Chapter 18 – Answers to end of chapter questions

1  a  B, C and D  
   b  A and E  
   c  d  A = 3-methylpentan-2-one; B = pentanal  
   d  B, C and D  
   e  A  
   f  A and E

2  Both groups are unsaturated and undergo addition reactions, e.g. with H₂ in the presence of a nickel catalyst. Alkenes, however, react with electrophiles, while the carbonyl group is attacked by nucleophiles.  

\[
\text{Alkene} \quad \text{Carbonyl} \\
\begin{array}{c}
\text{CH₃CCH₂} + \text{NH₂OH} \\
\text{CH₃C} - \text{N} – \text{OH} \\
\text{CH₃} - \text{C} - \text{N} – \text{OH} \\
\text{CH₃} + \text{H₂O}
\end{array}
\]

In the case of the carbonyl group, some of the addition products undergo further reaction, in condensation reactions.

The carbonyls also undergo a greater variety of reactions: oxidation to acids (in the case of aldehydes) and the iodoform reaction. These arise as a result of the effect of the carbonyl group on adjacent atoms.

3  a  The π-electrons occupy the vacant d orbitals in Pd²⁺.  
   b  The π-electrons are no longer available, and their removal makes the ethene positively charged.  
   c  Yes. Propene.
4  a  \( \text{CH}_3\text{CH(OH)CH}_2\text{CH}_3 \)
   
   b  \( \begin{aligned} \text{C}_6\text{H}_5\text{C} & \xrightarrow{\text{NH}_2\text{NH}} \text{DNP} \\
    \text{CH}_3 & \end{aligned} \)

   c  \( \text{CH}_3\text{CH.C(OH)(CN)CH}_2\text{CH}_3 \)
   
   d  \( \text{CH}_3\text{CCl}_2\text{CHO} \)

5  A  \( \text{CH}_3\text{CH.CH.CH}_2\text{CHO} \)
   
   B  \( \begin{aligned} \text{CH}_3\text{CH} & \xrightarrow{\text{CHO}} \\
    \text{CH}_3 & \end{aligned} \)

   C  \( \text{CH}_3\text{CH}_2\text{COCH}_3 \)

A and B react with Tollens’ reagent, Fehling’s solution or other oxidising agents. To
distinguish between them, make derivatives (with 2,4-dinitrophenylhydrazine) and
measure the melting points.

C does not react with oxidising agents.

6  a  \( \text{A} = \text{OHCCH}_2\text{CH.CH}_2\text{CHO} \)
   
   B =

   \( \begin{aligned} \text{HO} & \\
    \text{CH} & \xrightarrow{\text{CH}_2\text{CH}_2\text{CH} \xrightarrow{\text{OH}} \\
    \text{NC} & \end{aligned} \)

   C = \text{HOOCCH}_2\text{CH.COOH} \)

A to B  Nucleophilic addition: \( \text{CN} \) attacks carbonyl groups to give addition product
A to C  Oxidation of aldehyde to acid

Number of moles \( \text{NaOH} \) added  \( \frac{16.9}{1000} \times 1.0 = 0.0169 \)

Number of moles \( \text{C} \) that this reacts with  \( \frac{1}{118} = 0.008474 \)

\( \therefore \) they react in ratio 2 moles \( \text{NaOH} \) to 1 mole \( \text{C} \) so \( \text{C} \) has
2 —COOH groups.
b  C : H : O
5.36 : 7.11 : 1.7875
3 : 4 : 1
so empirical formula = C₃H₄O

\[ M_r = 56 \implies \text{molecular formula} = C_3H_4O \]

number of moles X = \( \frac{0.1}{56} = 0.0178 \)

number of moles H₂ = \( \frac{80}{22400} = 0.00357 \)

\[ \therefore 1 \text{ mole } X \text{ reacts with } 2 \text{ moles } H_2; X \text{ has 2 double bonds.} \]

X is \[ CH_2=CH-C\underset{O}{\overset{0}{\backslash}}H \]

with Fehling’s solution \[ CH_2=CH-C\overset{0}{\overset{0}{\backslash}}O \text{ is formed (oxidation)} \]

with H₂ \[ CH.CH.CH.OH \text{ is formed (reduction)} \]

7  a  The —OH groups can both be oxidised to an aldehyde or an acid:

CH₂=CHO \hspace{1cm} CHO—CHO \hspace{1cm} CHO—COH

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<thead>
<tr>
<th>CH₂—COOH</th>
<th>COOH</th>
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<tbody>
<tr>
<td>CH₂—COOH</td>
<td>COOH</td>
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<td>OH</td>
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<td>OH</td>
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b  The C = O group makes the H atoms on the adjacent C atom slightly acidic:

\[ CH₂CHO + OH ⇌ CH₂CHO + H₂O \]

This ion removes D⁺ from D₂O

\[ CH₂CHO + D₂O ⇌ CH₂DCHO + OD \]

This continues until all three H atoms have been replaced

c  The Cl atoms are electron-withdrawing, and make the C atom more susceptible to attack by nucleophiles.

\[ \end{align*} \]
8  a  CH₃CH₂OH  
b  CH₃CH(OH)CH₃  
c  CH₃C(OH)(CH₃)CH₃  
d  CH₃COOH

9  a  CH₃CH₂CHO  propanal  
b  3000 C—H   1700 C = O  
c  \[
\begin{array}{c}
CH₃CH₂CHO  \\
1.2  2.5  9.8
\end{array}
\]