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Homi Bhabha Centre for Science Education
Tata Institute of Fundamental Research

In collaboration with

Gogate Joglekar College, Ratnagiri

Organic Chemistry Task IB

This workshop is organized by Centre for Excellence in Science and Mathematics Education (CESME-HBCSE) and set up under the Pandit Madan Mohan Malaviya National Mission for Teachers and Teaching Programme

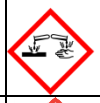
This experiment has been adapted from 45th International Chemistry Olympiad held in Moscow, Russia in 2013 which is available in the public domain and is accessed from: http://www.icho2013.chem.msu.ru/en/problems-solutions/icho-2013-problems

Tracking the supplied samples of substituted aldehydes by hydrazone derivatives

List of Glassware and equipment

Item	Quantity
5 mL Plastic tube with screw neck labeled "1"	1
5 mL Plastic tube with screw neck labeled "2"	1
Burette stand	1
50 mL beaker	2
15 mL test tube	4
Spatula	2
500 mL plastic washer bottle	1
10 mL measuring cylinder	1
Glass rod	1

List of Chemicals

Reagent	Quantity	Labeled	Safety
2,4-Dinitrophenylhydrazine	200 mg each, 2 vials	2,4 DNP	
Sulfuric acid, concentrated	1 mL each, 2 tubes	H_2SO_4 concentrated	
Aldehyde solution 1 mmol in ethanol	4 mL each, 2 bottles	Aldehyde 1 and Aldehyde 2	
NaOH solution	10 mL	NaOH 2M	
Acetone	10 mL	Acetone	
$NaHCO_3$ solution	10 mL	$NaHCO_3$ 10%	
Ethanol			

On the table for the common use
Ethanol, Liquid waste container, Solid waste container, Distilled Water, Filter paper, pH papers

Hazard Symbols

Corrosive 

Flammable 

Irritant 

Carcinogenic 

Toxic 

Hazard to environment 

Tracking the supplied samples of substituted aldehydes by hydrazone derivatives

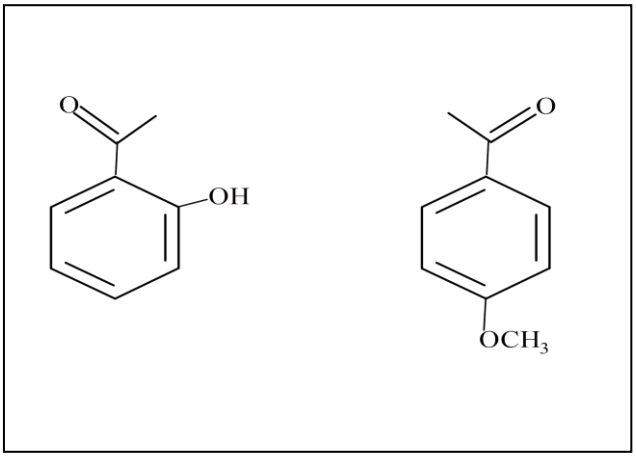
Introduction:

Hydrazones are organic compounds with the general formula, $R_1R_2C=N–NHR_3$. Reaction of hydrazine or substituted hydrazines (like 2,4-dinitrophenylhydrazine) with ketones or aldehydes lead to formation of hydrazones, (imine derivatives). The properties of hydrazones are largely due to the presence of the >C=N–N< structural unit, which contains two nitrogen atoms that are nucleophilic in nature. The carbon atom may act as either electrophile or nucleophile according to the reaction conditions and environment. The C=N bond of dialkyl hydrazones can be hydrolyzed, oxidized and reduced that gives variety of products. Similarly the N–N bond can be reduced to the free amine.

These derivatives are highly coloured solids, often stable and crystalline. You must have used formation of hydrazones as a qualitative test for confirming the presence of a carbonyl group. In fact, the concentration of low molecular weight aldehydes and ketones can be determined by converting them to their hydrazone derivatives. Hydrazone derivatives have various important pharmacological activities and are used for synthesis of a wide variety of medicinally active compounds.

References: i) Reactions, Mechanisms, and Structure, John Wiley & Sons, Milton, Australia, 6th edition, 2007.
ii) http://dx.doi.org/10.1155/2014/761030

In the current task, you will be preparing substituted hydrazones using 2,4-dinitrophenylhydrazine for the given samples of two substituted benzaldehydes (shown below). In fact, using the colour and some simple qualitative tests, you will identify the substituted benzaldehydes given to you.



Procedure

Preparation of 2,4-dinitrophenylhydrazones

Weigh 0.200 g of given 2,4-dinitrophenylhydrazine and transfer it to a 50 mL beaker and place a glass rod inside the beaker. Add 2 mL of the given concentrated sulfuric acid to this beaker in a dropwise manner using a **dropper and with constant stirring**. Then, using measuring cylinders, add 1.6 mL of water and 4 mL of ethanol to the reaction mixture. At the end, add one of the aldehyde sample solution and note its label (either **sample 1** or **sample 2**). A bright coloured precipitate will start forming at once. Continue stirring with the glass rod for 10 min, then add 10 mL of water and stir for another 3 min.

Separation and purification of the product

Filter the product using the Büchner funnel under suction. Wash the precipitate with small amounts of water (2 -3 mL each time) until the pH of the filtrate is almost neutral. Lastly, wash the precipitate twice with ethanol (2-3 mL each time). Air-dry the solid on the filter paper and record the mass of the product in the answer sheet.

Repeat the entire procedure with the other sample of the aldehyde provided to you.

Answer Sheet

Plastic Vial/stoppered tube 1 (Sample 1)		Plastic Vial/ stoppered tube 2 (Sample 2)	
Mass of empty vial/ stoppered tube		Mass of empty vial/ stoppered tube	
Mass of vial + product		Mass of vial + product	
Mass of product		Mass of product	

1. The structures of the aldehydes are given to you. Draw the structures of the two hydrazones that will be formed.

Product 1 (sample 1)	Product 2 (sample 2)

2a) In your opinion, will the hydrazones formed exhibit stereoisomerism?

Hydrazone formed for Sample 1 Yes ☐ No ☐

Hydrazone formed for Sample 2 Yes ☐ No ☐

b) If your answer is yes for one or both, the kind of stereoisomerism will be ☐

3. In your opinion, whether the acidic pH of the reaction mixture is a crucial factor which will affect the yield of the above synthesis? Explain your answer in brief.

4. In your opinion, whether the synthesis reaction will proceed in

a) neutral Yes ☐ No ☐

b) basic Yes ☐ No ☐

5. If the above synthesis is carried out with **p-nitro benzaldehyde** in acidic medium the rate of formation of product will be:

a) slower as compared to the synthesis done by you ☐

b) faster ☐

c) no change ☐

d) cannot say as more information will be required ☐

Characterization

Dissolve a **single crystal** of each hydrazone in a test tube in 10 mL of acetone and divide into two parts.

6. a) To I part add 1 drop of **saturated** $NaHCO_3$ solution and shake the resultant solution well. Record your observations of the solutions color changes in the box.

Observation for 2,4-DNPH derivative of Sample 1

The color of the solution does not change ☐

The color changes significantly ☐

Observation for 2,4-DNPH derivative of Sample 2

The color of the solution does not change ☐

The color changes significantly ☐

b) To the second part of the solution, add **2 drops** of NaOH solution and shake the resultant solution well. Record your observations of the solutions color change in the box.

Observation for 2,4-DNPH derivative of Sample 1

The color of the solution does not change ☐

The color changes significantly ☐

Observation for 2,4-DNPH derivative of Sample 2

The color of the solution does not change ☐

The color changes significantly ☐

7. What structural features of your products explain the color change (if any) in the reaction with $NaHCO_3$? Tick the appropriate box/es.

☐ presence of MeO group at position 4 in the benzene ring;
☐ presence of the OH group at position 2 in the benzene ring;
☐ presence of both >C=N-N< unit
☐ presence of both >C=N-N< and OH

8. What structural features of your products explain the color change (if any) in the reaction with NaOH? Tick the appropriate box/es.

☐ presence of MeO group at position 4 in the benzene ring;
☐ presence of the OH group at position 2 in the benzene ring;
☐ presence of both >C=N-N< unit
☐ presence of both >C=N-N< and OH

9. Which of the listed processes is responsible for the color change (if any) observed in the reaction of 2,4-dinitrophenylhydrazones with aqueous NaOH? Tick the appropriate box.

☐ alkaline hydrolysis	☐ dehydration	☐ hydration
☐ deprotonation	☐ dehydrogenation	

10. Draw the structures of the main organic species present in each test reaction medium in the answer box below.

Initial aldehyde	Solution with $NaHCO_3$	Solution with NaOH
Sample 1		
Sample 2		

11. Calculations

	Mass of aldehyde	**Molar Mass of aldehyde**	**Molar Mass of hydrazone**	**Mass of hydrazone**
Sample 1				
Sample 2				

12. Calculate the theoretical yield and the percentage yields of the hydrazones.

Sample 1

Sample 2