ring, it is not classified as an alcohol**

Alcohol

- **This is because the carbon atom it is attached to is not an sp^3 hybridized carbon atom but an sp^2 hybridized one – it is referred to as *phenol***



Phenol
This is not an alcohol



Phenylmethanol
This is an alcohol

- **Phenylmethanol however is an alcohol because the –OH is attached to an sp^3 carbon**

Nomenclature of Alcohols

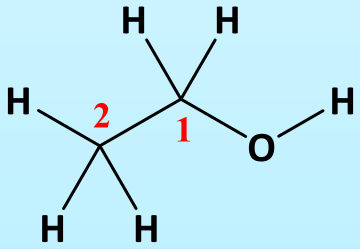
- **The rules for naming alcohols are very similar to those used for naming alkanes**
- **In the IUPAC system, the longest chain containing the –OH group is selected as the parent name and numbered starting from the end closer to the –OH group**
- **The suffix "*–e*" of the parent alkane is dropped and replaced by "*–ol*" and except for methanol and ethanol, a number is used to show the location of the –OH group**

Nomenclature of Alcohols

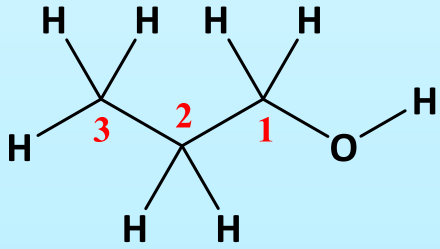
- In numbering the parent chain, the location of the –OH group takes precedence over alkyl groups, halogen substituents and unsaturation
- For cyclic alcohols, numbering begins at the carbon bearing the –OH group
- Common names of alcohols are derived by naming the alkyl group attached to the –OH and then adding the word "*alcohol*"

Nomenclature of Alcohols

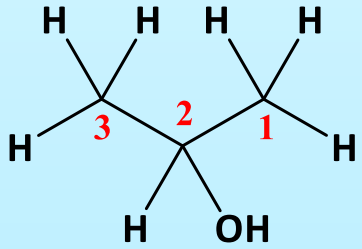
- **Given below are IUPAC names of some alcohols – common names in parenthesis**



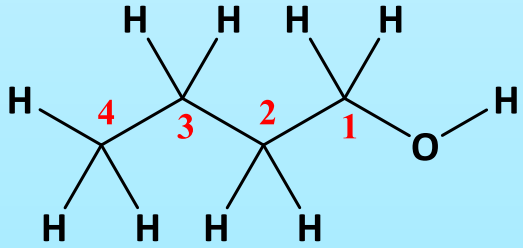
ethanol
(ethyl alcohol)



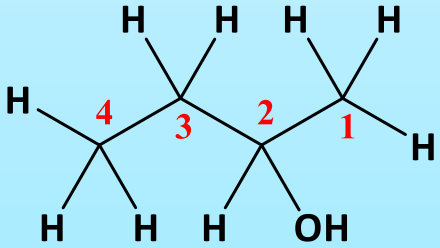
1-propanol
(propyl alcohol)



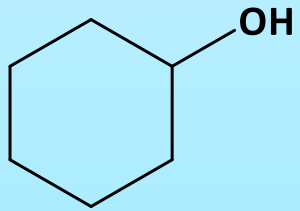
2-propanol
(isopropyl alcohol)



1-butanol
(butyl alcohol)

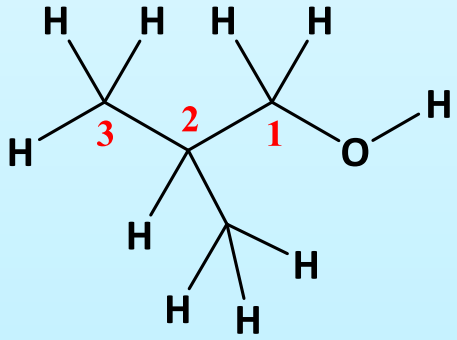


2-butanol
(*sec*-butyl alcohol)

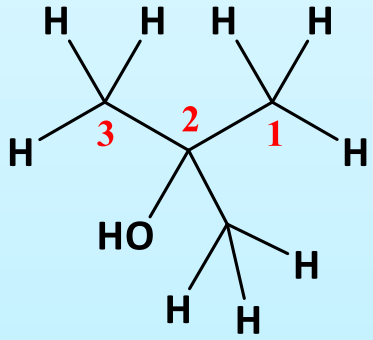


cyclohexanol
(cyclohexyl alcohol)

Nomenclature of Alcohols



2-methyl-1-propanol
(*sec*-butyl alcohol)

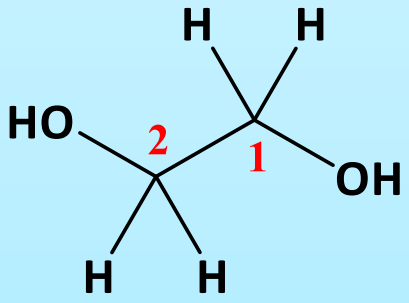


2-methyl-2-propanol
(*tert*-butyl alcohol)

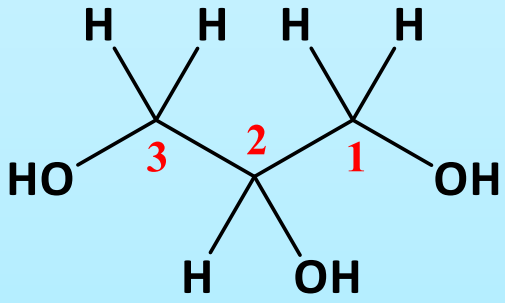
- **In the IUPAC system, a compound containing two hydroxyl groups is named as a *diol* while a compound that contains three hydroxyl groups is named as a *triol***

Nomenclature of Alcohols

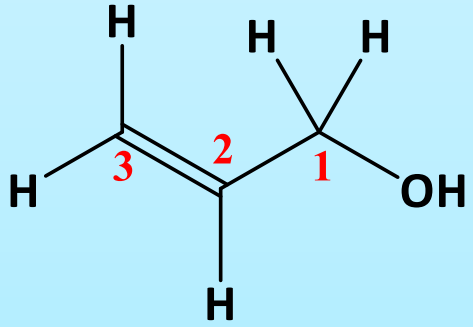
- **An alcohol that contains an unsaturation like a double bond or triple bond is named as *enols* or *ynols* respectively**



1,2-ethanediol



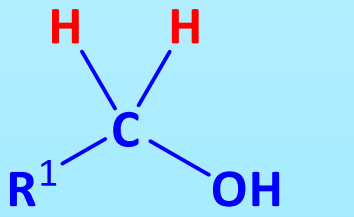
1,2,3-propanetriol



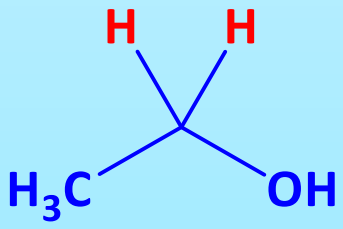
2-propen-1-ol

Classification of Alcohols

- Alcohols are classified as primary (1°), secondary (2°), or tertiary (3°) depending on the nature of the carbon atom to which the –OH group is attached
- If the carbon atom to which the –OH group is attached has two hydrogen atoms attached to it, then the alcohol is classified as a primary alcohol



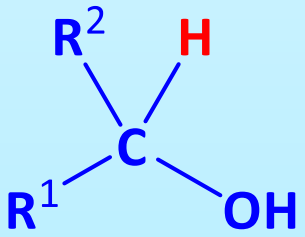
Primary alcohol



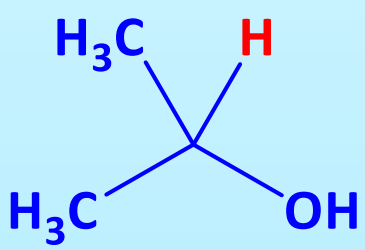
e.g. ethanol

Classification of Alcohols

- If the carbon atom to which the –OH group is attached has only one hydrogen atom attached to it, then the alcohol is classified as a secondary alcohol



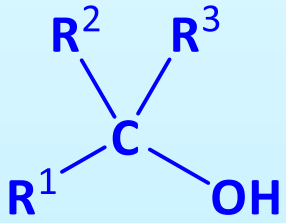
Secondary alcohol



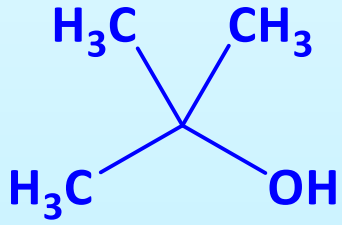
e.g. 2-propanol

- If the carbon atom to which the –OH group is attached has no hydrogen atom attached to it, then the alcohol is classified as a tertiary alcohol

Classification of Alcohols

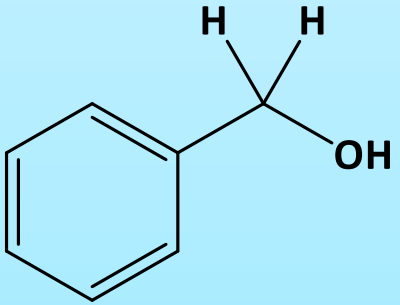


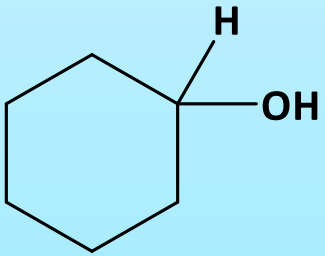
Tertiary alcohol

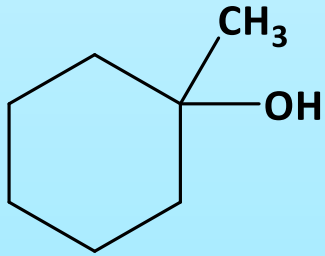


e.g. 2-methyl-2-propanol

- **Some more examples:**

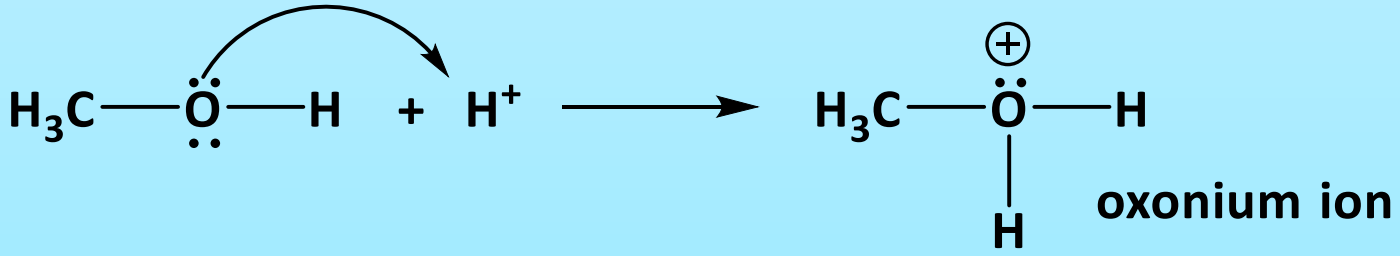






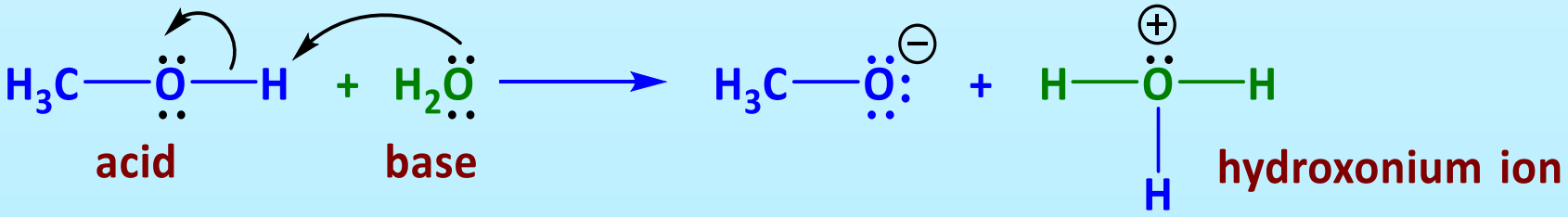
Reactions of Alcohols

- In the crudest sense, alcohols are amphoteric – i.e. they can act both as an acid or base depending on the situation
- In the presence of strong acids, the oxygen atom of an alcohol acts as a weak base and reacts with the acid by proton transfer to form the oxonium ion



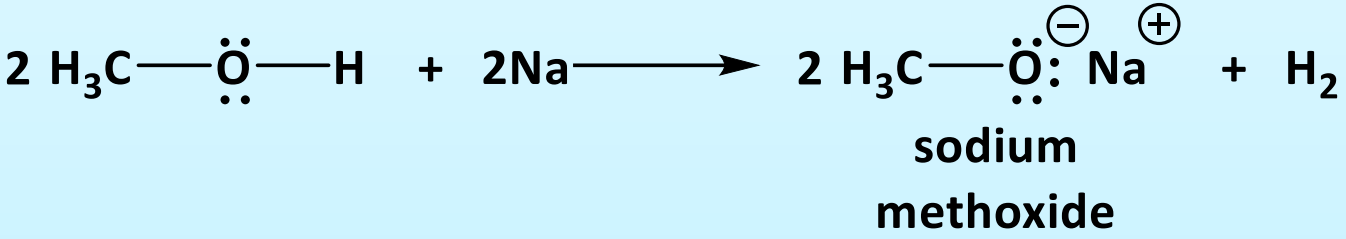
Reactions of Alcohols

- On the other hand, in dilute aqueous solution alcohols are very weak acids as illustrated by the ionization of methanol

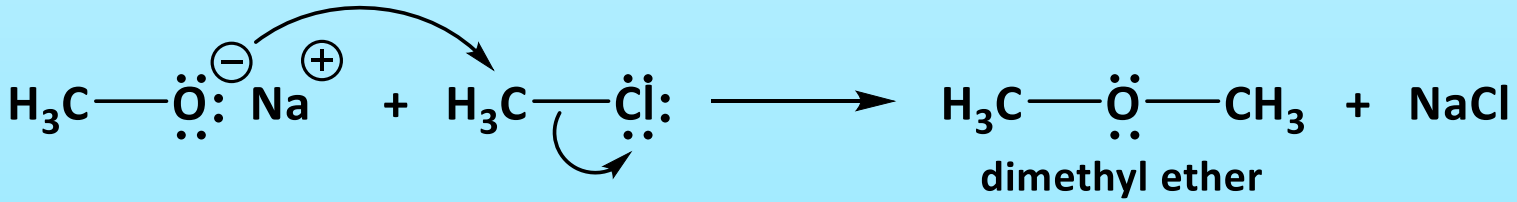


- Alcohols like water react with active metals such as Li, Na, K, Mg and others to liberate hydrogen gas and to form alkoxide salts

Reactions of Alcohols

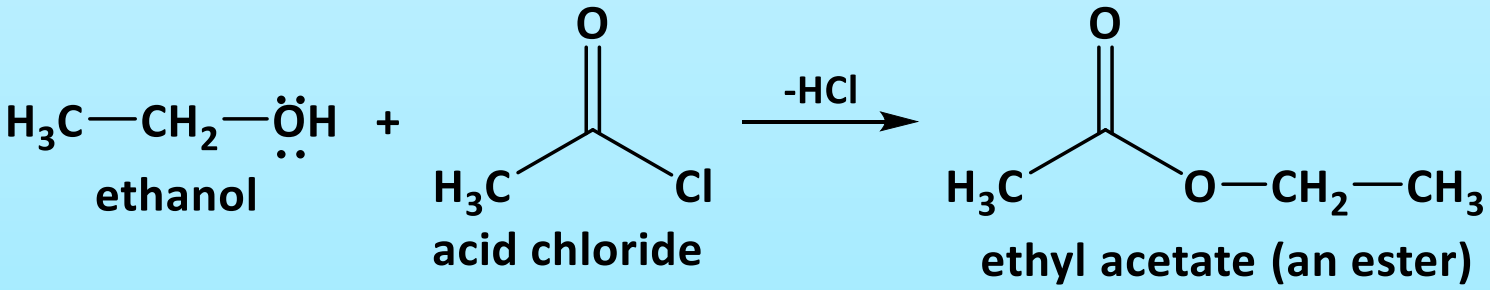


- The alkoxide salts are very useful intermediates indeed
- They can be reacted with haloalkanes to form ethers in a reaction known as the Williamson ether synthesis

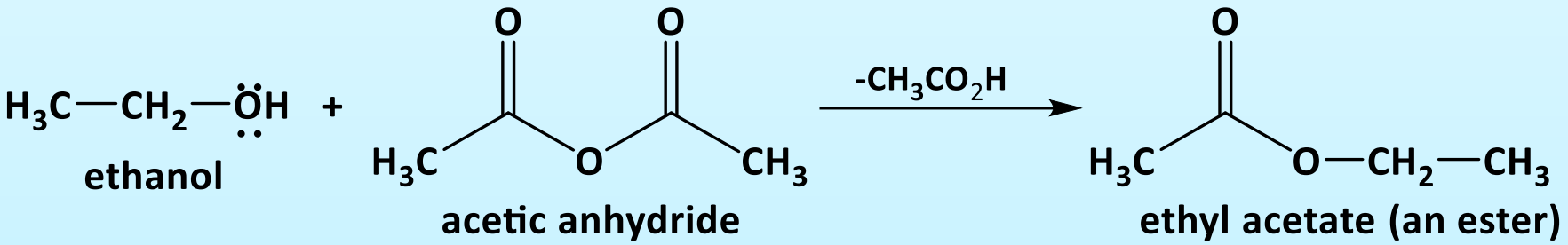


Reactions of Alcohols

- Another reaction that involves the use of the O–H groups and the non-bonding oxygen electrons, is the acylation reaction
- Here the alcohol is reacted with an acylating agent either an acid chloride or anhydride, to yield an ester



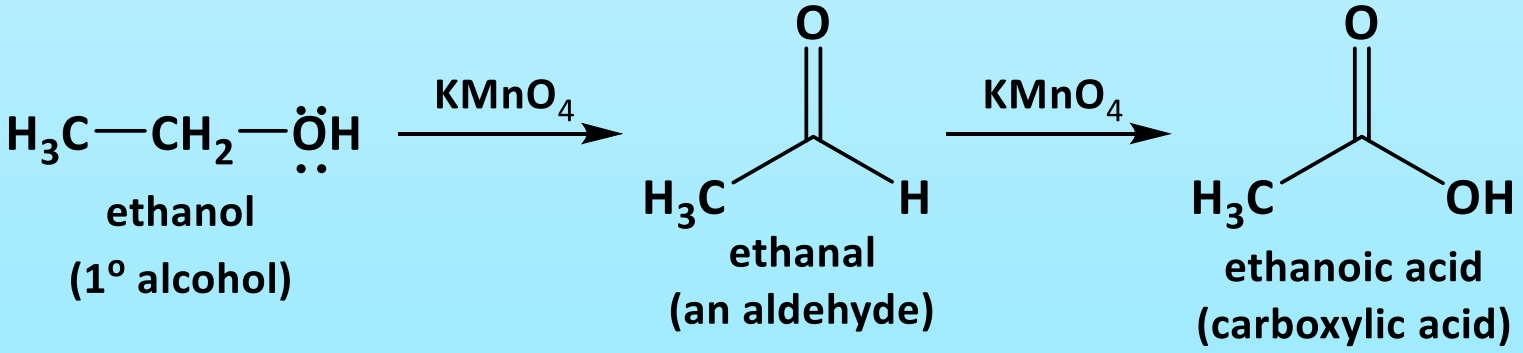
Reactions of Alcohols



- Here the hybridization of the carbon and oxygen (both sp^3 hybridized) is not altered
- There are other reactions, which involve the changing of the hybridization of both the carbon and the oxygen
- These are oxidation reactions

Reactions of Alcohols

- They occur in primary and secondary alcohols because the carbon atom to which the –OH group is attached also has a hydrogen atom attached to it
- Primary alcohols when oxidised are converted initially to an aldehyde and then on to a carboxylic acid



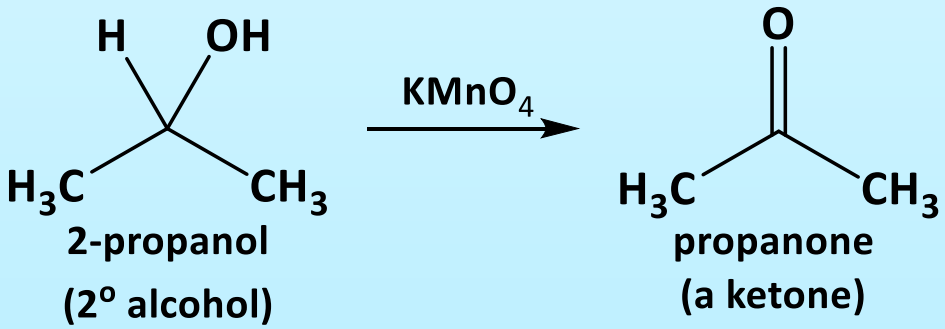
ethanol
(1° alcohol)

ethanal
(an aldehyde)

ethanoic acid
(carboxylic acid)

Reactions of Alcohols

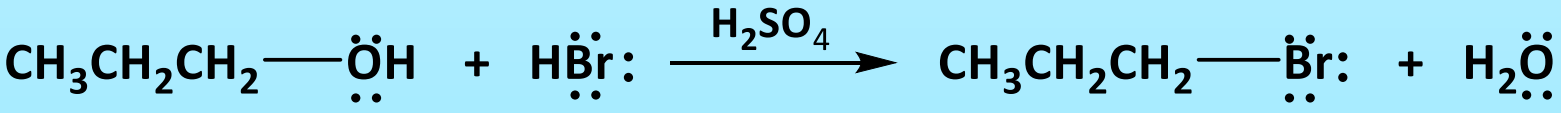
- Secondary alcohols when oxidized yield ketones



- Tertiary alcohols do not undergo oxidation because they do not possess a hydrogen atom on the carbon atom to which the –OH group is attached

Reactions of Alcohols

- There are other reactions where the C–O bond is cleaved
- One such reaction involves the halogenation of the alcohols in which the hydroxyl group is replaced by a halogen atom
- In primary and secondary alcohols, an acid catalyst (such as H_2SO_4, $ZnCl_2$) is necessary to get the reaction to proceed

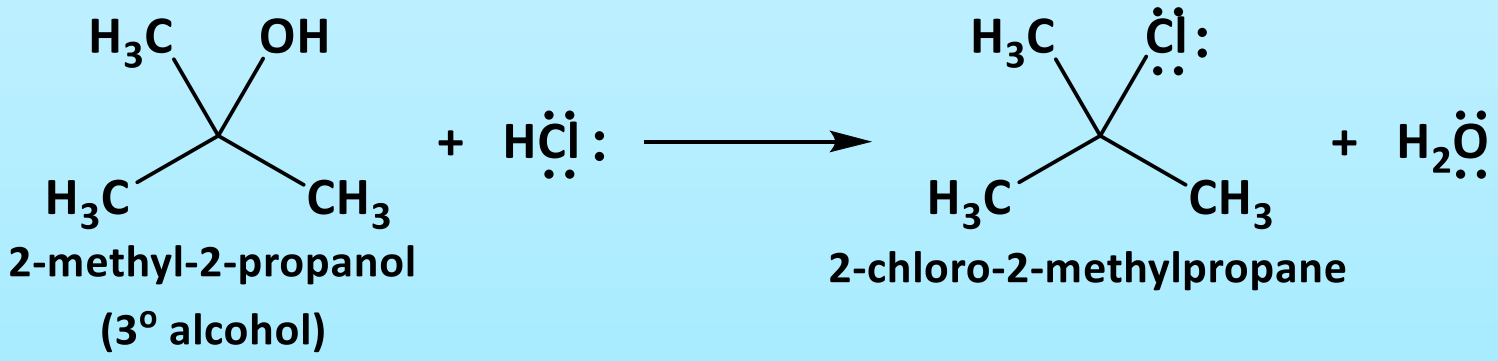


1-propanol
(1^o alcohol)

1-bromopropane

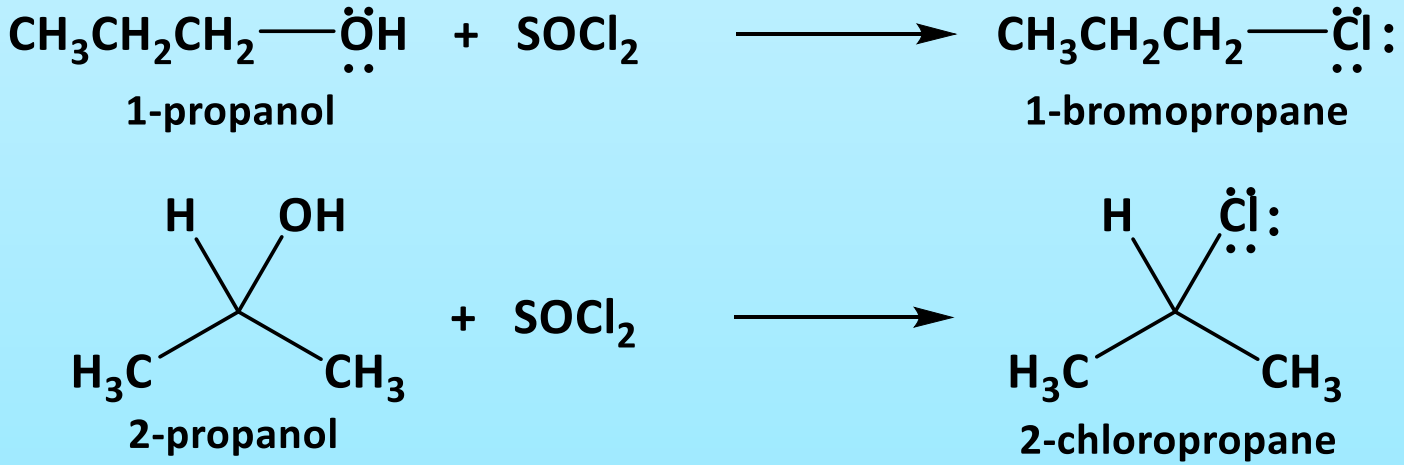
Reactions of Alcohols

- In the case of tertiary alcohols, no acid catalyst is required because the activation energy for the production of the cationic intermediate is quite low and is attained easily



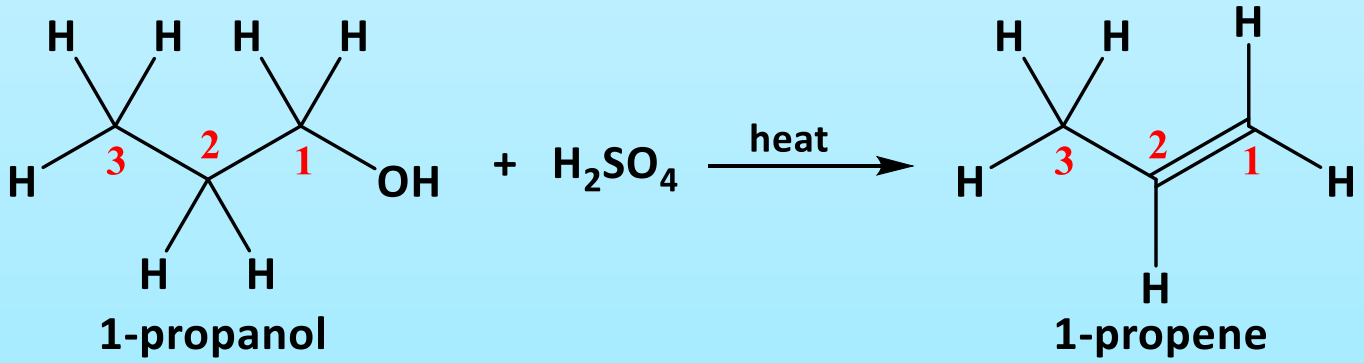
Reactions of Alcohols

- Halogenation, especially chlorination can also be achieved by reacting an alcohol with thionyl chloride ($SOCl_2$)
- The reagent is particularly useful when the alcohol used is a primary or secondary alcohol because no catalyst is necessary



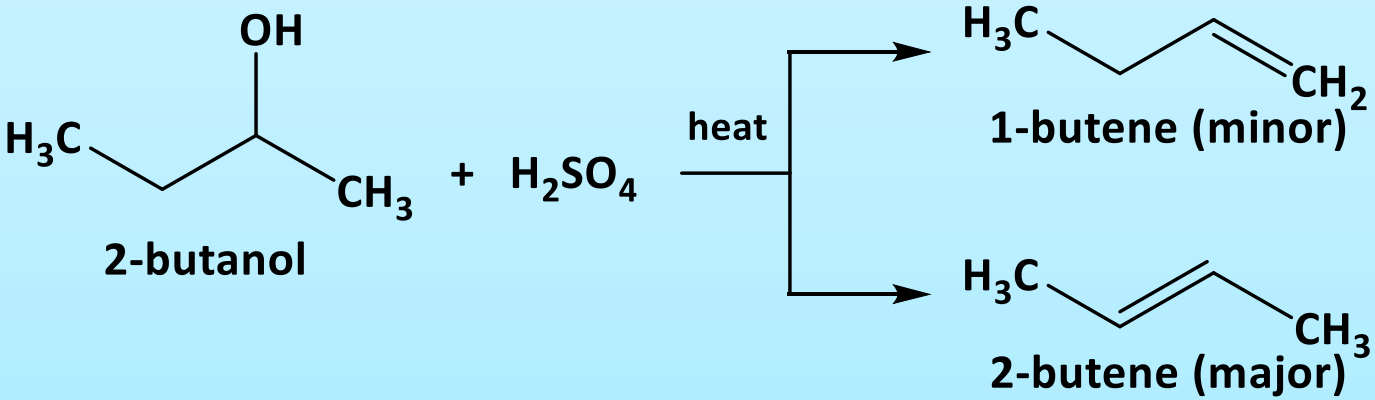
Reactions of Alcohols

- We have already seen that when alcohols are treated with an acid catalyst such as concentrated H_2SO_4, the alcohol undergoes a dehydration reaction (loses a water molecule) in which an alkene is produced



Reactions of Alcohols

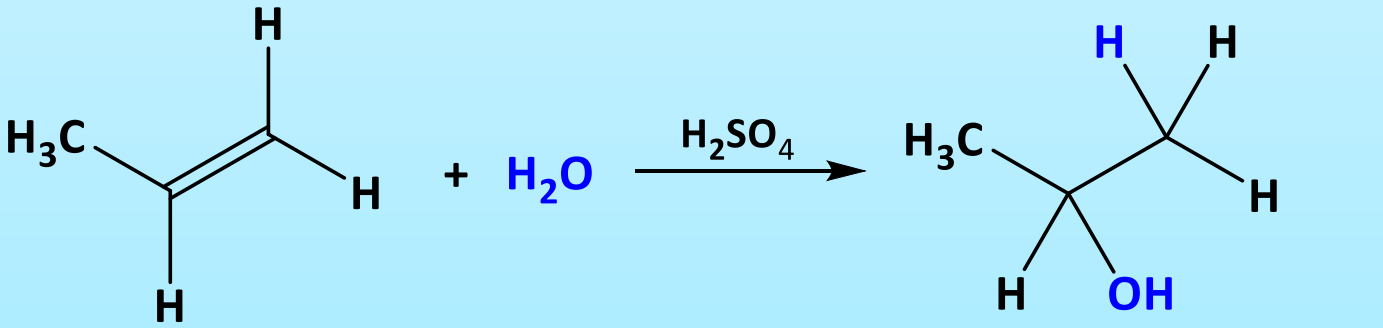
- When the dehydration reaction leads to the formation of two possible products, then the most substituted product will be preferentially formed – Zaitsev's rule



- In this case, 2-butene will be preferentially formed as it is the more substituted alkene

Synthesis of Alcohols

- Alcohols can be prepared in several ways
- A very common method is by adding water across a double bond of an alkene in the presence of a mineral acid like sulfuric acid

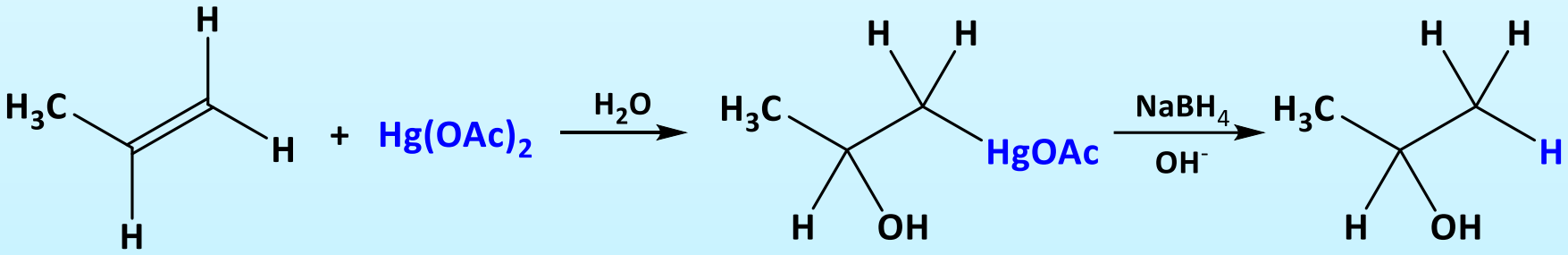


Markovnikov's addition product

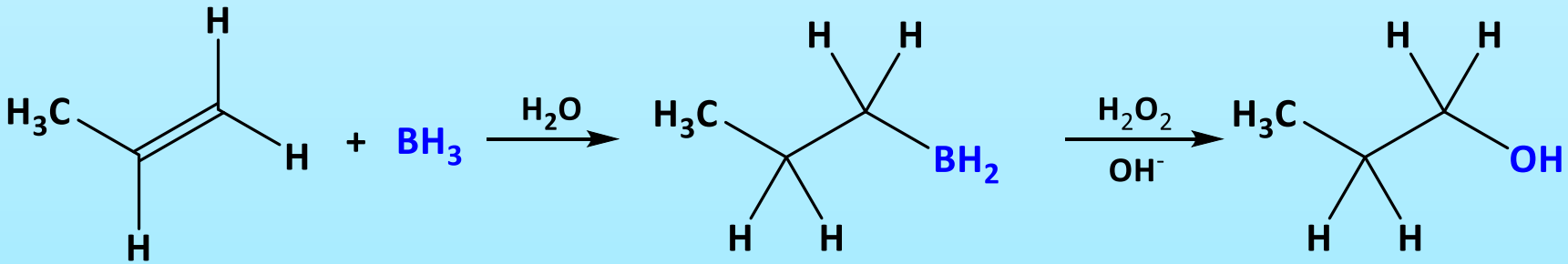
Synthesis of Alcohols

- There are two variants of this reaction which uses mercuric acetate [$Hg(OAc)_2$] and organoboranes [BH_3]
- In the first case, the reaction follows Markovnikov's rule, the mercury is reduced by a basic solution of $NaBH_4$ to yield an alcohol
- In the second case, the organoborane intermediate produced by the reaction of an alkene and BH_3 is oxidized by the basic hydrogen peroxide, H_2O_2 to yield a non-Markovnikov product

Synthesis of Alcohols



- In the second one, the boron derivative is oxidized with a peroxide to yield the alcohol

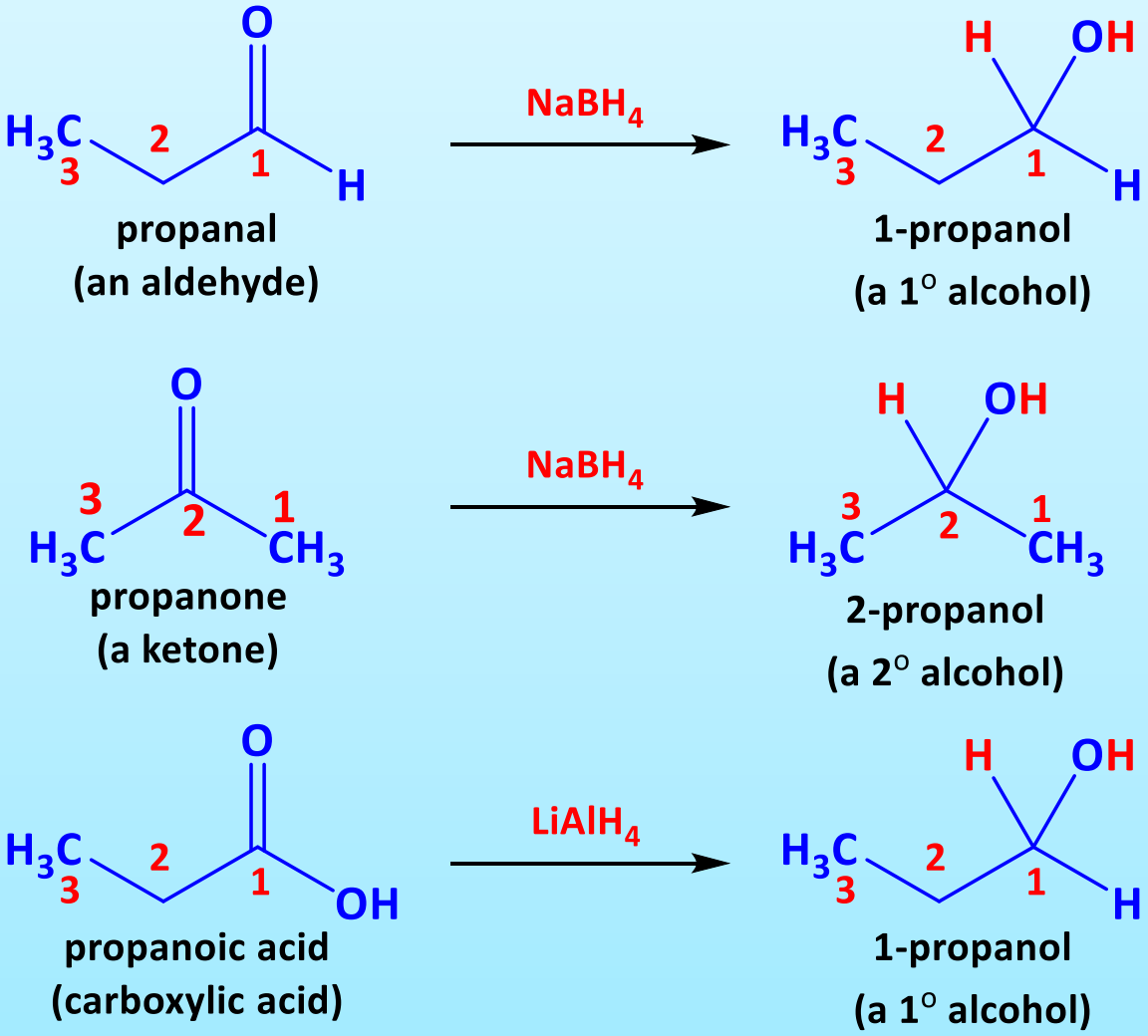


anti-Markovnikov's addition product

Synthesis of Alcohols

- We saw earlier that when primary and secondary alcohols are treated with oxidising agents, like $KMnO_4$, CrO_3, $K_2Cr_2O_7$, oxone, aldehydes and ketones are produced
- The reverse to these reactions is also true in that carboxylic acids and aldehydes when treated with reducing agents yield their corresponding primary alcohols
- Reduction of ketones yields the corresponding secondary alcohols

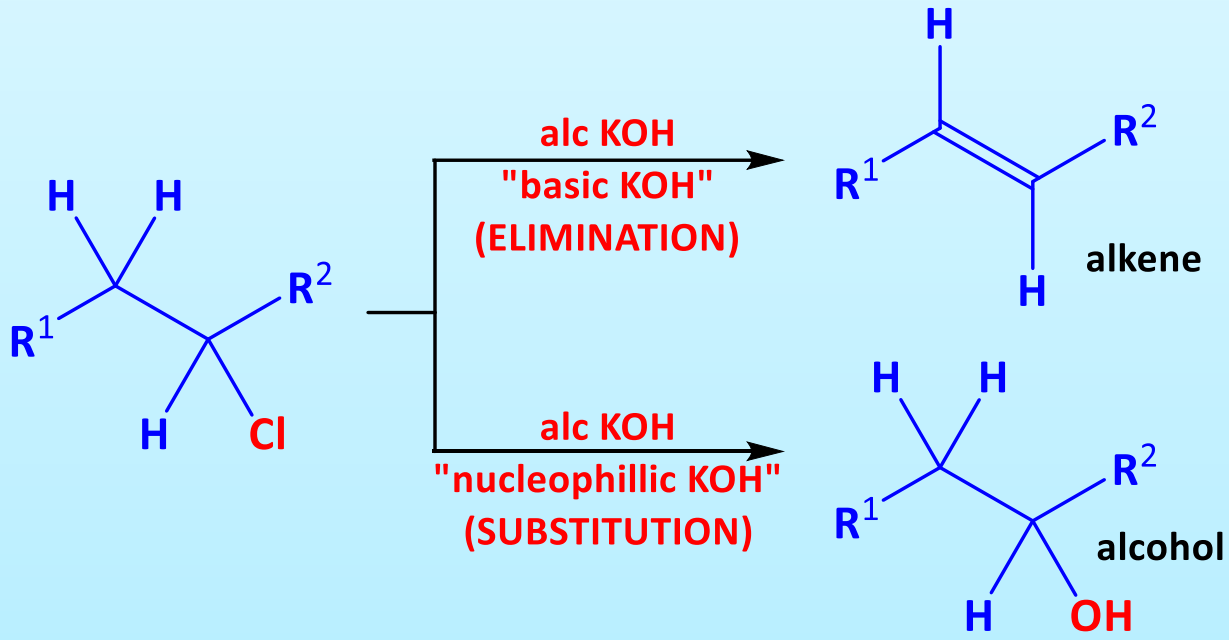
Synthesis of Alcohols



Synthesis of Alcohols

- Yet another method involves the substitution of haloalkanes with the hydroxide ion to produce alcohols
- As we saw in the section on the preparation of alkenes, when haloalkanes are treated with an alcoholic solution of KOH, two reactions are possible
- One involves elimination while the other involves displacement (substitution)

Synthesis of Alcohols



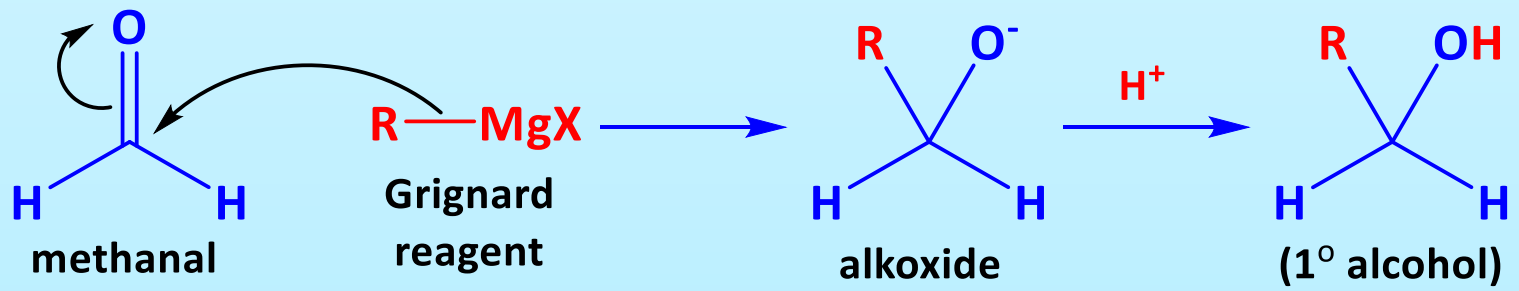
- To a great extent, the reaction conditions that are chosen will determine what product will be formed

Synthesis of Alcohols

- Alcohols can also be prepared by reacting aldehydes and ketones with Grignard reagents
- In these reactions, the Grignard reagent being strongly negatively charged will attack the electrophilic carbonyl carbon thus producing an alkoxide ion, which upon acidification yields the alcohol
- This method can be used to prepare primary, secondary and tertiary alcohols

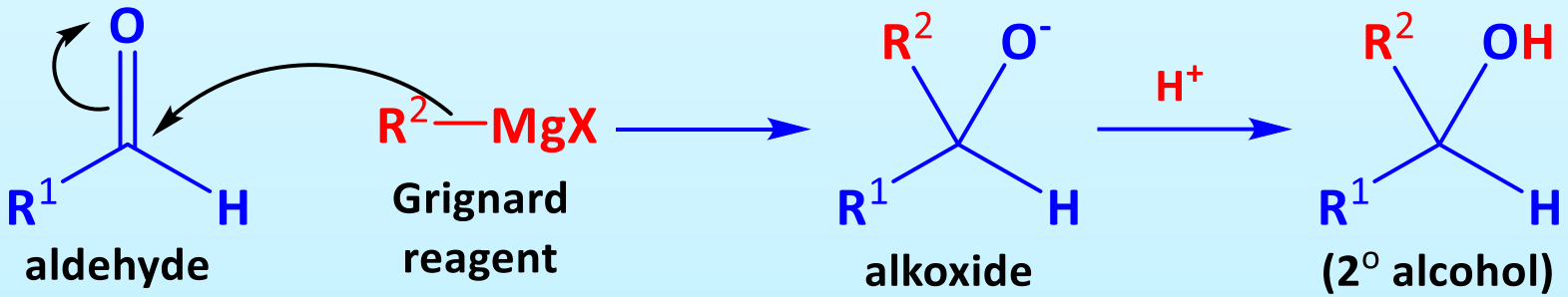
Synthesis of Alcohols

- **The reaction between methanal and a Grignard reagent will yield a primary alcohol**

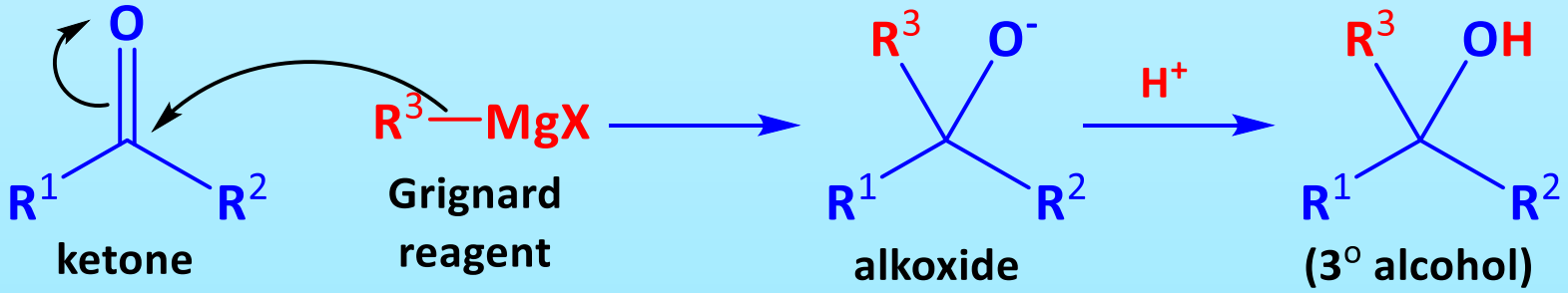


- **The reaction between an aldehyde and a Grignard reagent will yield a secondary alcohol**

Synthesis of Alcohols

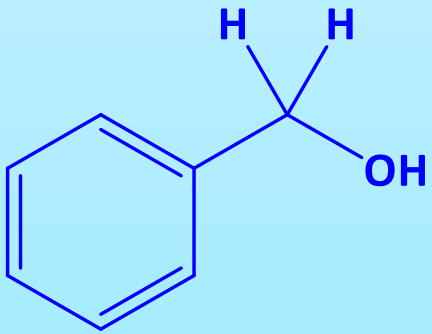


- **The reaction between a ketone and a Grignard reagent will yield a tertiary alcohol**

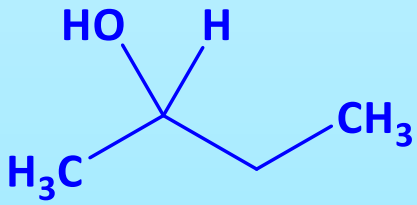


Synthesis of Alcohols

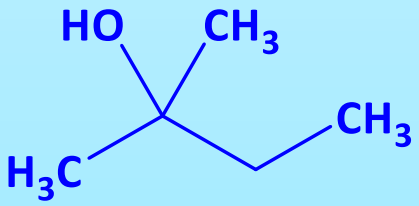
- Depending on what the desired product is, the appropriate reagents can be selected and the alcohol can be prepared
- For example, if you were asked to prepare phenylmethanol, 2-butanol, and 2-methyl-2-butanol, how could you prepare them?



phenylmethanol

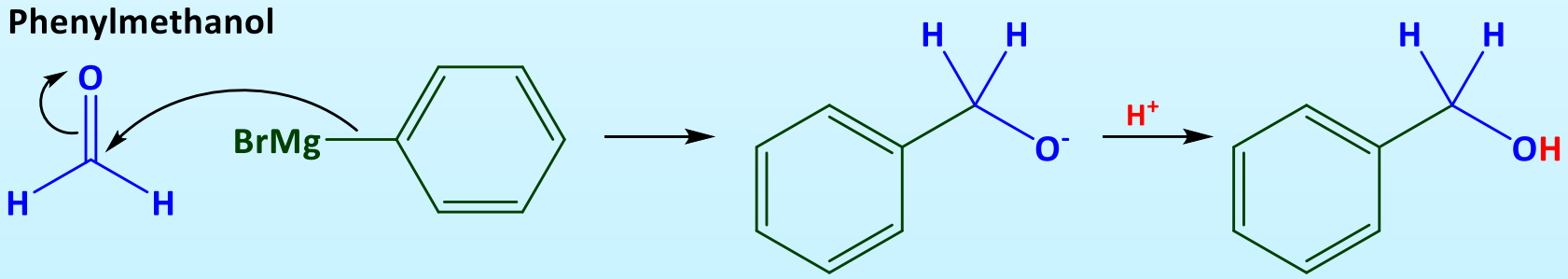


2-butanol

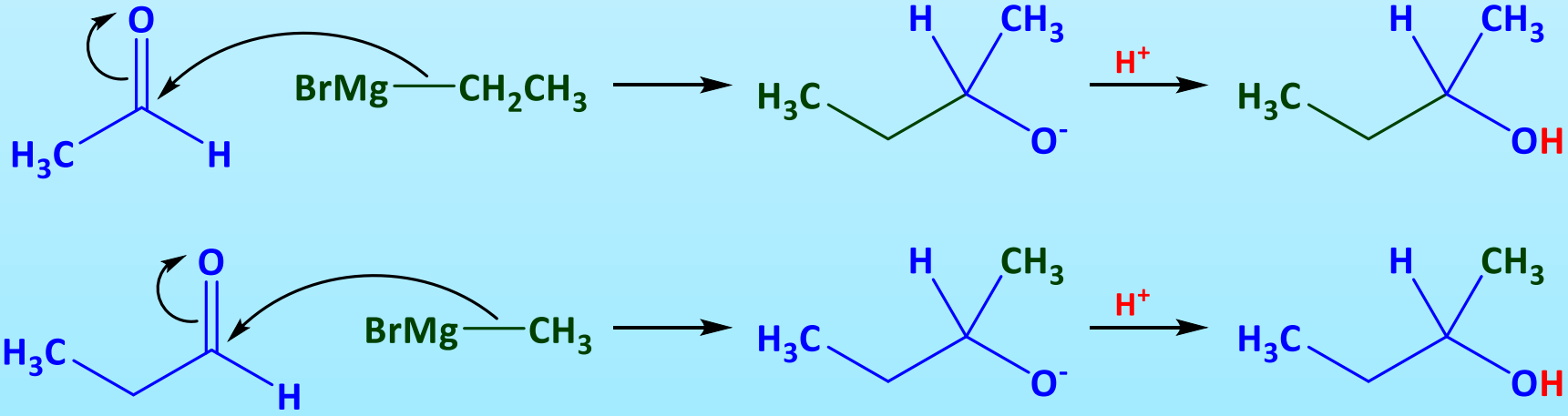


2-methyl-2-butanol

Synthesis of Alcohols



- For preparing 2-butanol, two approaches can be followed:



Synthesis of Alcohols

- Similarly for preparing 2-methyl-2-butanol, two approaches can also be followed: