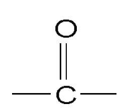
Aldehydes and ketones

Purpose of experimental

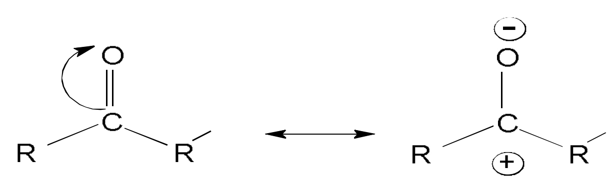
To learn identification of aldehydes , ketones and investigate the chemical properties of aldehydes and ketones.

Theory part of experimental

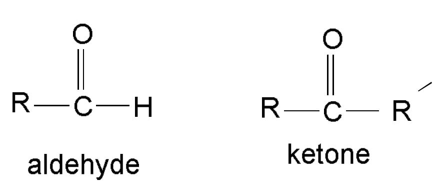
Aldehydes and ketones are representative of compounds which possess the carbonyl group. The carbonyl group (C=O), found in aldehydes and ketones, is a very important functional group that is involved in several common reactions. This particular functionality is unique because of the polarization (dipolar resonance) between the carbon-oxygen π bond.



The carbonyl group

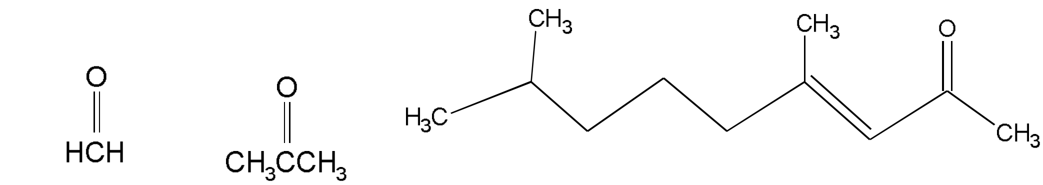


Aldehydes have at least one hydrogen attached to the carbonyl carbon; in ketones, no hydrogens are directly attached to the carbonyl carbon, only carbon containing R-groups:



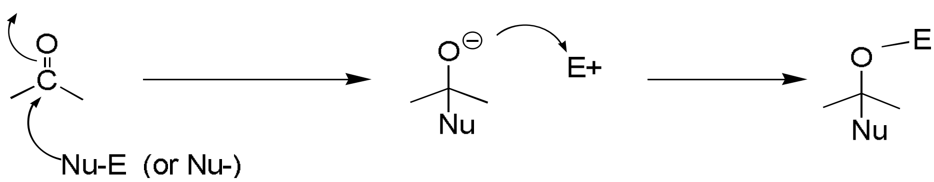
(R and R´ can be alkyl or aromatic)

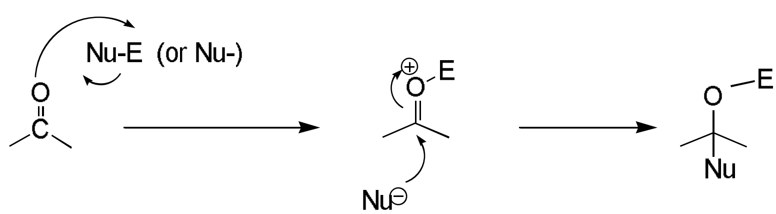
Aldehydes and ketones of low molecular weight have commercial importance. Many others occur naturally. Examples :



formaldehyde acetone citral (lemongrass oil)

Due to the resonance of the C-O bond, there are a variety of reactions where the electrophilic carbon is attacked by nucleophiles (Lewis bases) and the oxygen reacts with corresponding electrophiles (Lewis acids). The result of the reaction is the addition of a Nu-E to the π bond of the carbonyl group. The two most common mechanisms are outlined below, although they may vary based on the reagent and reaction conditions.

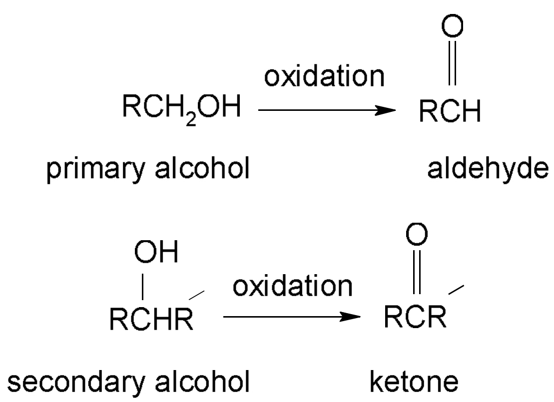




The carbonyl groups in both aldehydes and ketones will be examined in this experiment. Although the two groups often react similarly, aldehydes commonly react faster than ketones (with the same reagent) due to less steric hindrance at the carbonyl group. Aldehydes are also more easily oxidized than ketones. You will examine the similarities and differences between ketones and aldehydes and then use those skills to accurately identify an unknown compound containing a carbonyl group.

Physical properties and preparation

Aldehydes and ketones are polar compounds soluble in water and polar solvents. **Aldehydes** prepare by oxidation primary alcohols, while **ketones** prepare by oxidation secondary alcohols.



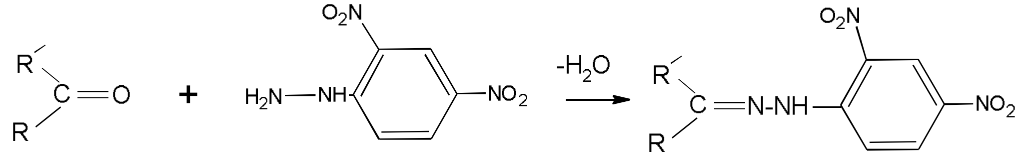
Chemical and Apparatus

Tollen's reagent (prepare from mixing (1ml) of 5% $AgNO_3$, (3 drops) of 5% NaOH), 2,4-dinitrophenylhydrazine, 10% NaOH, iodine (I_2) solution, aldehyde compound, ketone compound

Procedure of Experimental

1- General test for aldehydes and ketones- by reaction with nitrogen nucleophiles (2,4- Dinitrophenylhydrazine (DNP) Test), Brady's Test

2,4-dinitrophenylhydrazine can be used to qualitatively detect the carbonyl group functionality of an aldehyde or ketone functional group. A positive test is signaled by a yellow/red precipitate, known as a dinitrophenylydrazone. The solid derivatives are more stable than the original liquid compound.



Aldehyde : R = alkyl or aryl, R′ = hydrogen

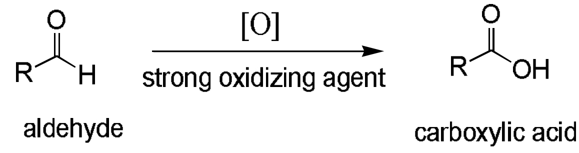
Ketone : R = alkyl or aryl, R′ = alkyl or aryl

Procedure :

- Place 5 drops of aldehyde or ketone into separately labeled clean, dry test tubes and add (1ml) of the 2,4-dinitrophenylhydrazine reagent to each. If no precipitate forms immediately, heat for 5 min. in a warm water bath (60 °C), cool.
- A positive test is denoted by a yellow→orange/red→red crystalline precipitate of the 2,4-dinitrophenylhydrazone derivative within a few minutes.
- Record your observations.

2- Oxidation

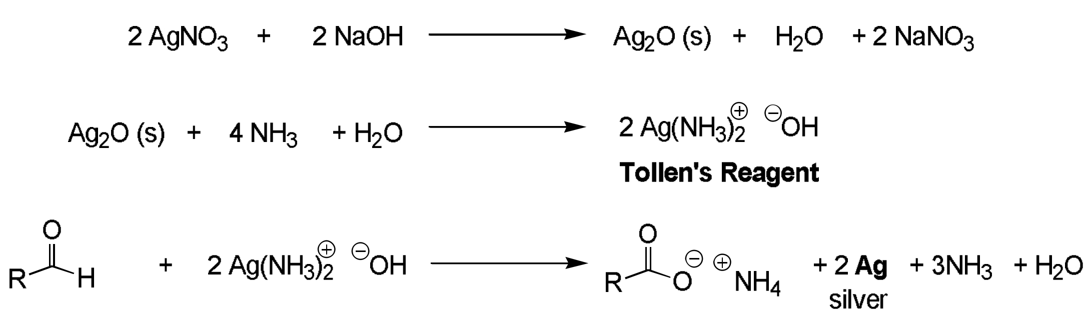
Aldehydes are more rapidly oxidized than ketones due to the hydrogen atom bonded to the α-carbon. Aldehydes are oxidized to carboxylic acids.



Ketones are not readily oxidized, which makes the two functional groups easily distinguishable. Only under extreme conditions (strong reagents and high temperature) can ketones be oxidized since the reaction requires the cleavage of a carbon-carbon bond.

Tollen's Test

Commonly known as the Silver Mirror Test, this distinctive qualitative test involves the oxidation of *aldehydes* to their corresponding carboxylic acid. The oxidizing agent is a silver complex ion $[Ag(NH_3)^{+}{}_2]$ which is reduced to a metallic silver which remains on the walls of the test tube as a mirror. Otherwise, the silver is deposited as a black precipitate. Tollen's reagent is prepared by dissolving silver oxide in ammonia:



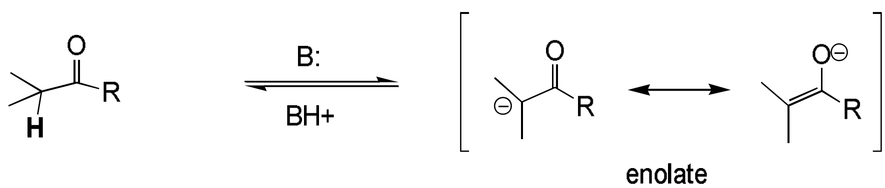
Procedure :

- Place 5 drops of aldehyde or ketone into separately labeled clean, dry test tubes Then, add (2 ml) of the prepared Tollens' reagent and mix.
- Place the test tube in a 60 °C water bath for 5 min. Remove the test tubes from the water and look for a silver mirror. If the tube is clean, a silver mirror will be formed; if not, a black precipitate of finely divided silver will appear.

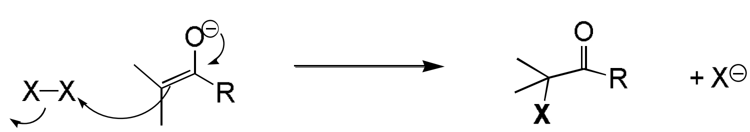
- Record your results on the report sheet.
- Clean your test tubes with 1 M HNO_3 and discard the solution in a waste container designated by your instructor.

3- The Haloform Reaction

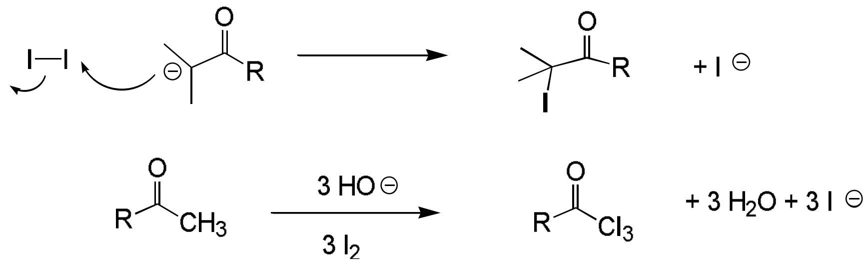
The haloform reaction is unique in the way that it occurs at the α-carbon of the carbonyl group. This reaction arises due to the increased acidity of the α-hydrogens and the resonance stabilization of the conjugate base (enolate anion).



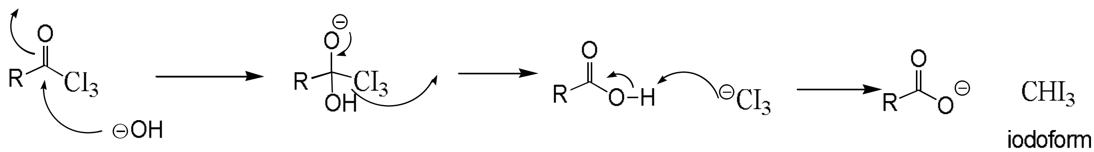
This reactive enolate anion acts as a nucleophile with halogens, generating an α-halo substitution product. Halogenation occurs to produce α-halocarbonyl compounds:



The first substituting halogens cause an electron withdrawing effect which makes any remaining hydrogens even more acidic. These hydrogens are then replaced quickly by other halogens. As seen below, a methyl group (α) to a carbonyl group is converted to a trihalomethyl group in a stepwise fashion.



With the addition of excess base, the electron withdrawing trihalo compound is cleaved, and the iodoform is generated.



Only carbonyl compounds with α-methyl groups undergo the carbon-carbon cleavage that produce the haloform and the corresponding carboxylic acid. This is due to the weakened bond that *only* results when three halogens are attached to the carbon (making it a sufficient leaving group).

When bromine or chlorine is used instead of iodine, the products are bromoform and chloroform, respectively. Most commonly, this reaction is used to test for the presence of methyl ketones, which uses iodine because it is safer and iodoform is a highly insoluble crystalline yellow solid that has a medicinal odor.

Procedure :

- Obtain two clean test tubes (not rinsed with acetone) and add 2-4 drops of aldehyde or ketone and Add about 2.5 mL of the base solution provided (NaOH) and then about 0.75 mL of the iodine solution. Shake well.

- Shake well and put into an ice bath if necessary.
- Record your observations.

Table of results

Compound	General test	Tollen's Test	Haloform test
Aldehyde			
Ketone			

Questions for discussion

1. How can Tollens' reagent be used to distinguish between an aldehyde and a ketone?
2. Explain, why Aldehydes are more active than ketones in oxidation?
3. Write the reaction of haloform reaction for ketone