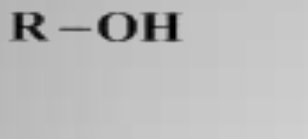
IDENTIFICATION OF ALCOHOLS

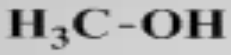
Alcohols are organic compounds that which considered as derivatives of water.

One of the hydrogen atoms of water molecule (H-O-H) has been replaced by an alkyl or substituted alkyl group.

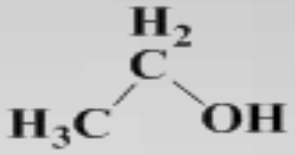
The alkyl group could be primary, secondary, or tertiary, and may be open chain or cyclic or it contain aromatic ring .



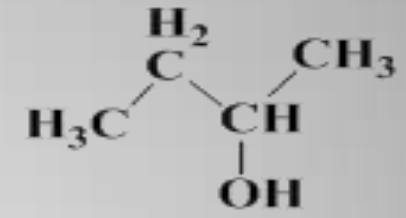
the general formula



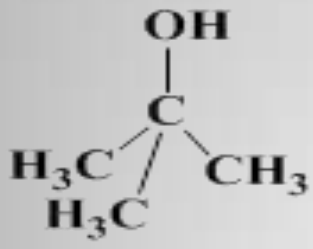
methanol



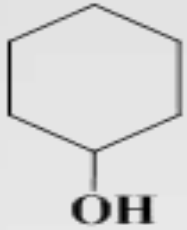
ethanol



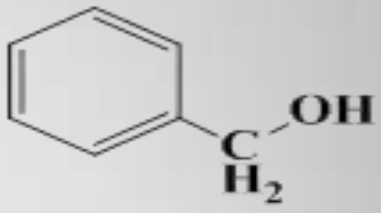
sec-butanol



tert-butanol



cyclohexanol
(cyclic)



benzyl alcohol
(aromatic)

Physical properties

- Alcohols are colourless liquids with a special faint odour.
- Aliphatic alcohols burn with blue flame (without smoke) while aromatic alcohols burn with yellow smoky flame
- B.p. of alcohols are considerably high;it is increase as the m.wt. increases.(alcohols has the ability to form H -bond).
- Alcohols are miscible with water except benzyl alcohol, cyclohexanol, and *sec*-butanol (which is very slightly soluble in water.

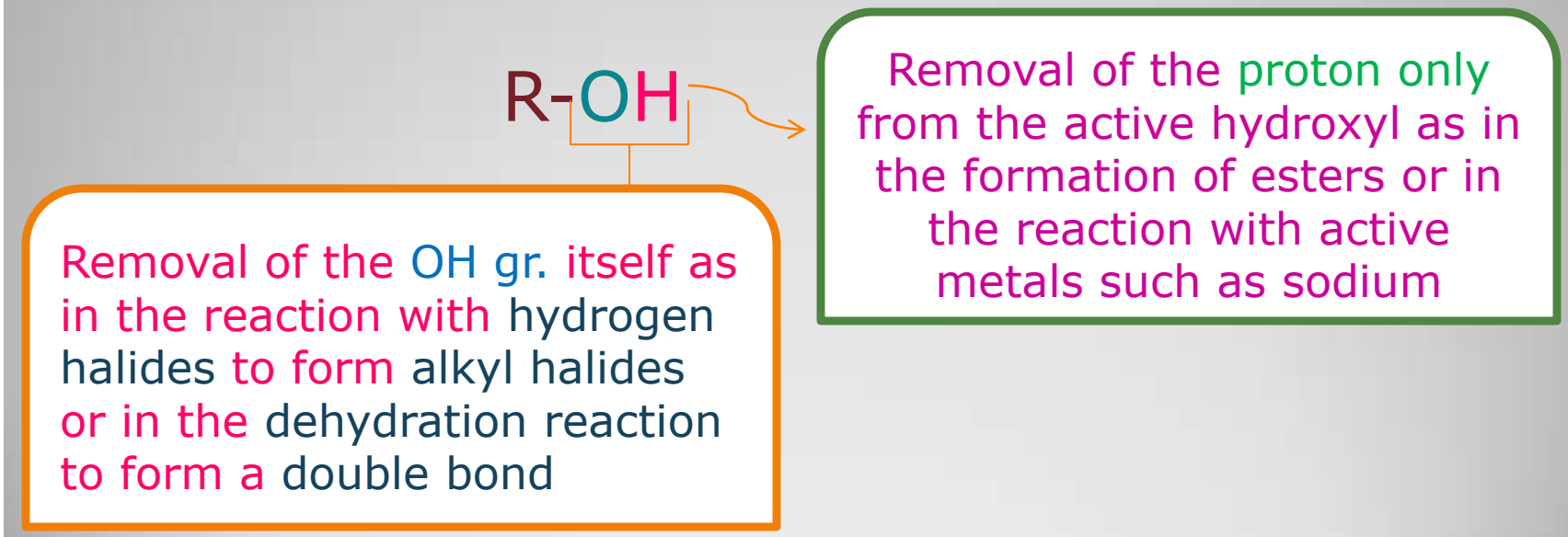
Solubility classification

- 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* and *methanol.*
- Alcohols that are insoluble in water are related to class ***N*** such as *benzyl alcohol*, *sec-butanol*, and *cyclohexanol*.

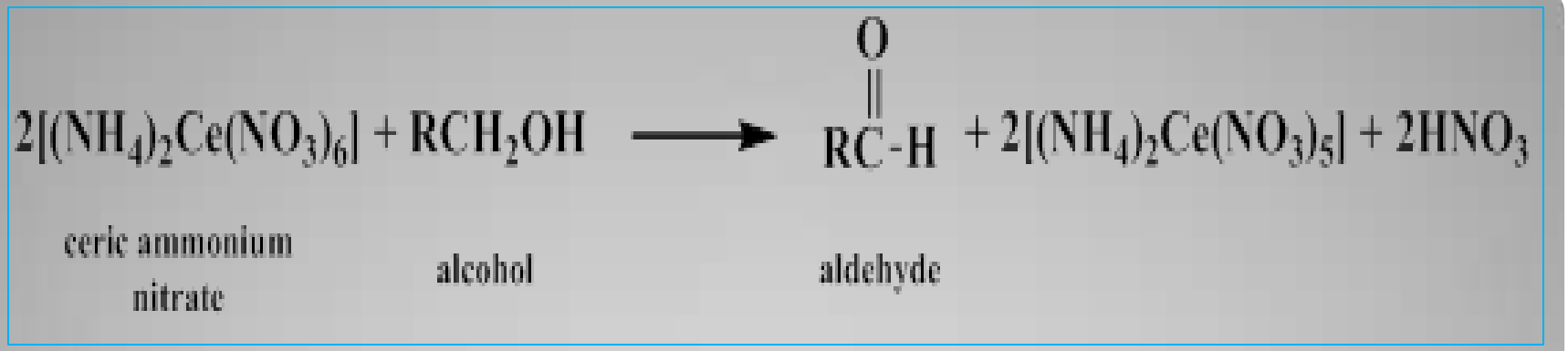
Chemical properties

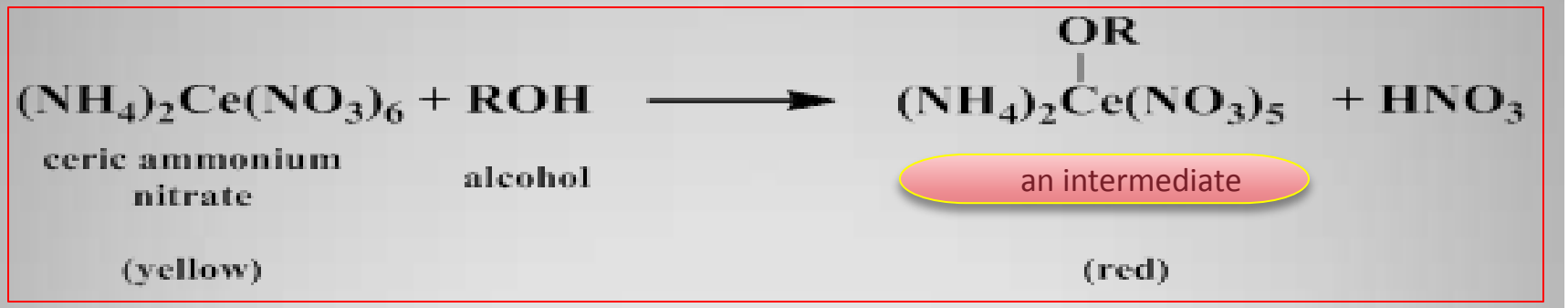
- Alcohols are neutral compounds that don't change the colour of litmus paper.
- All reactions of alcohols are related to its active hydroxyl group and are of two types:



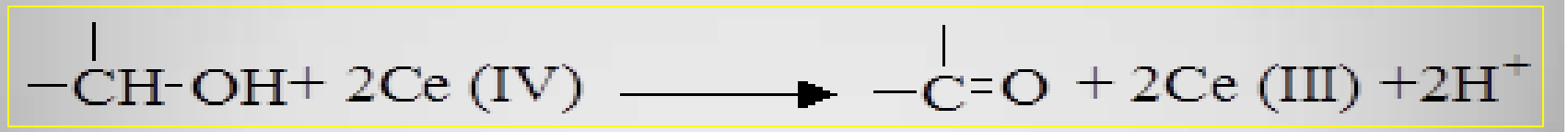
- **General test :**
  (Ceric ammonium nitrate reagent)

- Ceric ammonium nitrate (yellow soluion) is an oxidizing agent that reacts with alcohols to give a red complex and with phenols to give a brown to greenish brown precipitate.





This red colour disappears after a reason-able time due to complet-ing the oxidation of this intermediate.



- **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.

- This test gives positive results (+ ve) with :

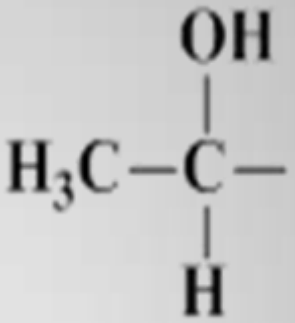
  primary, secondary, and tertiary alcohols (up to 10 carbons),

  poly hydroxylated compounds such as carbohydrates, and

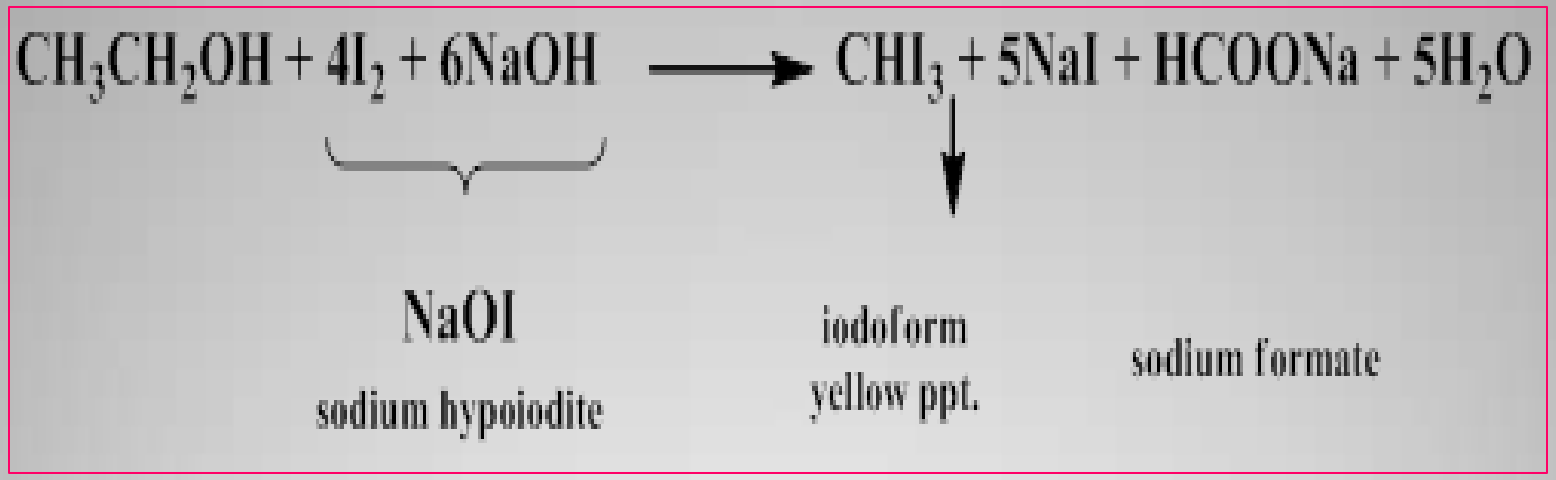
  hydroxylated carboxylic acids, aldehydes and ketones.

- **Specific tests**

- ***a) Iodoform (Haloform) test***
- This test is specific for alcohols which have a free methyl group (- CH_3)***and*** *a hydrogen attached* to the carbon bearing the hydroxyl group such as ethanol and *sec*-butanol.



The overall reaction is:



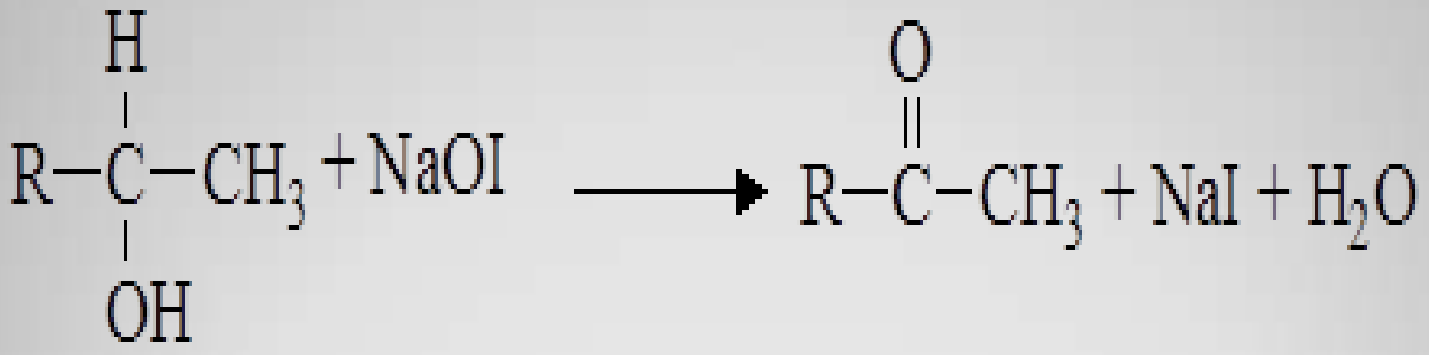
Tertiary alcohols show –ve result.

- The alcohol is oxidized to the corresponding aldehyde or ketone by the action of the produced oxidizing agent 'sodium hypoiodite', which also causes the aldehyde or ketone to be tri-iodinated on the terminal methyl group producing iodoform as a yellow precipitate.

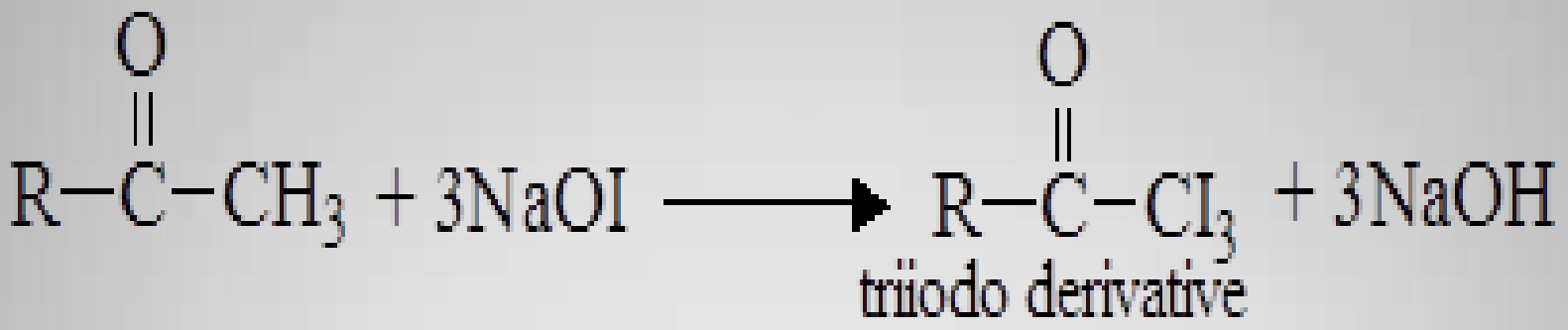
The ***mechanism*** of this reaction involves many steps, the first of which is the formation of the oxidizing agent sodium hypoiodate (NaOI).

The next steps are:

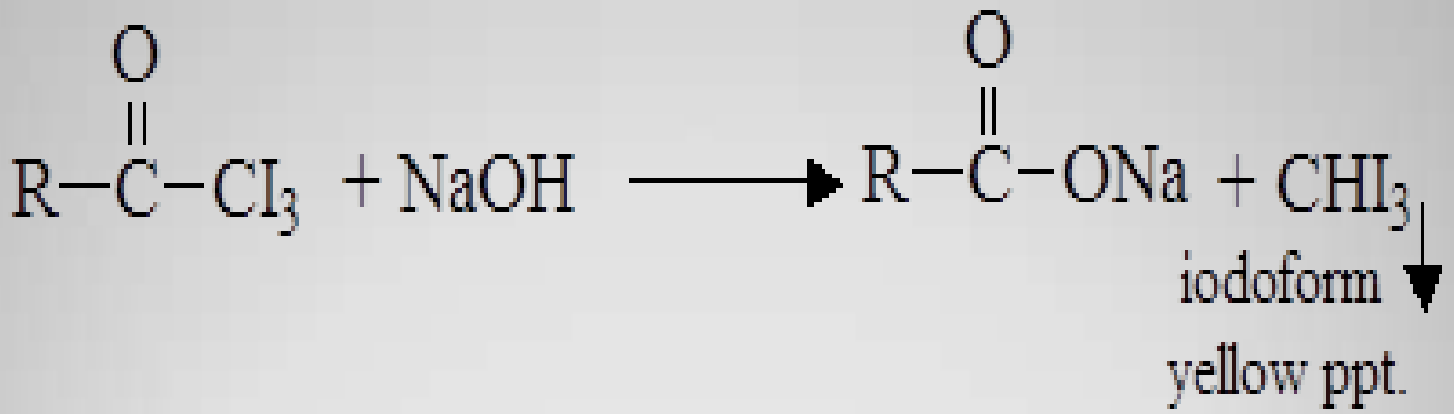
Oxidation of the alcohol to the correspond -ing aldehyde or ketone by sodium hypoiodate .



Halogenation of the produced aldehyde or ketone with three moles of sodium hypoiodate to form the triiodo derivative.



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



- Procedure
- 3 drops alcohol +1 mL of D.W (or 1mL of dioxane for water insoluble compounds).
- Add about 1 ml of 10% NaOH solution.
- Add iodine (I_2) solution drop wise with shaking until either a yellow iodoform precipitate is formed(test is positive and is completed) or the dark colour of the iodine solution is present.

- 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.

  If there is no precipitate

  Warm the solution in water bath(60°C) ~3 minutes with shaking from time to time and check for the yellow precipitate

- During warming, if the colour of iodine disappears, add few additional drops of iodine solution with shaking until either the yellow precipitate is formed or the dark iodine colour persists,& then complete warming
- Get rid of the excess iodine by the addition of 10% sodium hydroxide solution drop wise with shaking to obtain the yellow precipitate.
- If the precipitate is not formed, allow the solution to stand for 10 minutes to get the positive result.

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

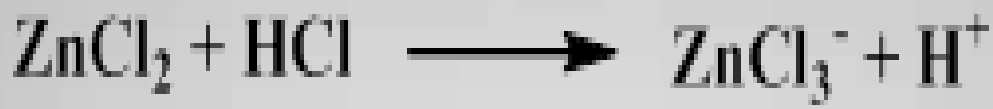
b) Lucas test:

provides classification informations on alcohols.

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 and concentrated HCl. Zinc chloride is added to increase the ionization of hydrochloric acid.



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>*tert*–alcohol>*sec*–alcohol> –ve primary alc.

All alcohols follow S_N1 mechanism except methanol and most primary alcohols that follow S_N2 mechanism

Benzyl alcohol shows the fastest positive result. 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.

tertiary alcohol

tertiary alkyl halide
insoluble in water

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