QUESTION 1

(a)  \[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 & \xrightarrow{\text{Cl}_2 \ (g), \ \text{uv light}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{NaOH \ (aq), heat}} \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{use excess propane}
\end{align*}
\]

Note: Free-radical substitution is not a good method to prepare halogenoalkanes in the laboratory as it gives a mixture of products. It is difficult to control the extent and position of substitution. However, for the first reaction in (a), (b) and (d), there is no other method because the starting compound is an alkane.

(b)  \[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}_3 & \xrightarrow{\text{Cl}_2, \ \text{UV light \ use excess propane}} \text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} \xrightarrow{\text{NaOH in ethanol \ heat}} \text{CH}_3\text{CH}==\text{CH}_2 \\
& \xrightarrow{\text{KMnO}_4 \ \text{solution,} \ \text{H}_2\text{SO}_4\text{(aq), heat}} \text{CH}_3\text{CO}_2\text{H}
\end{align*}
\]

(c)  \[
\begin{align*}
\text{CH}_3\text{CH}==\text{CH}_2 & \xrightarrow{\text{HBr(g) \ or \ in \ CCl}_4 \ \text{solvent \ r.t.p}} \text{CH}_3\text{CH}==\text{CH}_3 \\
& \xrightarrow{\text{KCN in ethanol \ heat}} \text{CH}_3\text{CH}==\text{CH}_3 \\
& \xrightarrow{\text{H}_2\text{SO}_4\text{(aq), heat}} \text{CH}_3\text{CH}==\text{CH}_3
\end{align*}
\]

(d)  cyclohexane $\rightarrow$ hexanedioic acid

\[
\begin{align*}
\text{Cl}_2 & \xrightarrow{\text{UV light \ use excess cyclohexane}} \text{Cl} \\
& \xrightarrow{\text{NaOH in ethanol \ heat}} \text{K MnO}_4 \ \text{solution,} \ \text{H}_2\text{SO}_4\text{(aq), heat} \text{CO}_2\text{H}
\end{align*}
\]
(e) \[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CH}=&=\text{CH}_2 \\
\text{HBr(g) or in } \text{CCl}_4 \text{ solvent, } \text{r.t.p} \\
\text{CH}_3\text{CH}_2\text{CHBrCH}_3 & \xrightarrow{\text{NaOH in ethanol, heat}} \text{CH}_3\text{CH}=&=\text{CHCH}_3 \\
& \xrightarrow{\text{KMnO}_4 \text{ solution, } \text{H}_2\text{SO}_4(\text{aq}), \text{heat}} \text{CH}_3\text{CO}_2\text{H}
\end{align*}
\]

(f) \[
\begin{align*}
\text{Br}_2(l) \text{ or } \text{Br}_2 \text{ in } \text{CCl}_4, \text{ absence of UV light} & \xrightarrow{\text{NaOH in ethanol, heat}} \text{Cyclohexane}
\end{align*}
\]

**QUESTION 2**

(a) Name of mechanism: nucleophilic substitution

- \(\delta^+\) and \(\delta^-\) on the C–Cl bond to indicate electron-deficient carbon atom.
- Arrows must originate from the lone pair on the nitrogen atom of NH\(_3\) and from the C–Cl bond; and also from the lone pair on the Cl\(^-\) ion and from the N–H bond.
- Transition state is neutral (conservation of charge).
- One-step reaction. There is no slow step.
- Lone pair of electrons must be shown on Cl\(^-\) ion (this step is optional)

[See Peter Cann pg468]

Further reaction with excess NH\(_3\):

\[
\text{CH}_3\text{CH}_2\text{NH}_3^+ + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{CH}_2\text{NH}_2 + \text{NH}_4^+
\]
(b) As bond length of C–Br > bond C–Cl, bond strength of C–Br < C–Cl

Therefore C–Br bond breaks more easily during nucleophilic substitution.
Reaction is faster for bromoethane.

Note from Data booklet: BE of C–Cl +280 vs. BE of C–Br +340 kJ mol\(^{-1}\).

(c) Structure of compound:

\[
\begin{array}{c}
\text{CH}_2\text{CH}_3 \\
\text{CH}_3\text{CH}_2\text{N}---\text{CH}_2\text{CH}_3 \\
\text{CH}_2\text{CH}_3
\end{array} + \text{Cl}^{-}
\]

Note: Cl\(^{-}\) exists as free ion, and hence able to form immediate precipitate with AgNO\(_3\).

QUESTION 3

(a) 

F undergoes nucleophilic substitution with OH\(^{-}\) and CH\(_3\)CH\(_2\)O\(^{-}\) to produce G and H respectively.

Normally under ethanolic conditions, elimination to form a C=C double bond is favoured.
However, the benzene C atom is not attached to any hydrogen atom. Thus, elimination cannot occur, nucleophilic substitution occurs instead.

Nucleophile (OH\(^{-}\) and CH\(_3\)CH\(_2\)O\(^{-}\) respectively) attacks partially-positively charged C atom of \(\delta^+\)C–Cl\(^{-}\). C–Cl bond breaks, Cl\(^{-}\) substituted by OH and OCH\(_2\)CH\(_3\) groups respectively.
(b) \( \text{Cl} \) does not react with hot ethanolic KOH

(Reason: p orbital of chlorine atom overlaps with the deocalised \( \pi \) electron cloud of the benzene ring. As a result, the C–Cl bond is strengthened and has partial double bond character and cannot be broken easily.)

\[
\text{H} \quad \text{H} \\
\text{H} \quad \text{Cl} \\
\text{H} \quad \text{C}=\text{C} \quad \text{H}
\]
undergoes elimination to form

\[
\text{H} \quad \text{H} \\
\text{H} \quad \text{C}=\text{C} \quad \text{H}
\]

**QUESTION 4**

(a) Add \( \text{Br}_2(aq) \). Yellow-orange colour of \( \text{Br}_2(aq) \) disappears only for \( \text{CH}_3\text{CH=CH}_2 \).

\[
\text{CH}_3\text{CH=CH}_2 + \text{Br}_2 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH(OH)CH}_2\text{Br} + \text{HBr}
\]

(b) Heat with \( \text{NaOH}(aq) \). Then cool & add excess dilute \( \text{HNO}_3 \). Then add \( \text{AgNO}_3(aq) \)

If yellow precipitate is obtained, the compound is

\[
\text{Br} \\
\text{CH}_2\text{I}
\]

If cream precipitate is obtained, the compound is

\[
\text{CH}_2\text{Br}
\]

\[
\text{Br} \\
\text{CH}_2\text{OH} + \text{I}^- \\
\text{Ag}^+ + \text{I}^- \rightarrow \text{AgI}
\]

\[
\text{CH}_2\text{Br} \\
\text{I} \\
\text{CH}_2\text{Br}
\]

\[
\text{CH}_2\text{OH} + \text{Br}^- \\
\text{Ag}^+ + \text{Br}^- \rightarrow \text{AgBr}
\]
QUESTION 5

R (C\textsubscript{10}H\textsubscript{11}Br) \rightarrow P (C\textsubscript{10}H\textsubscript{12}O) + Q (C\textsubscript{10}H\textsubscript{10})

The changes in molecular formula suggests that R has undergone
1. nucleophilic substitution to give P, and
2. elimination to give Q

Q does not contain any chiral carbon, so it does not rotate plane-polarised light.

P contains a chiral carbon (C\textsc{*}). But it is stated that P does not rotate plane-polarised light. Therefore, P must have been obtained as a racemic mixture containing both optical isomers in 1:1 mole ratio.

R has the structure of a tertiary halogenoalkane, it undergoes the S\textsubscript{N}1 reaction mechanism during nucleophilic substitution to give the following carbocation intermediate in step 1 of the mechanism. The carbocation is trigonal planar about C\textsuperscript{+}. In step 2 of the mechanism, OH\textsuperscript{-} may approach C\textsuperscript{+} from either above or below the plane with equal probability hence producing both optical isomers in equal quantities.
Further Practice Questions

QUESTION 1

\[
\text{Br} \quad \text{Br} \quad \quad [1] \quad \quad 1,5\text{-dibromoctane} \quad [1]
\]

QUESTION 2

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 & \rightarrow \quad \text{CH}_3\text{CH}_2\text{Br} & \rightarrow & \quad \text{CH}_3\text{CH}_2\text{CN} & \rightarrow & \quad \text{CH}_3\text{CH}_2\text{CO}_2\text{H} \\
\text{HBr(g)} & \quad \text{KCN(alc)} & \quad \text{dilute H}_2\text{SO}_4 & \quad \text{heat} & \quad \text{heat}
\end{align*}
\]

QUESTION 3

✓ High C : H ratio with more than 6 C, A and B contains a benzene ring.
✓ Nucleophilic substitution of Cl to OH, A is not an arylbenzene (i.e. Cl is \textit{not} directly bonded to the benzene ring).
  ➢ Compound C is C\textsubscript{6}H\textsubscript{5}CH\textsubscript{2}OH
✓ No nucleophilic substitution of Cl to OH possible, J is an arylbenzene (i.e. Cl is directly bonded to the benzene ring).
✓ A is \begin{align*}
\text{Cl} \\
\text{C}
\end{align*}
and
B is \begin{align*}
\text{Cl} \\
\text{C}
\end{align*}
(other position of substitution is possible)

QUESTION 4

(a) Refrigerants in air-conditioner
(b) Utraviolet light initiates homolytic fission of C-Cl bond, forming Cl• free radicals
(c) Steps 2 and 3
(d) Any steps which involves the collision of 2 radicals
   \[
   \begin{align*}
   2 \text{Cl}• & \rightarrow \text{Cl}_2 \\
   2 \text{OCl}• & \rightarrow \text{Cl}_2 + \text{O}_2 \\
   2 \text{CFCl}_2 & \rightarrow \text{C}_3\text{F}_2\text{Cl}_4 \\
   \text{Cl}• + \text{OCl}• & \rightarrow \text{Cl}_2\text{O}
   \end{align*}
   \]
(e) Decomposition of oxygen by ultraviolet light (refer to first equation in question)
(f) Depletion of ozone layer will cause more UV light to reach us, with subsequent increase in incidences of skin cancers and eye cataracts.