CODS
SUMMER CHEMISTRY OLYMPIAD
Silver Tier

| | | | |
|---|---|---|---|
| NAME | | | |
| DATE | | PROCTOR'S NAME | |
| CIN | | | |
| TIER | **SILVER** | | |

| **For Proctor's Use** | |
|---|---|
| **Time start:** | |
| **Time end:** | |

**INSTRUCTIONS:**
Fill in your team name, date, proctor's name, team captain's CIN and tier above.

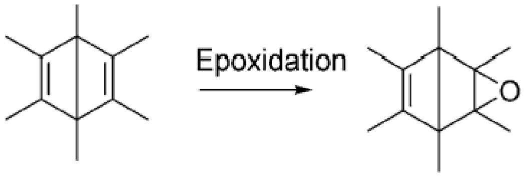
All results must be written in the appropriate answer boxes with pen or pencil on the answer sheets.

The number of marks is given in the table at the top of each question.

This document consists of **37** printed pages.

| **Problem 1** *(20% of total)* | **Question** | 1.1 | 1.2 | 1.3 | 1.4 | 1.5 | 1.6 | 1.7 | 1.8 | **Total** |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Points** | 4 | 7 | 6 | 3 | 18 | 20 | 6 | 2 | 66 |

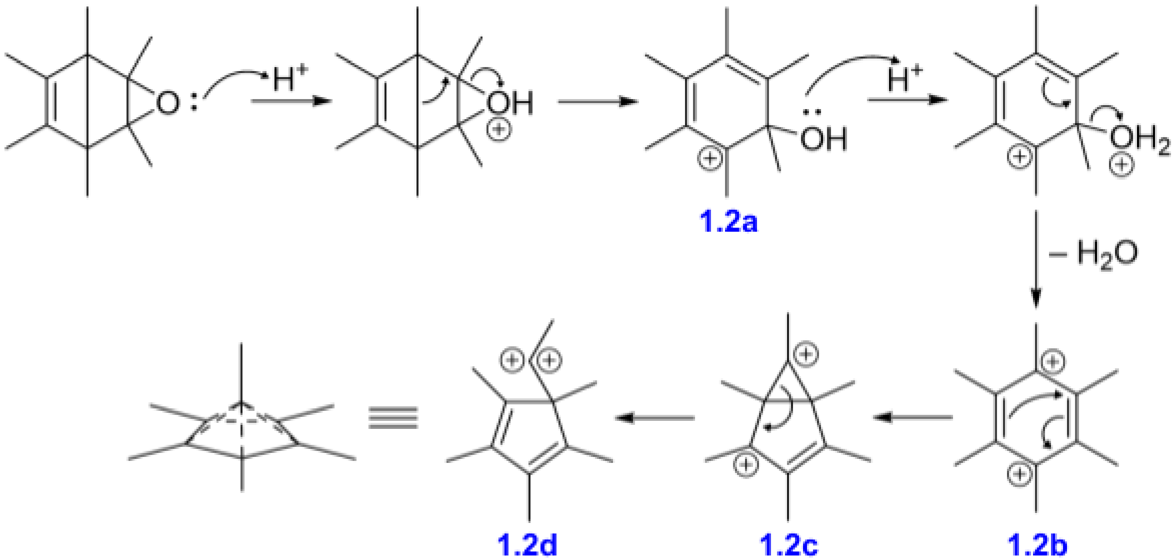
## 1.1)




**A** **B**

**2 points per correct structure (Total: 4 points).**
**Award partial credit as appropriate.**

## 1.2)



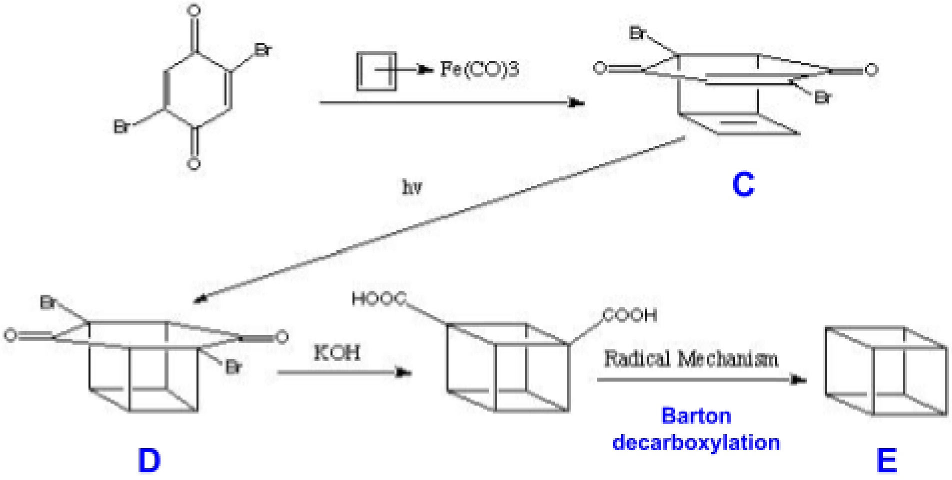

**2 points for forming intermediate 1.2a.**
**1 point for forming intermediate 1.2b.**
**2 points for forming intermediate 1.2c.**
**2 points for formation of 1.2d (compound 1).**

**Award partial credit as appropriate, and accept any other plausible mechanisms.**

**Penalties:**
–1 if side products (e.g. $H_2O$) are not explicitly shown.
–1 for labelling carbocation wrongly/wrong arrows, etc.

## 1.3)

The completed scheme is as follows:



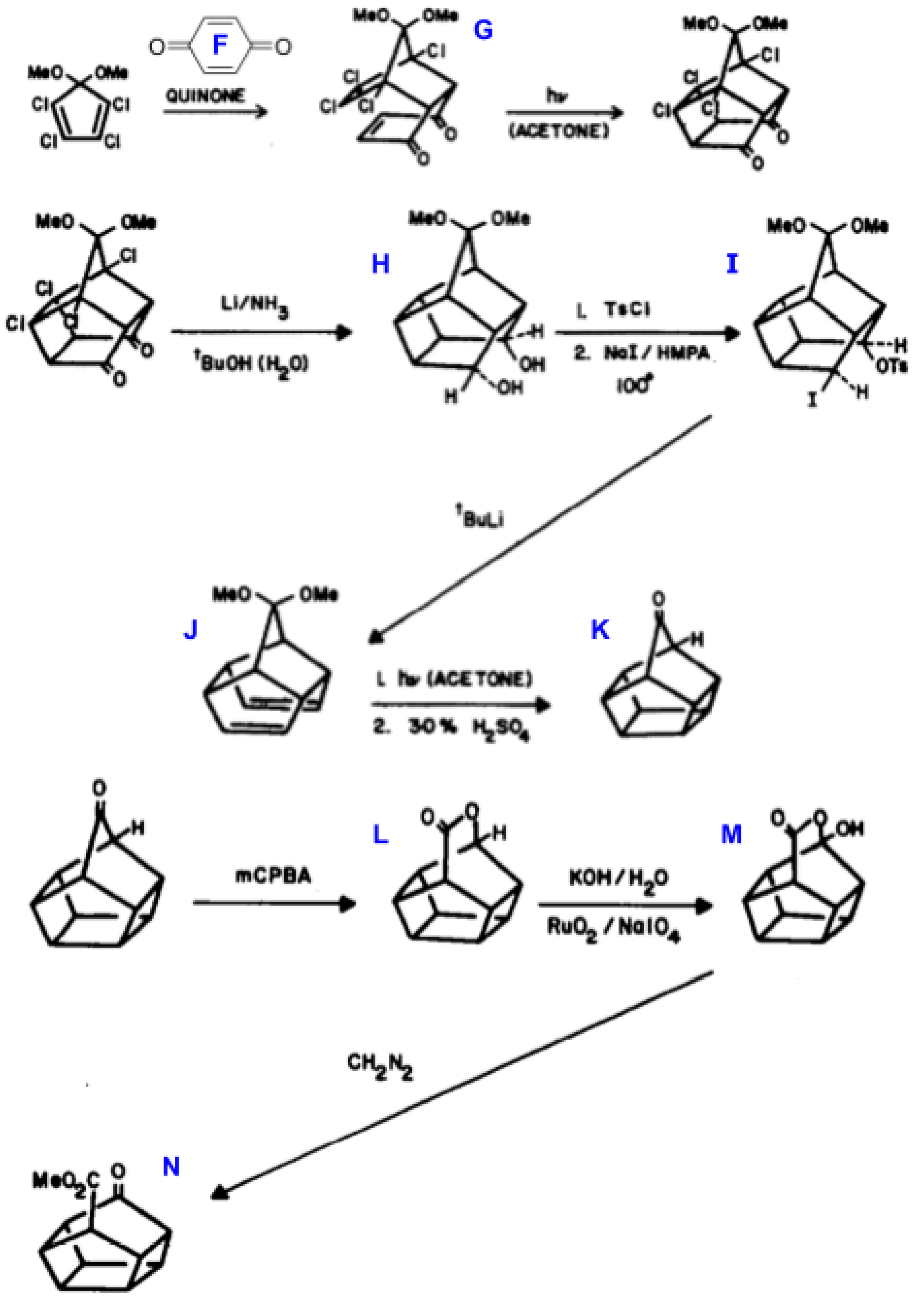

**2 points per correct structure (Total: 6 points).**
**Award partial credit as appropriate.**

## 1.4)

The iron cyclobutadiene complex is more stable than cyclobutadiene/does not dimerize spontaneously before the reaction/protects cyclobutadiene from self-reaction. Furthermore, Fe can easily be removed, so it is hence used to form **C**.

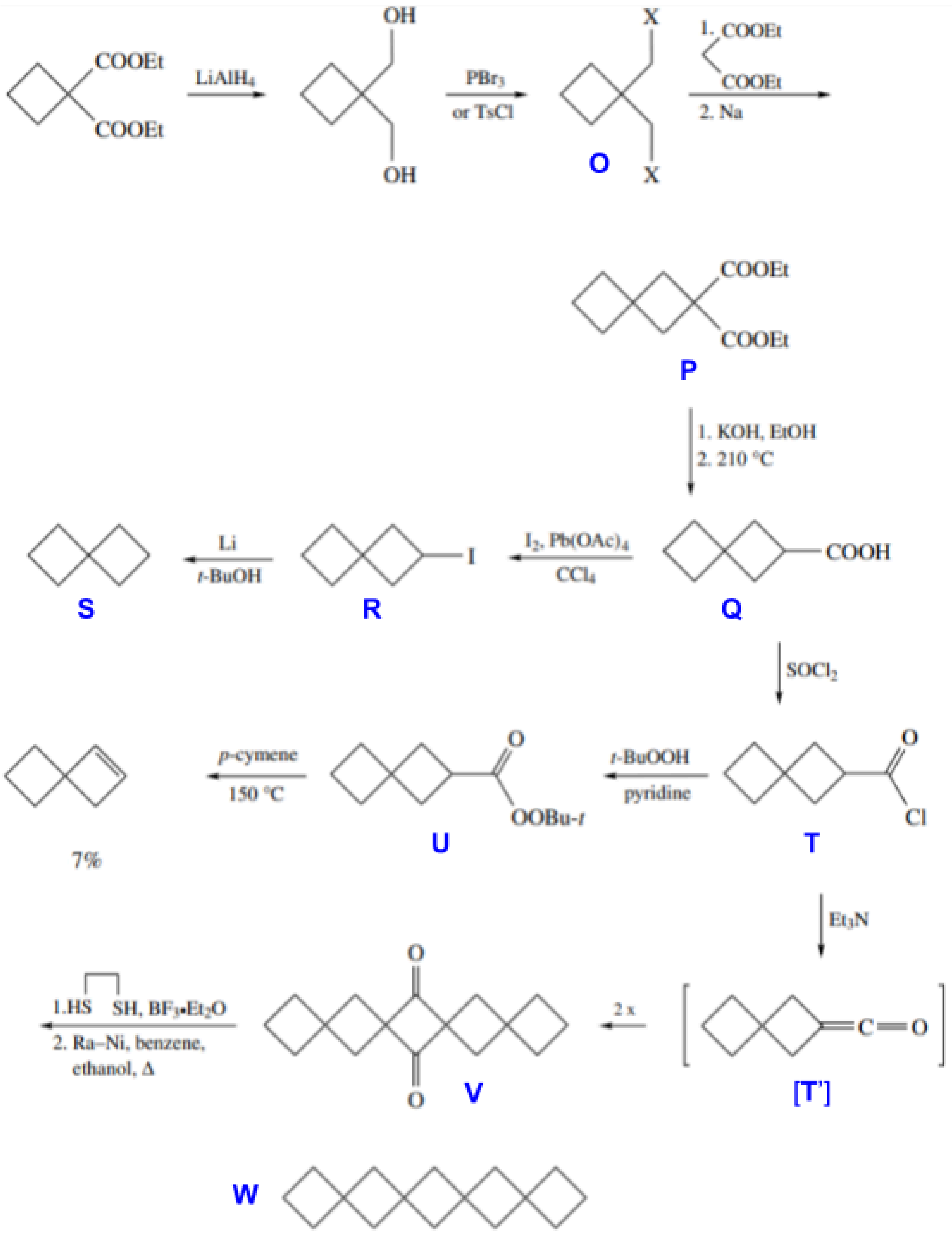
**2 points for discussing the stability of the complex as compared to cyclobutadiene.**
**1 point for stating that Fe can be easily removed.**

**1.5)**




**2 points per correct structure (Total: 18 points).**
**Award partial credit as appropriate.**

**1.6)**




**2 points per correct structure (Total: 20 points)**
**Award partial credit as appropriate.**



**[Turn Over]**

**1.8)**

Spiro compounds are compounds that have at least two molecular rings with only one common atom.

**1 point for suggesting that spiro compounds should have at least two ring structures.**
**1 point for suggesting that the two ring structures have one common atom.**
*Accept if candidates suggest that these ring structures have at least one common atom, as the fact that spiro compounds only have one common atom cannot be deduced from the information given.*

**Accept any reasonable responses.**

| Problem 2 *(15% of total)* | Question | 2.1 | 2.2 | 2.3 | 2.4 | 2.5 | 2.6 | Total |
|---|---|---|---|---|---|---|---|---|
| | Points | 20 | 3 | 2 | 2 | 1 | 2 | 30 |

**2.1)**

Obviously, compound **B** is PhCl and compound **C** is PhMgCl.

We know that compound **D** is shaped like a sandwich and does not contain any Cl atoms. This heavily implies that 2 Ph groups are coordinated to the Cr metal centre, i.e. compound **D** is $Cr(\eta^6\text{-}C_6H_6)_2$.

**Note:** hapticity should be explicitly shown (i.e. either full structure is drawn or "$\eta^6$" is written) or for the full points to be awarded for the identity of compound **D**.

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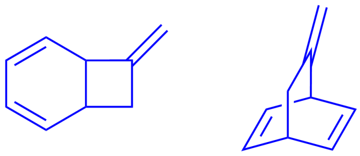
For the formation of compounds **E** and **F**, the presence of a diradical intermediate strongly implies that the first step is a radical-radical coupling process, which then reacts intramolecularly to form two different bicyclic products. Hence, the structures of **E** and **F** are:



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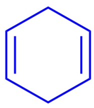
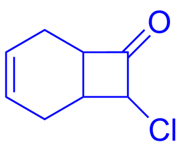
The transformation of benzene to compound **G** is the Birch reduction. Hence, the major product, compound **G** is



In the transformation of compound **G** to compound **L**, the initial reaction of the acyl chloride with Zn is an elimination, forming the ketene CHCl=C=O. The ketene then reacts with benzene in a thermally allowed [2 + 2] cycloaddition reaction to form compound **L**. Hence, the structure of compound **L** is




*Accept answers that suggest that both alkene functional groups in **D** reacted.

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Compound **I** is $PhNH_3$. This is confirmed by the fact that $PhNH_3$ reacts with $NaNO_2$ to form compound **J**, which is the diazonium salt $PhN_2^+Cl^-$ (which indeed has a planar carbocation).

Compound **K** is phenol, which is formed by hydrolysis of compound **J**.

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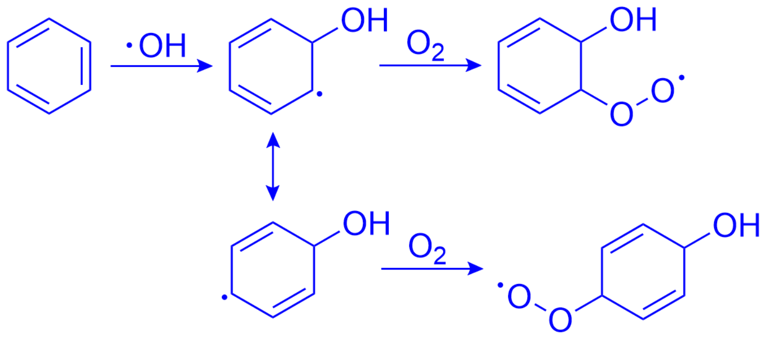
Notice that $M_r(OH) + M_r(O_2) + M_r(PhH) = 127.116 = 127.12$ (2 d.p.).
This implies that the molecular formula of **A** is $C_6H_7O_3$.

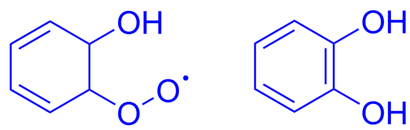
It is most likely that benzene first reacts with the reactive •OH species, which then reacts with oxygen to form compound **A**. There are currently two possible structures for compound **A**:




In the transformation of compound **A** to compound **H**, $HNO_2$ is the likely byproduct. Since compound **A** and NO are both radicals, they will most likely react in a 1 : 1 stoichiometric ratio:

$$C_6H_7O_3 + NO \rightarrow HNO_2 + C_6H_6O_2$$

The molecular formula of **H** is hence $C_6H_6O_2$. This implies that compound **H** contains 2 alcohol functional groups. Since compound **H** is polar, compounds **A** and **H** cannot be 1,4-disubstituted. Hence, the structures of compounds **A** and **H** are respectively:




**[1] for stating the identity of compound B.**
**[1] for stating the identity of compound C.**
**[2] for deducing the identity of compound D.**

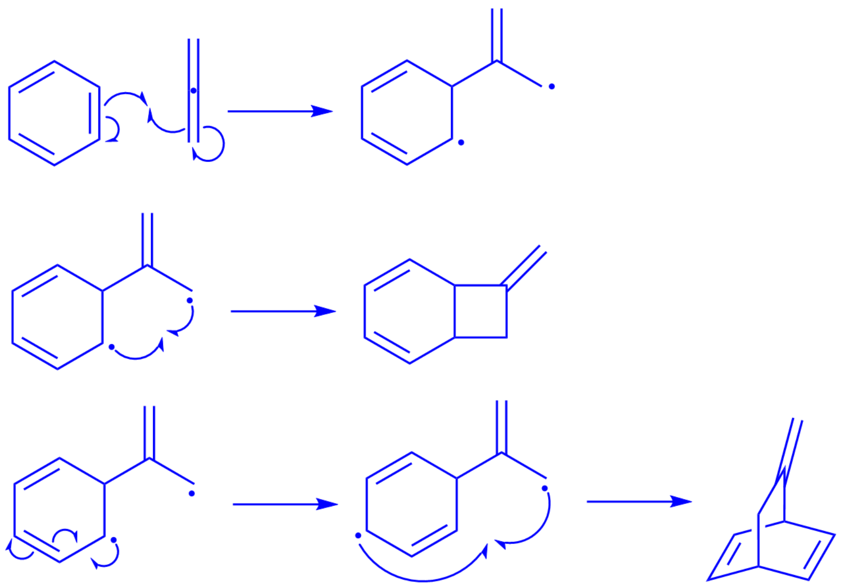
**[4] for deducing the identities of compounds E and F ([2] each).**

**[1] for stating the identity of compound G.**
**[2] for deducing the identity of compound L (accept reaction in 1 : 2 ratio).**

**[1] for stating the identity of compound I.**

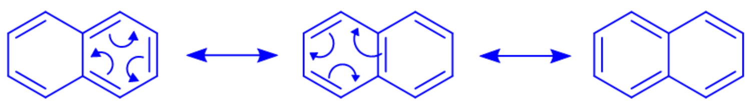
**[1] for stating the identity of compound J.**
**[1] for stating the identity of compound K.**
**[1] for deducing the molecular formula of compound A.**
**[1] for deducing the 2 possible structures of A.**
**[1] for deducing the byproduct of the reaction from compound A to compound H.**
**[1] for deducing the 2 possible structures of H.**
**[2] for deducing the correct structures of A and H (seen or implied).**
*Note: Process of elimination of 1,4-disubstitution need not be explicitly shown for full marks to be awarded.*

## 2.2)



**[1] for formation of diradical intermediate.**
**[1] for formation of the non-bridged product.**
**[1] for formation of the bridged product.**

## 2.3)



(given)

**[1] for each correct resonance structure drawn (Total: 2 points)**
*Note: arrows showing movement of electrons are* ***not*** *required.*

| 2.4) | | | | |
|---|---|---|---|---|

In bond c, two of its resonance structures contain the π-bond while in bonds a, b and d, only one of its resonance structures contains the π-bond.

Bond c has the greatest (partial) double bond character and hence has the shortest C–C bond length while bonds a, b and d have similarly longer C–C bond lengths.

**[1] for comparing the number of times each bond contains a π-bond across all resonance structures.**
**[1] for stating that bond c has the greatest C=C character.**

| 2.5) | | | | |
|---|---|---|---|---|

There is greater extent of delocalisation of the arenium cation intermediate in naphthalene than benzene. Since the intermediate is more stable (i.e. $E_a$ of RDS is lower), hence the reaction proceeds faster in naphthalene than benzene.

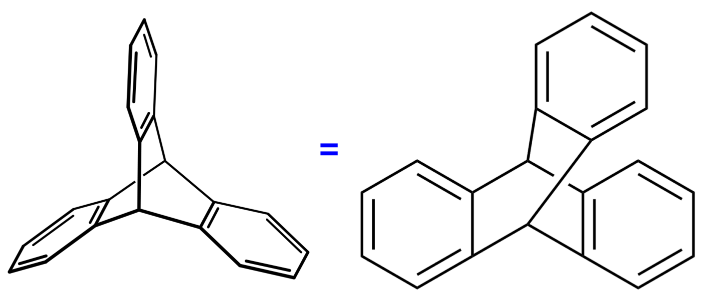
**[1] for discussing the relative stabilities of the intermediate cations.**

**OR**

Naphthalene has a greater extent of conjugation than benzene. Hence, its HOMO-LUMO gap is smaller, and the HOMO of naphthalene has a higher energy level than that of benzene. As a result, the donation of electrons from the HOMO of naphthalene to the LUMO of the electrophile is more likely to confer additional stability and is hence more favourable, resulting in the greater reactivity in naphthalene.

**[0.5] for explaining that the HOMO of naphthalene is higher than that of benzene.**
**[0.5] for discussing more favourable HOMO-LUMO interaction with electrophiles.**

| 2.6) | | | | |
|---|---|---|---|---|



**[2] for the correct structure of compound X.**
*Award [1] if the candidate shows an understanding of what a Diels-Alder reaction is.*

| Problem 3 *(10% of total)* | Question | 3.1 | 3.2 | 3.3 | 3.4 | Total |
|---|---|---|---|---|---|---|
| | Points | 6 | 6 | 6 | 6 | 24 |

## 3.1)

One strange clue to start with is "numerical value of percentage mass of **X** in **C** is very close to the molar mass of **X** (g/mol)".

The most straightforward scenario that this applies is when the molar mass of the compound is around 100 g/mol, and 1 mole of compound contains 1 mole of **X**.

Furthermore, calcination of **X** forms metal oxide $\mathbf{MO_n}$. Now tell me, what compound decomposes to an oxide when calcined, and has a molar mass of around 100 g/mol?

It's chalk. Fun fact - both "calcium" and "calcine" have their etymologies arising from the Latin word "calcis", meaning limestone. In fact, calcination was **named after** the process of calcining chalk - an archetypical example.

Hence, **C** is $CaCO_3$, and $\mathbf{MO_n}$ is CaO. By some element tracing, you would need to introduce **carbon** at some point in time, so element **X** should be **carbon**.

Reaction of carbon with CaO forms a carbide of calcium. As for the stoichiometry, from **A** to **B**, one carbon atom eventually goes into **C**, while the other is produced as elemental carbon. Hence, we can assume that there are two atoms of carbon in **A**, and **A** is $CaC_2$. By ensuring that the oxidation states of elements do not change from **B** to **C**, the carbon atom in **B** will need to exist as $\mathbf{CN_2^{2-}}$**.** Hence **B** is $CaCN_2$. 2 marks for each unknown **A**, **B** and **C**.

## 3.2)

Reactions (2m each, -1m for no state symbols)

$$CaO(s) + 3C(s) \rightarrow CaC_2(s) + CO(g)$$

$$CaC_2(s) + N_2(g) \rightarrow CaCN_2(s) + C(s)$$

$$CaCN_2(s) + 3H_2O(l) \rightarrow CaCO_3(s) + 2NH_3(aq)$$

## 3.3)

$CaC_2$ hydrolyses to protonate the acetylide ion, generating $Ca(OH)_2$ (limewater) and acetylene ($C_2H_2$) gas, which is the identity of **D**.

The next part is interesting. The nitration of acetone is coincidentally analogous to another well-known reaction - the haloform reaction, a distinguishing test for methyl ketones. Replacement of a halogen with nitric acid yields $NO_2^+$ as the electrophile. And instead of a haloform being produced, we produce **nitroform** ($HC(NO_2)_3$), which is **E**. The lone proton is easily removed by the formation of a vividly yellow, resonance stabilised anion. **Would you look at the title?**

## 3.4)

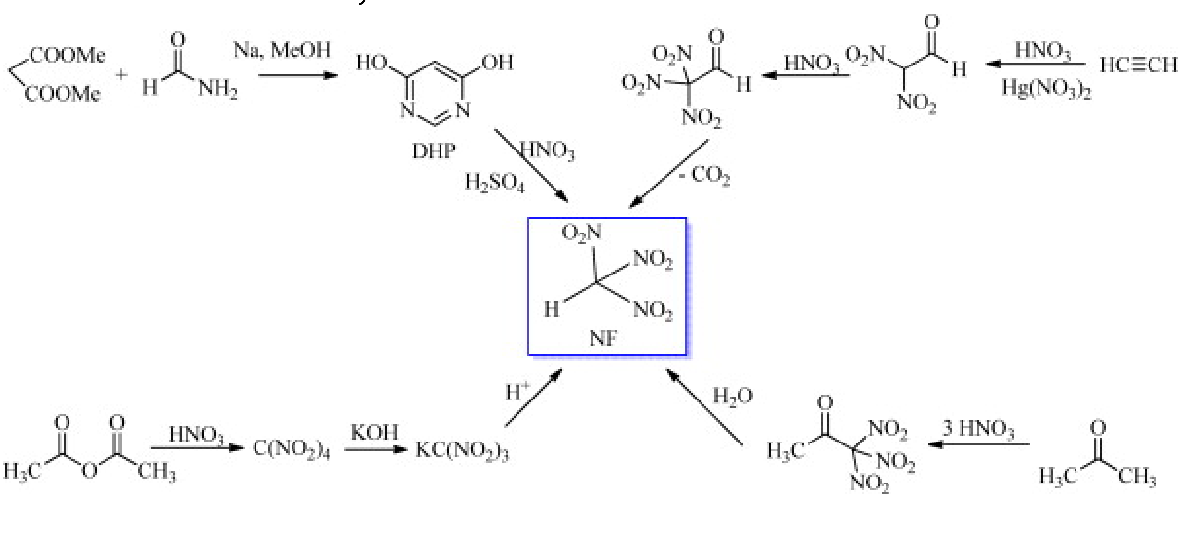
To truly balance the acetylene equation, one needs to know the stoichiometry of gases given off:

Molar mass of air = 0.79(14.01*2) + 0.21(16.00*2) = 28.86 g/mol
Density of emitted gases = 28.86 * 1.57 = 45.3 g/mol
The presence of orange gas suggests production of $NO_2$ ($M_r$ = 46.01) due to the net oxidation of acetylene. The molar mass of emitted gases is **very close** to $M_r$ of $NO_2$, but not quite. Hence, the other gas present in the mixture must also have a similar mass, which can be $CO_2$ ($M_r$ = 44.01).

Some button bashing will yield you the ratio of $NO_2$ to $CO_2$ being 2:1. Hence, the reactions are **(3m each)**:

$$C_2H_2 + 5HNO_3 \rightarrow CO_2 + 2NO_2 + HC(NO_2)_3 + 3H_2O$$
$$C_3H_6O + 3HNO_3 \rightarrow C_2H_4O_2 + HC(NO_2)_3 + 2H_2O$$

Here's a nice scheme of ways to access nitroform:



| Problem 4 *(15% of total)* | Question | 4.1 | 4.2 | 4.3 | 4.4 | 4.5 | 4.6 | 4.7 | Total |
|---|---|---|---|---|---|---|---|---|---|
| | Points | 2 | 5 | 2 | 7 | 1 | 4 | 1 | 22 |

**4.1)**

A = $H_3BO_3$ or $B(OH)_3$ **(2p.)**

**4.2)**

B= $(NH_4)HF_2$ or $NH_4F*HF$ **(2 pt. , 1.5 pt for $NH_5F_2$)**
D = $NH_3$ **(1p.)**
E = HF **(1p.)**
F = $NH_4F$ **(1p.)**

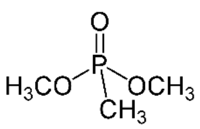
**4.3)**

$SiO_2 + 4\ (NH_4)(HF_2) \rightarrow SiF_4 + 4\ (NH_4)F + 2\ H_2O$ **(2p.)**

**4.4)**

C = $Na_2PO_3F$ **(2p.)**
G = P vai $P_4$ **(1p.)**
H = $PCl_3$ **(1p.)**
I = $P(OMe)_3$ or $P(OCH_3)_3$ vai $PO_3C_3H_9$ vai $C_3H_9O_3P$ **(1p.)**
J = HCl **(1p.)**
K= $PCl_5$ **(1p.)**

**4.5)**

L =  **(1p.)**



**[Turn Over]**

**4.6)**

X = $(NH_4)_3(PO_3F)(BF_4)$ **(3p.)**
M = NaF **(1p.)**

**4.7)**

5 tetrahdrons **(1p.)**

| Problem 5 (15% of total) | Question | 5.1 | 5.2 | 5.3 | 5.4 | 5.5 | Total |
|---|---|---|---|---|---|---|---|
| | Points | 2 | 2 | 2 | 1 | 7 | 14 |

**5.1)**

**NO ANSWERS AVAILABLE - WILL BE UPDATED IN FUTURE**

**5.2)**

**NO ANSWERS AVAILABLE - WILL BE UPDATED IN FUTURE**

| 5.3) |
| --- |
| **NO ANSWERS AVAILABLE - WILL BE UPDATED IN FUTURE** |

| 5.4) |
| --- |
| **NO ANSWERS AVAILABLE - WILL BE UPDATED IN FUTURE** |

| 5.5) |
| --- |
| **NO ANSWERS AVAILABLE - WILL BE UPDATED IN FUTURE** |

| **Problem 6** | **Question** | 6.1 | 6.2 | 6.3 | 6.4 | **Total** |
| --- | --- | --- | --- | --- | --- | --- |

| (10% of total) | Points | 8 | 10 | 5 | 8 | 31 |
|---|---|---|---|---|---|---|

**6.1)**

**NO ANSWERS AVAILABLE - WILL BE UPDATED IN FUTURE**

**6.2)**

**NO ANSWERS AVAILABLE - WILL BE UPDATED IN FUTURE**

**6.3)**

**NO ANSWERS AVAILABLE - WILL BE UPDATED IN FUTURE**

**6.4)**

**NO ANSWERS AVAILABLE - WILL BE UPDATED IN FUTURE**

| Problem 7 *(15% of total)* | Question | 7.1 | 7.2 | 7.3 | 7.4 | 7.5 | 7.6 | 7.7 | Total |
|---|---|---|---|---|---|---|---|---|---|
| | Points | 1 | 2 | 1 | 1 | 4 | 1 | 4 | 14 |

**7.1)**

For this, we need to understand which spike corresponds to the molecular ion. This would be the rightmost peak, which is at 152 g/mol. Thus, this must be the molar mass.

**7.2)**

First, we need to find the mole ratio of the compounds involved. It is clear that we have 0.13158 mol Jones reagent, from the given info. To find the amount of the mystery compound we added, divide the mass by the molar mass, giving us 0.19737 mol mystery compound. Thus, we have a 2:3 ratio of $CrO_3$ to the mystery compound at the equivalence point. This suggests that we have one oxygen-containing functional group that is capable of oxidation. Thus, we can say that there is one oxygen atom in the molecule. From here, we can use the fact that the molar mass has to add up to 152, to conclude that the molecular formula must be $C_{10}H_{16}O$. **(grading guidelines, give 1 point to any answer in the form $C_xH_yO$, where $12x + y = 136$).**

**7.3)**

We know that there is only 1 oxygen atom present as a heteroatom, and that it oxidizes in the presence of $CrO_3$. This leaves us with two possible functional groups, an aldehyde, or an alcohol. However, note that by the mole ratio in part 2, we have that the compound oxidizes only once. This is incompatible with an alcohol functional group, as that would oxidize to form an aldehyde, then a carboxylic acid. Thus, the answer must be aldehyde. **(give 0.5 point for alcohol)**

**7.4)**

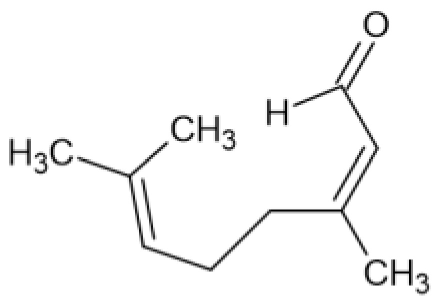
We know the molecular formula of the compound, and that it reacts with Jones reagent to form a carboxylic acid . Thus as we have the reactants and the products, this is quite straightforward. $\underline{C_{10}H_{16}O + CrO_3 + H_2SO_4 \rightarrow C_{10}H_{16}O_2 + Cr_2(SO_4)_3 + H_2O}$ **(-⅓ point for anything without the correct chromium product)**

**7.5)**

This is the meat of the problem.
From the CNMR spectrum,

| PPM | Bonds / functional groups responsible for absorption |
|---|---|
| 190 | Aldehyde, note that its ppm is very LOW. This indicates that it is likely conjugated to an alkene. |
| 120 - 165 | Alkene, the 4 peaks here correspond to 2 double bonds, with the 4 carbons being in 4 different chemical environments, as opposed to an alkyne Note that one of the peaks is much higher than usual. This corresponds to conjugation of the alkene with the carbonyl. |
| 17 - 37 | Alkane peaks. Note that it seems that there are only 4 different chemical environments for the 5 allylic carbons. |

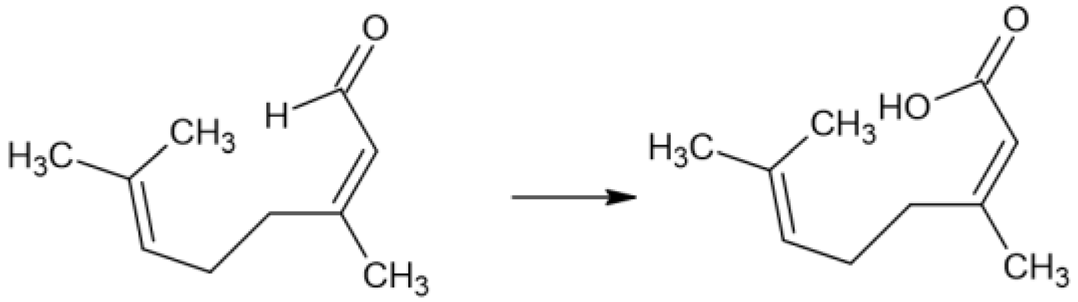
From here, we know that our compound has an aldehyde group, conjugated to an alkene, has 4 different chemical environments for its 5 allylic carbons, and 2 alkene groups. Using all of this, the structure can be deduced, as this:




Or its trans isomer. **Award 1/3 points for each of the 3 justifications (ppm table) and 3 points for the correct final structure (or its trans isomer).**

**7.6)**

For this part, we can use the fact from part three that the oxidation forms a carboxylic acid. As we know the structure from part 5, we have the following. **(1 point for the correct structure, with the same configuration as the structure given in 5)**



## 7.7)

First, from the reagents, we can identify all the reactions that occur. First, the Br2 + hv is usually for the bromination of an alkane, in order to form the non-markovnikov product. Then, the addition of Mg metal is to perform an oxidative insertion, forming an organometallic. Then, the organometallic compound A, is added to acetaldehyde in a nucleophilic carbonyl addition, forming an aldehyde. For the final reaction, a crossed aldol condensation occurs, forming the final product. The entire scheme is below. **Award 1 point for each compound A,B,C,D identified correctly. Ignore cis-trans isomerism when applicable.**