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IDENTIFICATION OF ALDEHDES AND KETONES

BACKGROUND

- Aldehydes are compounds of the general formula RCHO; ketones are compounds of the general formula R,COR. The groups R and R, may be aliphatic or aromatic, and in one aldehyde, formaldehyde , R is a hydrogen atom. Both contain the carbonyl group (C=O), which lends to their chief chemical and physical properties. Examples of them include formaldehyde, acetaldehyde, propionaldehyde, benzaldehyde ,salicylaldehyde, acetophenone, benzyl methyl ketone, and benzophenone.

PHYSICAL PROPERTIES

- 1- All aldehydes and ketones are liquids except formaldehyde which is a gas (boiling point = -21°C) and benzophene, which is a solid (milting point=48°C). Formaldehyde is handled either as an aqueous solution (formalin)or as one of its solid polymers: Para formaldehydes,(CH2O)n, or trioxune, (CH2O)3 .
- 2-The lower aldehydes and ketones are appreciably soluble in water (containing five or less carbon atoms), aromatic one are insoluble in water, and all of them are soluble in organic solvents.
- 3-They are colorless except benzaldehyde, which has a pale yellow color(due to oxidation) with characteristic odors.
- 4-The boiling points of aldehydes and ketones are lower than those of the alcohols from which they are derived. For example, isopropyl alcohol boils at 82.5°C while its oxidation product, acetones, boils at 56°C;ethanol boils at 78 °C while its oxidation product, acetaldehyde, and boils at 21°C .
- 5-Igonition: Aliphatic aldehydes and ketones burn with a blue flame (without smoke) while aromatic ones burn with a smoky yellow flame.

SOLUBILITY CLASSIFICATION

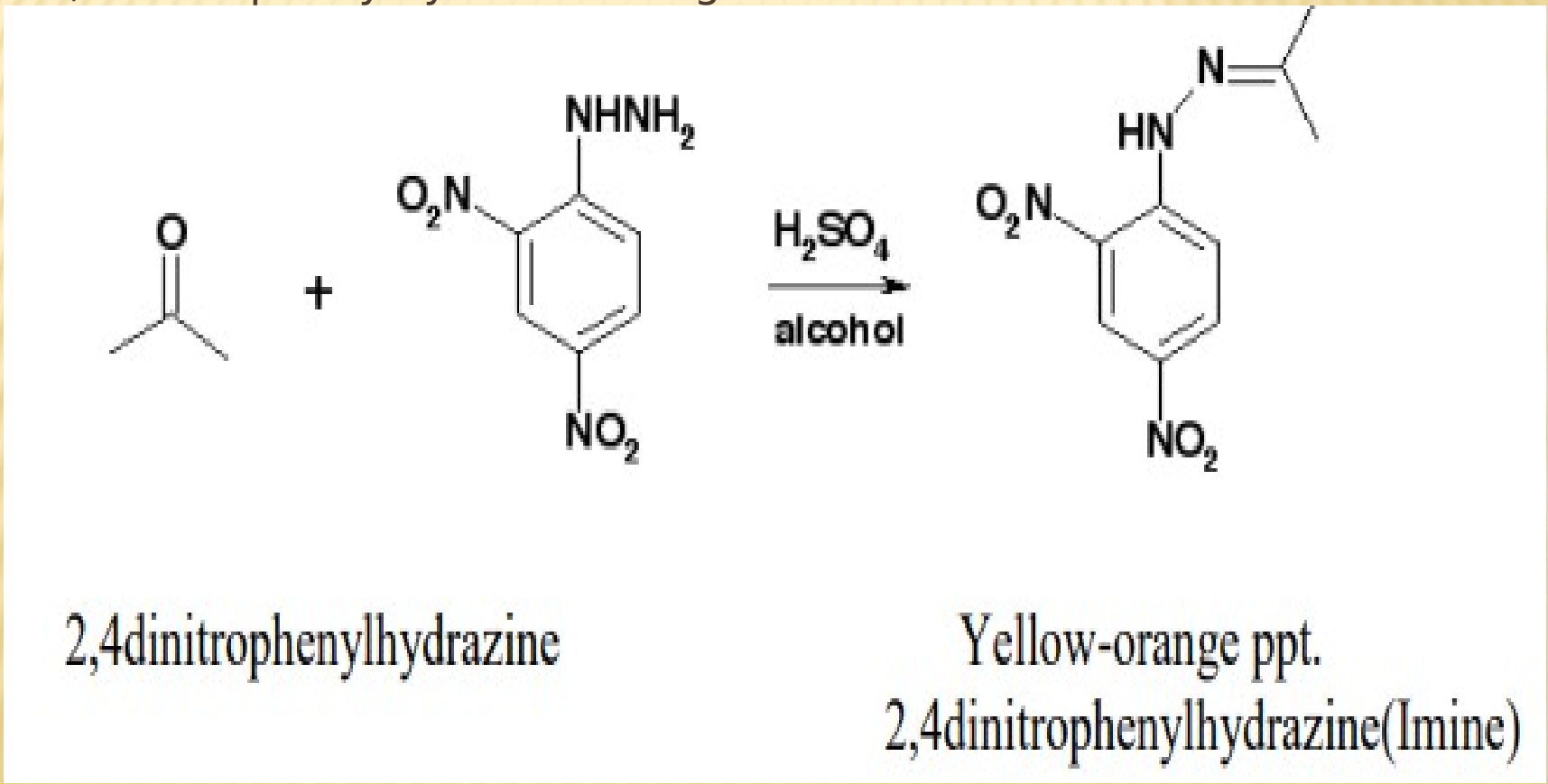
- Aldehydes and ketones, unlike alcohols, have no ability to form hydrogen bonding.
- 1-Aldehydes and ketones that are water – soluble are soluble in ether too and are classified under class S1(e.g. formaldehyd and acetone).
- 2-Aldehydes and ketones that are not soluble in water are classified under class N such as benzaldehyde and benzophenone.

CHEMICAL PROPERTIES

- 1-All reactions of aldehydes and ketones are related to the carbonyl group (the active group).
- 2- Aldehydes contain a hydrogen atom attached to its carbonyl while ketones donot.This difference in the chemical structure effects their chemical properties in tow ways:
- a)Aldehydes are easily oxidized to the corresponding acids and have reducing properties while ketones are not oxidized under similar conditions and do not show reducing properties.
- b)Aldehydes are usually more reactive than ketones towards nucleophilic addition, the characteristic reaction of carbonyl groups.
- 3- Aldehydes and ketons differ from alcohols by tow hydrogen atoms. Removel of these tow hydrogens from a primary alcohol as a result of oxidation yields an aldehyde; where as their removel from a secondary alcohol as a result of oxidation gives a ketone. The relation between them and alcohol is oxidation-reduction reaction.Tertiary alcohols canot undergo this reaction.
- 4-Both aldehydes and ketones are neutral compounds that donot change the color of litmus paper.

CHEMICAL REACTIONS

- 1-General test (2,4-dinitrophenylhydrazine reagent) (Brady test):Both aldehydes and ketones gives yellow or orange precipitate with 2,4dinitrophenylhydrazine reagent.



PROCEDURE

- 1-Add to 2 drops of the compound 3 drops of the reagent, a yellow or orange precipitate will be formed. If the compound is insoluble in water, dissolve it in 1 ml of methanol and then add the reagent.
- 2-Tests for differentiation between aldehydes and ketones. Differentiation between aldehydes and ketones is achieved by taking the advantage of the fact that aldehydes can easily oxidizing while ketones cannot (they need stronger oxidizing agents). Two reagents can be used for this purpose, Tollen,s reagent or Fehlings reagent. Only aldehydes give positive results with these tow reagents.

A. TOLLEN TEST (REDUCTION OF AMMONICAL-2 SILVER NITRATE)

- Tollens reagent is the combination of silver nitrate solution with ammonium hydroxide in the presence of sodium hydroxide solution. This reagent gives a silver mirror in the presence of aldehydes becuese the reaction between them involves the oxidation of the aldehyde to the corresponding carboxylic acid with an accompanyingreduction of silver ion from this reagent to silver element in the form of a silver
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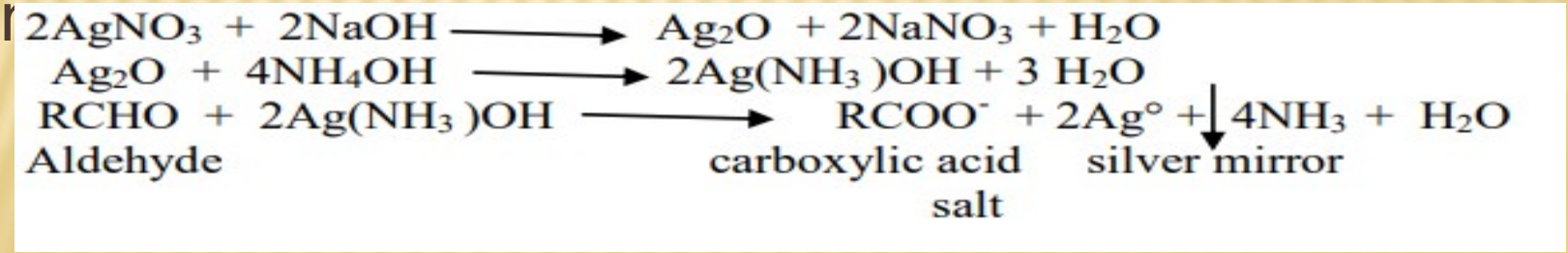
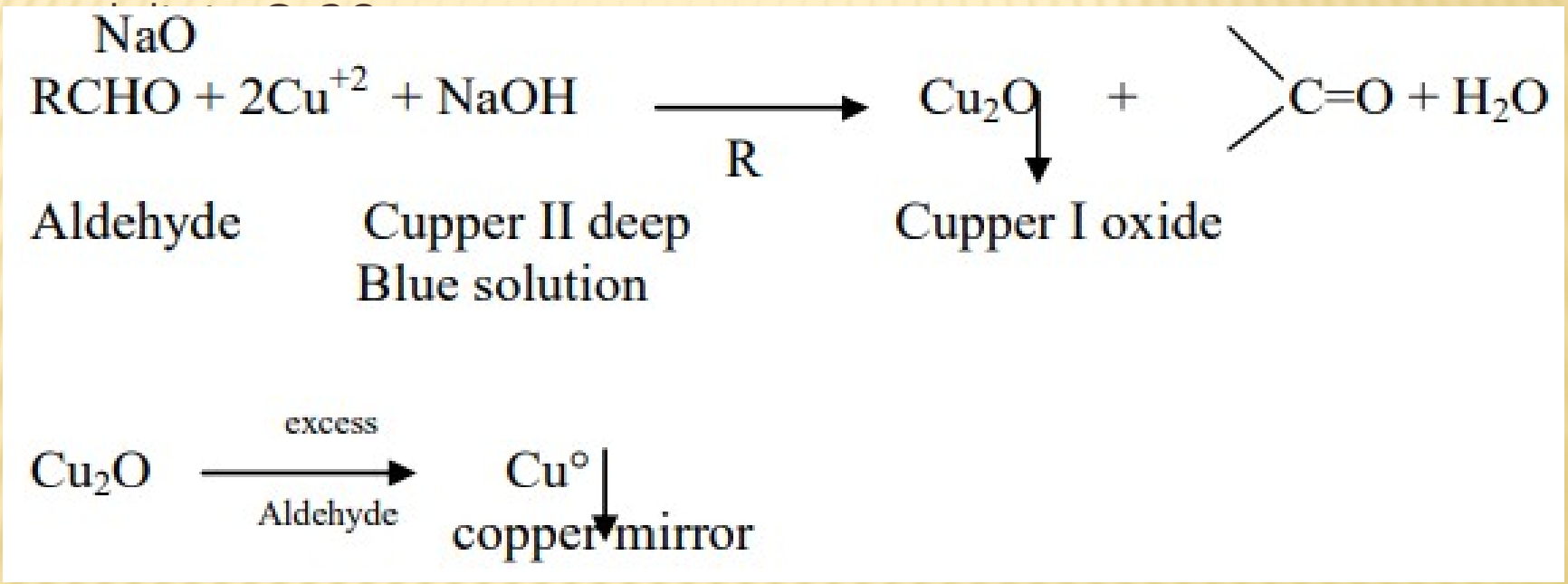


- The oxidation process needs alkaline medium, Therefore sodium hydroxide solution is used, and in order to overcome the formation of the brown silver oxide precipitate (Ag2O), ammonium hydroxide is used to serve as a complexing agent for this precipitate making it a water soluble complex.Note that since the medium is alkaline, salts of produced carboxylic acid are formed rather than the acid itself.

PROCEDURE

- To 5 ml of silver nitrate solution add 2-3 drops of 10% of sodium hydroxide solution, and then add very dilute ammonia solution drop by drop with continues shaking until all brown precipitate of silver oxide is dissolved. This reagent should be freshly prepared prior to use.
- -Add 2-3 drops of the compound to 2-3 ml of Tollens reagent, a silver mirror will be formed. If no reaction occurs, warm the test tube in water bath for few minutes

- Reduction of Fehlings reagent.This test, like Tollens test, is used to distinguish aldehydes from ketones. Only aldehydes can reduce Fehling,s reagent (a deep blue solution)to give a red cuprous oxide



- 1- Add 5 drops of the compound to 1 ml of Fehling,s solution, and then heat in water bath for 5 minutes (with shaking for water insoluble compounds).Aldehydes change the color of Fehling,s solution from blue to green, orange precipitate, and then red precipitate or copper mirror. Ketones donot change the color of this reagent. On the other hands, this test does not give sharp results with aromatic aldehydes.
- 2-Test for aldehydes and ketones containing a terminal methyl group.CH3C=OThese include acetaldehyde, acetone, acetophenone, and benzyl methyl ketone.

OTHER TEST

- 1-Iodoform(Haloform) test.
- 2-Sodium nitroprusside test (Na2[Fe(CN)5NO].2H2O)
- 3-Polymerization Reaction (test)
- 4-Cannizzaro reaction