<table>
<thead>
<tr>
<th>Question number</th>
<th>Answer</th>
<th>Marks</th>
<th>Guidance</th>
</tr>
</thead>
</table>
| 1              | conc HNO₃  
cconc H₂SO₄  
HNO₃ + 2H₂SO₄ → NO₂⁻ + H₃O⁺ + 2HSO₄⁻  
or HNO₃ + H₂SO₄ → NO₂⁻ + H₂O + HSO₄⁻  
or HNO₃ + H⁺ → NO₂⁻ + H₂O  
Electrophilic substitution | 1 | If both ‘conc’ missing you can score one for both acids.  
This can also be done in two equations.  
Benzene can also be written as C₆H₆ and nitrobenzene as C₆H₅NO₂.  
One mark is for the arrow from within hexagon to N or to the + on N (M1).  
The ‘horseshoe’ must not extend beyond C₂ to C₆.  
Mark 3 is for the arrow into the hexagon (M3).  |
| 2              | CH₃COCl + AlCl₃ → CH₃⁺CO + AlCl₄⁻  
Electrophilic substitution | 2 | One mark is for the correct reactive species and one for the equation.  
This cannot be F/C acylation.  
Horseshoe must not extend beyond C₂ to C₆.  
The + must be on the C of RC⁺O.  |
| 3              | CH₃COCl + AlCl₃ → CH₃⁺CO + AlCl₄⁻  
Electrophilic substitution | 2 | There is no mark for the acylium ion here. The mark is for the aluminium chloride and the second mark is for the balanced equation.  
You could have FeCl₃.  
The position of + on electrophile can be on O or C.  
The M1 arrow from within hexagon to C or to + on C.  
The + must be on C of RCO.  |
|                |        | 1 | This is not F/C acylation.  |
### Practice questions

#### 4 (a)
\[ CH_3CO^+ \]

1 point

#### 4 (b)

<table>
<thead>
<tr>
<th>Chemical Reaction</th>
<th>Tips</th>
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<tbody>
<tr>
<td>[ CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO+ + AlCl_4^- ]</td>
<td>Horseshoe must not extend beyond C2 to C6. The + must be on the C of RC=O.</td>
</tr>
</tbody>
</table>

3 points

#### 5 (a)

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>CH_3CH_2COCl OR CH_3CH_2CClO OR propanoyl chloride OR (CH_3CH_2CO)_2O OR propanoic anhydride</td>
<td>could score in equation</td>
</tr>
</tbody>
</table>

1 point

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<tr>
<td>AlCl_3 or FeCl_3 or names</td>
<td>could score in equation</td>
</tr>
</tbody>
</table>

1 point

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<tr>
<td>CH_3CH_2COCl + AlCl_3 \rightarrow CH_3CH_2CO+ + AlCl_4^-</td>
<td>allow + on C or O in equation</td>
</tr>
</tbody>
</table>

1 point

#### 5 (b)

<table>
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<tr>
<td>M1 arrow from circle or within it to C or to + on C</td>
<td>M1 arrow from circle or within it to C or to + on C</td>
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3 points

Horseshoe must not extend beyond C2 to C6 but can be smaller + not too close to C1 M3 arrow into hexagon unless Kekule allow M3 arrow independent of M2 structure Ignore base removing H in M3

#### 5 (c)

<table>
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<tbody>
<tr>
<td>Tollens or ammoniacal silver nitrate</td>
<td>penalise wrong formula</td>
</tr>
</tbody>
</table>

1 point

1 point

#### 6 (a)

Benzene is more stable than cyclohexatriene

1 point

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<tr>
<td>Expected ( \Delta H^\circ_{\text{hydrogenation}} ) of C_6H_6 is ( 3(\sim 120) = -360 \text{ kJ mol}^{-1} )</td>
<td>more stable than cyclohexatriene must be stated or implied</td>
</tr>
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</table>

1 point

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<tr>
<td>Actual ( \Delta H^\circ_{\text{hydrogenation}} ) of benzene is 152 kJ mol(^{-1}) (less exothermic) or 152 kJ mol(^{-1}) different from expected</td>
<td>If benzene more stable than cyclohexene, then penalise M1 but mark on</td>
</tr>
</tbody>
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1 point

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<tr>
<td>Because of delocalisation or electrons spread out or resonance</td>
<td>If benzene less stable: can score M2 only</td>
</tr>
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1 point

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<tr>
<td>Allow in words e.g. expected ( \Delta H^\circ_{\text{hydrogenation}} ) is three times the ( \Delta H^\circ_{\text{hydrogenation}} ) of cyclohexene</td>
<td>Ignore energy needed</td>
</tr>
</tbody>
</table>

1 point
### 6 (b)

**Conc HNO₃**

Conc H₂SO₄

2 H₂SO₄ + HNO₃ → 2 HSO₄⁻ + NO₂⁺ + H₂O

OR H₂SO₄ + HNO₃ → HSO₄⁻ + NO₂⁺ + H₂O

OR via two equations

H₂SO₄ + HNO₃ → HSO₄⁻ + H₂NO₃⁺

H₂NO₃⁺ → NO₂⁺ + H₂O

**Diagram:**

- M₁ arrow from within hexagon to N or + on N
- Allow NO₂⁺ in mechanism
- Horseshoe must not extend beyond C₂ to C₆ but can be smaller
- + not too close to C₁
- M₃ arrow into hexagon unless Kekule
- Allow M₃ arrow independent of M₂ structure ignore base removing H in M₃
- + on H in intermediate loses M₂ not M₃

**Marking:**

- 1 mark: If either or both conc missing, allow one; this one mark can be gained in equation
- 1 mark: Allow + anywhere on NO₂⁺
- 3 marks: M₁ arrow from within hexagon to N or + on N

### 7

**[CH₃CH₂CO]⁺**

CH₃CH₂COCl + AlCl₃ → [CH₃CH₂CO]⁺ + AlCl₄⁻

**Diagram:**

- M₁ arrow into hexagon unless Kekule
- Allow M₁ arrow into hexagon unless Kekule
- The horseshoe should extend from C₂ to C₆ only

**Marking:**

- 1 mark: You can gain the electrophile mark from the equation if not stated separately. Therefore the correct balanced equation is worth 2 marks.
- 1 mark: In the equation, the position of the + can be on O or C or outside square brackets, however you do not need to show the square brackets.
- 3 marks: The arrow for M₁ must be to C or to the + on C.

### 8

Cyclohexane evolves 120 kJ mol⁻¹

Therefore expect triene to evolve 360 kJ mol⁻¹; or 3 × 120 = 360 kJ mol⁻¹

360 – 208 = 152 kJ;

Benzene lower in energy / more stable; due to delocalisation;

**Marking:**

- 4 marks: Cannot estimate 150 kJ, you must use the values in the question. Therefore 152 kJ can score first 2 marks in this part.
- Any mention of ‘bond breaking needing energy’ will not score marks.

### 9 (a)

- nitric acid and sulfuric acid

### 9 (b)

- explosives / dyes / fibres / pharmaceuticals

### 9 (c) (i)

- C₆H₆ + HNO₃ → C₆H₅NO₂ + H₂

### 9 (c) (ii)

- it accepts a pair of electrons

### 9 (c) (iii)

- electrophilic substitution