Lab 4: Carbonyl Reactions

Anjali Chandrasekhar, Enkhsanaa Enkhbayar, Max Shi, Mariam Siam

-I pledge my honor that I have abided by the Stevens Honor System

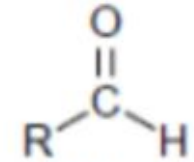
Reagents (Part 1)

Name	**M.W.** (0.5 pts)	**Density** (0.5 pts)	**Amount (grams/mL)** (0.5 pts)	**Moles** (0.5 pts)	**Hazards/Precautions (MSDS data) and melting point or boiling point** (2 pts)	**Role of the reagent** (1 pts)*
2,4-dinitrophenyl hydrazine	198.14 g/mol	0.843 g/mL	0.8 g	0.004	Flammable solid, harmful if swallowed. BP: 378.6°C, MP: 194.0°C	Reactant
Conc. Sulfuric Acid	98.079 g/mol	1.840 g/mL	4 mL	0.08	Very strong acid. Corrosive, eye damage, respiratory irritation and organ toxicity. Reacts violently with water. BP: 337°C, MP: 10°C	Catalyst
Methanol	31.04 g/mol	0.791 g/mL	45 mL	1.1	Flammable liquid and vapor. Toxic by ingestion and inhalation. May be fatal or cause blindness is swallowed. BP: 64.7°C MP: -98°C	Solvent
Ethanol	46.07 g/mol	0.789 g/mL			Flammable liquid and vapor, respiratory tract, skin and eye irritation. BP: 78.37°C MP: -114.1°C	Solvent

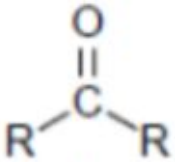
Reagents (Part 2)

Ethyl Acetate	88.11 g/mol	0.902 g/mL			Flammable liquid and vapor, eye, skin, digestive tract, and respiratory tract irritation. BP: 76.5-77.5°C MP: -84°C	Solvent
Semicarbazide hydrochloride	111.53 g/mol	740 kg/m^3	0.25 g	0.0022	Toxic if swallowed. MP: 175-117°C	Reactant
Sodium Acetate	82.0343 g/mol	1.5 g/mL	0.4 g	0.005	May cause, eye, skin, and respiratory tract irritation. Hygroscopic. BP: 881.4°C MP: 324°C	Reactant
3,5-dinitrobenzoyl chloride	230.56 g/mol	1.7 g/cm^3			Can cause skin burns and eye damage. BP: 339.0°C MP: 69°C	Reactant
Sodium Carbonate	105.989 g/mol	2.54 g/mL			Harmful if inhaled. Causes eye and skin irritation. May cause respiratory tract irritation. Hygroscopic. BP: 1600°C MP: 851°C	

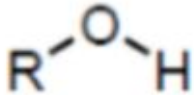
Main Compounds/Synthesis



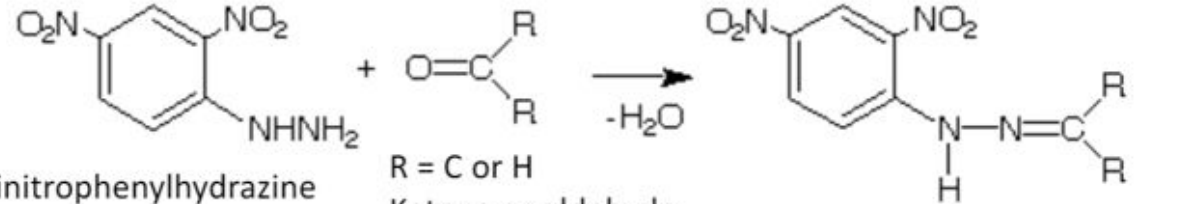
aldehyde



ketone



Alcohol



2,4-dinitrophenylhydrazine

R = C or H
Ketone or aldehyde

2,4-dinitrophenylhydrazone
(precipitate)

Procedure

1) Make a stock solution of DNP test reagent as follows: Weigh 0.8 g of 2,4 dinitrophenylhydrazine into a 125 mL Erlenmeyer flask and add 4 mL of water and (DROPWISE) 4 mL of conc. Sulfuric Acid. Cool if needed and add 40 mL of methanol. The solution should be clear. If not, warm a little and filter. Divide the solution into three portions.

2) Dissolve 0.3 g of each of the three unknowns A, B, and C in 5 mL of methanol in three separate small flasks. (Don't forget to label the flasks).

3) TO CLASSIFY THE UNKNOWNS: Add each of the unknown solutions dropwise to each of the three portions of the DNP reagent (one unknown to each flask, again make sure the flasks are labeled)

4) Record your observations, i.e. no reaction, precipitate, color of precipitate, etc. If no reaction occurs, warm the reaction mixture gently on a steam bath for about 5 mins and allow to cool.

5) If a precipitate (positive test for aldehyde or ketone) is observed, cool the mixture in ice for a few minutes and collect the product by suction filtration. Wash the crystals with a small amount of COLD METHANOL and dry thoroughly. These are the DNP derivatives of the unknowns.

6) TO IDENTIFY THE UNKNOWNS: Carefully record the melting point of the DNP derivative(s) and compare them with the table given in Wilcox and Wilcox, p188

7) If in doubt, recrystallize portion of the derivates from methanol-water or ethanol-ethyl acetate. Dry thoroughly. The melting point should be accurate.

8) For the carbonyl compounds make a second derivative (semicarbazine) using the procedure outline on p189 of Wilcox and Wilcox. Collect the product by suction filtration, dry thoroughly and record the melting point carefully.

9) THE MELTING POINTS OF BOTH DERIVATIVES SHOULD BE AS CLOSE TO THE LISTED VALUES AS POSSIBLE. If not, you need to recrystallize the compounds. DRY THOUROUGHLY

10) Make a tentative identification based on the melting points of both the derivatives. Confirm identities on the basis of IR and NMR spectra provided.

11) IF THE UNKOWN TESTED NEGATVIE WITH THE DNP REAGENT: Examine the spectra provided. If it appears that one of the compounds could be an alcohol. Make a 3,5-dinitrobenzoate derivative using the procedure outlined on page 181 of Wilcox and Wilcox. Collect the crystals by suction filtration, Dry thoroughly. Record the melting point carefully.

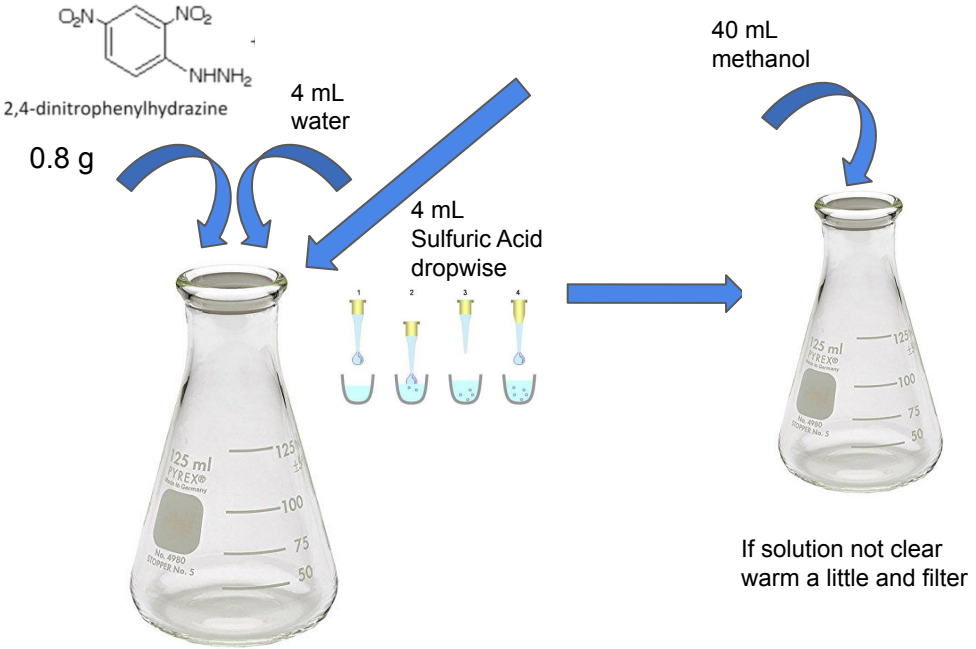
Semicarbazones Preparation

Semicarbazones Preparation:

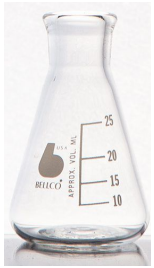
1. Take 0.25 g of semicarbazide HCl in an Erlenmeyer flask
2. Make a solution of 0.4 g of sodium acetate in 3 mL of H2O
3. Add solution from step 2 to step 1 flask
4. Add 0.25 g of unknown carbonyl compound to step 3 flask
5. Swirl/Stir with a glass rod. Crystals will appear
6. Vacuum filter crystals from step 5
7. Wash with cold water
8. Dry and take the melting point

Stepwise Procedure

1. Make a stock solution of DNP test reagent as follows: Weigh 0.8 g of 2,4 dinitrophenylhydrazine into a 125 mL Erlenmeyer flask and add 4 mL of water and (DROPWISE) 4 mL of conc. Sulfuric Acid. Cool if needed and add 40 mL of methanol. The solution should be clear. If not, warm a little and filter. Divide the solution into three portions.
2. Dissolve 0.3 g of each of the three unknowns A, B, and C in 5 mL of methanol in three separate small flasks. (Don't forget to label the flasks).

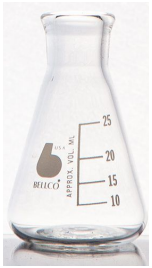


A



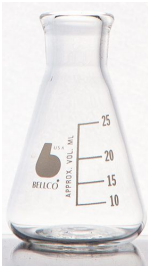
5 mL
methanol,
0.3 g A

B



5 mL
methanol,
0.3 g B

C

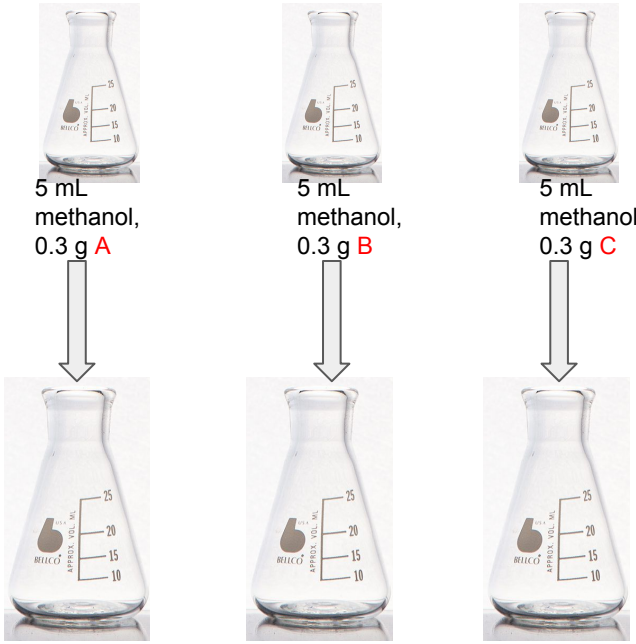


5 mL
methanol,
0.3 g C

Stepwise Procedure

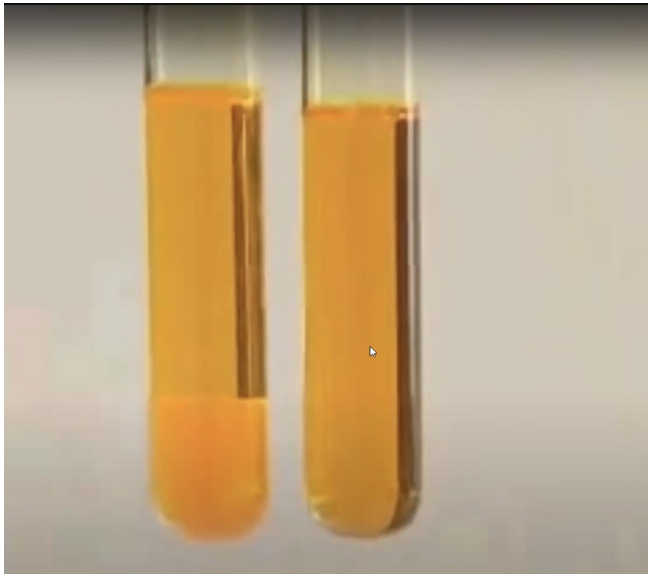
3. TO CLASSIFY THE UNKNOWNS: Add each of the unknown solutions dropwise to each of the three portions of the DNP reagent (one unknown to each flask, again make sure the flasks are labeled)

4. Record your observations, i.e. no reaction, precipitate, color of precipitate, etc. If no reaction occurs, warm the reaction mixture gently on a steam bath for about 5 mins and allow to coo



Three portions of DNP reagent

Add each unknown solution

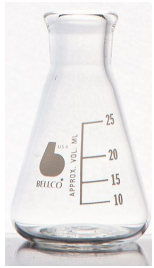


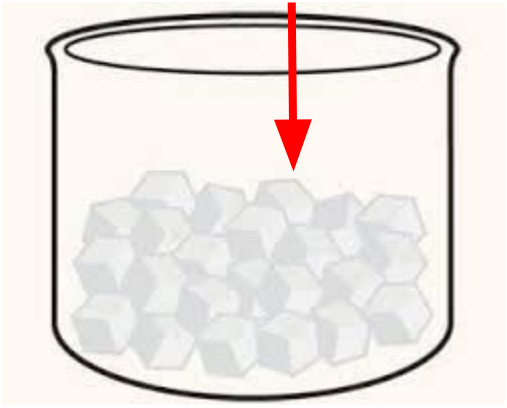
Observations: precipitate, no rxn

5) If a precipitate (positive test for aldehyde or ketone) is observed, cool the mixture in ice for a few minutes and collect the product by suction filtration. Wash the crystals with a small amount of COLD METHANOL and dry thoroughly. These are the DNP derivatives of the unknowns.

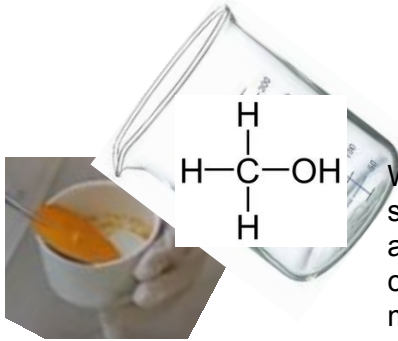
6) TO IDENTIFY THE UNKNOWNS: Carefully record the melting point of the DNP derivative(s) and compare them with the table given in Wilcox and Wilcox, p188

Cool for a few minutes

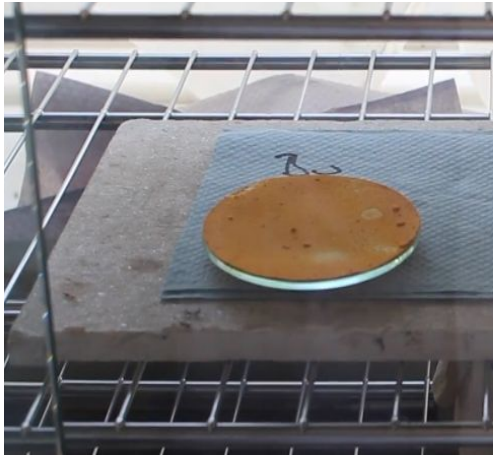




Collect Product by Suction Filtration



Wash with small amount of cold methanol



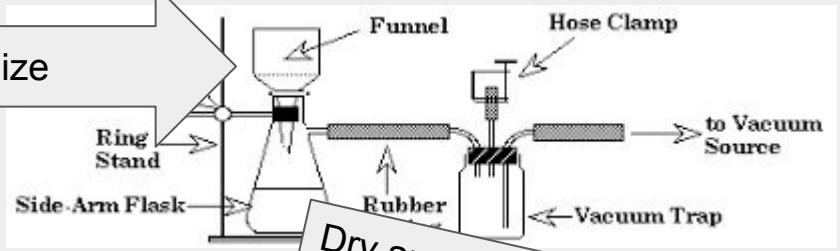
Dry thoroughly

7) If in doubt, recrystallize portion of the derivatives from methanol-water or ethanol-ethyl acetate. Dry thoroughly. The melting point should be accurate.

8) For the carbonyl compounds make a second derivative (semicarbazine) using the procedure outline on p189 of Wilcox and Wilcox. Collect the product by suction filtration, dry thoroughly and record the melting point carefully. (Refer to later slide)

Heat to dissolve

Cool to recrystallize

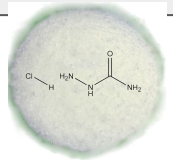


Dry and collect precipitate

Methanol-water or ethanol-ethyl acetate solvent

Recrystallize only if necessary

Create second derivative with semicarbazide



Stepwise Procedure

9. THE MELTING POINTS OF BOTH DERIVATIVES SHOULD BE AS CLOSE TO THE LISTED VALUES AS POSSIBLE. If not, you need to recrystallize the compounds. DRY THOROUGHLY

10. Make a tentative identification based on the melting points of both the derivatives. Confirm identities on the basis of IR and NMR spectra provided.

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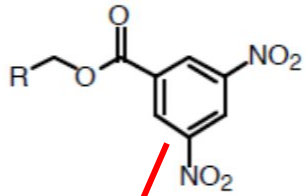
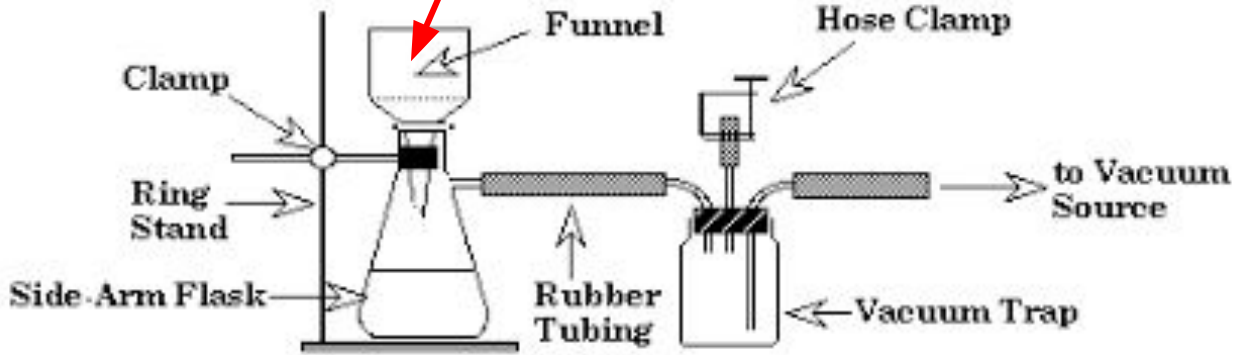
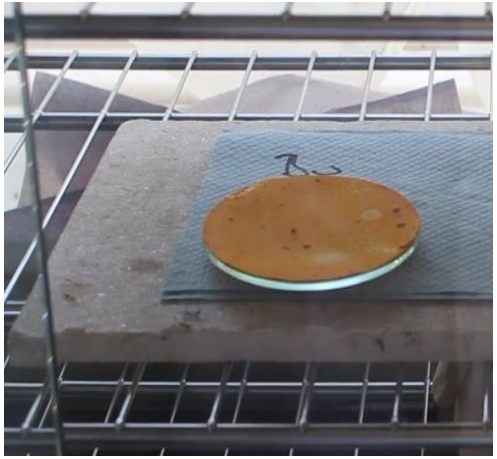
3,5-dinitrobenzoate derivative



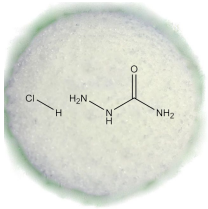


Dry Thoroughly



Stepwise Procedure (Carbazone)

1. Take 0.25 g of semicarbazide HCl in an Erlenmeyer flask
2. Make a solution of 0.4 g of sodium acetate in 3 mL of H2O
3. Add solution from step 2 to step 1 flask

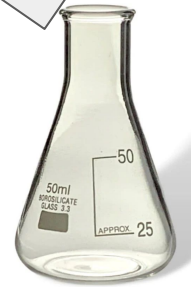


0.25 g

Step 1 flask

combine

0.4 g



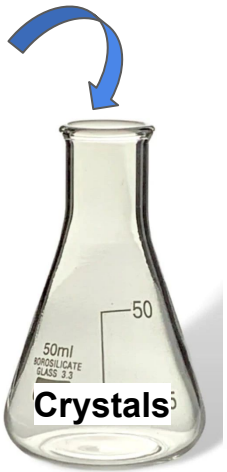
Step 2
solution flask

3 mL

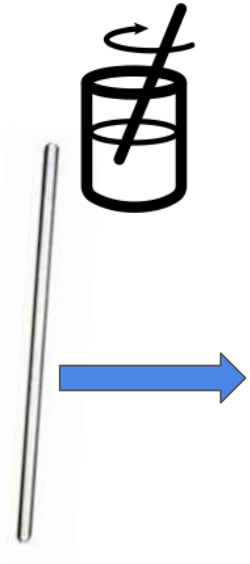
Stepwise Procedure (Carbazone)

4. Add 0.25 g of unknown carbonyl compound to step 3 flask
5. Swirl/Stir with a glass rod. Crystals will appear
6. Vacuum filter crystals from step 5
7. Wash with cold water
8. Dry and take the melting point

0.25 g unknown carbonyl



Step 3 flask



Wash with cold water

Vacuum the Crystals

Dry and take the melting point

Results

Reagents	Unknown A Formula: $C_6H_{10}O$	Unknown B Formula: C_7H_6O	Unknown C Formula: $C_4H_{10}O$
2,4-dinitrophenylhydrazine	Precipitate color: orange precipitate Melting Point = 160-162℃ Literature MP = 162℃	Precipitate color: orange precipitate Melting point = 237-240℃ Literature MP = 237℃	No precipitate
Semicarbazide hydrochloride	Precipitate color: white precipitate Melting point = 164-166℃ Literature MP = 166℃	Precipitate color: white precipitate Melting point = 220-225℃ Literature MP = 222℃	No precipitate
Result	Cyclohexanone	Benzaldehyde	2-Butanol (from NMR)

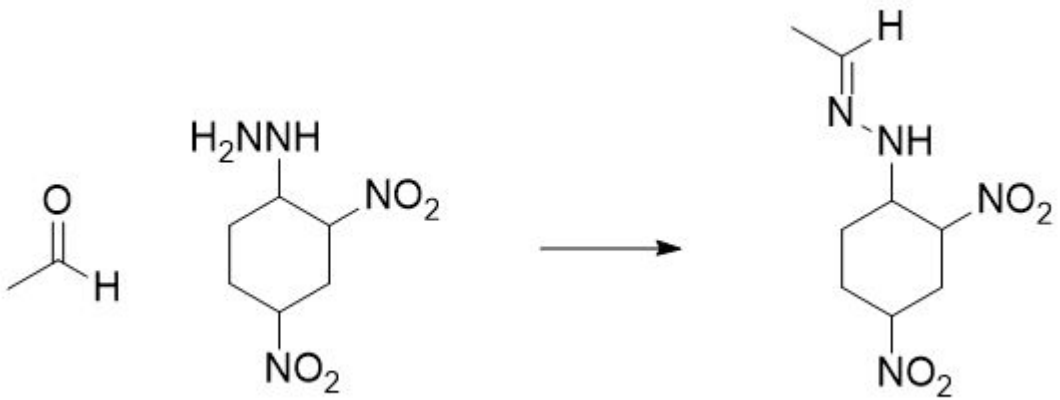
Conclusion

In this lab, we accomplished identification of aldehydes and ketones using their derivatives from carbonyl reactions with 2,4-dinitrophenylhydrazine and semicarbazone. From the three unknowns, two of them reacted to form derivatives, signifying their identity as either aldehydes or ketones. Melting point determinations of the four precipitates lead to the conclusion that compound A was cyclohexanone and compound B was benzaldehyde. Compound C tested negative with both tests, so it was concluded to be a form of butanol, given the chemical formula. From the 1H NMR spectra of the compound, compound C was determined to be 2-butanol. Through this experiment, we learned about how certain carbonyl reactions can be used as a test to determine the identity of compounds, and a commonly used methodology to deduce the identity of ketones and aldehydes. There were no issues and no future recommendations for this experiment, as it was conducted remotely. The DNP test is commonly used for this purpose in the real world.

Postlab Questions

1) Which of the following compounds will show positive results from 2,4-dinitrophenylhydrazine? Draw the reaction and product of one of them.

Acetaldehyde, cyclohexanone, and acetophenone will show positive results from 2,4-dinitrophenylhydrazine.



Postlab Questions (cont.)

2) You determined your unknown compounds structures in the lab from melting points of their derivatives. One of the unknown compounds was Benzaldehyde.Spectroscopy can also be used to determine the structures.Spectra belongs to three unknown compounds are given in the back.

a) Which of the following set of spectra belongs to benzaldehyde?

Set 2

b) Provide the unique peaks value below for both IR and NMR spectra which helped you make the decision.
The 1H NMR spectra gives the best evidence, as the hydrogen in the aldehyde group has a large chemical shift, visible at ~10 ppm on set 2, and not present on set 1. Set 3 is not benzaldehyde due to the large peak in the 3000-3500 cm^{-1} region, which signifies an OH bond.