

The oxidation of 2,4-dinitrophenylhydrazone to Carbonyl compound Emphasizing on the HMTA-2Br₂

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Abstract

HMTA-2Br₂ is a yellow solid with uniform shape which makes the oxidation of 2,4- dinitrophenylhydrazone made of Aldehyde and Ketone to carbonyl combination possible. The advantages in using the HMTAB are mentioned as the hydrolysis with minimum period of time, moderate condition for the reaction, the optimal characteristic of the oxidant to the Br₂ and most of the common oxidants, the certainty of the end of the reaction, the facilitation of the reaction collection which is possible with the simple extraction process, and the lack of using the complex system and the lack of extra oxidation.

Keywords: Hexamethylenetetramine-bromine complex, oxidation, 2, 4-Dinitrophenylhydrazone, aldehyde, ketone

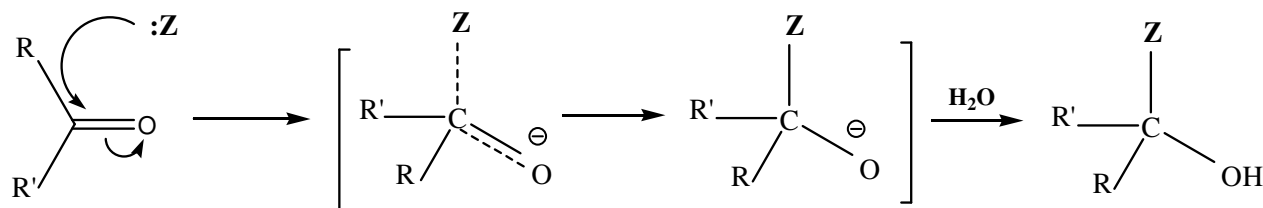
Introduction

The structure of Aldehyde and Ketone: The Aldehyde compounds are known with the formula "RCHO" and the Ketone compounds are known with the formula "RR'CO". The R and R' groups may be Aliphatic or Aromatic. The Aldehyde and Ketone both involve the carbonyl group, C=O and mainly are called the carbonyl compounds. The structural difference in the Aldehyde and Ketone compounds put the effect on their properties. As a matter of fact, the Aldehyde compounds get easily oxidized, whereas the Ketone compounds get oxidized with difficulty. Generally, the Aldehyde compounds are more reactionary against the increase of the nucleus, whereas about the carbonyl compounds-the Aldehyde compounds are more reactionary than the ketone compounds¹.

The protection of carbonyl group by 2,4- dinitrophenylhydrazone and using hexamethylenetetramine-bromine complex as a synthetic reagent for oxidation of 2,4- dinitrophenylhydrazone to its carbonyl group. The carbonyl group, C=O, are very effective in the Aldehyde and Ketone compounds. Aldehyde and ketone compounds are organic compounds which incorporate a carbonyl functional group, C=O. The carbon atom of this group has two remaining bonds that may be occupied by hydrogen or alkyl or aryl substituents. If at least one of these substituents be hydrogen, the compound would be an aldehyde.

If neither is hydrogen, the compound is a ketone. Where the carbon-oxygen double bond occurs in organic compound-it is called a carbonyl group. The interesting thing is the nature of carbon-oxygen double bond-not what's it attached to, So that, Due to the point that the electrons go forward the oxygen, thus the carbon in the carbonyl group is poor at electrons which the oxygen of carbonyl is rich of electrons. Also, due to the fact that the carbonyl group is flat, so those, the molecule against the attacks in the flat from the upward or inward sides come to the carbonyl group in a vertical position. The important stage in the reactions which develop on the carbonyl group is the very the development of the bond with carbon within low electrons in the carbonyl group. The carbonyl group are ready to be stood against the reactions with so many electrons; In fact, the reaction in the nucleus is the particular reaction provided for the Aldehyde and Ketone compounds which makes it interesting.

In 1962, NMR studies on the 2,4-dinitrophenylhydrazone and semicarbazone were provided. The magnetic resonance of the α , β and γ have been used in the syn and anti hydrogens which the contribution of the syn and anti isomers were obtained in these compounds. The increase of the solutions which have the capability to develop the hydrogen bond with N-H leads to the increase of the ratio of syn to anti².



Scheme-1

Allen-Bradley method is the method prepared for making the derivatives of the hydrazine compounds. Due to more solubility characteristic of the 2,4-dinitrophenylhydrazone in sulphuric acid, Bradley method is extensively used. Notwithstanding, this method results the consequences with the uncertain melting temperature and low melting temperature, by which the continuous crystallization would be resulted which this makes the optimal melting temperature provided. In addition, the observation about the previous studies gives us the consequences by which through the certain compounds in the studies accomplished by different individuals, the derivatives with various melting temperatures and physical characteristics have been obtained. For instance, three various melting temperature—148 C° ,154 C° OR 156 C° have been reported for the Propionaldehyde-2,4-dinitrophenylhydrazone^{3,4}, which six various melting temperatures have been reported for Acetaldehyde as well^{5,6}.

Main body: Using hexamethylenetetramine bromine complex in dichloromethane solvent. Benzophenone and 2,4-dinitrophenylhydrazone oxidation to benzophenone.

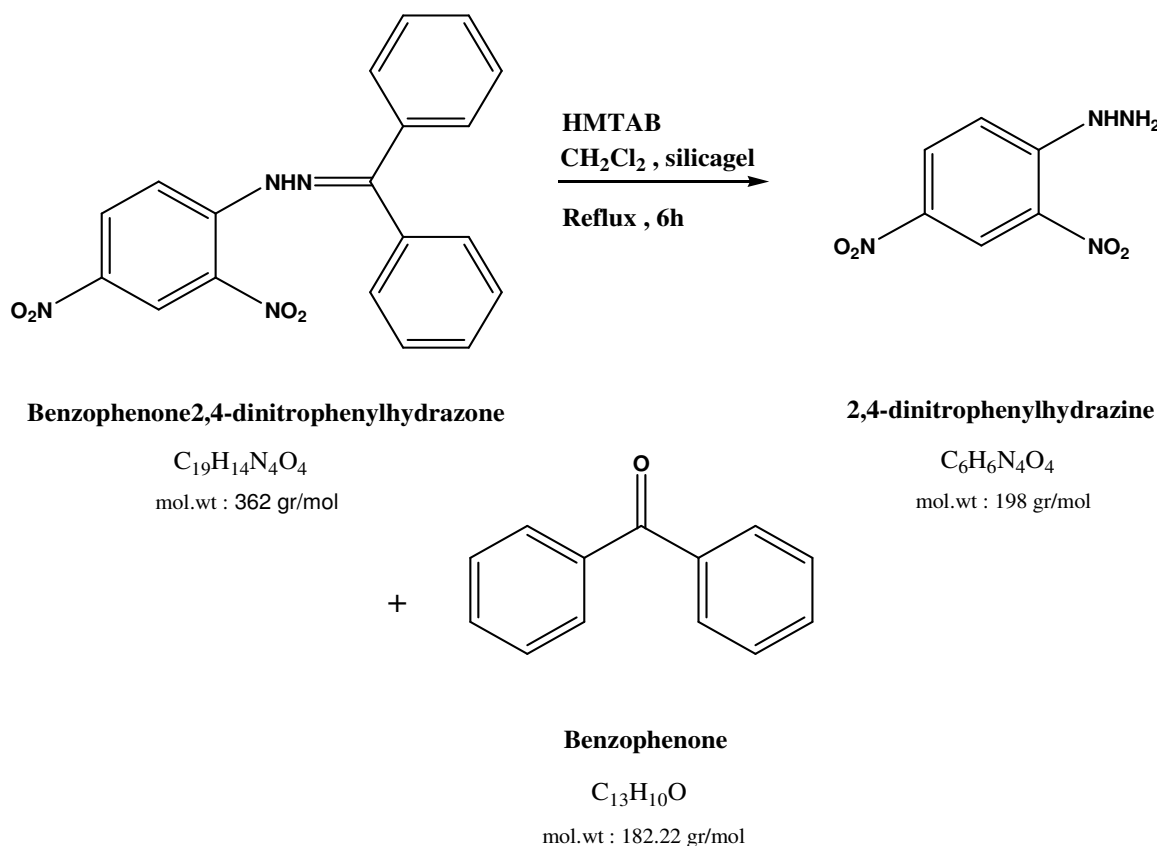
In a two span laboratorial flask(250 milliliters) we add .72 grams benzophenone, 2,4-dinitrophenylhydrazone and 20 milliliters

dichloromethane solvent, after absolute dissolving of hydrazones in dichloromethane solvent, 1/00 gram hexamethylenetetramine bromine and 1/00 silica gel is added to it.

The combination of reaction would be reflected in 40 degree temperature and for 6 hours through shaking it quickly so that its yellow color disappears. All different stages were taken from TLC reaction, and reaction progress was controlled by it.

After reflecting time, without evaporating reaction solvent, reaction combination would be left in environment temperature for 24 hours, and then reaction combination would be filtered so that its solvent would be evaporated and IR spectrum would be achieved from the rest of it. (IR spectrum, number 3)

IR spectrum, number 3:IR (KBr):1658 cm⁻¹: Aldehydes and ketones have carbonyl group (C=O), this group creates a strong absorption in 1650- 1850cm⁻¹ as a result of making changes in dipole moment. Moreover, since stretching vibration frequency C=O is sensitive to neighbor atoms, main mentioned groups have specific absorptions. With this brief introduction, we study spectrums 1, 2 and 3.



Scheme-2
 Benzophenone and 2,4-dinitrophenylhydrazone oxidation to benzophenone via HMTAB complex

IR spectrum number 1 is related to pure benzophenone and peak related to carbonyl group available in benzophenone is observable in frequency equal to 1651 cm^{-1} .

IR spectrum number 2 is related to benzophenone and 2,4-dinitrophenylhydrazone hydrazones. In frequency related to carbonyl group available in benzophenone, no peak is observed and it shows that pure benzophenone does not exist in this combination.

IR spectrum number 3 is related to reaction product and it is expected to see in this spectrum in frequency 1651 cm^{-1} , peak related to pure benzophenone. There is a little difference in frequencies related to spectrums number 1 and 3 that are resulted from possible impurity in reaction medium, and then it could be neglected. Therefore, with study of spectrums number 1, 2 and 3, one can conclude that it is possible to gain benzophenone via oxidation of benzophenone and 2,4-dinitrophenylhydrazone by hexamethylenetetramine bromine complex.

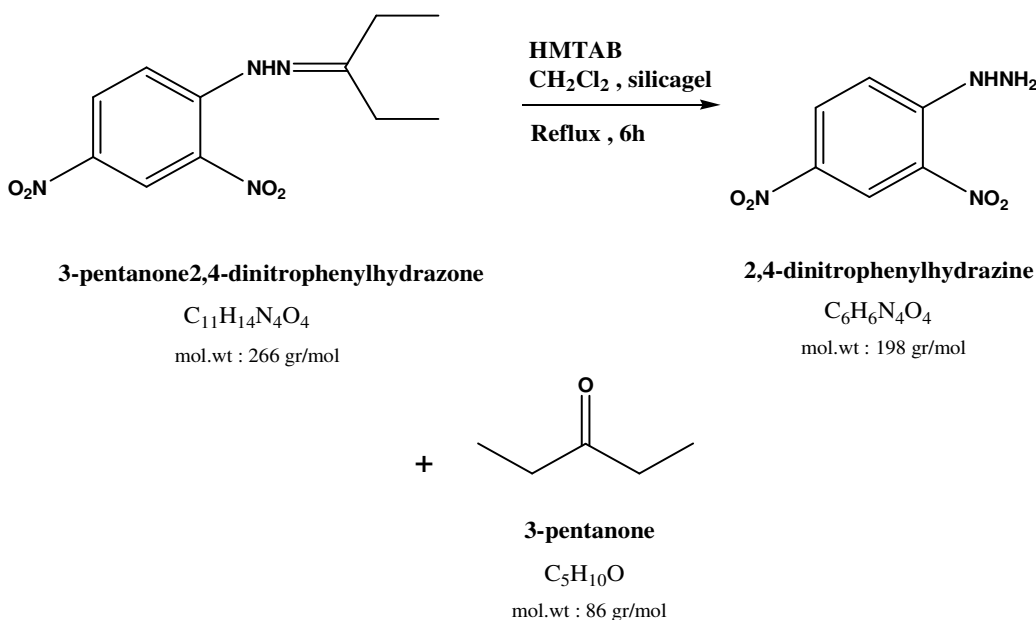
3-pentanone and 2,4-dinitrophenylhydrazone oxidation to 3-pentanone: In a two span laboratorial flask (250 milliliters), we add .12 grams of 3-pentanone and 2,4-dinitrophenylhydrazone and 20 milliliters dichloromethane solvent. Then, after complete dissolving of hydrazones in dichloromethane, 1/00 gram of hexamethylenetetramine bromine and silica gel would be added as well.

The combination of reaction would be reflected in 40 degree temperature, for 6 hours through shaking it quickly so that its yellow color disappears. All different stages were taken from TLC reaction, and reaction progress was controlled by it.

After reflecting time, without evaporating reaction solvent, reaction combination would be left in environment temperature for 24 hours, and then reaction combination get filtered to let its solvent get evaporated, and then IR spectrum would be achieved from the rest of it. (IR spectrum number 6)

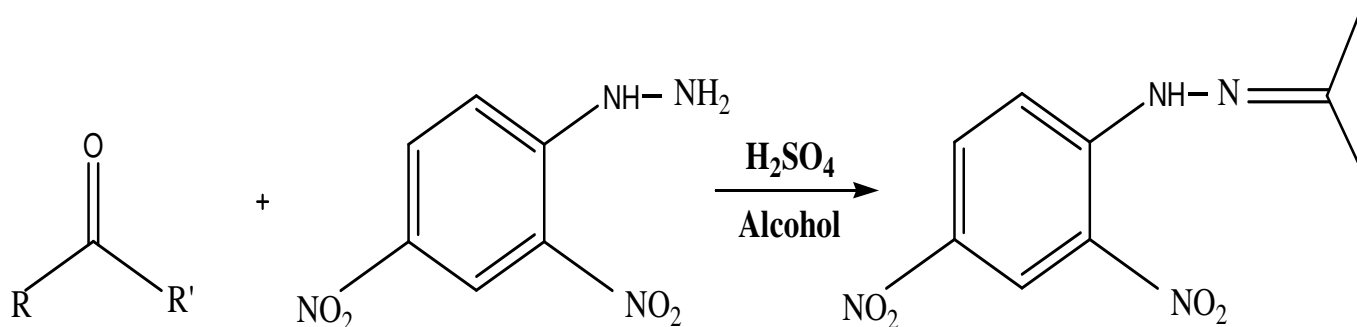
IR spectrum number 6: IR (KBr): 1722 cm^{-1} : IR spectrum number 4 is related to pure 3-pentanone. Peak related to carbonyl group available in 3-pentanone is observable in frequency 1733 cm^{-1} . IR spectrum number 5 is related to 3-pentanone and 2,4-dinitrophenylhydrazone. In frequency related to carbonyl group available in 3-pentanone, no peak is observed and it shows that 3-pentanone is not present in this combination. IR spectrum number 6 is related to reaction product and it is expected to see in this spectrum and in frequency 1733 cm^{-1} , peak related to 3-pentanone.

From The most useful derivatives of the Aldehyde compounds, we could mention the 2,4-dinitrophenylhydrazone, phenylhydrazine and 4-dinitrophenylhydrazone. Among these derivatives, we have chosen the 2,4-dinitrophenylhydrazone in present paper which this is due to the fact that the solid characteristic is more observed in this compound. As a matter of fact, through the molecular bazon Ketone within the 2,4-dinitrophenylhydrazone or 4-dinitrophenylhydrazone, the pertinent derivatives could be produced in this case. For the high molecular bazon Ketone, phenylhydrazine and 4-dinitrophenylhydrazone could be produced through the Aldehyde and Ketone reactions with the 2,4-dinitrophenylhydrazone, phenylhydrazine and 4-dinitrophenylhydrazone reactions⁷.



Scheme-3

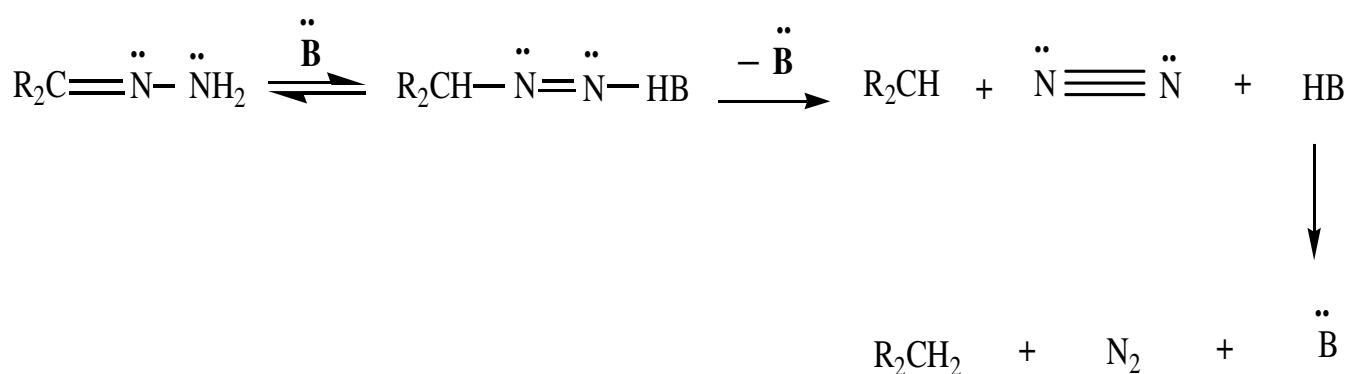
3-pentanone and 2,4-dinitrophenylhydrazone oxidation to 3-pentanone via HMTAB complex



Aldehyde or Ketone

2,4-dinitrophenylhydrazine

2,4-dinitrophenylhydrazone



Scheme-4

The reaction of the 2,4-dinitrophenylhydrazone: The carbonyl compounds with double bond of hydrazine, C=N, could be developed and changed to the hydrazine and azines (Aldehyde and setarin).

Hydrazones could be easily hydrolyzed in acidic environment, whereas the Hydrazones are sustainable in surrounding the bases. The prototrophy could be accomplished on the Hydrazones with 200 degree in surrounding the Alcoholate sodium which finally it could be separated from the compound, through this the CH₂ as the carbonyl factor would be decreased—This reaction is well-known with the Wolff-kishner reduction.

In this case, the Hydrazones particularly “phenylhydrazines” could be easily crystallized which they could be also used for determining the nature of the Aldehyde and Ketone compounds with the measurement of melting temperature.

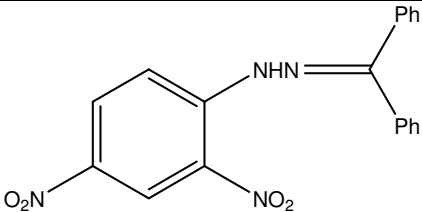
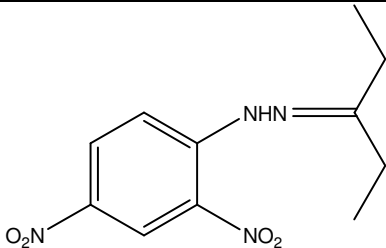
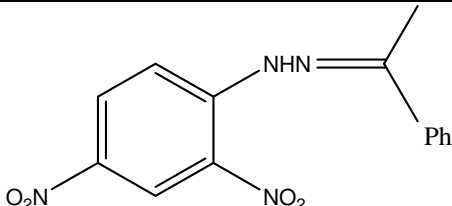
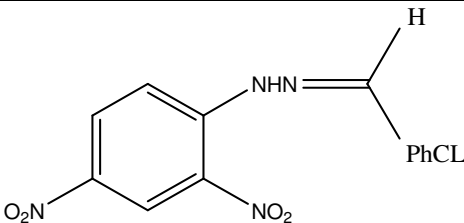
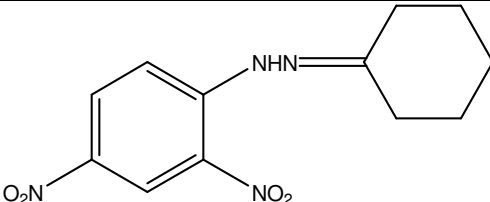
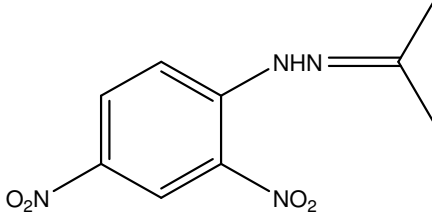
“Phenylhydrazines” relate to the crystal solid acetaldehyde melting at 99C° melting temperature. The extraction of atom which is melted at 99C° melting temperature tells the point that through the extraction of the oxygen atom from the carbonyl group in the molecule and the entrance of the heavy part, = NNH₂C₆H₅, in the molecule-the solubility of the Aldehyde and Ketone would be obviously decreased.⁸

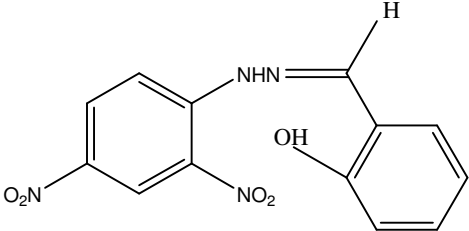
Produce the 2,4-dinitrophenylhydrazones reaction with the Aldehyde and Ketone compounds with Phosphoric acid Solubilize 4 g of 2,4-dinitrophenylhydrazones in 50 ml Phosphoric acid, act for this through 85% heating temperature, thereafter post the total solubility of the solution , make it cold as the room temperature, so that try to separate the negligible solid particles in order to get the transparent solution. Then, add 2mmol Aldehyde or Ketone compound to the new 10 ml solution of the 2,4-dinitrophenylhydrazone, so that act to warm the solution with the warm vapor, with this situation the solution gradually would become crystallized. After these stages, the solution has to be filtered and washed with cold water, which then it has to be drained⁹.

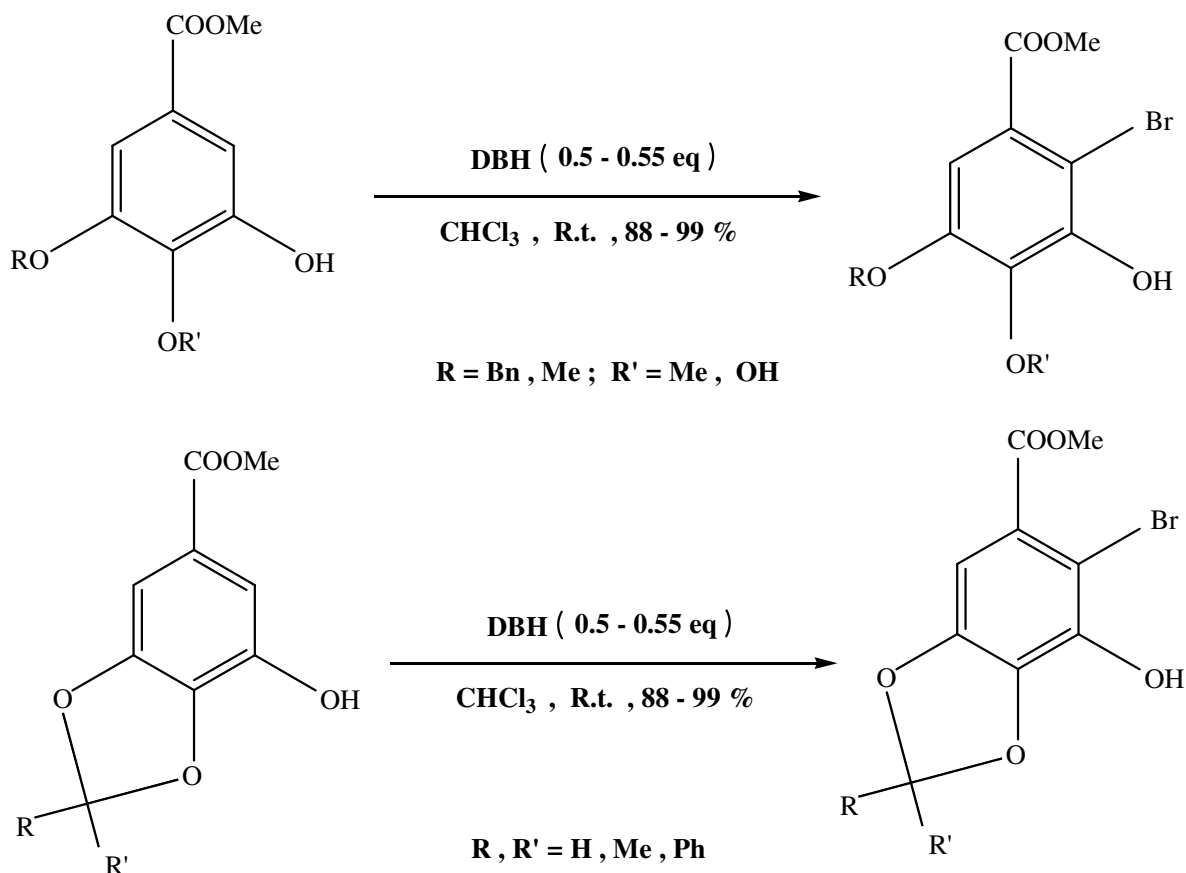
The reason for washing the solution with cold water is that there are extra acid in the solution which through the cold water, we could remove it .Through the methods provided for the generation of the 2,4-dinitrophenylhydrazone, in present paper the 2,4-dinitrophenylhydrazones reaction was generated through the first method. (Generation of the 2,4-dinitrophenylhydrazone involving Aldehyde and Ketone compounds with sulphuric acid and water)

Table-1

The table provided for melting temperature for the dinitrophenylhydrazones with the Aldehyde and Ketone compounds

2,4-Dinitrophenylhydrazone		
Name of compounds	Hydrazones of aldehyde or ketone	Derivative mp(°C)
Benzophenone		239
3-pentanone		156
Acetophenone		237; 250
4-chlorobenzaldehyde		270; 254
2,4-Dinitrophenylhydrazone		
Name of compounds	Hydrazones of aldehyde or ketone	Derivative mp(°C)
Cyclohexanone		162
Acetone		-

Salicylaldehyde		252d
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Scheme-5

Methodology

The characteristics of consumed materials in the laboratories: The materials used in the laboratories are as following which based on the requirements; they have been filtrated as well: i. Bromine, ii. Hexamethylenetetramine, iii. Chloroform, iv. Dichloromethane, v. 2,4-Dinitrophenylhydrazone, vi. Methanol, vii. Ethanol, viii. Sulfuric acid, ix. Phosphoric acid, x. Benzophenone, xi. 3-pentanone, xii. Acetophenone, xiii. 4-Chlorobenzaldehyde, xiv. Cyclohexanone, xv. Acetone, xvi. Salicylaldehyde, xvii. N-hexane, xviii. Ethylacetate.

The instrumentations and tools used in the laboratories: i. FT-IR spectrum, ii. The device determining the melting point,

iii. 500 MHz, ¹H NMR spectrum, iv. Magnetic stirrer heater, v. Condenser, vi. 250 ml two-necked flasks, vii. Buchner Funnel, viii. Crystalizor.

Activating hexamethylenetetramine bromine complex: Hydrazine resulted from aldehyde or relevant ketone (.12 grams) and dichloromethane (20 milliliter) are poured into a two span laboratorial flask and then *hexamethylenetetramine* bromine complex(1/00) plus silica gel would be added to it. The mixture would be reflected in temperature equal to 40 centigrade with quick shaking for 6 hours. Oxidation would be continued up to the time that yellow color disappears. Moreover, development of reaction is controlled via TLC method.

Determining adequate solvent: Oxidation of hydrazones to carbonyl compounds related to other solvents such as chloroform, carbon tetrachloride, and n-hexane was done via hexamethylenetetramine bromine, however, later it was clarified that oxidation of hydrazones to carbonyl compounds via hexamethylenetetramine bromine in dichloromethane solvent with mol ratio (one to five) of hydrazone to HMTAB complex would have a better output.

The quantitative measurement of active Bromine in the complex: The amount of active Bromine is in terms of 1 mol from the 1.5 Bromine complex which it could be determined with the Titration Method using Sodium Thiosulfate.

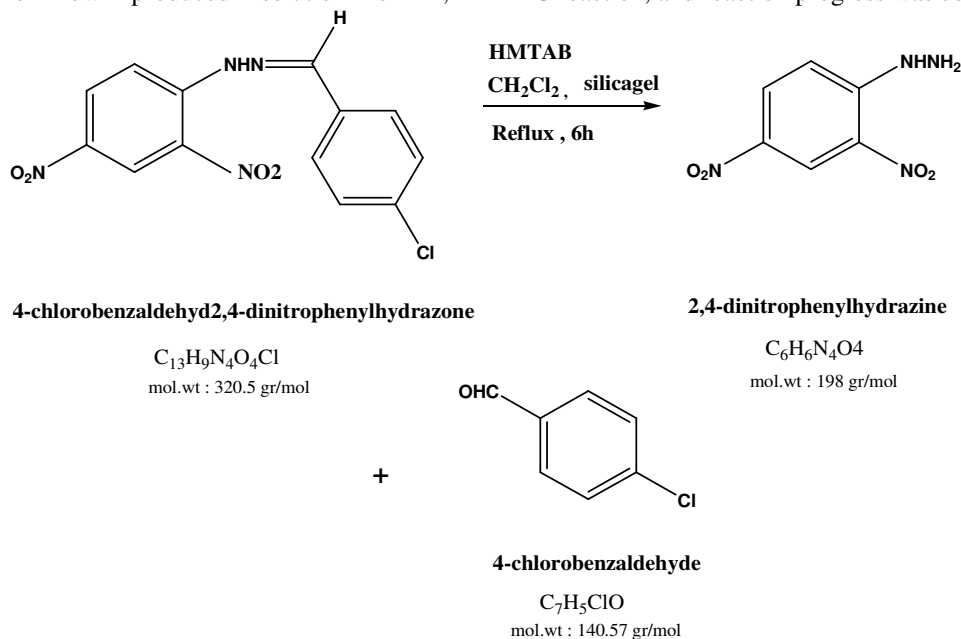
The oxidation reactions for the hydrazines to the carbonyl compounds. All the oxidation reactions for the hydrazines to the carbonyl compounds have been repeated for several times; this is done in order to get the optimal temperature, time, molar ratio of complex to the hydrazine and also the optimal solution. Therefore, here the best consequences have been provided.

The method to produce the hydrazines: Through several methods, producing the hydrazines from the aldehyde or ketone compounds is possible. Here, two methods in order to produce the hydrazines have been mentioned: i. Producing the 2,4-dinitrophenylhydrazone involving the aldehyde or ketone compounds with 0.4 g, thick sulphuric acid in Ethanol in a small flask, in this case add the 4-dinitrophenylhydrazone to the 2 ml thick sulphuric acid—thereafter add 3 ml water drop by drop, so that shake the flask which this would solubilize the 2,4-dinitrophenylhydrazone. In this case, add 10 ml ethanol -95%, and then add the new produced solution of 2,4-

dinitrophenylhydrazone to the complex with 0.5 g aldehyde or ketone compound which has been solubilized in 20 ml ethanol-95%, in this case let the solution be in a room temperature for some while. The separation of 2,4-dinitrophenylhydrazone crystals from the solution takes 5-10 minutes. In this case, it has to be mentioned that if the precipitation was not observed, so that the solution has to be remained in the room temperature for a night. Through warming the 2,4-dinitrophenylhydrazone with the vapor and also through the 30 ml ethanol-95%, act for the re-crystallization process. If the 2,4-dinitrophenylhydrazone was immediately solubilized, so that in this case add the water in order to make it turbid, which for this you could also add 5 ml water in order to make it turbid. If the compound was not solubilized, in this case you could add the ethyl estate in order to provide the solution, and then filtrate the solution and let the solution remained in the room temperature for nearly 12 hours, then put the attempt to separate the crystals with Buchner Funnel⁷.

4-chlorobenzaldehyde, 4-dinitrophenylhydrazone oxidation to 4-chlorobenzaldehyde: In a two span laboratorial flask (250 milliliters), .12 grams of 4-chlorobenzaldehyde, 4-dinitrophenylhydrazone and 20 milliliters of dichloromethane solvent is added, after completely dissolving hydrazone in dichloromethane solvent, 1/00 grams of hexamethylenetetramine bromine and silica gel would be added as well.

The combination of reaction would be reflected in 40 degree temperature for 6 hours through shaking it quickly so that its yellow color disappears. All different stages were taken from TLC reaction, and reaction progress was controlled by it.



Scheme-6

4-chlorobenzaldehyde, 4-dinitrophenylhydrazone oxidation to 4-chlorobenzaldehyde via HMTAB complex

IR spectrum number 12: IR (KBr): 1683 cm⁻¹: IR spectrum number 10 is related to pure 4-chlorobenzaldehyde. Peak related to carbonyl group available in 4-chlorobenzaldehyde is observable in frequency 1683 cm⁻¹. IR spectrum number 11 is related to 4-chlorobenzaldehyde and 2, 4-dinitrophenylhydrazone. In frequency related to carbonyl group available in 4-chlorobenzaldehyde, no peak is observable and it shows that pure 4-chlorobenzaldehyde is not present in this combination. IR spectrum number 12 is related to reaction product and it is expected to see in this spectrum and in frequency 1683 cm⁻¹, peak related to 4-chlorobenzaldehyde.

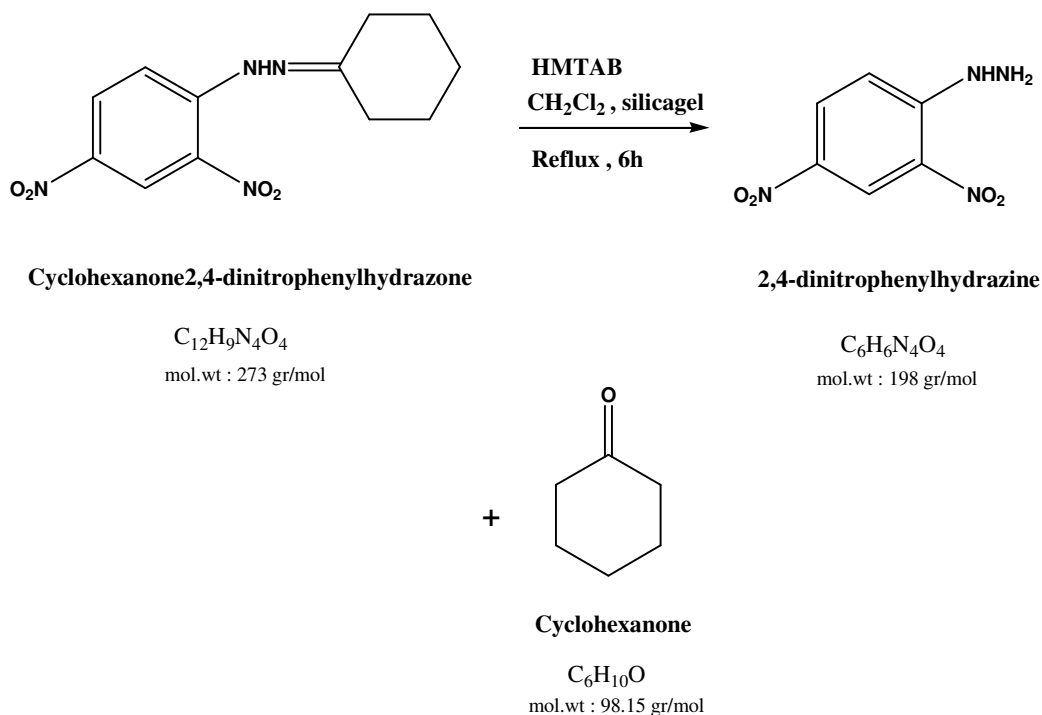
Cyclohexanone2, 4-dinitrophenylhydrazone oxidation to cyclohexanone: In a two span laboratorial flask (250 milliliters), .2 grams of cyclohexanone, 4-dinitrophenylhydrazone and 20 milliliters of dichloromethane solvent is added, after completely dissolving hydrazone in dichloromethane solvent, 1/00 grams of hexamethylenetetramine bromine and silica gel would be added as well. The combination of reaction would be reflected in 40 degree temperature for 6 hours through shaking it quickly so that its yellow color disappears. All different stages were taken from TLC reaction, and reaction progress was controlled by it.

IR spectrum number 15: IR(KBr): 1715 cm⁻¹: IR spectrum number 13 is related to pure cyclohexanone and peak related to carbonyl group available in cyclohexanone is observable in frequency 1715 cm⁻¹. IR spectrum number 14 is related to cyclohexanone and 2, 4-dinitrophenylhydrazone. In frequency related to carbonyl group available in cyclohexanone, no peak is observable and it shows that pure cyclohexanone is not

present in this combination. IR spectrum number 15 is related to reaction product and it is expected to see in this spectrum and in frequency 1715 cm⁻¹, peak related to pure cyclohexanone. As it is obvious, in frequency 1715 cm⁻¹, peak related to cyclohexanone is observed.

Salicylaldehyde2, 4-dinitrophenylhydrazone oxidation to salicylaldehyde: In a two span laboratorial flask (250 milliliters), .2 grams of salicylaldehyde2, 4-dinitrophenylhydrazone and 20 milliliters of dichloromethane solvent is added, after completely dissolving hydrazone in dichloromethane solvent, 1/00 grams of hexamethylenetetramine bromine and silica gel would be added as well. The combination of reaction would be reflected in 40 degree temperature for 6 hours through shaking it quickly so that its yellow color disappears. All different stages were taken from TLC reaction, and reaction progress was controlled by it.

IR spectrum number 21: IR (KBr): 1733 cm⁻¹: IR spectrum number 19 is related to pure salicylaldehyde. Peak related to carbonyl group available in salicylaldehyde is observable in frequency 1710 cm⁻¹. IR spectrum number 20 is related to salicylaldehyde and 2, 4-dinitrophenylhydrazone. In frequency related to carbonyl group available in salicylaldehyde, no peak is observable and it shows that salicylaldehyde is not present in this combination. IR spectrum number 21 is related to reaction product and it is expected to see in this spectrum and in frequency 1710 cm⁻¹, peak related to pure salicylaldehyde. As it is obvious, in frequency 1710 cm⁻¹, peak related to salicylaldehyde is observed.



Scheme-7

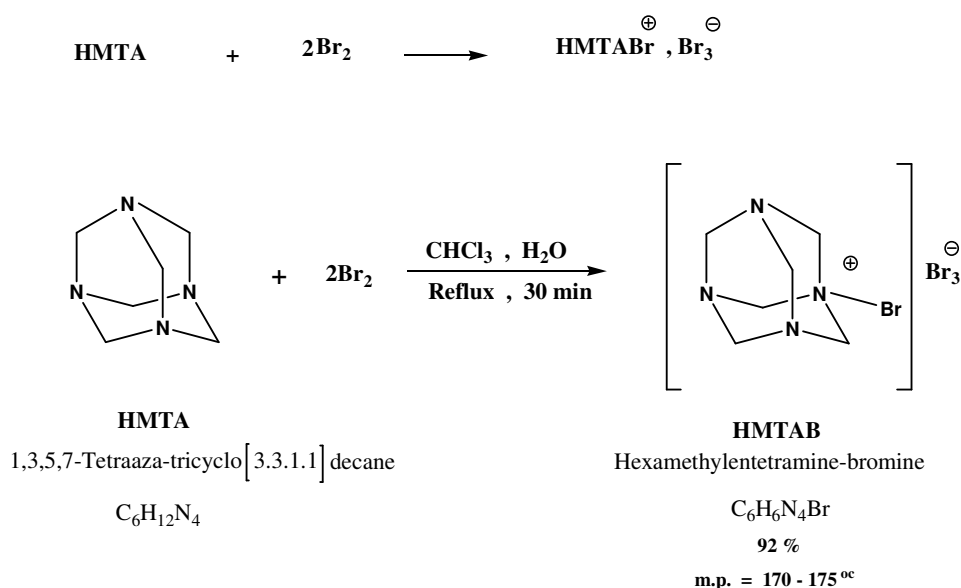
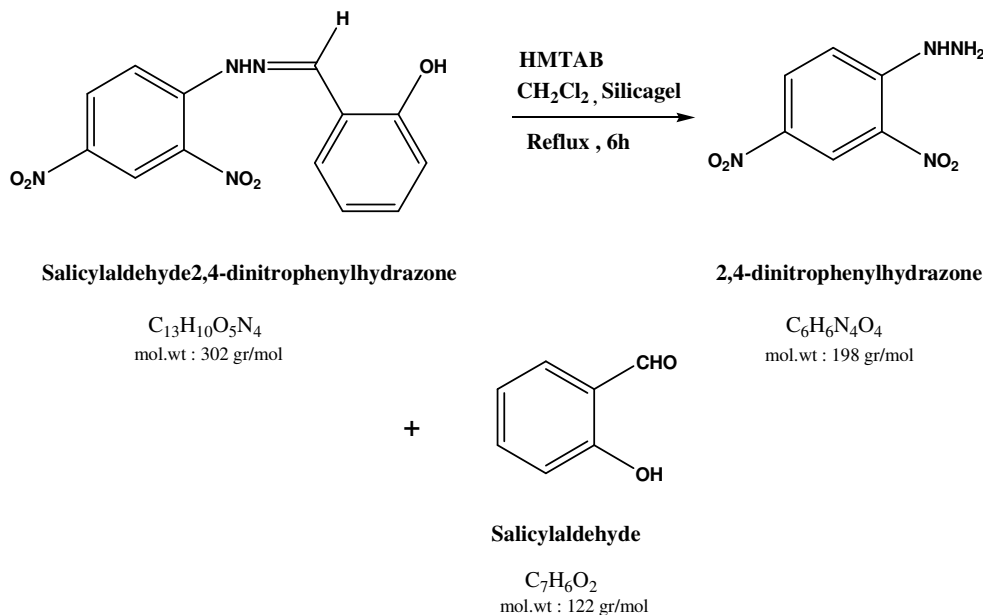
Cyclohexanone2, 4-dinitrophenylhydrazone oxidation to cyclohexanone

Results and Discussion

In 2005, Tsubi et al found out that DBH is a pertinent and optimal reactive to produce the phenols and poly phenols to the mono-ortho Bromide with very optimal efficiencies¹⁰.

The description of the Hexamethy lenetetramine-Bromine(HMTAB): Hexamethylenetetramine-Bromine is an orange yellow solid which through putting the Bromine on the Hexamethylenetetramine, it could be easily produced which in

normal situation, it is sustainable. Due to the fact that based on the following reaction between Bromine and Hexamethylenetetramine the complex is resulted, so that the Bromine could be gradually get into the reaction. As a matter of fact, this complex is neither solubilized in water, nor in any other organic solutions like Chloroform, Dichloromethane, and etc .Only if the Bromine be separated from the complex, in this case the complex would be solubilized.



Change the Oxime to carbonyl compounds using the Hexamethylenetetramine-Bromine complex in surrounding the aluminum. In this reaction, the oxime in surrounding the hexamethylenetetramine-bromine complex and aluminum in the CH_2Cl_2 solution become refluxed. In this case, clay desiccants and silica gel have been used as well, but the best consequences have been reported about the Aluminum.¹¹In present paper, the Hexamethylenetetramine-Bromine complex has been mentioned as an efficient oxidant for the oxidation of 2,4-dinitrophenylhydrazone to carbonyl compound in a condition with 40 C° temperature and reflux with the optimal consequence and less time in the Dichloromethane solution and Hexamethylenetetramine- Bromine complex. From the advantages of this oxidant method for the hydrogen, we could mention the advantages such as moderate condition for the reaction, less time, the optimal index of oxidant rather than Bromine and the existence of so many common oxidants, the certain fact about the end of the reaction, disappearance of yellow color; In fact, in this case there is no need to the complex device.

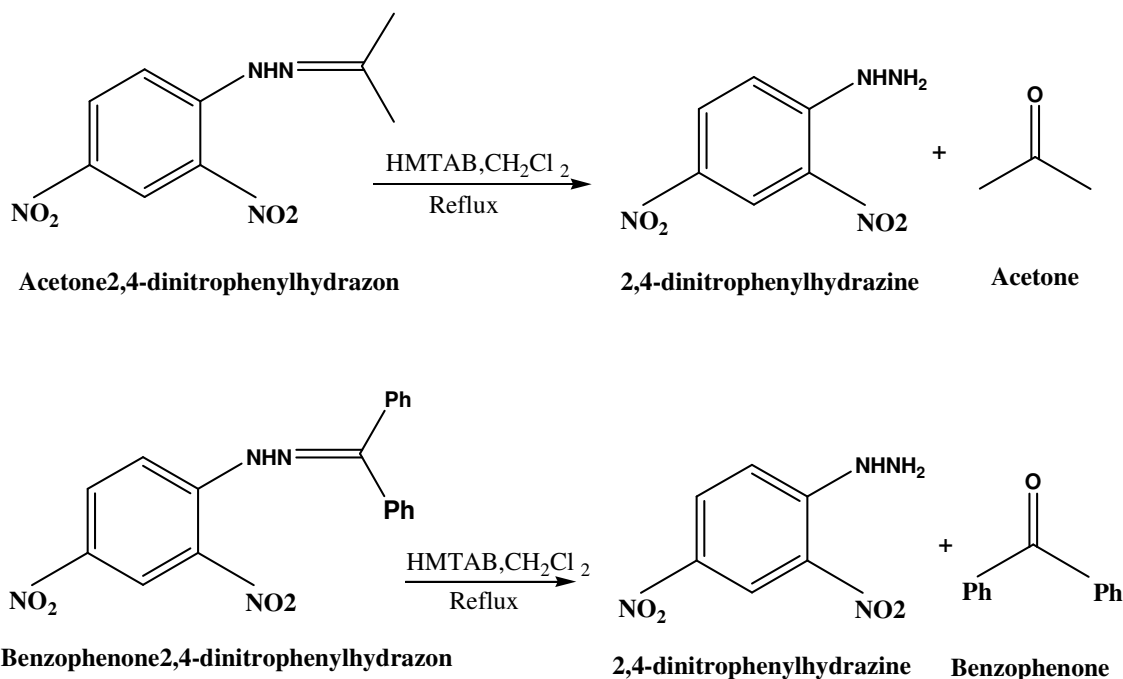
Conclusion

Due to the necessity of the process of changing the 2, 4-dinitrophenylhydrazone to the aldehyde or ketone compounds and the Synthesis application of this compound, present paper has been prepared to access a pertinent method for the hydrolysis of 2, 4-dinitrophenylhydrazone to carbonyl compound using the Hexamethylenetetramine-Bromine complex

as the reactive. Along this, to achieve the objectives, the aldehyde and ketone hydrazines were chosen by which the approach provided for the Oxidation using the HMTAB complex was observed. Through the reactions provided for the oxidation of 2, 4-dinitrophenylhydrazone to carbonyl compounds. The aldehyde or ketone compounds using HMTAB complex, it was specified that the various types of hydrazines in Dichloromethane solution give us the best consequences related to the aldehyde or ketone compounds.

Considered purposes of the present paper could be summarized in the following cases: i. Finding access to a method for oxidizing hydrogen to aldehydes and related ketones, a method that does not need long processes and separation of products. ii. Using a cheap reagent. iii. Finding access to aldehydes and ketones without producing lateral products or spending a huge amount of money. iv. Increasing efficiency of reagent hexamethylenetetramine bromine in dichloromethane which was previously used for oxidizing different types of organic compounds.

In this figure, acetone 2,4 dinitrophenylhydrazone have been analyzed via formula HMTAB, CH_2Cl_2 and 2,4 dinitrophenylhydrazone, acetone have been achieved. Moreover, benzophenone 2,4 dinitrophenylhydrazone have been analyzed via formula HMTAB, CH_2Cl_2 and 2,4 dinitrophenylhydrazone, benzophenone have been achieved.



Scheme-10

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