US04CHHE21 : ORGANIC CHEMISTRY

UNIT-II : ALCOHOL, PHENOS, ALDEHYDES, KETONES, AMINE

Compiled By Dr. B. C. Dixit

Alcohols

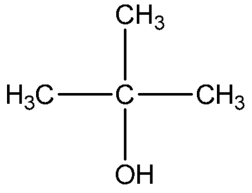
Structure of alcohols

Alcohols are compounds of the general formula ROH, where R is any alkyl or substituted alkyl group. The group may be primary, secondary, or tertiary;

$$R-OH$$

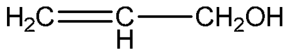
An alcohol

It may be open chain or cyclic; it may contain a halogen atom, additional hydroxyls, or one of the many groups that are still unfamiliar to us: a double bond, for example, or an aromatic ring. For example:



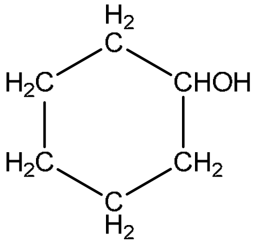
$$H_3C-\overset{CH_3}{\underset{OH}{C}}-CH_3$$

2-Methyl-2-propanol
tert-Butyl alcohol

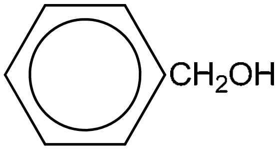


$$H_2C=\underset{H}{C}-CH_2OH$$

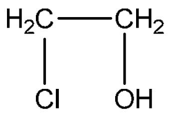
2-Propen-1-ol
Allyl alcohol



Cyclohexanol

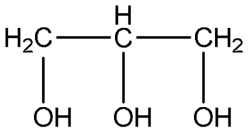


Benzyl alcohol



$$\underset{Cl}{H_2C}-\underset{OH}{CH_2}$$

2-Chloroethanol
Ethylene chlorohydrin



$$\underset{OH}{H_2C}-\overset{H}{\underset{OH}{C}}-\underset{OH}{CH_2}$$

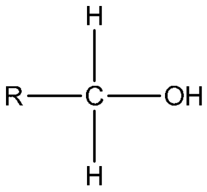
1,2,3-Propanetriol
Glycerol

All alcohols contain the hydroxyl (-OH) group, which, as the functional group, determines the properties characteristic of this family. Variations in structure of the R-group may affect the rate at which the alcohol undergoes certain reactions, and even, in a few cases, may affect the kind of reaction.

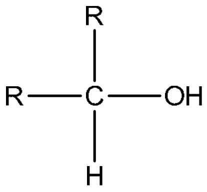
(Compounds in which the hydroxyl group is attached directly to an aromatic ring are not alcohols; they are phenols).

Classification of alcohols

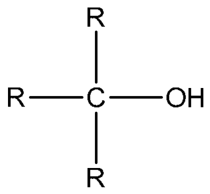
An alcohol is classified as primary, secondary, or tertiary according to the kind of carbon that bears the –OH group:



Primary (1°)



Secondary (2°)



Tertiary (3°)

Reactions of alcohols

The chemical properties of an alcohol, ROH, are determined by its functional group, -OH, the hydroxyl group.

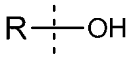
Reactions of an alcohol can involve the breaking of either of two bonds: the C-OH bond, with removal of the –OH group; or the O-H bond, with removal of -H. Either kind of reaction can involve substitution, in which a group replaces the –OH or –H, or elimination, in which a double bond is formed.

Differences in the structure of the group R- cause difference in reactivity, and in a few cases even profoundly alter the course of reaction. We shall see what these effects of structure on reactivity alter the course of reaction.

Some of the more important reactions of alcohols are listed below :

REACTIONS OF ALCOHOLS

C---H Bond Cleavge



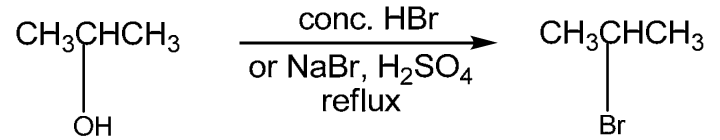
1. Reaction with hydrogen halides.

$$R\text{—}OH + HX \longrightarrow R\text{—}X + H_2O \qquad \text{R may rearrange}$$

Reactivity of HX: HI > HBr > HCl

Reactivity of ROH: allyl, benzyl $>3^o > 2^o > 1^o$

Examples:

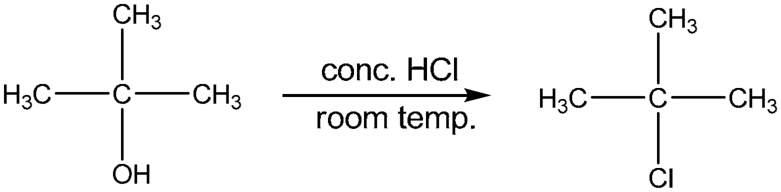


$$\underset{\text{OH}}{CH_3\overset{|}{C}HCH_3} \xrightarrow[\text{or NaBr, } H_2SO_4 \text{ reflux}]{\text{conc. HBr}} \underset{\text{Br}}{CH_3\overset{|}{C}HCH_3}$$

Isopropyl alcohol Isopropyl bromide

$$CH_3CH_2CH_2CH_2CH_2OH \xrightarrow[\text{heat}]{\text{HCl, } ZnCl_2} CH_3CH_2CH_2CH_2CH_2Cl$$

n-Pentyl alcohol n-Pentyl chloride



$$H_3C-\underset{OH}{\overset{CH_3}{C}}-CH_3 \xrightarrow[\text{room temp.}]{\text{conc. HCl}} H_3C-\underset{Cl}{\overset{CH_3}{C}}-CH_3$$

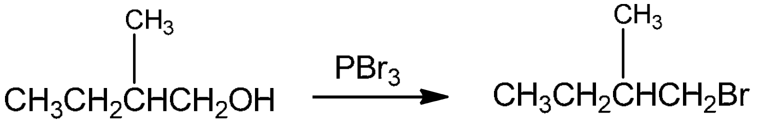
tert-Butyl alcohol tert-Butyl chloride

2. Reaction with phosphorus trihalides.

$$3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$$

$$(Px_3 = PBr_3, PI_3)$$

Examples:



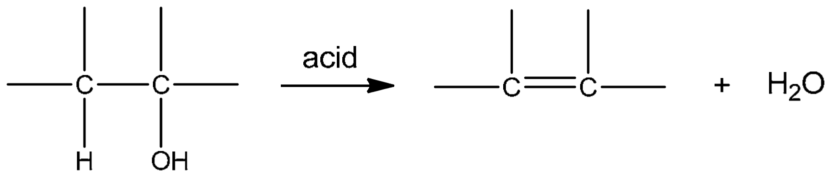
$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH \xrightarrow{PBr_3} CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2Br$$

2-Methyl-1-butanol 2-Methyl-1-bromobutane

$$CH_3CH_2OH \xrightarrow{P + I_2} CH_3CH_2I$$

Ethyl alcohol Ethyl iodide

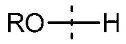
3. Dehydration.



Rearrangement may occur

Reactivity of ROH: 3° > 2° > 1°

O---H Bond cleavage



4. Reaction as acids : reaction with active metals.

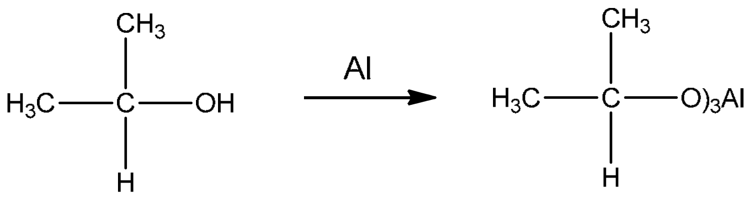
$RO-H + M \longrightarrow RO^-M^+ + \frac{1}{2}H_2$ M=Na, K, Mg, Al, etc.

Reactivity of ROH: CH_3OH > 1° > 2° > 3°

Examples:

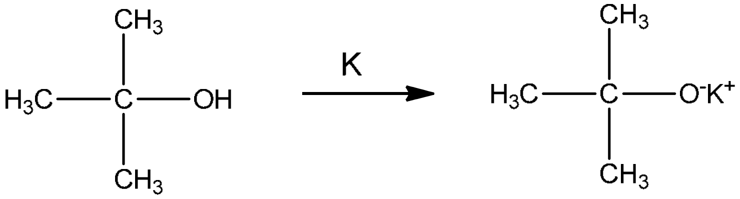
$CH_3CH_2OH \xrightarrow{Na} CH_3CH_2O^-Na^+ + \frac{1}{2}H_2$

Ethyl alcohol — Sodium ethoxide



$H_3C-\overset{CH_3}{\underset{H}{C}}-OH \xrightarrow{Al} H_3C-\overset{CH_3}{\underset{H}{C}}-O)_3Al$

Isopropyl alcohol — Aluminum isopropoxide

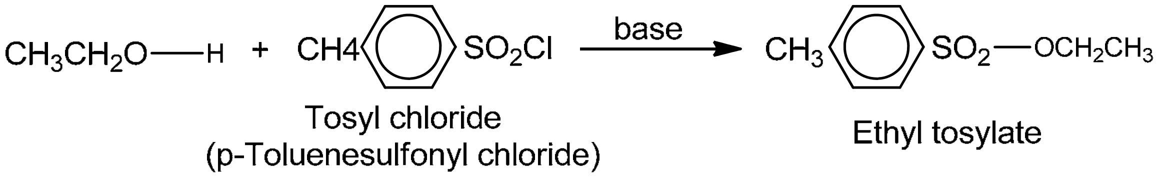


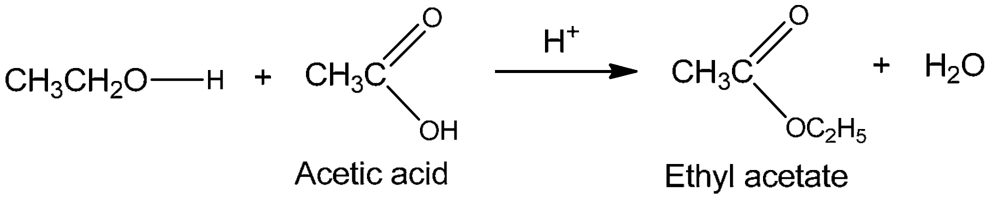
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-OH \xrightarrow{K} H_3C-\overset{CH_3}{\underset{CH_3}{C}}-O^-K^+$

tert-Butyl alcohol — Potassium tert-butoxide

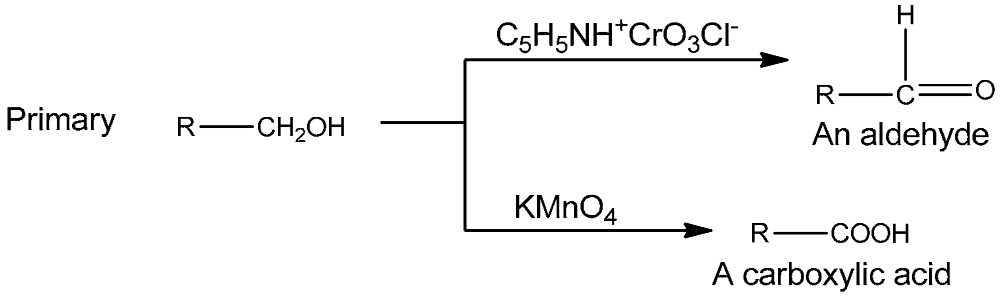
5. Ester formation.

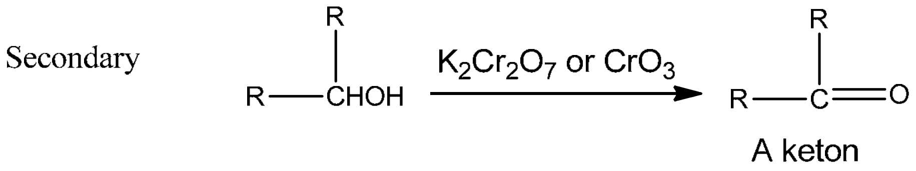
Examples:

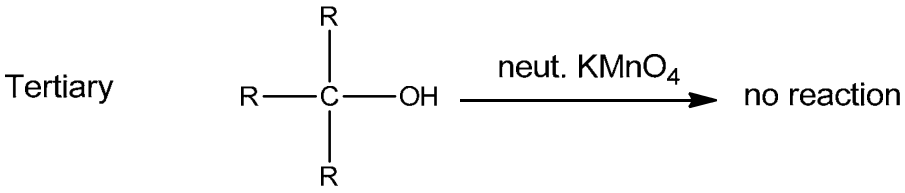




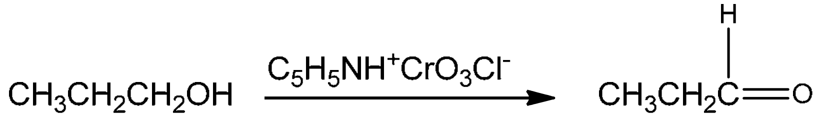
6. Oxidation.







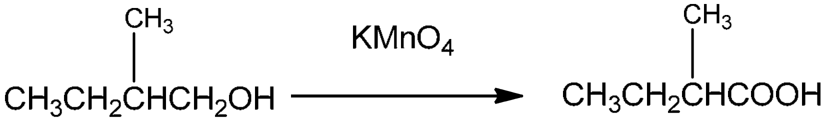
Examples:



$$CH_3CH_2CH_2OH \xrightarrow{C_5H_5NH^+CrO_3Cl^-} CH_3CH_2\overset{H}{\overset{|}{C}}{=}O$$

n-Propyl alcohol (1°)

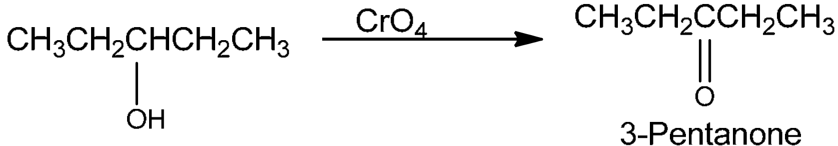
Propionaldehyde



$$CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2OH \xrightarrow{KMnO_4} CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCOOH$$

2-Methyl-1-butanol (1°)

2-Methylbutanoic acid



$$CH_3CH_2\underset{OH}{\underset{|}{C}}HCH_2CH_3 \xrightarrow{CrO_4} CH_3CH_2\underset{O}{\underset{||}{C}}CH_2CH_3$$

3-Pentanol (2°)

3-Pentanone

Alcohols undergo many kinds of reactions, to yield many kinds of products. Because of the availability of alcohols, each of these reactions is one of the best ways to make the particular kind of product.

Alcohols as acids and bases

Question : Alcohol is a weaker acid than water.

Of the varied chemical properties of alcohols : their acidity and basicity. These properties reside, of course, in the functional group of alcohols: the hydroxyl group, --OH. This group is like the hydroxyl group of water, a compound with which we are already familiar. Like water, alcohols are weak acids and weak bases—roughly, about as acidic and as basic as water.

It is oxygen, with its unshared electron pairs, that makes an alcohol basic. Like water, alcohols are basic enough to accept a proton from strong acids like hydrogen chloride and hydrogen sulfate, and thus bring about complete dissociation of these acids. For example:

$$\underset{\text{Alcohol stronger base}}{ROH} + H_2SO_4 \rightleftharpoons \underset{\text{Protonated alcohol}}{ROH_2^+} + \underset{\text{weaker base}}{HSO_4^-}$$

In alcohols, hydrogen is bonded to the electronegative element oxygen. The polarity of the O-H bond facilities the departure of a proton ; viewed differently, electronegative oxygen readily accommodates the negative charge of electrons left behind.

The acidity of alcohols is shown by their reaction with active metals to liberate hydrogen gas.

$$\underset{\substack{\text{An}\\\text{alcohol}\\\text{A weak acod}}}{ROH} + Na \longrightarrow \underset{\substack{\text{A sodium}\\\text{alkoxide}\\\text{A strong base}}}{RONa} + \tfrac{1}{2}H_2$$

The products are called alkoxides: sodium ethoxide, for example, or potassium isopropoxide.

Just how acidic are alcohols? With the possible exception of methanol, they are somewhat weaker acids than water. When water is added to an alkoxide, these are obtained sodium hydroxide and the parent alcohol.

$$\underset{\substack{\text{Stronger}\\\text{base}}}{RO^-Na^+} + \underset{\substack{\text{Stronger}\\\text{acid}}}{H\text{-}OH} \longrightarrow \underset{\substack{\text{Weaker}\\\text{base}}}{Na^+OH^-} + \underset{\substack{\text{Weaker}\\\text{acid}}}{RO\text{-}H}$$

The weaker acid, RO-H, is displaced from its salt by the stronger acid, HO-H. In other word, the stronger base, RO^-, pulls the proton away from the weaker base, HO^-; if RO^- holds the proton more tightly than HO^-, then RO-H must be a weaker acid than HO-H.

Like water and ammonia, alcohols are enormously stronger acids than alkanes, and readily displace them from their “salts” : from Grignard reagents, for example.

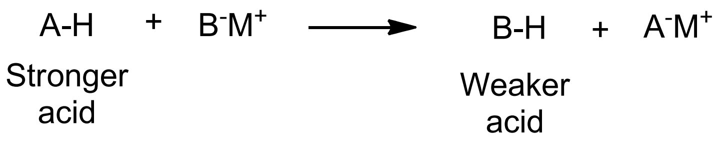
$$\underset{\substack{\text{Stronger}\\\text{acid}}}{ROH} + R'MgX \longrightarrow \underset{\substack{\text{Weaker}\\\text{acid}}}{R'H} + Mg(OR)X$$

We can thus place alcohols in a sequence of acidity relative to other familiar compounds. And when we do this, we necessarily arrive at an order of relative basicity for the corresponding conjugate bases.

Relative acidities $H_2O > ROH > NH_3 > RH$

Relative basicities $OH^- < OR^- < NH_2^- < R^-$

The method we have just described for comparing acidities is a general one, and has been used to determine the relative acidities of a number of extremely weak acids. One compound is shown to be a stronger acid than another by its ability to displace the second compound from salts.



$$\underset{\text{Stronger acid}}{\text{A-H}} + \text{B}^-\text{M}^+ \longrightarrow \underset{\text{Weaker acid}}{\text{B-H}} + \text{A}^-\text{M}^+$$

Let us look more closely at the relative acidities of alcohols and water. The difference between an alcohol and water is, of course, the alkyl group. Not only does the alkyl group make an alcohol less acidic than water, but the bigger the alkyl group, the less acidic the alcohol; methanol is the strongest and tertiary alcohols are the weakest. For a long time, this acid-weakening effect in alcohols was believed to be a polar effect: electron release by alkyl groups intensifies the negative charge of alkoxide ions and makes them stringer bases. But then it was found that in the gas phase the relative acidities of the various alcohols and of alcohols and water are reversed; evidently here the easily polarized alkyl groups are helping to accommodate the negative charge, just as they help to accommodate the positive charge in carbonations. Alcohols are weaker acids than water in solution-which is where we are normally concerned with acidity and this is a salvation effect; a bulky group interferes with ion-dipole interactions that stabilize the anion.

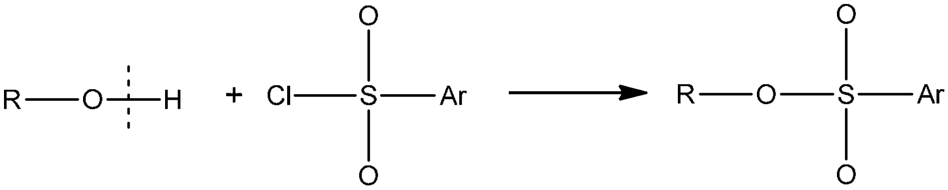
Since an **alcohol is a weaker acid than water**, an alkoxide is not prepared by the reaction of the alcohol with sodium hydroxide, but rather by reaction of the alcohol with the active metal itself.

Alkoxides are extremely useful reagents. They are powerful bases stronger than hydroxide and, by varying the alkyl group, we can vary their degree of basicity, their steric requirements, and their solubility properties. As nucleophiles, they can be used to introduce the alkoxy group into molecules.

Now, any preparation of a halide from an alcohol must involve breaking of the carbon-oxygen bond, and hence is accompanied by the likelihood of stereochemistry

$$\text{R—O—H} \xrightarrow{\text{HX or PX}_3} \text{R—X}$$

inversion and the possibility of racemization. Preparation of a sulfonate, on the other hand, does not involve the braking of the carbon-oxygen bond, and hence proceeds with complete retention; when we carry out a reaction with this sulfonate, we know exactly what we are starting with.

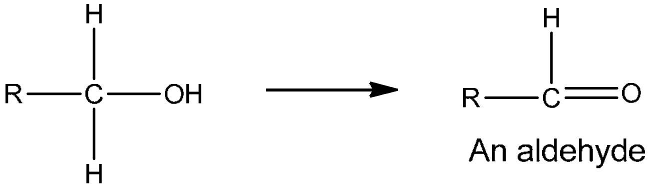


As a way of changing the –OH group of an alcohol into a good leaving group, conversion into sulfonates is just about ideal. We do out disturb the stereochemistry of the alkyl group. We can vary the structure of the sulfonate group and thus vary its leaving ability over a tremendous range. Although protonation of alcohols also generates a good leaving group, it limits our choice of reagents to those compatible with an acidic medium; but we can allow these alkyl sulfonates to react with just about any nucleophile or base we care to use.

Oxidation of alcohols

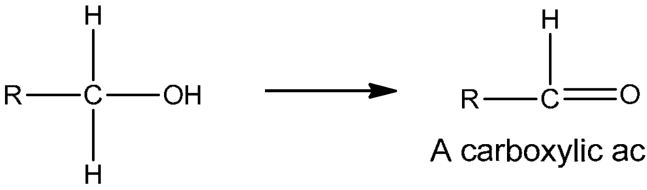
The oxidation of an alcohol involves the loss of one or more hydrogen's (α-hydrogen's) from the carbon bearing the –OH group. The kind of product that is formed depends upon how many of these α-hydrogens the alcohol contains, that is, upon whether the alcohol is primary, secondary, or tertiary.

A primary alcohol contains two α-hydrogens, and can either lose one them to form an aldehyde or both of them to form a carboxylic acid.



A 1° alcohol

An aldehyde

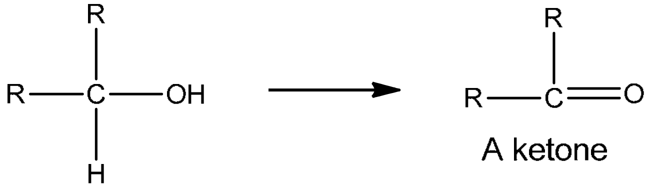


A carboxylic acid

A 1° alcohol

(Under the proper conditions, as we shall find, an aldehyde can itself be oxidized to a carboxylic acid.)

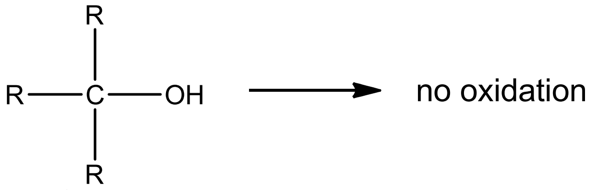
A secondary alcohol can lose its only α-hydrogen to form a ketone.



A 2° alcohol

A ketone

A tertiary alcohol contains no α-hydrogens and is not oxidized. (An acidic oxidizing agent can, however, dehydrate the alcohol to an alkene and then oxidize this)

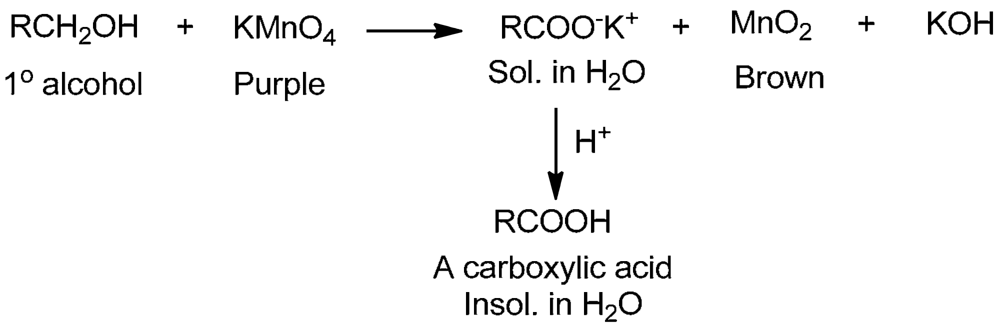


A 3° alcohol

These oxidation products aldehydes, ketones, and carboxylic acids are new to us, and at this point we need only learn to recognize their structures. As we shall find, they are extremely important compounds, and their preparation by the oxidation of alcohols is an essential part of organic synthesis.

The number of oxidizing agents available to the organic chemist is growing at a tremendous rate. As with all synthetic methods, emphasis is on the development of highly selective reagents, which will operate on only one functional group in a complex molecule, and leave the other functional groups untouched. Of the many reagents that can be used to oxidize alcohols, we can consider only the most common ones, those containing Mn(VII) or Cr(VI). Heptavalent manganese is used in the form of potassium permanganate, $KMnO_4$. Also widely used is hexavalent chromium, chromic acid essentially, in a form selected for the job at hand: acidic aqueous K_2CrO_7, CrO_3 in glacial acetic acid, CrO_3 in pyridine, etc.

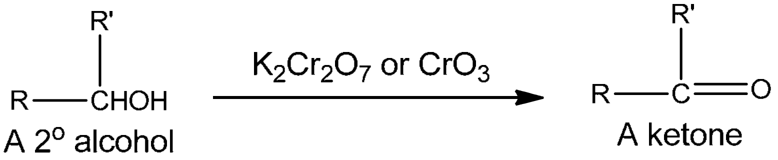
Oxidation of primary alcohols to carboxylic acids is usually accomplished by use of potassium permanganate. (Best yield are obtained if the permanganate and the alcohol are brought together in a non- polar solvent by use of phase-transfer catalysis, When reaction is complete, an aqueous solution of the soluble potassium salt of the carboxylic acid is filtered form MnO_2, and the acid is liberated by the addition of a stronger mineral acid.



$$\underset{1^\circ\text{ alcohol}}{RCH_2OH} + \underset{\text{Purple}}{KMnO_4} \longrightarrow \underset{\text{Sol. in }H_2O}{RCOO^-K^+} + \underset{\text{Brown}}{MnO_2} + KOH$$

$$RCOO^-K^+ \xrightarrow{H^+} \underset{\substack{\text{A carboxylic acid}\\ \text{Insol. in }H_2O}}{RCOOH}$$

Oxidation of alcohols to the aldehyde or ketone stage is usually accomplished by the use of Cr(VI) in one of the forms described above. Oxidation of secondary alcohols to ketones is generally straightforward.



$$\underset{\text{A }2^\circ\text{ alcohol}}{R{-}\overset{R'}{\overset{|}{C}}HOH} \xrightarrow{K_2Cr_2O_7\text{ or }CrO_3} \underset{\text{A ketone}}{R{-}\overset{R'}{\overset{|}{C}}{=}O}$$

Because aldehydes are susceptible to further oxidation, the conversion of primary alcohols to aldehydes can be troublesome. One of the best and most convenient reagents for this purpose is pyridinium chlorochromate ($C_5H_5NH^+CrO_3Cl^-$) formed by the reaction between chromic acid and pyridinium chloride.

$$RCH_2OH \xrightarrow[\text{in }CH_2Cl_2]{C_5H_5NHCrO_3Cl} RCHO + Cr^{3+}$$

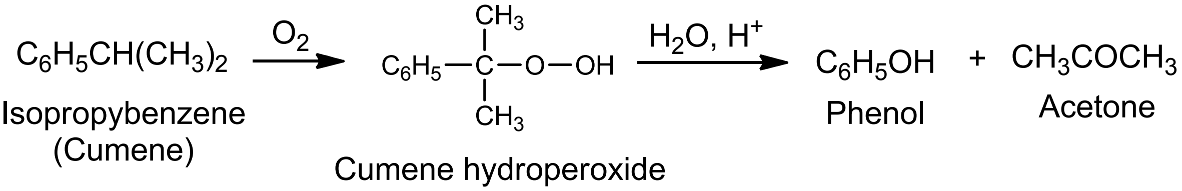
PHENOL

Rearrangement of hydroperoxides: Migration to electron-deficient oxygen:

Question : Give reaction mechanism for migration to electron-deficient oxygen.

Question : Give reaction mechanism for the synthesis of phenol via cumene hydroperoxide.

During synthesis of phenol via cumene hydroperoxide from cumene, in the second stage of the process, the conversion of the hydroperoxide into phenol and acetone involves migration of phenyl group from hydroperoxide to oxygen in the phenol takes place via rearrangement.



$$C_6H_5CH(CH_3)_2 \xrightarrow{O_2} C_6H_5-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-O-OH \xrightarrow{H_2O,\ H^+} C_6H_5OH + CH_3COCH_3$$

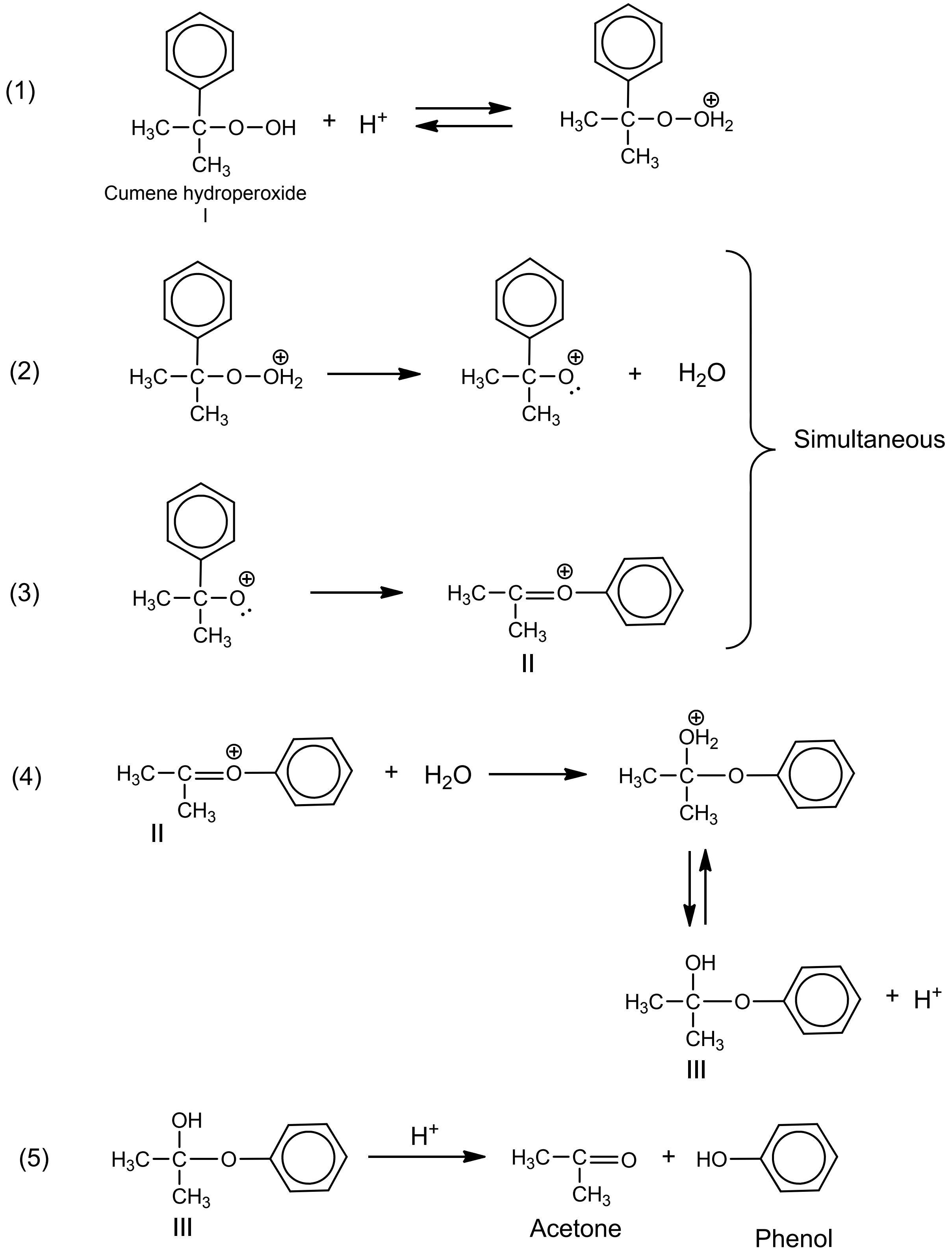
Isopropybenzene (Cumene)

Cumene hydroperoxide

Phenol

Acetone

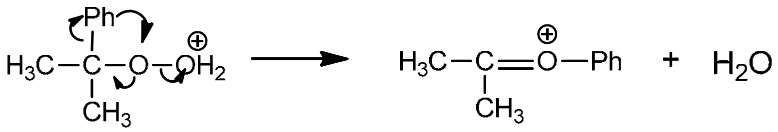
Mechanism :


(1)
Cumene hydroperoxide
I
+ H⁺
(2)
+ H₂O
Simultaneous
(3)
II
(4)
II
+ H₂O
+ H⁺
III
(5)
III
H⁺
Acetone
Phenol

Acid converts (step 1) the peroxide- I into the protonated peroxide, which loses (step 2) a molecule of water to form an intermediate in which oxygen bears only six electrons. A 1,2-shift of the phenyl group from carbon to electron-deficient oxygen yields (step 3) the “carbocation-II”, which reacts with water to yield (step 4) the hydroxyl compound -III. Compound- III is a hemiketal which breaks down (step 5) to give phenol and acetone.

Here, steps (2) and (3) are simultaneous (rearrangement involves a 1,2-shift to electron-deficient oxygen), in which the migrating phenyl group helping to push out (2,3) the molecule of water ; that is to say, water is lost with anchimeric assistance.

(2,3)



$$H_3C-\overset{Ph}{\underset{CH_3}{C}}-O-\overset{\oplus}{O}H_2 \longrightarrow H_3C-\underset{CH_3}{C}=\overset{\oplus}{O}-Ph + H_2O$$

This concerted mechanism is supported by:

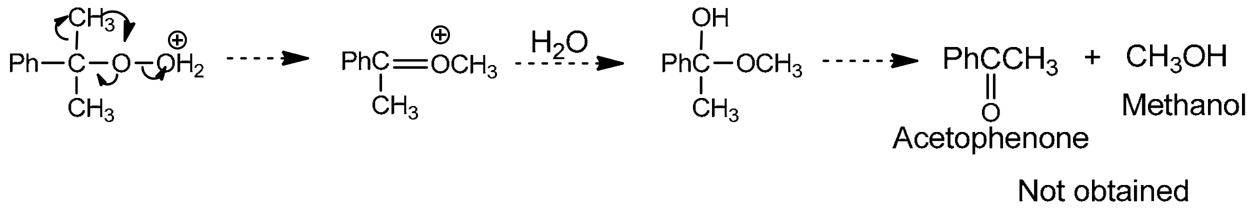
(a) A highly unstable intermediate containing oxygen with only a sextet of electrons should be very difficult to form.

(b) There is evidence that, if there is such an intermediate, it must undergo rearrangement as fast as it is formed ; that is, if (2) and (3) are separate steps, (3) must be fast compared with (2).

(c) The rate of overall reaction is speeded up by electron-releasing substituent’s in migrating aryl groups, and in a way that resembles, quantitatively, the effect of these groups on ordinary electrophilic aromatic substitution. Almost certainly, then, substituent’s affect the overall rate of reaction by affecting the rate of migration, and hence migration must take place in the rate-determining step. This rules out the possibility of a fast (3), and leaves us with the concerted reaction (2,3).

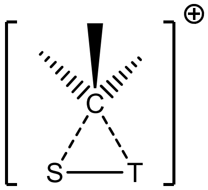
Rearrangement of hydroperoxides. Migratory aptitude

In the rearrangement of hydroperoxides the preferential migration of one group rather than another takes place. That is, we can observe the relative speeds of migration-the relative migratory aptitudes of two groups, not as a difference in rate of reaction, but as a difference in the product obtained. In cumene hydroperoxide, any one of three groups could migrate : phenyl and two methyl. If, instead of phenyl,



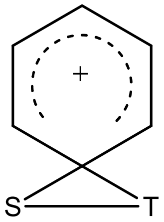
If methyl were to migrate, reaction would be expected to yield methanol and acetophenone. Actually, phenol and acetone are formed quantitatively, showing that a phenyl group migrates much faster than a methyl.

In 1,2-shifts aryl groups have greater migratory aptitudes than alkyl groups (methyl). Migration of an alkyl group must involve a transition state containing pentavalent carbon (IV). Migration of an aryl group, on the other hand, takes place via a structure of the Benzenonium ion type (V) ; transition state or actual intermediate, V clearly offers an easier path for migration than does IV.



IV

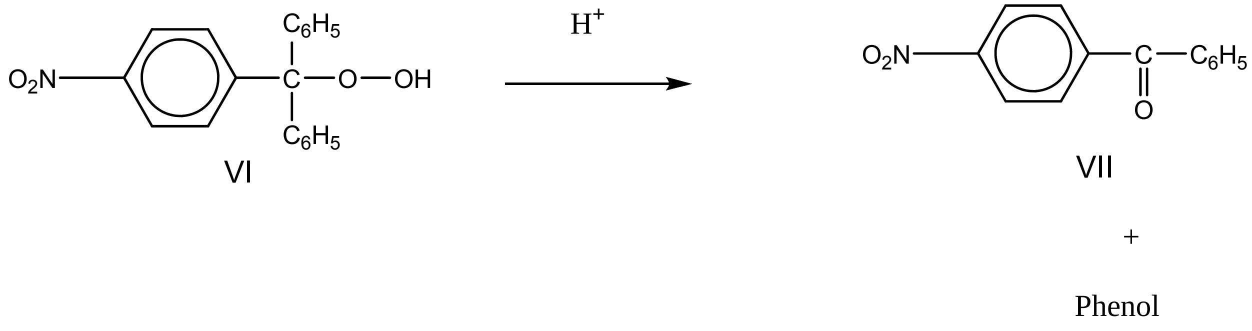
alkyl migration :
pentavalent carbon



V

Aryl migration :
benzenonium ion

The hydroperoxide may contain several aryl groups and, if they are different, we can observe competition in migration between them.



The relative migratory aptitude of an aryl group is raised by electron-releasing substituent's, and lowered by electron-withdrawing substituent's. For example, when pnitro triphenyl methyl hydroperoxide (VI) is treated with acid, it yields exclusively phenol and p-nitrobenzophenone (VII); as we would have expected, phenyl migrates in preference to p-nitrophenyl.

In the migrating aryl group, rearrangement is simply electophilic aromatic substitution with the electron-deficient atom oxygen, here acting as an electrophile. Benzene undergoes electrophilic substitution faster than nitrobenzene and, for the same basic reason, phenyl migrates faster than p-nitrophenyl.

Preparation :

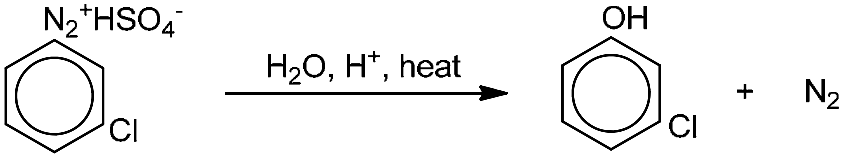
Phenols are generally prepared by one the methods outlined below :

PREPARATION OF PHENOLS

1. Hydrolysis of diazonium salts.

$$Ar{-}N_2^+ + H_2O \longrightarrow Ar{-}OH + H^+ + N_2$$

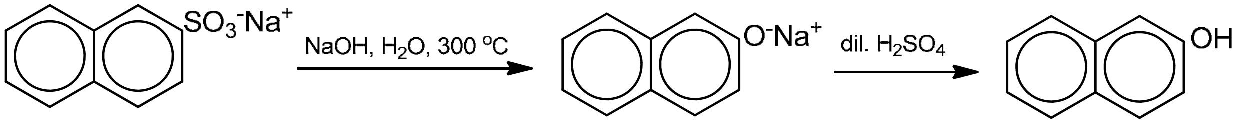
Example :



m-Chlorobenzenediazonium hygrogen sulfate

m-Chlorophenol

2. Alkali fusion of sulfonates.



Sodium 2-naphthalenesulfonate

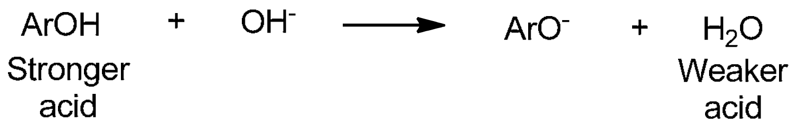
Sodium 2-naphthoxide

2-Naphthol
β-Naphthol

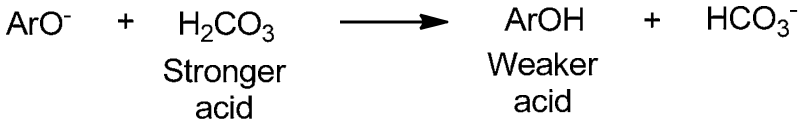
Acidity of phenols :

Q : Explain phenol is acidic in nature.

Phenols are converted into their salts by aqueous hydroxides, but not by aqueous bicarbonates. The salts are converted in to the free phenols by aqueous mineral acids, carboxylic acids, or carbonic acid.



$$\underset{\text{Stronger acid}}{ArOH} + OH^- \longrightarrow ArO^- + \underset{\text{Weaker acid}}{H_2O}$$



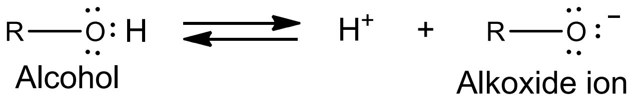
$$ArO^- + \underset{\text{Stronger acid}}{H_2CO_3} \longrightarrow \underset{\text{Weaker acid}}{ArOH} + HCO_3^-$$

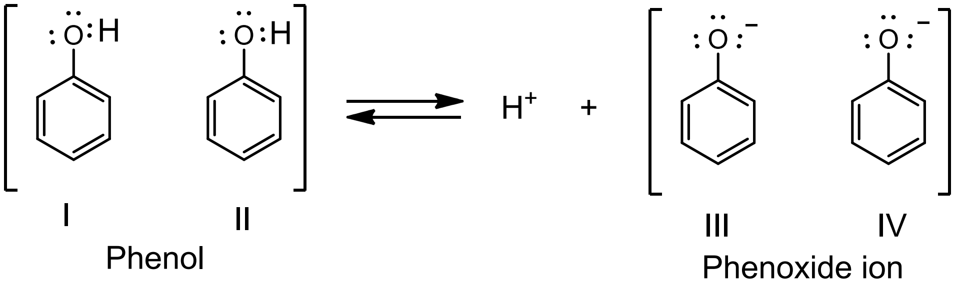
Phenols must therefore be considerably stronger acids than water, but considerably weaker acids than the carboxylic acids. Most phenols have K_a values of about 10^{-10}, whereas carboxylic acids have K_a values of about 10^{-5}.

Although weaker than carboxylic acids, phenols are tremendously more acidic than alcohols, which have K_a values in the neighborhood of 10^{-16} to 10^{-18}.

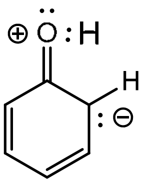
[*How does it happen that an –OH attached to an aromatic ring is so much more acidic than an –OH attached to an alkyl group? The answer is to be found in an examination of the structures involved. As usual we shall assume that differences in acidity are due to differences in stabilities of reactants and products.]*

Let us examine the structures of reactants and products in the ionization of an alcohol and of phenol. We see that the alcohol and the alkoxide ion are each represented satisfactorily by a single structure. Phenol and the phenoxide ion contain a benzene ring and therefore must be hybrids of the Kekule structures- I and -II, and -III and -IV. This resonance presumably stabilizes both molecule and ion to the same extent. It lowers the energy content of each by the same number of kilocalories per mole, and hence does not affect the difference in their energy contents. If there were no other factors involved, then, we might expect the acidity of a phenol to be about the same as the acidity of an alcohol.

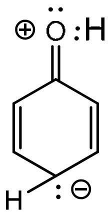




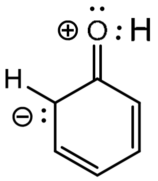
However, there are additional structures to be considered. Being basic, oxygen can share more than a pair of electrons with the ring; this is indicated by contribution from structures V-VII for phenol, and VIII-X for the phenoxide ion.



V

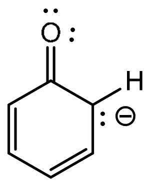


VI

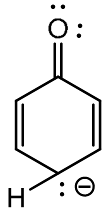


VII

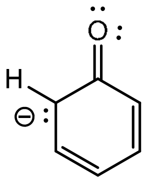
Phenol



VIII



IX



X

Phenoxide ion

Now, are these two sets of structures equally important? Structures V-VII for phenol carry both positive and negative charges; structures VIII-X for phenoxide ion carry only a negative charge. Since energy must be supplied to separate opposite charges, the structures for the phenol should contain more energy and hence be less stable than the structures for phenoxide ion. The net effect of resonance is therefore to stabilize the phenoxide ion to a greater extent than the phenol, and thus to shift the equilibrium toward ionization and make K_a larger then for an alcohol.

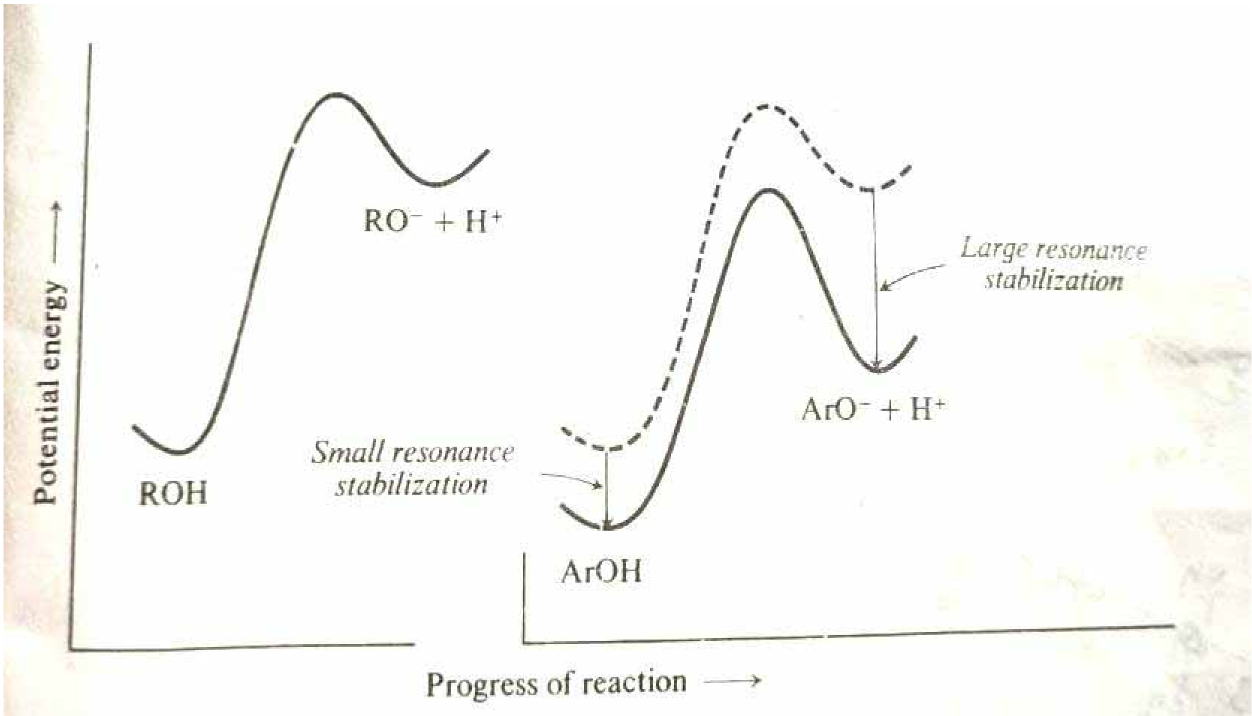
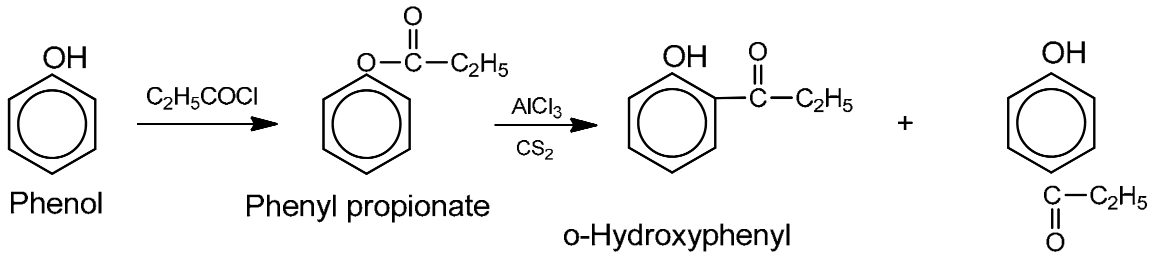


Figure : Molecular structure and position of equilibrium. Phenol yields a resonance-stabilized anion, and is a stronger acid than is alcohol. (The plots are aligned with each other for easy comparison.)

Ester formation. Fries rearrangement

Q. Write a note on Fries rearrangement.

When esters of phenols are heated with aluminum chloride, the acyl group migrates from the phenolic oxygen to an ortho- or para- position of the ring, thus yielding a ketone. This reaction, called the Fries rearrangement, is often used instead of direct acylation for the synthesis of phenolic ketones.



Phenol

Phenyl propionate

o-Hydroxyphenyl
ethyl ketone
(o-Hydroxypropiophenone)
Volatile in steam

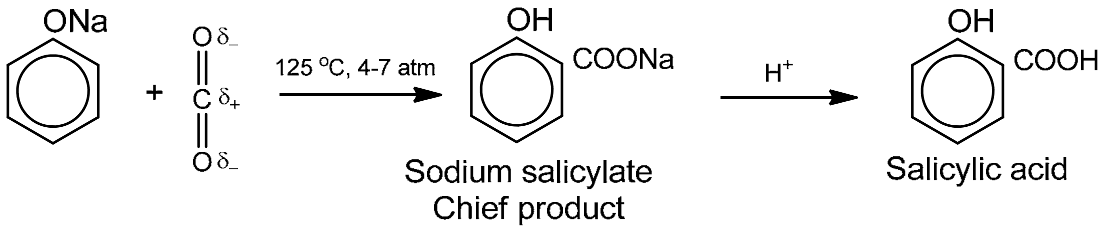
p-Hydroxyphenyl
ethyl ketone
(p-Hydroxypropiophenone)
Non-volatile in steam

In some cases, rearrangement appears to involve generation of an acylium ion, RCO^+, which then attacks the ring as in ordinary Friedel-Crafts acylation.

Kolbe reaction. Synthesis of phenolic acids

Q. Write a note on Kolbe reaction.

Treatment of the salt of a phenol with carbon dioxide brings about substitution of the carboxyl group, -COOH, for hydrogen of the ring. This reaction is known as the Kolbe reaction; its most important application is in the conversion of phenol itself into o-hydroxy benzoic acid, known as salicylic acid. Although some p-hydroxy benzoic acid is formed as well, the separation of the two isomers can be carried out readily by steam distillation, the ortho isomer being the more volatile.

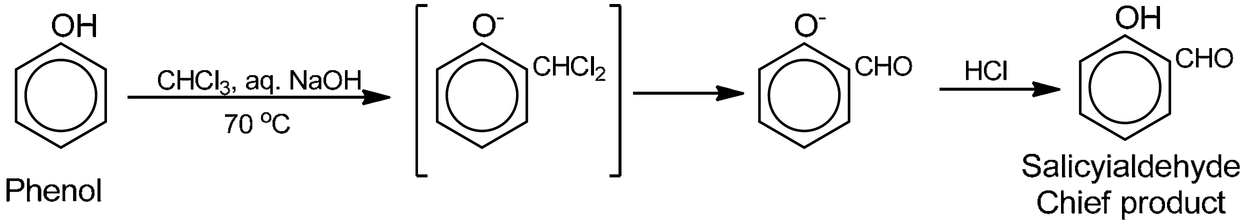


It seems likely that CO_2, attaches itself initially to phenoxide oxygen rather than to the ring. In any case, the final product almost certainly results from electrophilic attack by electron-deficient carbon on the highly reactive ring.

Reimer-Tiemann reaction. Synthesis of phenolic aldehydes. Dichlorocarbene

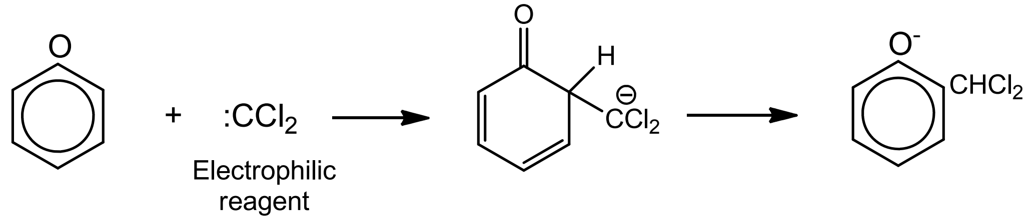
Q. Write a note on Reimer-Tiemann reaction.

Treatment of a phenol with chloroform and aqueous hydroxide introduces an aldehyde group, -CHO, onto the aromatic ring, generally ortho- to the-OH. This reaction is known as the Reimer-Tiemann reaction. A substituted benzal chloride is initially formed, but is hydrolyzed by the alkaline reaction medium.



The Reimer-Tiemann reaction involves electrophilic substitution on the highly reactive phenoxide ring. The electrophilic reagent is dichlorocarbene, $:CCl_2$, generated from chloroform by the action of base. Although electrically neutral, dichlorocarbene contains a carbon atom with only a sextet of electrons and hence is strongly electrophilic.

$$\underset{\text{Chloroform}}{OH^- + CHCl_3} \rightleftharpoons H_2O + {}^-{:}CCl_3 \longrightarrow Cl^- + \underset{\text{Dichlorocarbene}}{:CCl_2}$$



We encountered dichlorocarbene earlier as a species adding to carbon-carbon double bonds. There, it is considered to be formed from chloroform by the action of a strong base.

$$\text{(1)}\quad CHCl_3 + OH^- \rightleftharpoons CCl_3^- + H_2O$$

$$\text{(2)}\quad CCl_3^- \rightleftharpoons Cl^- + :CCl_2 \xrightarrow{\text{fast}} \text{Products (addition to alkenes, Reimer-Tiemann reaction, hydrolysis, etc.)}$$

REFERENCE BOOK : Organic chemistry by Morrison and Boyd, 6th Ed.