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# Identification of Alcohols

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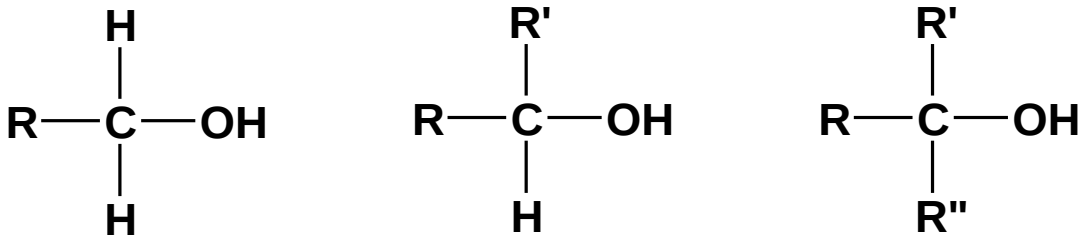
**Structurally, an alcohol is a composite of an alkane & water.**

**It contains an alkane - like alkyl group & a water – like hydroxyl group.**

**It is the –OH group that gives the alcohol it's characteristic physical properties, & the alkyl group , depending on it's size and shape , modifies these properties .**

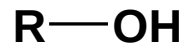
| R—H | H—OH | R—OH |
| --- | --- | --- |
| An alkane | Water | An alcohol |

**Alcohols** are organic cpd.s of the general formula ROH , where **R** is any alkyl or substituted alkyl group ,
The group may be primary , secondary or tertiary according to the kind of carbon that bears the –OH group.

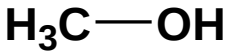



Primary ( $1^{o}$ ) Secondary ( $2^{o}$ ) Tertiary ( $3^{o}$ )

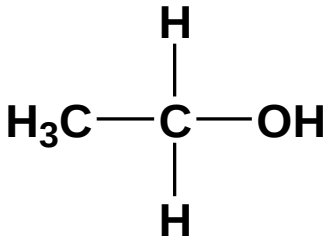
It may be open chain or cyclic.
It may contain a halogen atom, additional hydroxyls, or a double bonds or an aromatic ring.



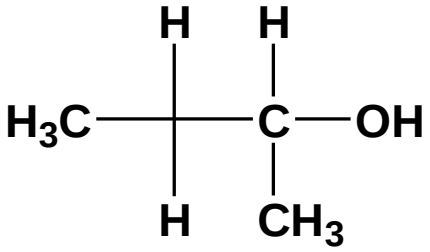

The general formula



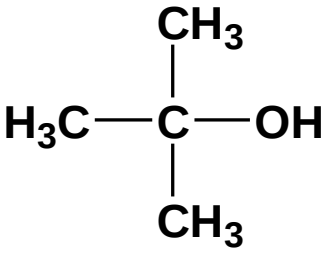

Methanol



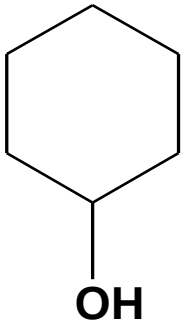

Ethanol



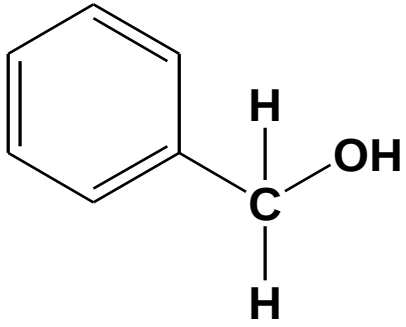

*sec*-Butanol




*tert*-Butanol




Cyclohexanol ( *cyclic* )

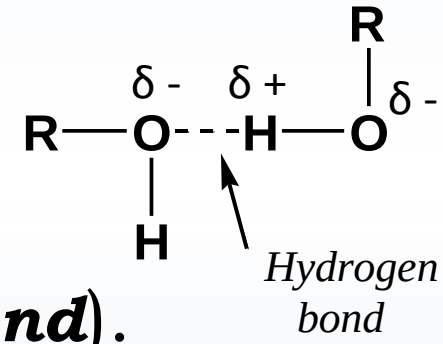



Benzyl alcohol ( *aromatic* )

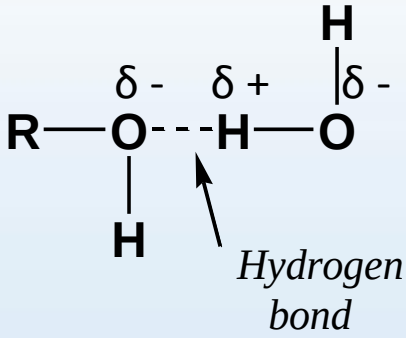
***Note:*** ***Compounds in which the –OH group is attached directly to an aromatic ring is not alcohols , they are phenols , and differ markedly from the alcohols.***

# Physical properties

- Alcohols are colorless liquids with a special faint odor.
- Aliphatic alcohols burn with blue flame (without smoke), while aromatic alcohols burn with yellow smoky flame.
- B.p. of alcohols are considerably high, it increases as the m.wt. increases.
  (***alcohols have the ability to form H -bond***).




- The lower alcohols are miscible with water, as the alkane-like alkyl group becomes larger , water solubility decreases.



# Solubility classification

Alcohols are polar compounds because of the presence of the –OH group which is also responsible for their ability to form hydrogen bonding.

The degree of polarity depends on the size of the alkyl side chain.

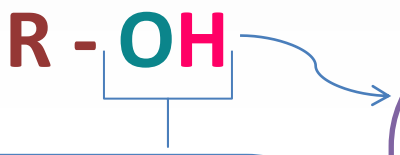
As the hydroxyl group /hydrocarbon ratio of alcohols increases , their water solubility increases and *vice versa*.

Therefore, alcohols that are soluble in water and ether are classified under class $S_1$ *such as ethanol & methanol.*

While those that are insoluble in water are related to class N *such as benzyl alcohol, sec-butanol & cyclohexanol.*

# Chemical properties

- Alcohols are neutral compounds that don't change the color of litmus paper.
- All reactions of alcohols are related to its active hydroxyl group & are of two types:




1- Removal of the -OH group itself as in the reaction with hydrogen halides to form alkyl halides or in the dehydration reaction to form a double bond.

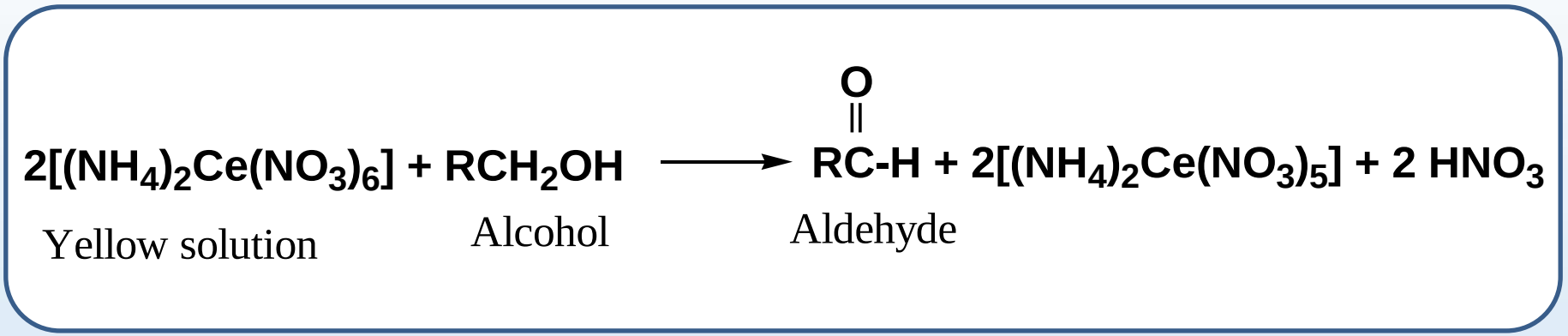
2- Removal of the proton only from the active hydroxyl as in the formation of esters or in the reaction with active metals such as sodium.

## General test

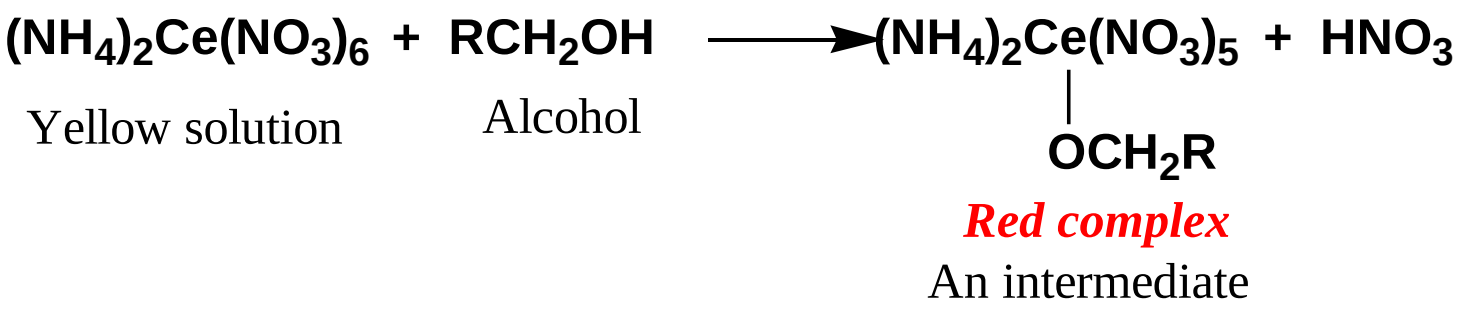
**Several methods are available for the analysis of the – OH group , the functional group present in alcohols.**

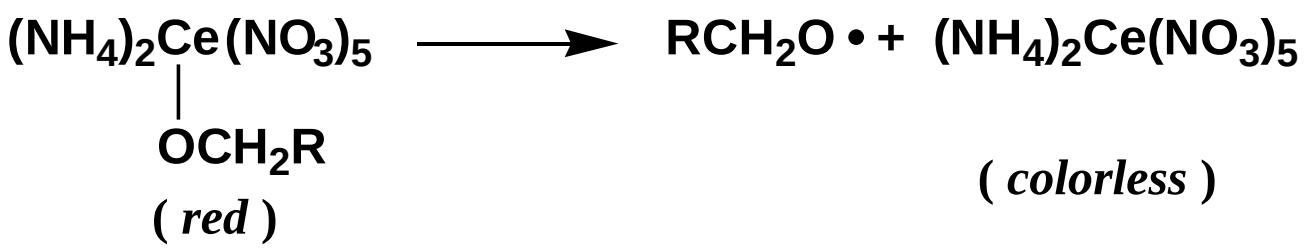
## Ceric ammonium nitrate reagent:

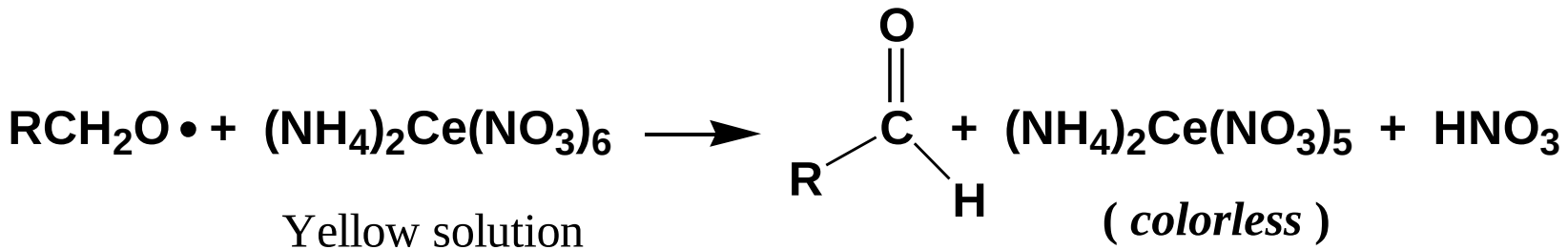
**Ceric ammonium nitrate, (yellow solution), is an oxidizing agent that reacts with alcohols to give a red complex & with phenols to give a brown to greenish brown precipitate.**



# The overall sequence of reaction for a primary alcohol is as follows:

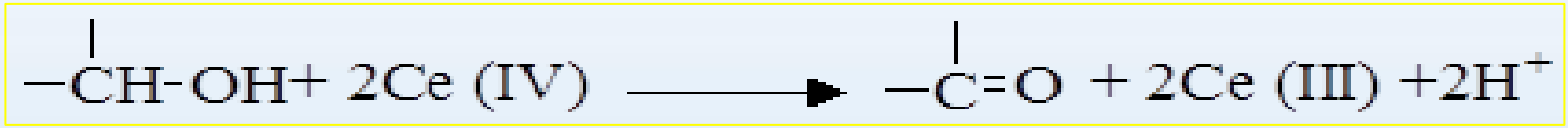


**Each mole of the alcohol requires two moles of the reagent.**

**The red colored complex is an intermediate for the oxidation of alcohols by the Ce ( *IV* ) solution. This red color disappears after a reasonable time due to completing the oxidation of this intermediate and the reduction to the colorless Ce ( *III* ) solution producing the corresponding aldehyde or ketone.**



# Procedure:

- ***Water soluble (miscible) alcohols:-***

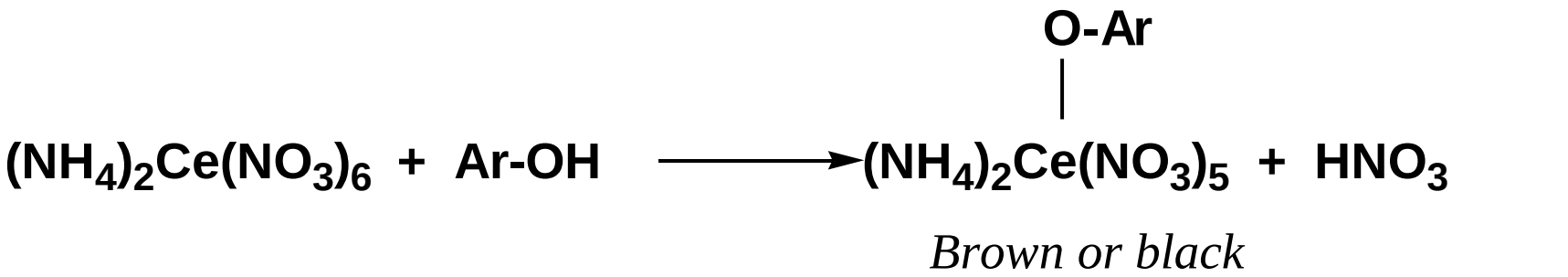
**Mix two drops of the alcohol with one drop of ceric ammonium nitrate solution ( reagent ) . A red complex indicates a positive test.**

- ***Water insoluble (immiscible) alcohols:***

**Mix two drops of the alcohol with 0.5 ml dioxane, shake well, and add one drop of the reagent to get a positive red complex.**

**The ceric ammonium nitrate reagent forms red complexes ( + ve result ) with :**
***Primary*, *secondary* and *tertiary* alcohols of up to 10 carbons.**
**Also all types of poly hydroxylated cpd.s such as carbohydrates and hydroxylated carboxylic acids , hydroxy aldehydes and hydroxy ketones .**

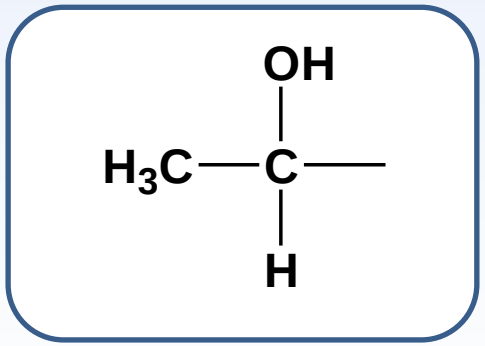
- **Phenols give a brown color or precipitate.**



# Specific Tests:

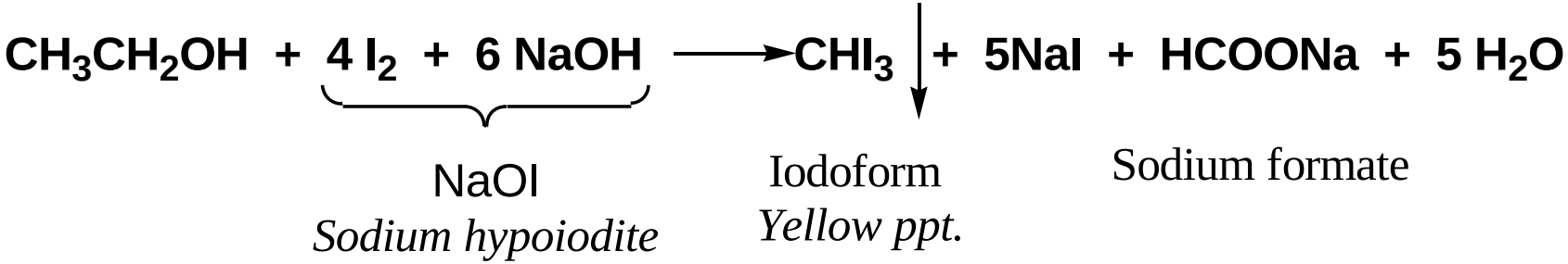
## a) Iodoform (Haloform) test

**This test is specific for alcohols which have a free methyl group (- $CH_3$ ) & *a hydrogen attached* to the carbon bearing the –OH group such as ethanol & *sec*-butanol.**



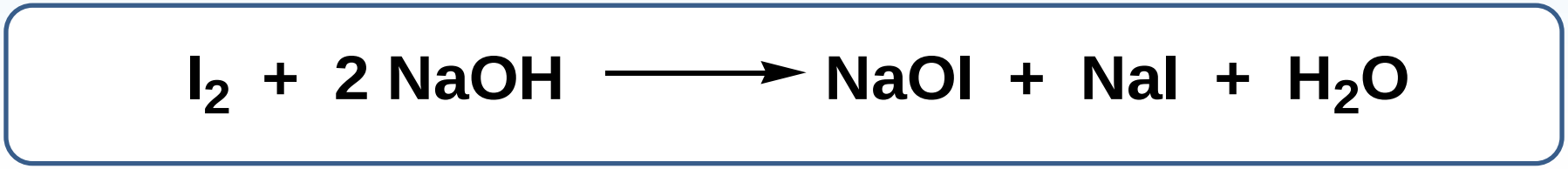

- **Tertiary alcohols show negative (-ve) result.**

The overall reaction is:

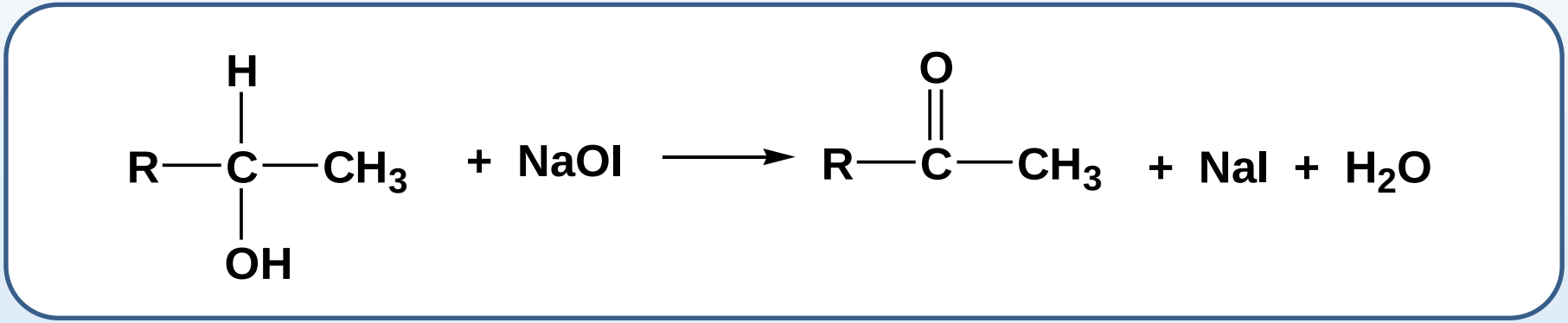


**The mechanism of the reaction involves many steps,**

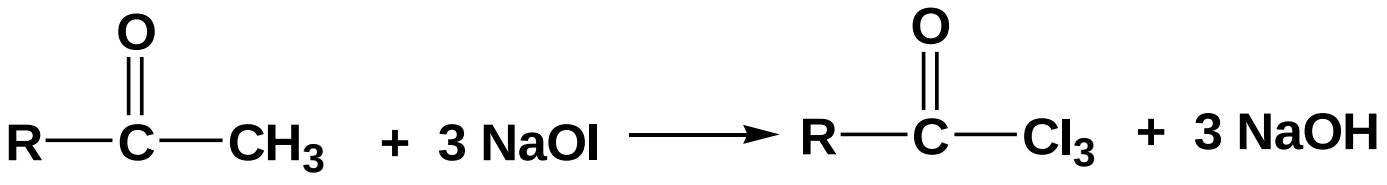
- **The formation of the oxidizing agent sodium hypoiodite (NaOI).**




- **Oxidation of the alcohol to the corresponding aldehyde or ketone by NaOI.**

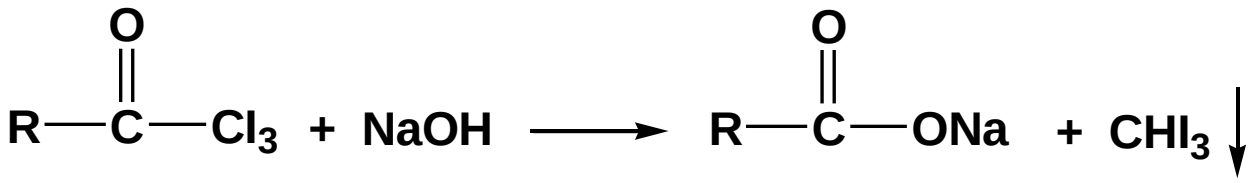


- **Halogenation of the produced aldehyde or ketone with 3 moles of NaOI to form the triiodo derivative.**




Triiodo derivative

- **Cleavage of the triiodo derivative by NaOH to an acid containing one less carbon atom than the starting alcohol.**




Iodoform
Yellow ppt.

## Procedure:

**1- Dissolve about 3 drops of the alcohol in about 1 ml of D.W ( or 1 ml of dioxane for water insoluble compounds ).**

**2- Add about 1 ml of 10% NaOH solution.**

**3- Add iodine ( $I_2$ ) solution drop wise with shaking until either a yellow iodoform ppt. is formed, *in which case* the test is positive & is completed, or the dark color of the iodine solution is present.**

**4- *In the latter case*, allow the solution to stand for 3 minutes during which period check for the appearance of the yellow precipitate at the bottom of the test tube.**

**5- If there is no ppt., warm the solution in water bath (60˚C) for ~3 minutes with shaking from time to time & check for the yellow ppt.**

**6- During warming , if the color of iodine disappears, add few additional drops of iodine solution with shaking until either the yellow precipitate is formed or the dark iodine color persists & then complete warming.**

**7- Get rid of the excess iodine by the addition of 10% NaOH solution drop wise with shaking to obtain the yellow ppt..**

**8- If the ppt. is not formed, allow the solution to stand for 10 minutes to get the positive result.**

**9-** Finally, **if no precipitate is formed after the 10 minutes – standing period, dilute the solution with an equal volume of distilled water to obtain the iodoform ppt..**

***It is important to proceed through all these steps so that only at the final step you can say that the test is negative.***

***Both ethanol & sec-butanol give positive iodoform test & they can be differentiated only by testing their solubility in water ; sec-butanol is less soluble in water than ethanol.***

## b) Lucas test:

**This test provides classification information for alcohols , so it is used to distinguish between the different types of alcohols ( primary, secondary, or tertiary ) .**

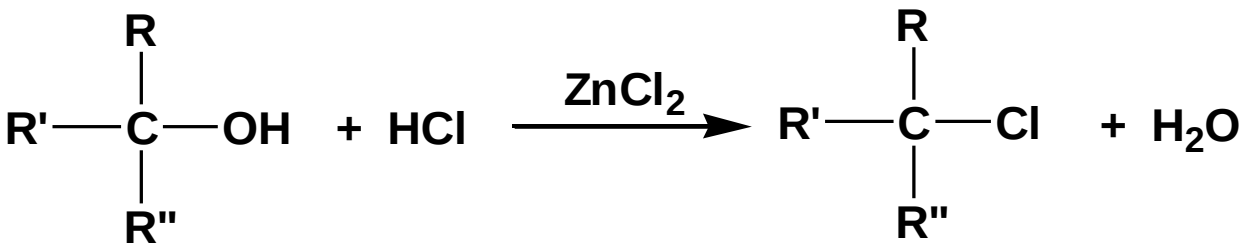
**It depends on the formation of alkyl chloride as a second liquid phase .**

Lucas reagent **is prepared from anhydrous zinc chloride & concentrated HCl.**

**$ZnCl_2$ is added to increase the ionization of HCl.**

$$ZnCl_2 + HCl \longrightarrow ZnCl_3^- + H^+$$

## The overall reaction is,



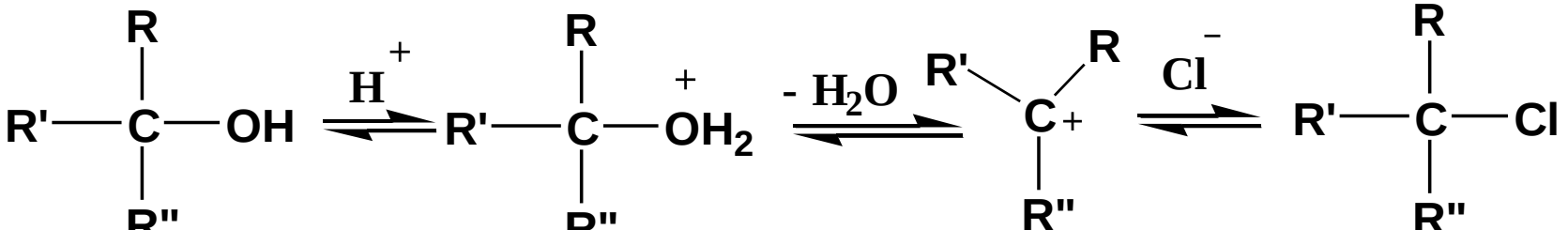

*3° alcohol*

*3° alkyl halide*

*insoluble in water*

## The mechanism of the reaction is,

**The mechanism of the Lucas test is an $S_N1$ type process as follows:**



- **The reaction depends on the formation of a stable carbonium ion.**
**The more stable the carbonium ion formed, the faster the reaction is.**

- **The rate of the reaction among different alcohols is shown below:**
**Benzyl alcohol > allyl alcohol > 3° alcohol > 2° alcohol > 1° alcohol ( 1° *alcohol & methanol give –ve test* ) .**

- **Benzyl alcohol shows the fastest +ve result.**

- **Allyl alcohol , although it is a 1° alcohol , it reacts rapidly with the Lucas reagent.**

- **Tertiary alcohols are faster in the formation of conjugated halides than secondary alcohols.**

- **Primary alcohols and methanol don't react and don't form two layers.**

- **All alcohols follow $S_N1$ mechanism except methanol and most primary alcohols that follow $S_N2$ mechanism.**

## Procedure

**Mix 2-4 drops of the alcohol with few drops of Lucas reagent & observe the results:**

- **Benzyl alcohol gives immediate result as shown by the appearance of two phases.**
- **Tertiary alcohols give two phases that separate within 2 – 3 minutes.**
- **Secondary alcohols give two phases that separate after 15 – 20 minutes ( giving a cloudy solution ).**
- **In primary alcohols one layer appears.**

# Questions & Exercises :

**1- Which alcohol has solubility class $S_2$, what are the structural requirements present in this alcohol that made it under this solubility class ?**

**2- By performing Lucas test , how would you account for the difference in the behavior of:**

**(*a*) Allyl alcohol & *n*-propyl alcohol?**

**(*b*) Benzyl alcohol & *n*-pentyl alcohol?**

**3- List two tests , *with equations* , that will give a positive result for 2-butanol.**

# References


* Robert T. Morrison, Robert N. Boyd : *" Alcohols and Ethers"*. **Organic Chemistry**, (6th) edition, Prentice-Hall Inc.

* Shriner R.L., Hermann C.K.F., Morrill T.C., Curtin D.Y. and Fuson R.C.: *" Chemical tests for functional groups "* . **The Systemic Identification of Organic Compounds** , (8th) edition, John Wiley and Sons Inc., New York. 2004; 247-350.

* Azhar M. Jasim , Duraid H. Mohammad, **A Laboratory Manual on Practical Organic Chemistry for 2nd year students**, *University of Baghdad , College of Pharmacy, Department of Pharmaceutical Chemistry, 2012.*