

Problem x x% of total	Question	x.1	x.2	x.3	x.4	x.5	x.6	x.7	x.8	x.9	x.10	Total
	Points	1	3	1	2	1	2	5	1	2	2	20

Problem x: An Organic Elucidation

By Lim Dillion, Singapore

Compound **A**, $\text{C}_6\text{H}_3\text{ClN}_2\text{O}_4$, is a common precursor for a common laboratory reagent, compound **B**, $\text{C}_6\text{H}_6\text{N}_4\text{O}_4$. This question will focus on the determination of what these unknown compounds are, as well as some transformations of these reagents.

NaOH was added to compound **A**, before it was subsequently placed in a hot water bath. After 5 minutes, excess dilute HNO_3 was then added before AgNO_3 was added. A precipitate formed, and this precipitate dissolved in dilute NH_3 (aq) to give a colourless solution.

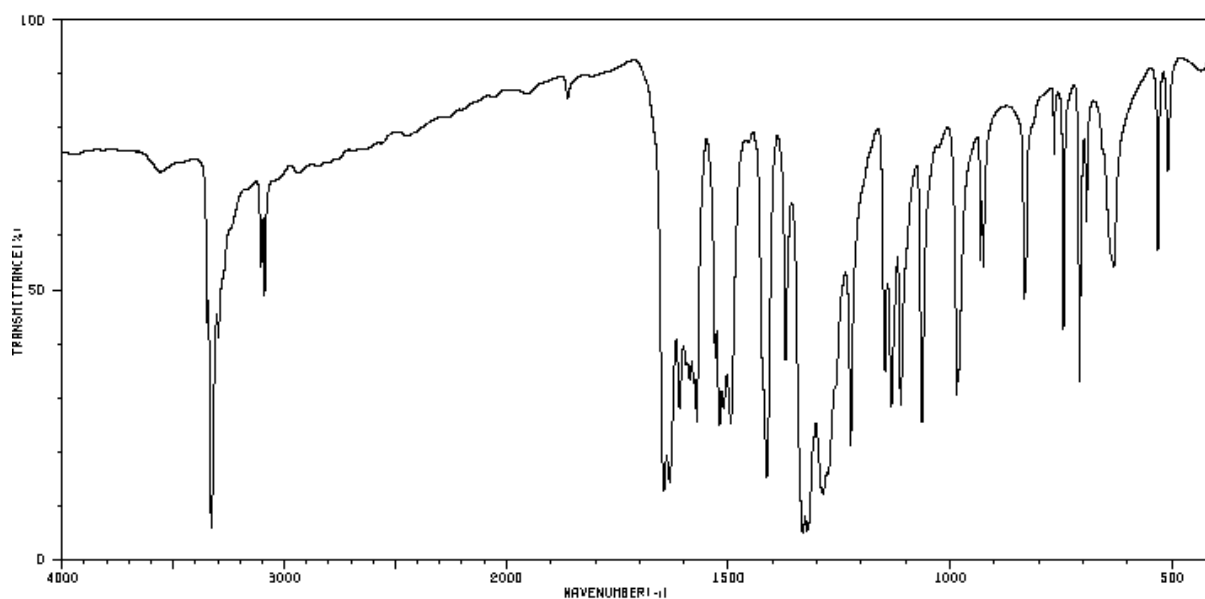
- 1) State the functional group present in compound **A** as shown by the test above.
- 2) When a particular atom in compound **A** was substituted for another atom in the same group and the test was repeated, a precipitate formed that was insoluble, even in concentrated NH_3 (aq). What is the identity of the new atom which was substituted? Justify why the precipitate formed was insoluble in concentrated NH_3 , while the precipitate of compound **A** was soluble in dilute NH_3 .

10mg of compound **A** was then added to 1 mL of Mohr's salt, $(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2(\text{H}_2\text{O})_6$ in a test tube. Ethanolic KOH was then added and the test tube was stoppered and shaken. After 1 minute, a reddish-brown precipitate formed and an organic product, **C** with molecular formula $\text{C}_6\text{H}_7\text{ClN}_2$ after aqueous workup was obtained.

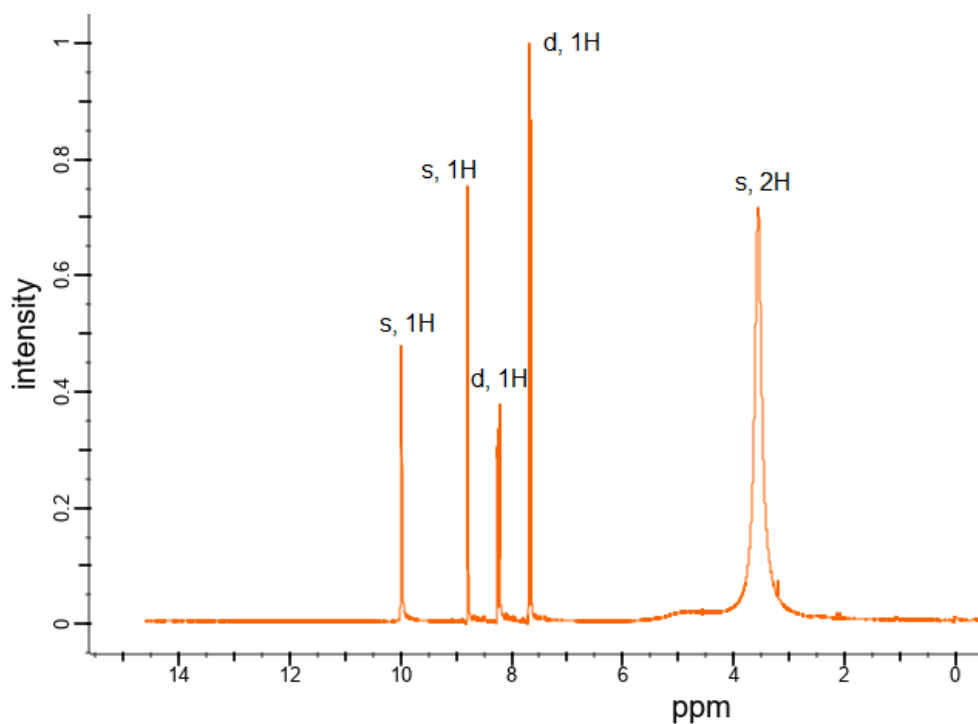
- 3) From the test above, state the functional group that is present in compound **A**.
- 4) Write a balanced equation for the reaction conducted above. You can abbreviate the rest of the compound, excluding the functional group as R.
- 5) Suggest another set of reagents that can convert the compound **A** to compound **C**.
- 6) Hence, suggest a possible structure of compound **A**. Explain your answer clearly.

Compound **A** is transformed to compound **B** by the addition of reagent **D**.

Compound **B** also produced a reddish-brown precipitate when the test above was conducted. Upon conducting an infra-red spectroscopy and NMR spectroscopy, the following spectra was obtained.



IR Spectrum of compound **B**



NMR Spectrum of compound **B**

- 7) Using the above IR and NMR spectra, deduce the structure of compound **B**. Justify your answer using spectroscopic data **clearly**. [s = singlet, d = doublet]
- 8) Suggest a possible reagent **D** for the conversion of compound **A** to **B**.
- 9) When propanone was added to compound **B**, a precipitate was observed. State the colour of this precipitate and draw the structure of this precipitate.
- 10) Explain why no precipitate was formed when compound **B** is added to propanoic acid or propanamide instead.

Problem x: Solution

- 1) State the functional group present in compound **A** as shown by the test above.

Chloroalkane / alkyl chloride.

1 point for the correct functional group stated.

0.5 points for stating halogenoalkane / alkyl halide.

- 2) When a particular atom in compound **A** was substituted for another atom in the same group and the test was repeated, a precipitate formed that was insoluble, even in concentrated NH_3 (aq). What is the identity of the new atom which was substituted? Justify why the precipitate formed was insoluble in concentrated NH_3 , while the precipitate of compound **A** was soluble in dilute NH_3 .

Iodine / I atom was substituted.

The K_{sp} of AgCl is greater than that of AgI .

For AgCl , when dilute NH_3 is added, the precipitate dissolves completely because the addition of dilute NH_3 is sufficient to lower $[\text{Ag}^+]$ such that the ionic product becomes smaller than the K_{sp} of AgCl .

For AgI , the K_{sp} is extremely low, thus the ionic product remains greater than K_{sp} regardless of the concentration of NH_3 added. Hence, the precipitate remains when concentrated NH_3 is added.

0.5 points for stating iodine.

0.5 points for stating K_{sp} of AgCl is larger than AgI .

1 point for justifying the solubility of AgCl in terms of ionic product & K_{sp} .

1 point for justifying the insolubility of AgI in terms of ionic product & K_{sp} .

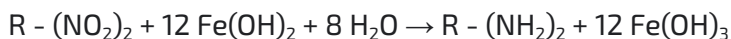
- 3) From the test above, state the functional group that is present in compound **A**.

Nitro / $-\text{NO}_2$ group.

[This is the common iron(II) hydroxide test]

1 point for the correct functional group stated.

- 4) Write a balanced equation for the reaction conducted above. You can abbreviate the rest of the compound, excluding the functional group as R.



1 point for correct reagents and products. [0.5 points awarded if the compound written is $\text{R} - \text{NO}_2$ instead.]

1 point for correct coefficients. [Error carry forward from above, do not double penalise from above.]

5) Suggest another set of reagents that can convert the compound **A** to compound **C**.

1. Sn/Fe/Zn, concentrated HCl, heat; 2. NaOH (aq) OR
H₂ (g), Ni/Pd/Pt catalyst, 25°C, 30 atm

1 point for any method that works. [0.5 points if the NaOH workup step is not present. 1 point even if the temperature/pressure for the hydrogenation method is not given.]

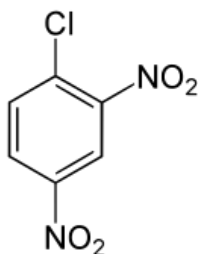
0.5 points if Zinin reduction is used: NH₃, H₂S. Only mono-reduction occurs.

6) Hence, suggest a possible structure of compound **A**. Explain your answer clearly.

Consider the double-bond equivalents of compound **A**.

DBE of **A** = 6.

It is known from the previous parts that there are 2 nitro groups, contributing to 2 DBE. Hence, there is 4 DBE left. A reasonable answer would hence be due to a benzene ring. Thus, **A** is 2,4-dinitrochlorobenzene.



1 point for considering double-bond equivalents, or any reasonable method to deduce the benzene ring.

1 point for deducing the structure of **A. [Accept any substitution pattern.]**

7) Using the above IR and NMR spectra, deduce the structure of compound **B**. Justify your answer using spectroscopic data **clearly**.

From the IR spectrum,

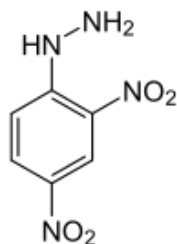
Wavenumber / cm ⁻¹	Bonds / functional groups responsible for absorption
3310 - 3300	Medium N-H stretch of primary amine (two bands are present), overlapping with weak N-H stretch of secondary amine.
3000	Medium aromatic C-H stretch of benzene ring
1600-1500	Aromatic C=C stretch of benzene ring
1510, 1310	Strong N-O stretch of nitro groups

Other deductions such as the N-H bend, C-N stretches can be included, but are not critical to the analysis.

From the NMR spectrum,

δ / ppm	Multiplicity	Integral	Deductions
10.00	Singlet	1	Highly deshielded proton next to a phenyl ring and next to an electronegative N atom. This exceptionally high value, however, is due to hydrogen-bonding between the H of the NH group and the neighbouring O atom of the nitro group.
8.90	Singlet	1	Highly deshielded, likely next to 2 electron-withdrawing groups.
8.35	Doublet	1	Highly deshielded, coupling, indicative of 2, 3-position substitution pattern in a phenyl ring.
7.90	Doublet	1	
3.50	Singlet	2	Slightly deshielded, likely next to electronegative N atoms.

Combining our knowledge from the NMR and IR spectrum, as well as our previous structure of **A**, we can deduce this to be the structure of **B**. This is 2, 4-dinitrophenylhydrazine, better known as 2,4-DNPH.



0.5 points for making each reasonable deduction drawn from the IR spectrum. (Total 1.5 points, 3 deductions to be made.)

0.5 points for analysing each NMR peak above. (Total 2.5 points, all 5 peaks must be analysed.)

1 point for drawing the correct structure of A. (0.5 points if the substitution pattern is wrong, but otherwise correct structure.)

8) Suggest a possible reagent **D** for the conversion of compound **A** to **B**.

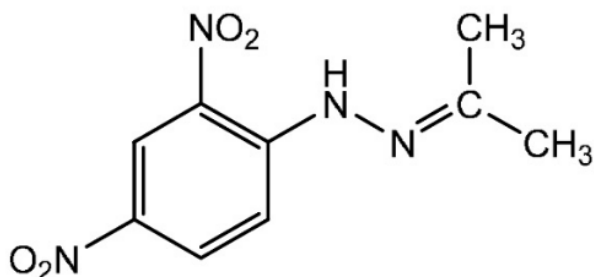
N_2H_4 or $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$

1 point for suggesting hydrazine, or any reasonable alternative.

- 9) When propanone was added to compound **B**, a precipitate was observed. State the colour of this precipitate and draw the structure of this precipitate.

Red/orange/yellow precipitate.

Precipitate formed is the hydrazone. Structure:



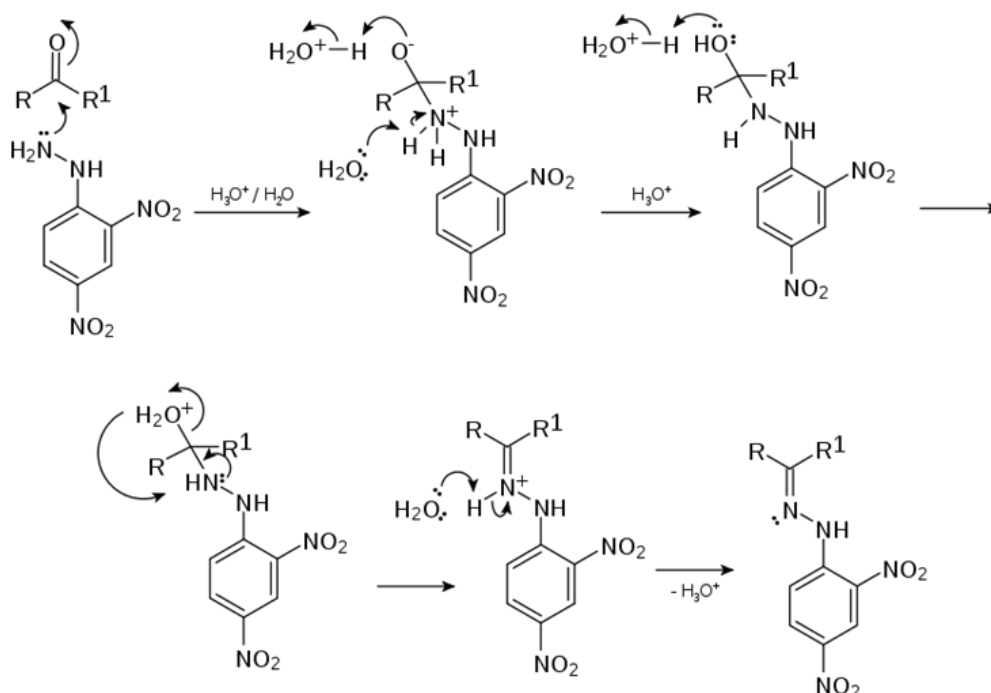
1 point for correct colour.

1 point for correct structure drawn.

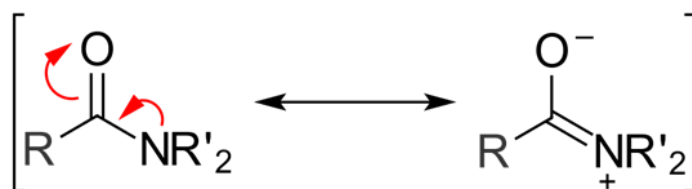
- 10) Explain why no precipitate was formed when compound **B** is added to propanoic acid or propanamide instead.

Consider the resonance structures of amides or carboxylic acids. In both cases, a lone-pair of electrons interacts with the p orbital of the carbonyl carbon resulting in increased delocalization in the molecule. This makes the carbonyl carbon less electrophilic and hence decreases the rate of nucleophilic attack in the first step of the condensation between these groups and 2,4-DNPH.

For reference, here is the mechanism for the condensation.



Resonance structures:



1 point for stating/drawing out resonance structures of amides and carboxylic acids.
1 point for stating that the carbonyl carbon is less electrophilic / less electron-deficient, or something to the same effect.