Alcohols

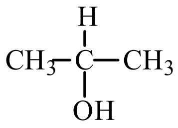
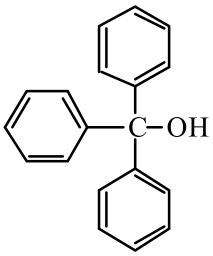
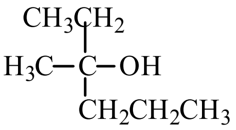
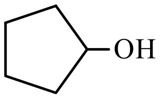
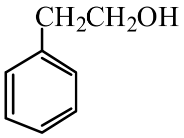
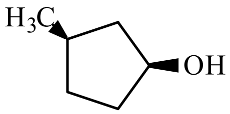
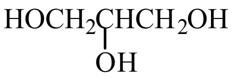
General formula R-OH

hydroxyl group

Nomenclature

IUPAC: name as for alkane dropping the -ane and adding -anol. Indicate the position of the hydroxyl group with a number. Number the longest alkane chain beginning at the end nearer the hydroxyl group.

e.g.

	IUPAC name	Trivial name
CH_3-OH	methanol	methyl alcohol
CH_3CH_2-OH	ethanol	ethyl alcohol
 $CH_3-\underset{OH}{\overset{H}{C}}-CH_3$	2-propanol	isopropanol
	triphenylmethanol	trityl alcohol
 $H_3C-\underset{CH_2CH_2CH_3}{\overset{CH_3CH_2}{C}}-OH$	3-methyl-3-hexanol	
$\overset{1}{HOCH_2}\overset{2}{CH}=\overset{3}{CH_2}$	2-propen-1-ol	allyl alcohol
$CH_3CHOHCH=CHCH_3$	3-butene-2-ol	
	cyclopentanol	
	2-phenylethanol	
	cis-3-methylcyclopentanol	
$HOCH_2CH_2OH$	1,2-ethanediol	ethylene glycol
 $HOCH_2\underset{OH}{C}HCH_2OH$	1,2,3-propantriol	glycerol

Properties of Alcohols

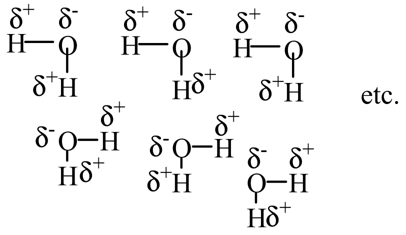
Boiling Points

Compound	M.W.	B.Pt.°C
CH_4	16	-161.5
CH_3Cl	50.5	-24
CH_3OH	32	64.5
CH_3CH_3	30	-88.6
$CH_3CH_2CH_3$	44	-42
CH_3OCH_3	46	-24

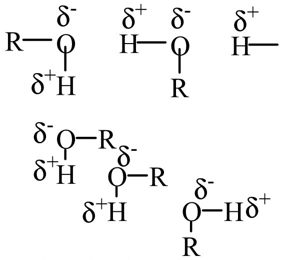
Compound	M.W.	B.Pt.°C
CH_4	16	-161.5
NH_3	17	-33
H_2O	18	100
HF	20	19

The low molecular weight alcohols, with 4 carbons or less, are water soluble. The hydrocarbons and aryl halides are not.

There are several types of intermolecular bonding: London or dispersion forces, dipole-dipole interactions and hydrogen bonding. Hydrogen bonding is the strongest type of intermolecular bonding. Hydrogen bonds exist between molecules having an H attached to a strongly electronegative atom such as O, N, or F. These forces are present in water and can build up a 3-D network.



Alcohols can also hydrogen bond in this way.

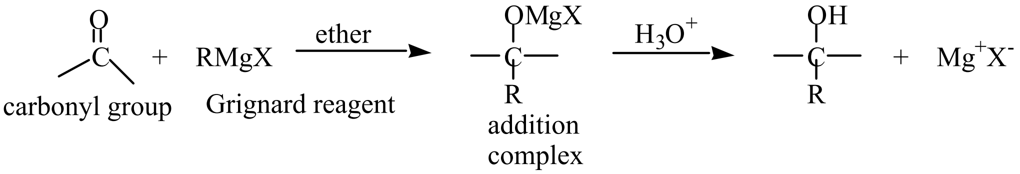


These hydrogen bonds have to be broken before the molecules break apart to form vapour and so they account for the relatively high boiling points.

Synthesis of Alcohols

Grignard reactions

Generalized reaction

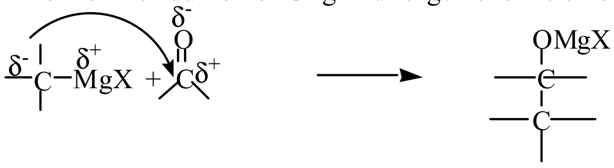


Preparation of Grignard reagent

$$R\text{-}X + Mg \xrightarrow{\text{ether}} RMgX$$

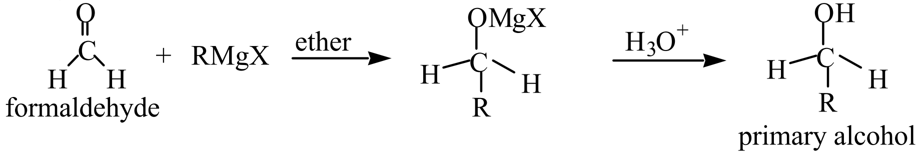
X = Br or I

Mechanism of the addition of Grignard reagents to the carbonyl group



Formation of primary, secondary and tertiary alcohols by the Grignard Reactions

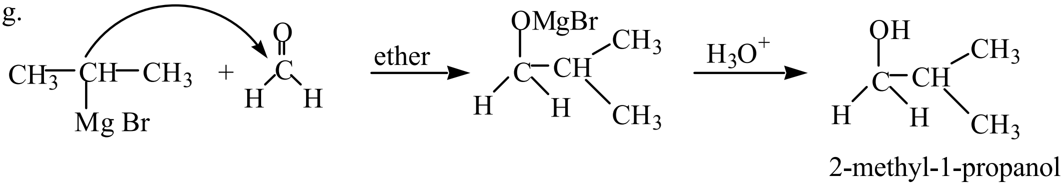
Primary alcohols



formaldehyde

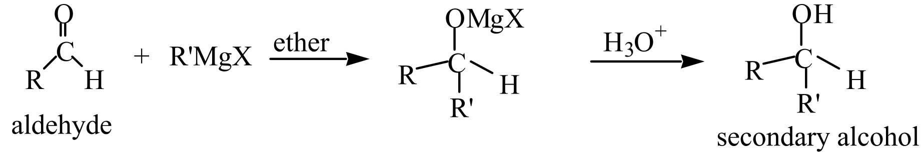
primary alcohol

e.g.



2-methyl-1-propanol

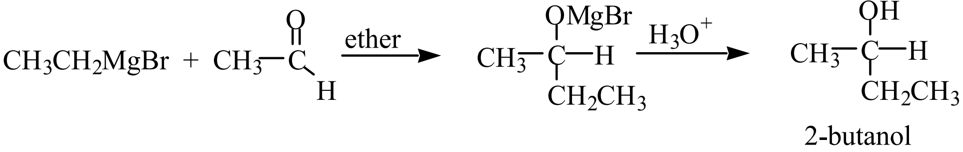
Secondary alcohols



aldehyde

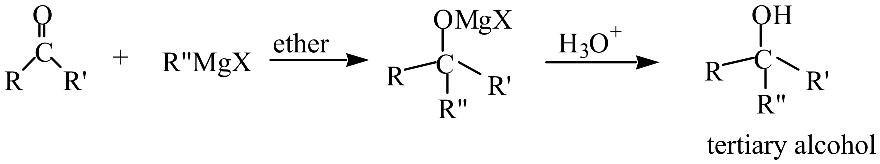
secondary alcohol

e.g.



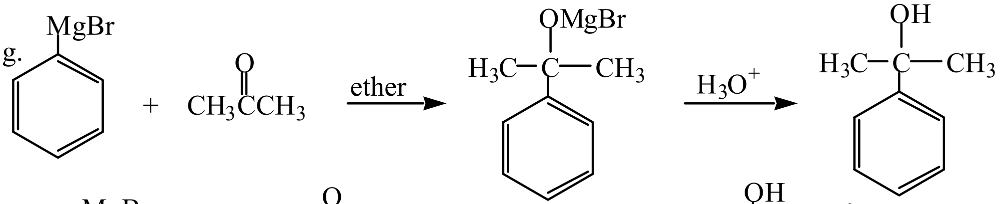
2-butanol

Tertiary alcohols

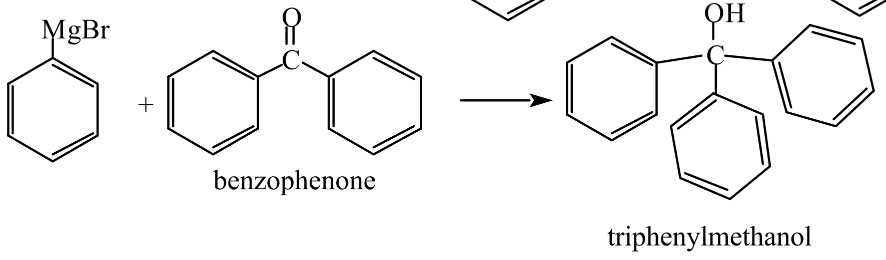


tertiary alcohol

e.g.



and



benzophenone

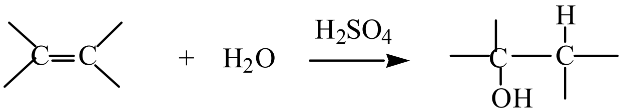
triphenylmethanol

Triphenylmethanol is an interesting compound. When treated with acid, it forms a very stable carbocation which has 10 resonance structures.

Hydration of Alkenes

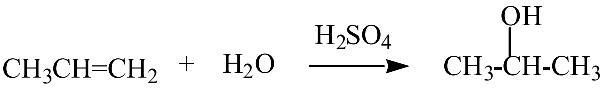
Acid-catalyzed addition of water to an alkene

General reaction



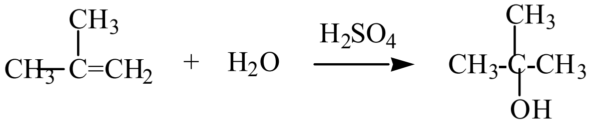
follows Markovnikov rule
get both syn and anti addition

e.g.



$$CH_3CH{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3\text{-}\overset{OH}{C}H\text{-}CH_3$$

75%

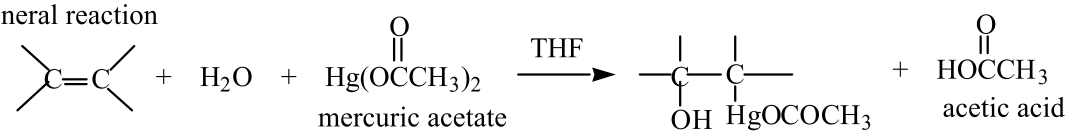


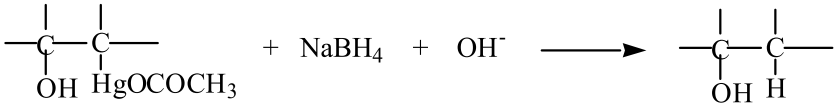
$$CH_3\text{-}\overset{CH_3}{C}{=}CH_2 + H_2O \xrightarrow{H_2SO_4} CH_3\text{-}\underset{OH}{\overset{CH_3}{C}}\text{-}CH_3$$

85%

Oxymercuration-demercuration reaction

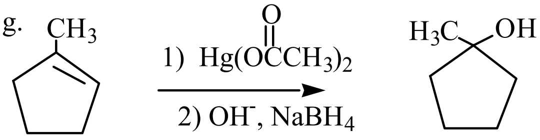
General reaction



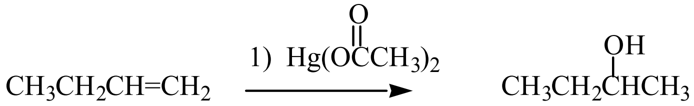


follows Markovnikov rule
get both syn and anti addition

e.g.



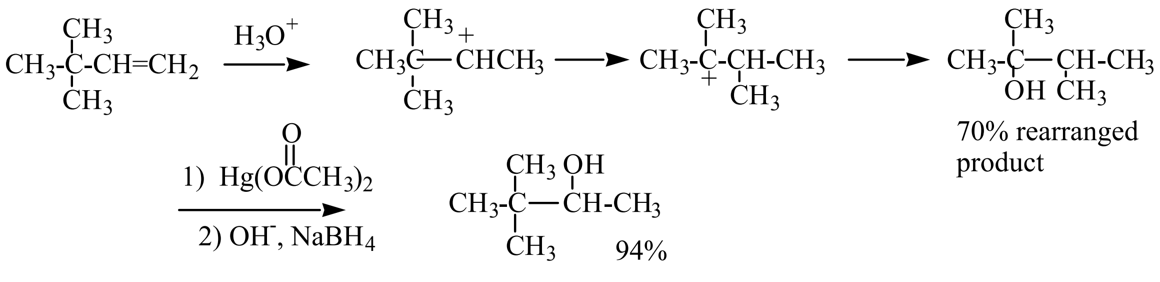
90%



$$CH_3CH_2CH{=}CH_2 \xrightarrow[\text{2) } OH^-,\ NaBH_4]{\text{1) } Hg(O\overset{O}{\overset{\|}{C}}CH_3)_2} CH_3CH_2\overset{OH}{C}HCH_3$$

95%

In oxymercuration-demercuration reactions, acid is not required so that carbocations are not formed and rearrangement does not occur

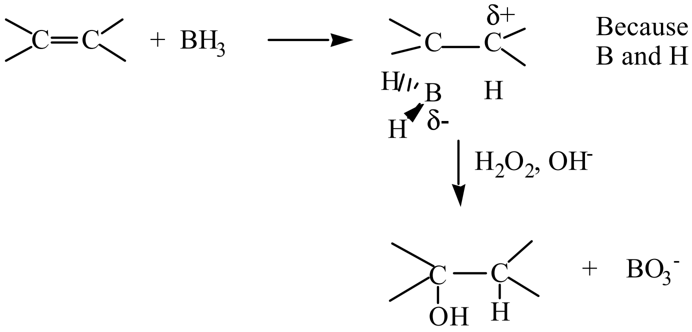


70% rearranged product

94%

Hydroboration - oxidation

This is a very important reaction since it gives Anti-Markovnikov addition and both the H and the OH add sy



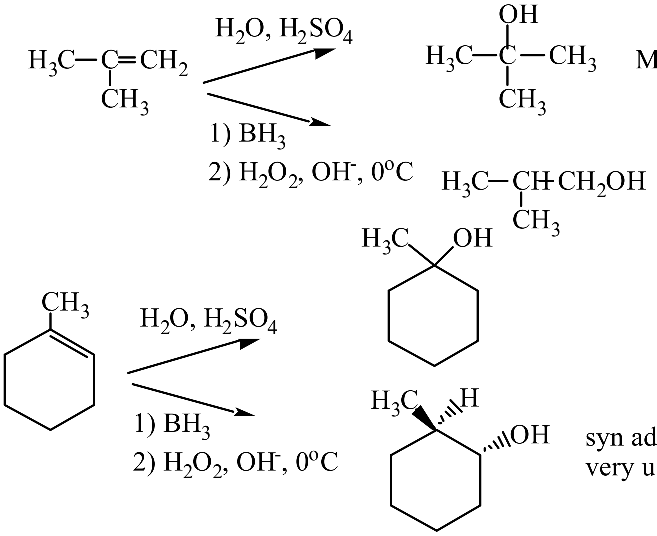
Because there is a cyclic compled formed, both B and H add to the same side of the double bond.

e.g.

$$3\ CH_3CH{=}CH_2 + BH_3 \longrightarrow B\text{-}(CH_2CH_2CH_3)_3 \xrightarrow{H_2O_2,\ OH^-,\ 0^oC} 3\ CH_3CH_2CH_2OH$$

tri-(1-propyl) borane   1-Propanol

Notice the different products from hydration and hydroboration of an alkene



Markownikov addition

anti-Markovnikov addition

syn addition, stereospecific reaction
very useful

Hydrolysis of alkyl halides

This reaction was studied in the context of S_N1 and S_N2 reactions.

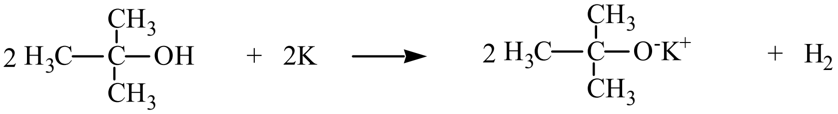
Reactions of Alcohols

Reactions with active metals

$2ROH + 2M \longrightarrow 2RO^-M^+ + H_2$ i.e., the hydrogen of the OH is slightly acidic

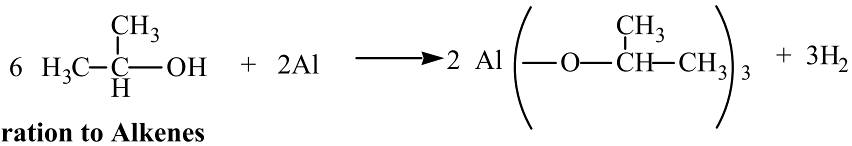
M = Li, Na, K fast reaction
Mg, Ca, Al very slow reaction

e.g. $2CH_3CH_2OH + 2Na \longrightarrow 2CH_3CH_2^-Na^+ + H_2$



$$2\,H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH + 2K \longrightarrow 2\,H_3C-\overset{CH_3}{\underset{CH_3}{C}}-O^-K^+ + H_2$$

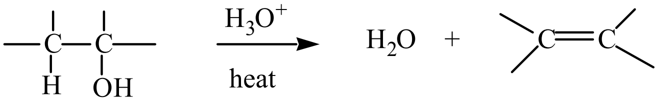
potassium t-butoxide



$$6\;H_3C-\overset{CH_3}{\underset{H}{C}}-OH + 2Al \longrightarrow 2\;Al\left(-O-\overset{CH_3}{CH}-CH_3\right)_3 + 3H_2$$

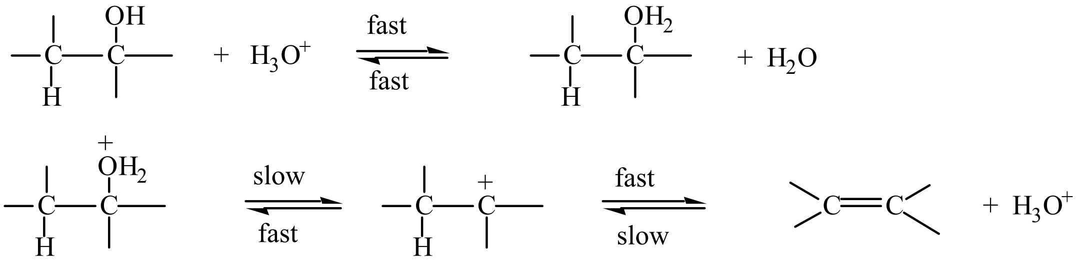
Dehydration to Alkenes

This reaction has been studied in the synthesis of alkenes



$$-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{OH}{C}}- \xrightarrow[\text{heat}]{H_3O^+} H_2O + \;>C=C<$$

Mechanism:

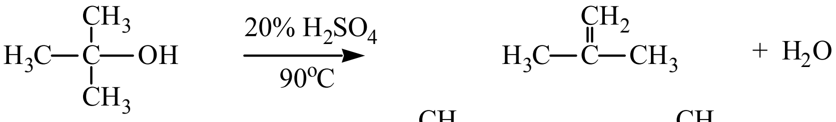


$$-\overset{|}{\underset{H}{C}}-\overset{OH}{\underset{|}{C}}- + H_3O^+ \underset{\text{fast}}{\overset{\text{fast}}{\rightleftharpoons}} -\overset{|}{\underset{H}{C}}-\overset{\overset{+}{O}H_2}{\underset{|}{C}}- + H_2O$$

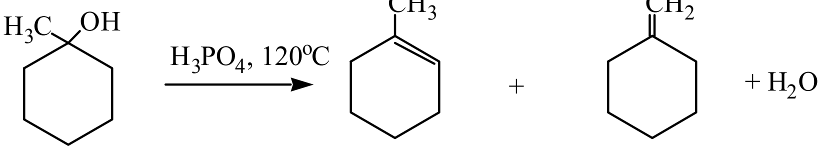
$$-\overset{|}{\underset{H}{C}}-\overset{\overset{+}{O}H_2}{\underset{|}{C}}- \underset{\text{fast}}{\overset{\text{slow}}{\rightleftharpoons}} -\overset{|}{\underset{H}{C}}-\overset{+}{\underset{|}{C}}- \underset{\text{slow}}{\overset{\text{fast}}{\rightleftharpoons}} >C=C< + H_3O^+$$

Note that all of the reactions are reversible. Therefore the alkene has to be removed from the solution as rapidly as it is formed. The slow rate-determining step is the formation of the carbocation. Tertiary alcohols react more rapidly than secondary which react more rapidly than primary.

e.g.



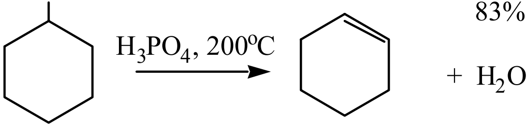
$$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow[90^\circ C]{20\%\ H_2SO_4} H_3C-\overset{\overset{CH_2}{\|}}{C}-CH_3 + H_2O$$



83%

very small amount

Dehydration follows the Saytzeff rule - the most highly substituted alkene is formed as the major product. This is also the more stable alkene.

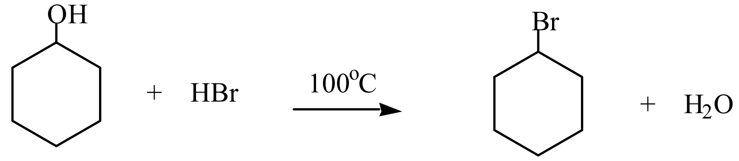


Conversion to Alkyl Halides

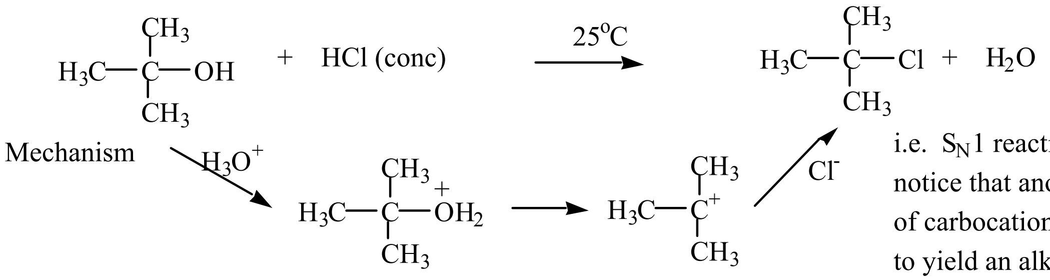
$$R\text{-}OH \xrightarrow[\text{or } PX_3]{HX} RX + H_2O \text{ or } P(OH)_3$$

This is one of the most important methods of synthesis of alkyl halides

e.g.

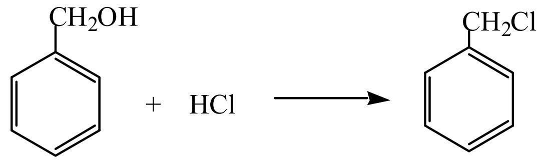


cyclohexanol



i.e. S_N1 reaction
notice that another reaction of carbocations is loss of H^+ to yield an alkene. In this example, the nucleophile Cl^- is in large excess and so the formation of the alkyl halide is favored.

and

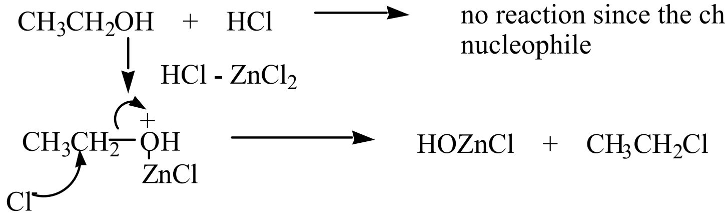


benzyl alcohol

benzyl chloride

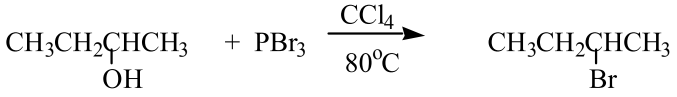
The benzylic cation is more stable than a tertiary carbocation.

but



no reaction since the chloride ion is not a strong enough nucleophile

Primary alcohols and methyl alcohols react with phosphorus trihalides by an S_N2 reaction

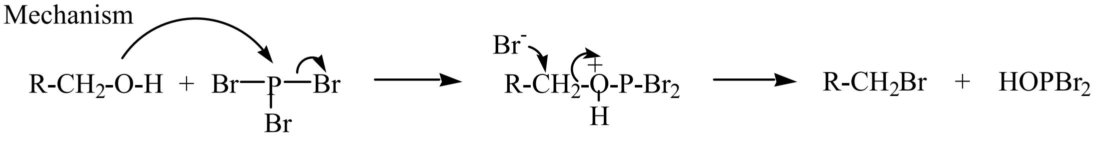


$$CH_3CH_2\underset{OH}{C}HCH_3 + PBr_3 \xrightarrow[80^{\circ}C]{CCl_4} CH_3CH_2\underset{Br}{C}HCH_3$$

$$CH_3CH_2CH_2CH_2OH + PCl_3 \xrightarrow[80^{\circ}C]{CCl_4} CH_3CH_2CH_2CH_2Cl$$

Using PBr_3 there is no carbocation formed and so we do not get rearrangements and this is usually the preferred reagent for converting alcohols to alkyl bromides.

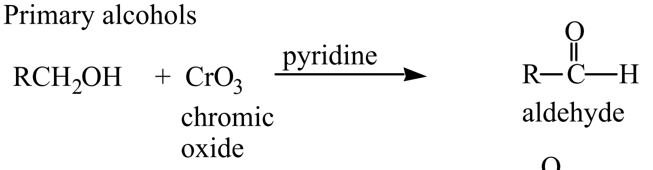
Mechanism



This is an S_N2 type of reaction

Oxidation of Alcohols

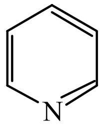
Primary alcohols



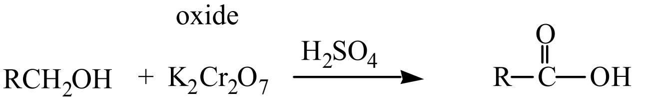
$$RCH_2OH + CrO_3 \xrightarrow{pyridine} R-\overset{O}{\overset{\|}{C}}-H$$

chromic oxide

aldehyde



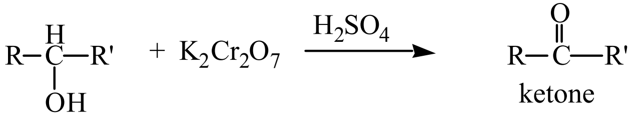
pyridine



$$RCH_2OH + K_2Cr_2O_7 \xrightarrow{H_2SO_4} R-\overset{O}{\overset{\|}{C}}-OH$$

carboxylic acid

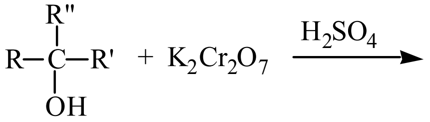
Secondary alcohols



$$R-\underset{OH}{\overset{H}{C}}-R' + K_2Cr_2O_7 \xrightarrow{H_2SO_4} R-\overset{O}{\overset{\|}{C}}-R'$$

ketone

Tertiary alcohols

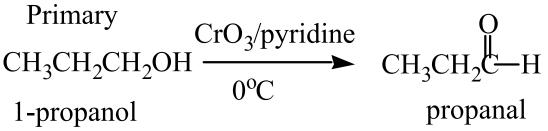


$$R-\underset{OH}{\overset{R''}{C}}-R' + K_2Cr_2O_7 \xrightarrow{H_2SO_4}$$

no reaction
black tar if the temperature is high enough!
oxidation would require breaking of C-C bond

Examples

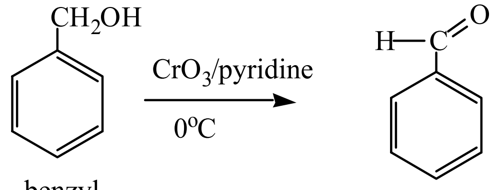
Primary



$$CH_3CH_2CH_2OH \xrightarrow[0^oC]{CrO_3/pyridine} CH_3CH_2\overset{O}{\overset{\|}{C}}-H$$

1-propanol

propanal



benzyl allcohol

benzaldehyde

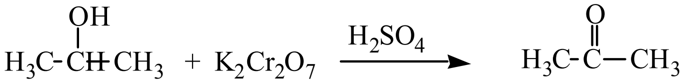
$$CH_3CH_2CH_2CH_2OH + K_2Cr_2O_7 \xrightarrow{H_2SO_4} CH_3CH_2CH_2COOH$$

butanoic acid

This reaction was the basis of the breathalyzer test: $Cr_2O_7^{=} \longrightarrow Cr^{3+}$ by ethanol oxidation

orange green

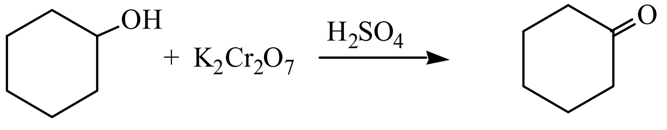
Secondary



$$H_3C-\overset{OH}{\overset{|}{C}H}-CH_3 + K_2Cr_2O_7 \xrightarrow{H_2SO_4} H_3C-\overset{O}{\overset{\|}{C}}-CH_3$$

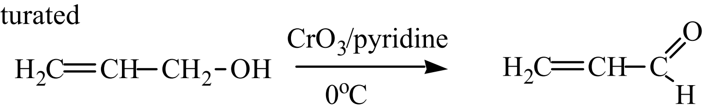
2-propanol

2-propanone (acetone)



cyclohexanone

Unsaturated



$$H_2C=CH-CH_2-OH \xrightarrow[0^oC]{CrO_3/pyridine} H_2C=CH-C(=O)H$$

propenal

Using a stronger oxidising agent would oxidise the double bond