Chapter 6: Haloalkanes and Haloarenes

Exercises — Exercises

Q1 Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:
(i) $(CH_3)_2CHCH(Cl)CH_3$
(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$
(iii) $CH_3CH_2C(CH_3)_2CH_2I$
(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$
(v) $CH_3CH(CH_3)CH(Br)CH_3$
(vi) $CH_3C(C_2H_5)_2CH_2Br$
(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$
(viii) $CH_3CH=C(Cl)CH_2CH(CH_3)_2$
(ix) $CH_3CH=CHC(Br)(CH_3)_2$
(x) p-$ClC_6H_4CH_2CH(CH_3)_2$
(xi) m-$ClCH_2C_6H_4CH_2C(CH_3)_3$
(xii) o-Br-$C_6H_4CH(CH_3)CH_2CH_3$

SOLUTION

(i) $(CH_3)_2CHCH(Cl)CH_3$:
Longest chain = 4C. Cl at C_2, methyl branch at C_3 (numbering from the Cl end).
Name: 2-Chloro-3-methylbutane. The C bearing Cl is bonded to 2 carbon groups ($CH(CH_3)_2$ and CH_3) and 1H — secondary.

(ii) $CH_3CH_2CH(CH_3)CH(C_2H_5)Cl$:
Longest chain runs through the C bearing Cl, taking its C_2H_5 group into the main chain → 6C (hexane).
Number to give Cl the lowest locant: Cl at C_3, methyl branch at C_4.
Name: 3-Chloro-4-methylhexane. C bearing Cl has 2 carbon groups → secondary.

(iii) $CH_3CH_2C(CH_3)_2CH_2I$:
The C bearing I = CH_2I → bonded to only 1 carbon group → primary.
Longest chain: I-CH_2-$C(CH_3)_2$-CH_2-CH_3 = 4C (butane), with two methyl branches at C_2 from the I end.
Name: 1-Iodo-2,2-dimethylbutane. Primary alkyl halide.

(iv) $(CH_3)_3CCH_2CH(Br)C_6H_5$:
C bearing Br = CH(Br): bonded to $CH_2C(CH_3)_3$ (alkyl) and C_6H_5 (aryl) → 2 carbon groups → secondary benzyl halide.

Main chain (excluding phenyl): 4C → butane. From phenyl end C_1=CH(Br)(C_6H_5), C_2=CH_2, C_3=C(CH_3)$_3$ gives 3C + 3 methyl branches at C_3.
Name: 1-Bromo-1-phenyl-3,3-dimethylbutane. Secondary benzyl halide.

(v) $CH_3CH(CH_3)CH(Br)CH_3$:
Longest chain = 4C; Br at C_2, methyl at C_3 (from Br end).
Name: 2-Bromo-3-methylbutane. C bearing Br bonded to 2 carbon groups → secondary alkyl halide.

(vi) $CH_3C(C_2H_5)_2CH_2Br$:
C bearing Br = CH_2Br → primary (1 carbon group attached).
Central C bonded to CH_3, two C_2H_5 (ethyl) groups and CH_2Br. Take one ethyl into the main chain: C_1=CH_2Br, C_2=C(CH_3)(C_2H_5), C_3=CH_2, C_4=CH_3 — 4C (butane), with ethyl and methyl branches at C_2.
Name: 1-Bromo-2-ethyl-2-methylbutane. Primary alkyl halide.

(vii) $CH_3C(Cl)(C_2H_5)CH_2CH_3$:
C bearing Cl bonded to CH_3, C_2H_5, and CH_2CH_3 → 3 carbon groups → tertiary.
Longest chain through C(Cl): CH_3CH_2-C(Cl)(CH_3)-CH_2CH_3. Take one ethyl on each side: C_1=CH_3, C_2=CH_2, C_3=C(Cl)(CH_3), C_4=CH_2, C_5=CH_3 — 5C main chain, methyl branch at C_3.
Name: 3-Chloro-3-methylpentane. Tertiary alkyl halide.

(viii) $CH_3CH=C(Cl)CH_2CH(CH_3)_2$:
Cl is attached to a sp^2 carbon (part of C=C double bond) → vinyl (vinylic) halide.
Longest chain including C=C: C_1=CH_3, C_2=CH=, C_3=C(Cl), C_4=CH_2, C_5=CH(CH_3), C_6=CH_3 — 6C chain with double bond at C_2, Cl at C_3, methyl branch at C_5.
Name: 3-Chloro-5-methylhex-2-ene. Vinyl halide.

(ix) $CH_3CH=CHC(Br)(CH_3)_2$:
Br on C adjacent to C=C (allylic carbon) → allylic halide. C bearing Br has 3 carbon groups (2 methyls + vinyl C) → tertiary allylic halide.
Longest chain: C_1=CH_3, C_2=CH=, C_3=CH^-, C_4=C(Br)(CH_3), C_5=CH_3 — 5C chain (one methyl of the dimethyl becomes C_5, other is a branch).
Name: 4-Bromo-4-methylpent-2-ene. Tertiary allylic halide.

(x) p-$ClC_6H_4CH_2CH(CH_3)_2$:
Cl directly on the benzene ring → aryl halide. The $CH_2CH(CH_3)_2$ group is a 2-methylpropyl (isobutyl) substituent at para position.
Name: 1-Chloro-4-(2-methylpropyl)benzene. Aryl halide.

(xi) m-$ClCH_2C_6H_4CH_2C(CH_3)_3$:
Cl is on a CH_2 group attached to the benzene ring (benzylic position) → benzyl halide, primary (CH_2 bonded to ring C and Cl).
The other substituent is a 2,2-dimethylpropyl (neopentyl = $C(CH_3)_3$-CH_2^-) group at meta.
Name: 1-(Chloromethyl)-3-(2,2-dimethylpropyl)benzene. Primary benzyl halide.

(xii) o-Br-$C_6H_4CH(CH_3)CH_2CH_3$:
Br directly on the benzene ring → aryl halide. The sec-butyl group [$CH(CH_3)CH_2CH_3$ = 1-methylpropyl] is at ortho position.
Name: 1-Bromo-2-(1-methylpropyl)benzene (or 1-bromo-2-sec-butylbenzene). Aryl halide.

Answer: (i) 2-Chloro-3-methylbutane — secondary alkyl halide; (ii) 3-Chloro-4-methylhexane — secondary alkyl halide; (iii) 1-Iodo-2,2-dimethylbutane — primary alkyl halide; (iv) 1-Bromo-1-phenyl-3,3-dimethylbutane — secondary benzyl halide; (v) 2-Bromo-3-methylbutane — secondary alkyl halide; (vi) 1-Bromo-2-ethyl-2-methylbutane — primary alkyl halide; (vii) 3-Chloro-3-methylpentane — tertiary alkyl halide; (viii) 3-Chloro-5-methylhex-2-ene — vinyl halide; (ix) 4-Bromo-4-methylpent-2-ene — tertiary allylic halide; (x) 1-Chloro-4-(2-methylpropyl)benzene — aryl halide; (xi) 1-(Chloromethyl)-3-(2,2-dimethylpropyl)benzene — primary benzyl halide; (xii) 1-Bromo-2-(1-methylpropyl)benzene — aryl halide

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Q2 Give the IUPAC names of the following compounds:
(i) $CH_3CH(Cl)CH(Br)CH_3$
(ii) $CHF_2CBrClF$
(iii) $ClCH_2C{\equiv}CCH_2Br$
(iv) $(CCl_3)_3CCl$
(v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$
(vi) $(CH_3)_3CCH{=}CClC_6H_4I\text{-}p$

SOLUTION

(i) $CH_3CH(Cl)CH(Br)CH_3$:
4C chain: $C_1{=}CH_3$, $C_2{=}CH(Cl)$, $C_3{=}CH(Br)$, $C_4{=}CH_3$.
Two halogens — locant set {2,3} from either end. Alphabetical rule: bromo (B) cited before chloro (C) → Br gets the lower locant.
Number from right: $C_1{=}CH_3$, $C_2{=}CH(Br)$, $C_3{=}CH(Cl)$, $C_4{=}CH_3$ → Br@C_2, Cl@C_3.

Name: 2-Bromo-3-chlorobutane.

(ii) $CHF_2CBrClF$:
2C chain (ethane). Number from the CBrClF end → Br, Cl, F all at C_1; the two F of CHF_2 at C_2.
Substituents cited alphabetically: bromo, chloro, then the three fluoro (at 1,2,2).
Name: 1-Bromo-1-chloro-1,2,2-trifluoroethane.

(iii) $ClCH_2C{\equiv}CCH_2Br$:
4C chain with triple bond: $C_1{=}CH_2Cl$, $C_2{\equiv}C_3$, $C_4{=}CH_2Br$ (or from Br end: $C_1{=}CH_2Br$ ... same triple bond position).
Triple bond gets lowest locant: from either end it is at C_2. Alphabetical: Br (B) gets lower locant than Cl (C).
Number from Br end: $C_1{=}CH_2Br$, $C_2{\equiv}C_3$, $C_4{=}CH_2Cl$ → Br@C_1, Cl@C_4, triple bond@C_2.
Name: 1-Bromo-4-chlorobut-2-yne.

(iv) $(CCl_3)_3CCl$:
Central C bonded to 3 trichloromethyl (CCl_3) groups and 1 Cl.
Longest chain: CCl_3-C(Cl)-CCl_3 = 3C (propane); C_1 and C_3 each carry 3 Cl (1,1,1,3,3,3-hexachloro), the third CCl_3 is a branch at C_2, and one Cl sits on C_2.
Name: 2-(Trichloromethyl)-1,1,1,3,3,3-hexachloropropane.

(v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$:
4C main chain (excluding aryl groups): $C_1{=}CH_3$, $C_2{=}C(Ar)_2$, $C_3{=}CH(Br)$, $C_4{=}CH_3$.
Br@C_3, two (4-chlorophenyl) groups@C_2.
Name: 3-Bromo-2,2-bis(4-chlorophenyl)butane.

(vi) $(CH_3)_3CCH{=}CClC_6H_4I\text{-}p$:
Cl is on a sp^2 vinyl carbon adjacent to the (4-iodophenyl) group.
Main chain: from the C(Cl)(Ar)= end: $C_1{=}C(Cl)(p\text{-}IC_6H_4){=}$, $C_2{=}CH{=}$, $C_3{=}C(CH_3)_2$, then one methyl becomes $C_4{=}CH_3$, with 2 methyls as branches at C_3.
4C chain with double bond at C_1 (but-1-ene numbering); substituents: Cl and 4-iodophenyl at C_1, two methyls at C_3.
Name: 1-Chloro-1-(4-iodophenyl)-3,3-dimethylbut-1-ene.

Answer: (i) 2-Bromo-3-chlorobutane; (ii) 1-Bromo-1-chloro-1,2,2-trifluoroethane; (iii) 1-Bromo-4-chlorobut-2-yne; (iv) 2-(Trichloromethyl)-1,1,1,3,3,3-hexachloropropane; (v) 3-Bromo-2,2-bis(4-chlorophenyl)butane; (vi) 1-Chloro-1-(4-iodophenyl)-3,3-dimethylbut-1-ene

Q3 Write the structures of the following organic halogen compounds.

(i) 2-Chloro-3-methylpentane

(ii) p-Bromochlorobenzene

(iii) 1-Chloro-4-ethylcyclohexane

(iv) 2-(2-Chlorophenyl)-1-iodooctane

(v) 2-Bromobutane

(vi) 4-tert-Butyl-3-iodoheptane

(vii) 1-Bromo-4-sec-butyl-2-methylbenzene

(viii) 1,4-Dibromobut-2-ene

SOLUTION

(i) 2-Chloro-3-methylpentane:
5C chain, Cl at C_2, methyl branch at C_3.
Structure: CH_3-CH(Cl)-CH(CH_3)-CH_2-CH_3

(ii) p-Bromochlorobenzene (1-bromo-4-chlorobenzene):
Benzene ring with Br and Cl at 1,4 (para) positions.
Structure: C_6H_4(Br)(Cl) with Br and Cl para to each other (1-Br-4-Cl-C_6H_4)

(iii) 1-Chloro-4-ethylcyclohexane:
Cyclohexane ring with Cl at C_1 and ethyl (-CH_2CH_3) at C_4 (para positions).
Structure: cyclohexane ring — C_1(H)(Cl), C_2H_2, C_3H_2, C_4(H)(CH_2CH_3), C_5H_2, C_6H_2

(iv) 2-(2-Chlorophenyl)-1-iodooctane:
8C main chain (octane), I at C_1, 2-chlorophenyl group at C_2.
Structure: I-CH_2-CH(2-ClC_6H_4)-$CH_2CH_2CH_2CH_2CH_2CH_3$

(v) 2-Bromobutane:
4C chain, Br at C_2.
Structure: CH_3-CH(Br)-CH_2-CH_3

(vi) 4-tert-Butyl-3-iodoheptane:
7C chain, tert-butyl [$C(CH_3)_3$] at C_4, I at C_3.
Structure: CH_3-CH_2-CH(I)-CH[$C(CH_3)_3$]-CH_2-CH_2-CH_3

(vii) 1-Bromo-4-sec-butyl-2-methylbenzene:
Benzene ring: Br at C_1, CH_3 at C_2, sec-butyl [$CH(CH_3)CH_2CH_3$ = 1-methylpropyl] at C_4.
Structure: benzene ring with Br(C_1), CH_3(C_2), $CH(CH_3)(CH_2CH_3)$(C_4)

(viii) 1,4-Dibromobut-2-ene:
4C chain, double bond at C_2-C_3, Br at C_1 and C_4.

Structure: Br-CH_2-CH=CH-CH_2-Br

Answer: (i) CH_3-CH(Cl)-CH(CH_3)-CH_2-CH_3; (ii) 1-Bromo-4-chlorobenzene (Br and Cl at para positions of benzene); (iii) Cyclohexane ring with Cl at C_1, CH_2CH_3 at C_4; (iv) I-CH_2-CH(2-ClC_6H_4)-$(CH_2)_5$-CH_3; (v) CH_3-CH(Br)-CH_2-CH_3; (vi) $CH_3CH_2CH(I)$-CH[$C(CH_3)_3$]-$CH_2CH_2CH_3$; (vii) Benzene ring with Br(C_1), CH_3(C_2), $CH(CH_3)(CH_2CH_3)$(C_4); (viii) Br-CH_2-CH=CH-CH_2-Br

Q4 Which one of the following has the highest dipole moment?
(i) CH_2Cl_2 (ii) $CHCl_3$ (iii) CCl_4

SOLUTION

CCl_4 (tetrachloromethane): All four C-Cl bonds are identical and arranged tetrahedrally. The bond dipoles cancel completely by symmetry → net dipole moment = 0 D.

CH_2Cl_2 (dichloromethane): The two C-Cl bond dipoles add up (resultant along the Cl-C-Cl bisector), while the two C-H dipoles are much smaller. The resultant is large: dipole moment ≈ 1.60 D.

$CHCl_3$ (chloroform): The three C-Cl bond dipoles largely oppose one another (they point toward three corners of the tetrahedron), so their resultant is partly cancelled and reinforced only weakly by the single C-H dipole. Net dipole moment ≈ 1.04 D — smaller than in CH_2Cl_2.

Therefore CH_2Cl_2 has the highest dipole moment: the two large C-Cl dipoles reinforce, giving the largest vector sum of the three molecules.

Answer: CH_2Cl_2 (dichloromethane) has the highest dipole moment (≈1.60 D). Order: CH_2Cl_2 (1.60 D) > $CHCl_3$ (1.04 D) > CCl_4 (0 D)

Q5 A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

SOLUTION

Degree of unsaturation for C_5H_{10} = (2×5 + 2 - 10)/2 = 1.
One degree of unsaturation means one ring or one double bond.

Does not react with Cl_2 in the dark → NOT an alkene (alkenes react with Cl_2 via electrophilic addition in dark).
So the compound is a cycloalkane (ring = 1 degree of unsaturation, no reaction

with Cl_2 in dark).

Gives a SINGLE monochloro product in sunlight → free-radical chlorination → all H atoms in the molecule are equivalent.

Among C_5H_{10} cycloalkanes: cyclopentane (C_5H_{10}) has all 10 hydrogen atoms equivalent (all are CH_2 hydrogens on the ring, in identical environments).
Chlorination of cyclopentane gives only one product: chlorocyclopentane (C_5H_9Cl). ✓

Methylcyclobutane (C_5H_{10}) would give multiple products (non-equivalent H atoms), so it is ruled out.

Answer: Cyclopentane (C_5H_{10}). All 10 hydrogen atoms are equivalent; free-radical chlorination in sunlight gives a single product — chlorocyclopentane (C_5H_9Cl).

Q6 Write the isomers of the compound having formula C_4H_9Br.

SOLUTION

C_4H_9Br has no degree of unsaturation. The C_4H_9 group can be arranged in four ways:

1. 1-Bromobutane (n-butyl bromide): $CH_3CH_2CH_2CH_2Br$ — primary halide.

2. 2-Bromobutane (sec-butyl bromide): $CH_3CH(Br)CH_2CH_3$ — secondary halide.

3. 1-Bromo-2-methylpropane (isobutyl bromide): $(CH_3)_2CHCH_2Br$ — primary halide.

4. 2-Bromo-2-methylpropane (tert-butyl bromide): $(CH_3)_3CBr$ — tertiary halide.

These are all four structural isomers of C_4H_9Br.

Answer: Four isomers: (1) $CH_3CH_2CH_2CH_2Br$ (1-bromobutane, 1°); (2) $CH_3CH(Br)CH_2CH_3$ (2-bromobutane, 2°); (3) $(CH_3)_2CHCH_2Br$ (1-bromo-2-methylpropane, 1°); (4) $(CH_3)_3CBr$ (2-bromo-2-methylpropane, 3°)

Q7 Write the equations for the preparation of 1-iodobutane from
(i) 1-butanol
(ii) 1-chlorobutane
(iii) but-1-ene.

SOLUTION

(i) From 1-butanol ($CH_3CH_2CH_2CH_2OH$):

1-Butanol is treated with KI in the presence of H_3PO_4 (or with HI).
H_2SO_4 cannot be used because it oxidises I^- to I_2.
$CH_3CH_2CH_2CH_2OH + KI + H_3PO_4 \rightarrow CH_3CH_2CH_2CH_2I + KH_2PO_4 + H_2O$
Alternatively: $CH_3CH_2CH_2CH_2OH + I_2 + \text{red P} \rightarrow CH_3CH_2CH_2CH_2I + H_3PO_3$ (or analogous)

(ii) From 1-chlorobutane ($CH_3CH_2CH_2CH_2Cl$):
Finkelstein reaction: treatment with NaI in dry acetone.
$CH_3CH_2CH_2CH_2Cl + NaI \xrightarrow{\text{acetone}} CH_3CH_2CH_2CH_2I + NaCl\downarrow$
NaI is soluble in acetone; NaCl is insoluble and precipitates out, driving the SN_2 equilibrium to completion.

(iii) From but-1-ene ($CH_2=CHCH_2CH_3$):
Direct addition of HI would give 2-iodobutane (Markovnikov). To get 1-iodobutane:
Step 1: Add HBr in the presence of peroxide (anti-Markovnikov, free-radical addition):
$CH_2=CHCH_2CH_3 + HBr \xrightarrow{\text{peroxide}} CH_3CH_2CH_2CH_2Br$ (1-bromobutane)
Step 2: Finkelstein reaction:
$CH_3CH_2CH_2CH_2Br + NaI \xrightarrow{\text{acetone}} CH_3CH_2CH_2CH_2I + NaBr\downarrow$

Answer: (i) $CH_3CH_2CH_2CH_2OH + KI/H_3PO_4 \rightarrow CH_3CH_2CH_2CH_2I$; (ii) $CH_3CH_2CH_2CH_2Cl + NaI/\text{acetone} \rightarrow CH_3CH_2CH_2CH_2I + NaCl$ (Finkelstein); (iii) $CH_2=CHCH_2CH_3 + HBr/\text{peroxide} \rightarrow$ 1-bromobutane, then $+ NaI/\text{acetone} \rightarrow$ 1-iodobutane

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Q8 What are ambident nucleophiles? Explain with an example.

SOLUTION

An ambident nucleophile is a nucleophile that possesses two different nucleophilic sites (two different atoms carrying lone pairs or negative charge), either of which can attack an electrophilic carbon, giving two different products.

Example 1 — Cyanide ion (CN^-):
CN^- has lone pairs on both C and N. It can attack through:
(a) Carbon end: $R\text{-}X + CN^- \rightarrow R\text{-}C\equiv N + X^-$ (nitrile/alkyl cyanide)
(b) Nitrogen end: $R\text{-}X + CN^- \rightarrow R\text{-}N^+=C^-$ (isonitrile/alkyl isocyanide)
In SN_2 conditions, attack via the harder C-end predominates → nitrile is the major product.

Example 2 — Nitrite ion (NO_2^-):

NO_2^- can attack through:

(a) Nitrogen: R-X + NO_2^- -> R-NO_2 + X^- (nitroalkane)

(b) Oxygen: R-X + ONO^- -> R-O-N=O + X^- (alkyl nitrite)

With $AgNO_2$, nitrogen-attack (nitroalkane) is favoured; with KNO_2, a mixture forms.

Answer: An ambident nucleophile has two nucleophilic sites capable of attacking an electrophile. Example: CN^- attacks via C to give nitrile (R-CN) or via N to give isocyanide (R-NC). Example: NO_2^- attacks via N to give nitroalkane (R-NO_2) or via O to give alkyl nitrite (R-ONO).

Q9 Which compound in each of the following pairs will react faster in SN_2 reaction with -OH?

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3CCl$ or CH_3Cl

SOLUTION

(i) CH_3Br vs CH_3I:

In SN_2, the rate depends on (a) steric hindrance at the reaction centre and (b) the leaving group ability.

Both CH_3Br and CH_3I have the same substrate (methyl), so steric hindrance is identical.

Leaving group ability: I^- is a better leaving group than Br^- because iodide is a larger, more polarisable anion that is more stable after departure (weaker C-I bond).

∴ CH_3I reacts faster in SN_2.

(ii) $(CH_3)_3CCl$ vs CH_3Cl:

Both have Cl as the leaving group, so leaving group ability is the same.

Steric hindrance: $(CH_3)_3CCl$ (tertiary) has three methyl groups crowding the back of the C-Cl bond. Back-side attack by OH^- is severely hindered → extremely slow SN_2.

CH_3Cl (methyl chloride) has no substituents blocking back-side attack.

∴ CH_3Cl reacts much faster in SN_2.

(Note: $(CH_3)_3CCl$ essentially does not undergo SN_2 under ordinary conditions; it reacts by SN_1 or E_2 instead.)

Answer: (i) CH_3I reacts faster (I^- is a better leaving group); (ii) CH_3Cl reacts faster ($(CH_3)_3CCl$ is too sterically hindered for SN_2 back-side attack)

Q10 Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:
(i) 1-Bromo-1-methylcyclohexane
(ii) 2-Chloro-2-methylbutane
(iii) 2,2,3-Trimethyl-3-bromopentane.

SOLUTION

(i) 1-Bromo-1-methylcyclohexane:
Structure: methylcyclohexane with Br at C_1 (tertiary C). Beta-H atoms can be removed from:
(a) Ring C_2 or C_6 (equivalent by symmetry) → double bond enters the ring → 1-methylcyclohex-1-ene (endocyclic alkene, tetrasubstituted)
(b) The methyl group (-CH_3 at C_1) → exocyclic double bond → methylenecyclohexane (CH_2= exocyclic, less substituted)
Major product (Zaitsev's rule — more substituted alkene is favoured in E_2): 1-methylcyclohex-1-ene (endocyclic, more substituted).
Minor product: methylenecyclohexane.

(ii) 2-Chloro-2-methylbutane [CH_3-C(Cl)(CH_3)-CH_2-CH_3]:
C bearing Cl = C_2 (tertiary). Beta-H atoms can be removed from:
(a) C_1 (CH_3 group): gives CH_2=C(CH_3)-CH_2CH_3 → 2-methylbut-1-ene (disubstituted/monosubstituted, less substituted)
(b) C_3 (CH_2 group): gives CH_3-C(CH_3)=CH-CH_3 → 2-methylbut-2-ene (trisubstituted, more substituted)
Major product (Zaitsev): 2-methylbut-2-ene (trisubstituted double bond).
Minor product: 2-methylbut-1-ene.

(iii) 2,2,3-Trimethyl-3-bromopentane:
Main chain: C_1=CH_3, C_2=C(CH_3)$_2$ (quaternary — NO H), C_3=C(Br)(CH_3), C_4=CH_2, C_5=CH_3.
C_2 is quaternary (no beta-H on that side). Beta-H is available on C_4 (CH_2) and on the C_3-methyl.
(a) Remove H from C_4 → C_3=C_4 double bond: CH_3-C(CH_3)$_2$-C(CH_3)=CH-CH_3 = 3,4,4-trimethylpent-2-ene (trisubstituted).
(b) Remove H from the C_3-methyl → exocyclic C=CH_2: (CH_3)$_3$C-C(=CH_2)-CH_2CH_3

= 2-ethyl-3,3-dimethylbut-1-ene (disubstituted).
Major product (Zaitsev — more substituted): 3,4,4-trimethylpent-2-ene.

Answer: (i) Products: 1-methylcyclohex-1-ene (major) and methylenecyclohexane (minor); (ii) Products: 2-methylbut-2-ene (major, Zaitsev) and 2-methylbut-1-ene (minor); (iii) Products: 3,4,4-trimethylpent-2-ene (major, Zaitsev) and 2-ethyl-3,3-dimethylbut-1-ene (minor)

Q11 How will you bring about the following conversions?
(i) Ethanol to but-1-yne
(ii) Ethane to bromoethene
(iii) Propene to 1-nitropropane
(iv) Toluene to benzyl alcohol
(v) Propene to propyne
(vi) Ethanol to ethyl fluoride
(vii) Bromomethane to propanone
(viii) But-1-ene to but-2-ene
(ix) 1-Chlorobutane to n-octane
(x) Benzene to biphenyl

SOLUTION

(i) Ethanol (CH_3CH_2OH) to but-1-yne ($HC\equiv C\text{-}CH_2CH_3$):
Step 1: $CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$
Step 2: $CH_3CH_2Cl + KOH(alc) \rightarrow CH_2=CH_2 + KCl + H_2O$
Step 3: $CH_2=CH_2 + Br_2 \rightarrow CH_2Br\text{-}CH_2Br$
Step 4: $CH_2BrCH_2Br + 2KOH(alc) \rightarrow HC\equiv CH + 2KBr + 2H_2O$
Step 5: $HC\equiv CH + NaNH_2 \rightarrow HC\equiv C^-Na^+ + NH_3$
Step 6: $HC\equiv CNa + CH_3CH_2Br \rightarrow HC\equiv C\text{-}CH_2CH_3 + NaBr$ (but-1-yne)

(ii) Ethane (CH_3CH_3) to bromoethene ($CH_2=CHBr$):
Step 1: $CH_3CH_3 + Br_2\ (hv) \rightarrow CH_3CH_2Br + HBr$
Step 2: $CH_3CH_2Br + KOH(alc) \rightarrow CH_2=CH_2 + KBr + H_2O$
Step 3: $CH_2=CH_2 + Br_2 \rightarrow CH_2BrCH_2Br$
Step 4: $CH_2BrCH_2Br + KOH(alc) \rightarrow CH_2=CHBr + KBr + H_2O$ (one dehydrohalogenation)

(iii) Propene ($CH_3CH=CH_2$) to 1-nitropropane ($CH_3CH_2CH_2NO_2$):
Step 1: $CH_3CH=CH_2 + HBr$ (peroxide, anti-Markovnikov) $\rightarrow CH_3CH_2CH_2Br$
Step 2: $CH_3CH_2CH_2Br + AgNO_2 \rightarrow CH_3CH_2CH_2NO_2 + AgBr$

(Silver nitrite gives nitroalkane; attack via N of NO_2^-)

(iv) Toluene ($C_6H_5CH_3$) to benzyl alcohol ($C_6H_5CH_2OH$):
Step 1: $C_6H_5CH_3 + Cl_2$ (hv, high temp) -> $C_6H_5CH_2Cl + HCl$ (free-radical side-chain chlorination)
Step 2: $C_6H_5CH_2Cl + NaOH(aq) \rightarrow C_6H_5CH_2OH + NaCl$ (SN_2 hydrolysis)

(v) Propene ($CH_3CH=CH_2$) to propyne ($CH_3C\equiv CH$):
Step 1: $CH_3CH=CH_2 + Br_2 \rightarrow CH_3CHBr\text{-}CH_2Br$ (1,2-dibromopropane)
Step 2: $CH_3CHBrCH_2Br + 2KOH(alc) \rightarrow CH_3C\equiv CH + 2KBr + 2H_2O$

(vi) Ethanol (CH_3CH_2OH) to ethyl fluoride (CH_3CH_2F):
Step 1: $CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$
Step 2: $CH_3CH_2Cl + AgF \rightarrow CH_3CH_2F + AgCl$ (Swarts reaction)

(vii) Bromomethane (CH_3Br) to propanone (CH_3COCH_3):
Step 1: $CH_3Br + Mg$ (dry ether) -> CH_3MgBr (Grignard reagent)
Step 2: $CH_3MgBr + CH_3CHO$ (acetaldehyde) -> $CH_3CH(OMgBr)CH_3$, then H_3O^+ -> $(CH_3)_2CHOH$ (propan-2-ol)
Step 3: $(CH_3)_2CHOH + K_2Cr_2O_7/H_2SO_4 \rightarrow CH_3COCH_3 + H_2O$ (oxidation to propanone)

(viii) But-1-ene ($CH_2=CHCH_2CH_3$) to but-2-ene ($CH_3CH=CHCH_3$):
Step 1: $CH_2=CHCH_2CH_3 + HBr \rightarrow CH_3CH(Br)CH_2CH_3$ (Markovnikov → 2-bromobutane)
Step 2: $CH_3CH(Br)CH_2CH_3 + KOH(alc) \rightarrow CH_3CH=CHCH_3 + KBr + H_2O$ (Zaitsev: more substituted alkene = but-2-ene)

(ix) 1-Chlorobutane ($CH_3CH_2CH_2CH_2Cl$) to n-octane (C_8H_{18}):
$2\ CH_3CH_2CH_2CH_2Cl + 2Na$ (dry ether) -> $CH_3(CH_2)_6CH_3 + 2NaCl$
(Wurtz reaction: coupling of two 1-chlorobutane molecules gives n-octane)

(x) Benzene to biphenyl ($C_6H_5\text{-}C_6H_5$):
Step 1: $C_6H_6 + Br_2$ ($FeBr_3$) -> $C_6H_5Br + HBr$ (electrophilic aromatic substitution)
Step 2: $C_6H_5Br + Mg$ (dry ether) -> C_6H_5MgBr (Grignard reagent)
Step 3: $C_6H_5MgBr + C_6H_5Br \rightarrow C_6H_5\text{-}C_6H_5 + MgBr_2$ (biphenyl)
OR: Ullmann coupling: $2C_6H_5Br + Cu$ (heat) -> $C_6H_5\text{-}C_6H_5 + CuBr_2$

Answer: (i) EtOH -> EtCl -> ethylene -> 1,2-dibromoethane -> HC≡CH -> HC≡CNa -> but-1-yne; (ii) Ethane -> EtBr -> ethylene -> 1,2-dibromoethane -> CH_2=CHBr; (iii) Propene + HBr/peroxide -> 1-BrPr + $AgNO_2$ -> 1-nitropropane; (iv) Toluene + Cl_2/hv -> $PhCH_2Cl$ + NaOH(aq) -> benzyl alcohol; (v) Propene + Br_2 -> 1,2-dibromopropane + 2KOH(alc) -> propyne; (vi) EtOH -> EtCl + AgF -> EtF (Swarts); (vii) CH_3Br -> CH_3MgBr + CH_3CHO -> propan-2-ol -> oxidation -> propanone; (viii) But-1-ene + HBr -> 2-bromobutane + KOH(alc) -> but-2-ene; (ix) 2 nBuCl + 2Na -> n-octane (Wurtz); (x) Benzene -> PhBr -> PhMgBr + PhBr -> biphenyl

Q12 Explain why
(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?
(ii) alkyl halides, though polar, are immiscible with water?
(iii) Grignard reagents should be prepared under anhydrous conditions?

SOLUTION

(i) Dipole moment of chlorobenzene < cyclohexyl chloride:
In chlorobenzene (C_6H_5Cl), Cl is bonded to an sp^2 hybridised carbon of the aromatic ring.
Cl has lone pairs in p-orbitals that participate in p-π conjugation (overlap) with the benzene ring π-system.
This delocalisation results in partial double bond character of the C-Cl bond, and the electron density on Cl is effectively donated into the ring (Cl acts as a pi-donor).
Consequently, the C-Cl bond is shorter, stronger, and has REDUCED polarity compared to C-Cl in a purely sp^3 environment.

In cyclohexyl chloride ($C_6H_{11}Cl$), Cl is bonded to an sp^3 carbon. No resonance or conjugation is possible.
The C-Cl bond is a pure sigma bond with full polarity; the Cl atom withdraws electron density completely toward itself.
Therefore, the dipole moment of cyclohexyl chloride (2.16 D) is significantly higher than that of chlorobenzene (1.69 D).

(ii) Alkyl halides are immiscible with water:
For a compound to dissolve in water (a highly polar, H-bonded solvent), it must either:
(a) form hydrogen bonds with water (requires O-H or N-H groups), or

(b) be so ionic/polar that ion-dipole or dipole-dipole forces overcome water-water H-bonds.

Alkyl halides are polar at the C-X bond but the rest of the molecule is a hydrophobic alkyl chain.

They cannot form H-bonds with water (no -OH or -NH group to donate H-bonds).

The energy required to break water-water H-bonds cannot be compensated by weaker alkyl halide-water interactions.

Therefore, alkyl halides remain immiscible (or sparingly soluble) in water.

(iii) Grignard reagents under anhydrous conditions:

Grignard reagents (RMgX) are organometallic compounds in which C-Mg bond is highly polarised (C^(delta-)---Mg^(delta+)).

They are extremely reactive towards any protic source, especially water:

$RMgX + H_2O \rightarrow R\text{-}H + Mg(OH)X$

Even trace amounts of moisture decompose the Grignard reagent by protonation of the carbanion-like carbon.

This destroys the reagent before it can react with the intended electrophile.

Therefore, all glassware, solvents (usually anhydrous ether or THF), and reagents must be completely dry.

Answer: (i) In C_6H_5Cl, lone pairs of Cl conjugate with the ring (p-π overlap) reducing C-Cl bond polarity → lower dipole moment. In $C_6H_{11}Cl$, Cl on sp^3 C has full C-Cl polarity → higher dipole moment. (ii) Alkyl halides cannot form H-bonds with water (no -OH/-NH); hydrophobic alkyl chain makes solvation energetically unfavourable → immiscible. (iii) Grignard reagents are destroyed by water ($RMgX + H_2O \rightarrow RH + Mg(OH)X$); even traces of moisture decompose them → must be prepared in anhydrous conditions.

Q13 Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

SOLUTION

Freon 12 (CCl_2F_2, dichlorodifluoromethane):

- Used as refrigerant in refrigerators and air conditioners (now largely phased out under the Montreal Protocol).
- Used as aerosol propellant in spray cans.
- Used as a blowing agent for foam production.

Note: Freons are non-toxic, non-flammable and thermally stable, but they deplete the ozone layer.

DDT (2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane):
- First widely used synthetic insecticide/pesticide; effective against mosquitoes (malaria control) and lice (typhus control).
- Extensively used during World War II to control vector-borne diseases.
- Now BANNED in most countries because it is non-biodegradable, accumulates in food chains (biomagnification), and is toxic to birds and mammals; suspected carcinogen.

Carbon tetrachloride (CCl_4):
- Used as a solvent for fats, oils, rubber, waxes, and lacquers.
- Used in dry cleaning (now replaced by less toxic alternatives).
- Used in fire extinguishers (pyrene type) — it forms a heavy non-flammable vapour layer over fires (now discontinued due to toxicity).
- Used as a starting material in the manufacture of refrigerants (CFCs).

Iodoform (CHI_3, triiodomethane):
- Used as antiseptic for dressing wounds; the germicidal action is due to the slow liberation of iodine (I_2).
- Used in the iodoform test: methyl ketones (CH_3COR) and secondary alcohols with $CH_3CH(OH)^-$ group give a yellow precipitate of CHI_3 with I_2/NaOH — diagnostic test.

Answer: Freon 12: refrigerant, aerosol propellant (now banned — ozone depleting). DDT: insecticide/mosquito control (now banned — non-biodegradable, biomagnifies). CCl_4: solvent for oils/fats, fire extinguishers, refrigerant manufacture. Iodoform: antiseptic for wound dressing (liberates germicidal I_2); used in iodoform test for methyl ketones.

Q14 Write the structure of the major organic product in each of the following reactions:

(i) $CH_3CH_2CH_2Cl + NaI$ (acetone)

(ii) $(CH_3)_3CBr + KOH$

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH$

(iv) $CH_3CH_2Br + KCN$

(v) $C_6H_5ONa + C_2H_5Cl$

(vi) $CH_3CH_2CH_2OH + SOCl_2$

(vii) $CH_3CH_2CH=CH_2 + HBr$

(viii) $CH_3CH=C(CH_3)_2 + HBr$

SOLUTION

(i) $CH_3CH_2CH_2Cl$ + NaI (acetone):
Finkelstein reaction (SN_2). NaCl precipitates from acetone, driving reaction to completion.
Product: $CH_3CH_2CH_2I$ (1-iodopropane)

(ii) $(CH_3)_3CBr$ + KOH:
Tertiary substrate with strong base KOH in alcoholic medium → E_2 elimination (major).
Product: $(CH_3)_2C=CH_2$ (2-methylpropene / isobutylene)
(With aqueous KOH: SN_1 → $(CH_3)_3COH$ would be major; alcoholic KOH → alkene major)

(iii) $CH_3CH(Br)CH_2CH_3$ + NaOH (aqueous):
Secondary halide + NaOH(aq) → SN_2 substitution dominates.
Product: $CH_3CH(OH)CH_2CH_3$ (butan-2-ol)

(iv) CH_3CH_2Br + KCN:
SN_2; CN^- attacks via the harder C-end (harder nucleophile in SN_2 conditions).
Product: CH_3CH_2CN (propanenitrile / propionitrile)

(v) C_6H_5ONa + C_2H_5Cl:
Williamson ether synthesis: sodium phenoxide (nucleophile) attacks ethyl chloride (SN_2).
Product: $C_6H_5OC_2H_5$ (ethyl phenyl ether / phenetole / ethoxyethane)

(vi) $CH_3CH_2CH_2OH$ + $SOCl_2$:
$SOCl_2$ converts -OH to -Cl via SN_2 (with retention through chlorosulfite intermediate).
Product: $CH_3CH_2CH_2Cl$ (1-chloropropane)
By-products: SO_2 + HCl (both gaseous, escape easily — good for yield).

(vii) $CH_3CH_2CH=CH_2$ + HBr:
Electrophilic addition; Markovnikov's rule → H adds to $=CH_2$ (less substituted end).
Product: $CH_3CH_2CH(Br)CH_3$ (2-bromobutane)

(viii) $CH_3CH=C(CH_3)_2$ + HBr:
Markovnikov addition: H adds to $=CH^-$ (less substituted), Br to $=C(CH_3)_2$ (more substituted/more stable carbocation).
Product: CH_3CH_2-$C(Br)(CH_3)_2$ (2-bromo-2-methylbutane)

Answer: (i) $CH_3CH_2CH_2I$; (ii) $(CH_3)_2C=CH_2$ (isobutylene); (iii) $CH_3CH(OH)CH_2CH_3$ (butan-2-ol); (iv) CH_3CH_2CN (propanenitrile); (v) $C_6H_5OC_2H_5$ (phenetole); (vi) $CH_3CH_2CH_2Cl$; (vii) $CH_3CH_2CH(Br)CH_3$ (2-bromobutane); (viii) $CH_3CH_2C(Br)(CH_3)_2$ (2-bromo-2-methylbutane)

Q15 Write the mechanism of the following reaction:
n-BuBr + KCN -> n-BuCN

SOLUTION

n-Butyl bromide ($CH_3CH_2CH_2CH_2Br$) is a primary alkyl halide → undergoes SN_2 (bimolecular nucleophilic substitution).
KCN dissociates: KCN -> K^+ + CN^-
CN^- is an ambident nucleophile; in SN_2 the harder C-nucleophile end attacks preferentially → nitrile product.

Mechanism (SN_2 — one step, concerted):

Step 1 — Back-side approach:
CN^- approaches $CH_3CH_2CH_2CH_2Br$ from the side OPPOSITE to Br (180° approach angle).
As the C-CN bond begins to form, the C-Br bond begins to break.

Step 2 — Transition state:
$[N\equiv C----------CH_2CH_2CH_2CH_3----------Br]^-$
Pentacoordinate carbon in the transition state; both C-CN and C-Br bonds are partially formed/broken; the three remaining groups (H, H, $CH_2CH_2CH_3$) are in a plane (trigonal bipyramidal geometry).

Step 3 — Product formation:
C-Br bond breaks fully; C-CN bond completes. Configuration at C inverts (Walden inversion — umbrella flip of the three groups in the plane).
$N\equiv C-CH_2CH_2CH_2CH_3 + Br^-$

Product: $CH_3CH_2CH_2CH_2CN$ (pentanenitrile / n-butyl cyanide)

Rate law (bimolecular): rate = k[n-BuBr][CN^-]
Key features: single-step, no intermediate, inversion of configuration at the reaction centre.

Answer: SN_2 mechanism: CN^- attacks back-side of C-Br bond in n-BuBr (180° to Br). Concerted transition state $[NC{-}{-}{-}C(n\text{-}Bu){-}{-}{-}Br]^-$. C-Br breaks as C-CN forms. Product: n-BuCN (pentanenitrile) + Br^-. Rate = $k[n\text{-}BuBr][CN^-]$. Inversion of configuration at carbon.

Q16 Arrange the compounds of each set in order of reactivity towards SN_2 displacement:
(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane
(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 2-Bromo-3-methylbutane
(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane

SOLUTION

SN_2 reactivity decreases as steric hindrance at the reaction site increases:
Methyl > Primary > Secondary > Tertiary (≈ 0 for SN_2)
For same class, less branching near the C bearing X = faster SN_2.

(i) 2-Bromo-2-methylbutane [$CH_3C(Br)(CH_3)CH_2CH_3$, tertiary], 1-Bromopentane [$CH_3(CH_2)_3CH_2Br$, primary], 2-Bromopentane [$CH_3CH(Br)CH_2CH_2CH_3$, secondary]:
Order of SN_2 reactivity (fastest to slowest):
1-Bromopentane (1°) > 2-Bromopentane (2°) > 2-Bromo-2-methylbutane (3°, barely reacts by SN_2)

(ii) 1-Bromo-3-methylbutane [$(CH_3)_2CHCH_2CH_2Br$, primary], 2-Bromo-2-methylbutane [$CH_3C(Br)(CH_3)CH_2CH_3$, tertiary], 2-Bromo-3-methylbutane [$CH_3CH(Br)CH(CH_3)CH_3$, secondary]:
Order:
1-Bromo-3-methylbutane (1°) > 2-Bromo-3-methylbutane (2°) > 2-Bromo-2-methylbutane (3°)

(iii) All are primary bromides — compare steric bulk near the reaction site:
1-Bromobutane [$CH_3CH_2CH_2CH_2Br$]: no branching adjacent to C_1 → least hindrance.
1-Bromo-3-methylbutane [$(CH_3)_2CHCH_2CH_2Br$]: branch at C_3 (two carbons away from Br) → very little effect on SN_2.
1-Bromo-2-methylbutane [$BrCH_2CH(CH_3)CH_2CH_3$]: one methyl branch at C_2 (adjacent to C_1) → moderate steric hindrance.
1-Bromo-2,2-dimethylpropane (neopentyl bromide) [$(CH_3)_3CCH_2Br$]: three methyl

groups at C_2 (beta-carbon) → extreme steric hindrance at back-side of C_1 → SLOWEST.

Order (fastest → slowest in SN_2):
1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane

Answer: (i) 1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane; (ii) 1-Bromo-3-methylbutane > 2-Bromo-3-methylbutane > 2-Bromo-2-methylbutane; (iii) 1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane (neopentyl bromide)

Q17 Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

SOLUTION

$C_6H_5CH_2Cl$ = benzyl chloride (benzylic, primary)
$C_6H_5CHClC_6H_5$ = benzhydryl chloride / diphenylmethyl chloride (benzylic, secondary)

Hydrolysis by aqueous KOH for benzylic halides proceeds via SN_1 (ionisation to a stabilised carbocation is favourable).

$C_6H_5CH_2Cl$ ionises to: $C_6H_5CH_2^+$ (benzyl cation)
Stabilised by resonance with ONE phenyl ring.

$C_6H_5CHClC_6H_5$ ionises to: $C_6H_5CH^+C_6H_5$ (benzhydryl / diphenylmethyl cation)
Stabilised by resonance with TWO phenyl rings → greater delocalisation → more stable carbocation.

Greater stability of the benzhydryl cation means it forms more readily (lower activation energy for ionisation) → faster SN_1 hydrolysis.

∴ $C_6H_5CHClC_6H_5$ (benzhydryl chloride) is MORE easily hydrolysed by aqueous KOH.

Answer: $C_6H_5CHClC_6H_5$ (benzhydryl chloride) is more easily hydrolysed. It ionises to the benzhydryl cation ($C_6H_5CH^+C_6H_5$) stabilised by two phenyl rings, making SN_1 faster than for benzyl chloride (stabilised by only one ring).

Q18 p-Dichlorobenzene has higher m.p. than those of o- and m-isomers. Discuss.

SOLUTION

The melting point of a solid depends on the crystal lattice energy, which in turn depends on how efficiently the molecules pack in the crystal lattice.

p-Dichlorobenzene is the most symmetrical of the three isomers ($D_{2}h$ symmetry). Its linear, symmetric shape allows molecules to pack very efficiently and tightly in the crystal lattice.
→ Stronger intermolecular interactions (London dispersion + dipole-dipole) per unit cell → higher lattice energy → higher melting point.

o-Dichlorobenzene and m-dichlorobenzene are less symmetrical molecules.
Their irregular shapes lead to less efficient packing in the crystal lattice → weaker intermolecular forces → lower lattice energy → lower melting point.

This is a general principle: among structural isomers, the most symmetrical (usually para) isomer has the highest melting point due to most efficient crystal packing.

m.p. order: p-dichlorobenzene (53°C) **>** o-dichlorobenzene (-17°C) **~** m-dichlorobenzene (-25°C).
(Note: o-isomer has a higher b.p. than p-isomer because it has a larger dipole moment.)

Answer: p-Dichlorobenzene is the most symmetrical isomer, allowing closest/most efficient packing in the crystal lattice → highest lattice energy → highest melting point. The o- and m-isomers are less symmetrical → less efficient packing → lower melting points.

Q19 How the following conversions can be carried out?
(i) Propene to propan-1-ol
(ii) Ethanol to but-1-yne
(iii) 1-Bromopropane to 2-bromopropane
(iv) Toluene to benzyl alcohol
(v) Benzene to 4-bromonitrobenzene
(vi) Benzyl alcohol to 2-phenylethanoic acid
(vii) Ethanol to propanenitrile
(viii) Aniline to chlorobenzene
(ix) 2-Chlorobutane to 3,4-dimethylhexane
(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane
(xi) Ethyl chloride to propanoic acid
(xii) But-1-ene to n-butyliodide
(xiii) 2-Chloropropane to 1-propanol
(xiv) Isopropyl alcohol to iodoform
(xv) Chlorobenzene to p-nitrophenol
(xvi) 2-Bromopropane to 1-bromopropane
(xvii) Chloroethane to butane
(xviii) Benzene to diphenyl
(xix) tert-Butyl bromide to isobutyl bromide
(xx) Aniline to phenylisocyanide

SOLUTION

(i) Propene to propan-1-ol (anti-Markovnikov hydration):
$CH_3CH=CH_2 + B_2H_6 \rightarrow CH_3CH_2CH_2\text{-}BR_2$ (hydroboration, boron to less substituted C)
$CH_3CH_2CH_2\text{-}BR_2 + H_2O_2/NaOH \rightarrow CH_3CH_2CH_2OH$ (oxidation; propan-1-ol)

(ii) Ethanol to but-1-yne: (same as $Q_6.11(i)$)
$EtOH \rightarrow EtCl\ (SOCl_2) \rightarrow CH_2=CH_2\ (KOH/alc) \rightarrow CH_2BrCH_2Br\ (Br_2)$
$\rightarrow HC\equiv CH\ (2KOH/alc) \rightarrow HC\equiv CNa\ (NaNH_2) \rightarrow HC\equiv C\text{-}CH_2CH_3\ (EtBr)$ [but-1-yne]

(iii) 1-Bromopropane to 2-bromopropane:
Step 1: $CH_3CH_2CH_2Br + KOH(alc) \rightarrow CH_3CH=CH_2 + KBr + H_2O$
Step 2: $CH_3CH=CH_2 + HBr \rightarrow CH_3CH(Br)CH_3$ (Markovnikov → 2-bromopropane)

(iv) Toluene to benzyl alcohol: (same as $Q_6.11(iv)$)
$C_6H_5CH_3 + Cl_2(hv) \rightarrow C_6H_5CH_2Cl$; then $+ NaOH(aq) \rightarrow C_6H_5CH_2OH$

(v) Benzene to 4-bromonitrobenzene:

Step 1: $C_6H_6 + Br_2/FeBr_3 \rightarrow C_6H_5Br + HBr$ (bromobenzene)
Step 2: $C_6H_5Br + HNO_3(conc)/H_2SO_4 \rightarrow p\text{-}BrC_6H_4NO_2 + o\text{-}BrC_6H_4NO_2$
(Br is ortho/para director; para product isolated as the major product)
Product: 1-Bromo-4-nitrobenzene (4-bromonitrobenzene)

(vi) Benzyl alcohol to 2-phenylethanoic acid (phenylacetic acid):
Step 1: $C_6H_5CH_2OH + HBr$ (or PBr_3) $\rightarrow C_6H_5CH_2Br$
Step 2: $C_6H_5CH_2Br + KCN \rightarrow C_6H_5CH_2CN + KBr$
Step 3: $C_6H_5CH_2CN + H_3O^+$ (or OH^-, then H^+) $\rightarrow C_6H_5CH_2COOH + NH_3$

(vii) Ethanol to propanenitrile:
Step 1: $CH_3CH_2OH + HBr \rightarrow CH_3CH_2Br$ (or use $PBr_3/SOCl_2 + KBr$)
Step 2: $CH_3CH_2Br + KCN \rightarrow CH_3CH_2CN + KBr$ (propanenitrile)

(viii) Aniline to chlorobenzene (Sandmeyer reaction):
Step 1: $C_6H_5NH_2 + NaNO_2 + HCl$ (0–5°C) $\rightarrow C_6H_5N^+{\equiv}NCl^- + NaCl + 2H_2O$ (diazotisation)
Step 2: $C_6H_5N^+{\equiv}NCl^- + CuCl/HCl \rightarrow C_6H_5Cl + N_2 + CuCl_2$ (Sandmeyer)

(ix) 2-Chlorobutane to 3,4-dimethylhexane:
Wurtz reaction using sodium metal with 2-chlorobutane:
$2\ CH_3CH(Cl)CH_2CH_3 + 2Na$ (dry ether) $\rightarrow CH_3CH(CH_2CH_3)\text{-}CH(CH_3)CH_2CH_3 + 2NaCl$
Product: 3,4-dimethylhexane (C-C coupling at C_2 of each molecule)

(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane:
$CH_2{=}C(CH_3)_2 + HCl \rightarrow (CH_3)_3CCl$
(Markovnikov addition: H adds to $=CH_2$, Cl to $=C(CH_3)_2$; tertiary carbocation intermediate)

(xi) Ethyl chloride to propanoic acid:
Step 1: $CH_3CH_2Cl + KCN \rightarrow CH_3CH_2CN + KCl$ (propanenitrile)
Step 2: $CH_3CH_2CN + H_2O + H^+$ (or $H_2O + OH^-$) $\rightarrow CH_3CH_2COOH + NH_3$ (hydrolysis to propanoic acid)

(xii) But-1-ene to n-butyl iodide (1-iodobutane):
Step 1: $CH_2{=}CHCH_2CH_3 + HBr$ (peroxide) $\rightarrow CH_3CH_2CH_2CH_2Br$ (anti-Markovnikov, 1-bromobutane)
Step 2: $CH_3CH_2CH_2CH_2Br + NaI$ (acetone) $\rightarrow CH_3CH_2CH_2CH_2I + NaBr$ (Finkelstein)

(xiii) 2-Chloropropane to 1-propanol:

Step 1: $CH_3CHClCH_3$ + KOH(alc) -> $CH_3CH=CH_2$ + KCl + H_2O
Step 2: $CH_3CH=CH_2$ + B_2H_6 -> $CH_3CH_2CH_2$-B; then H_2O_2/NaOH -> $CH_3CH_2CH_2OH$ (anti-Markovnikov hydration)

(xiv) Isopropyl alcohol to iodoform:
$(CH_3)_2CHOH$ + I_2 + NaOH -> CHI_3 (yellow ppt, iodoform) + CH_3COONa + NaI + H_2O
Mechanism: NaOI oxidises isopropanol to acetone (CH_3COCH_3); then iodination of CH_3 group three times, followed by cleavage.

(xv) Chlorobenzene to p-nitrophenol:
Step 1: C_6H_5Cl + HNO_3(conc)/H_2SO_4 -> p-$ClC_6H_4NO_2$ + o-$ClC_6H_4NO_2$ (nitration; separate para isomer)
Step 2: p-$ClC_6H_4NO_2$ + NaOH(aq, 300°C, high pressure) -> p-O_2N-C_6H_4-ONa + NaCl (nucleophilic aromatic substitution; NO_2 activates ring)
Step 3: p-O_2N-C_6H_4-ONa + HCl -> p-O_2N-C_6H_4-OH (p-nitrophenol)

(xvi) 2-Bromopropane to 1-bromopropane:
Step 1: $CH_3CHBrCH_3$ + KOH(alc) -> $CH_3CH=CH_2$ + KBr + H_2O
Step 2: $CH_3CH=CH_2$ + HBr (peroxide) -> $CH_3CH_2CH_2Br$ (anti-Markovnikov → 1-bromopropane)

(xvii) Chloroethane to butane:
2 CH_3CH_2Cl + 2Na (dry ether) -> $CH_3CH_2CH_2CH_3$ + 2NaCl (Wurtz reaction)

(xviii) Benzene to diphenyl (biphenyl):
Step 1: C_6H_6 + Br_2/$FeBr_3$ -> C_6H_5Br + HBr
Step 2: C_6H_5Br + Mg (dry ether) -> C_6H_5MgBr
Step 3: C_6H_5MgBr + C_6H_5Br -> C_6H_5-C_6H_5 + $MgBr_2$
OR Ullmann reaction: 2C_6H_5Br + Cu (heat) -> C_6H_5-C_6H_5 + $CuBr_2$

(xix) tert-Butyl bromide to isobutyl bromide:
Step 1: $(CH_3)_3CBr$ + KOH(alc) -> $(CH_3)_2C=CH_2$ + KBr + H_2O (E_2; isobutylene)
Step 2: $(CH_3)_2C=CH_2$ + HBr (peroxide) -> $(CH_3)_2CHCH_2Br$ (anti-Markovnikov; isobutyl bromide)

(xx) Aniline to phenylisocyanide (Carbylamine reaction):
$C_6H_5NH_2$ + $CHCl_3$ + 3KOH(alc) -> C_6H_5NC + 3KCl + 3H_2O
(Primary amine + $CHCl_3$ + alc. KOH → isocyanide; carbylamine reaction — test for 1° amines)

Answer: (i) Propene + B_2H_6, then H_2O_2/NaOH -> propan-1-ol; (ii) EtOH -> HC≡CH (via EtCl, ethylene, 1,2-dibromoethane) -> HC≡CNa -> but-1-yne; (iii) 1-BrPr + KOH(alc) -> propene + HBr(Mkv) -> 2-BrPr; (iv) $PhCH_3$ + Cl_2/hv -> $PhCH_2Cl$ + NaOH(aq) -> $PhCH_2OH$; (v) Benzene -> PhBr -> p-$BrC_6H_4NO_2$ (nitration); (vi) $PhCH_2OH$ -> $PhCH_2Br$ -> $PhCH_2CN$ -> $PhCH_2COOH$; (vii) EtOH -> EtBr + KCN -> EtCN; (viii) $PhNH_2$ -> diazonium salt + CuCl -> PhCl (Sandmeyer); (ix) 2×2-chlorobutane + 2Na -> 3,4-dimethylhexane; (x) isobutylene + HCl -> $(CH_3)_3CCl$; (xi) EtCl + KCN -> EtCN + H_3O^+ -> propanoic acid; (xii) But-1-ene + HBr/peroxide -> 1-BrBu + NaI/acetone -> 1-IBu; (xiii) 2-ClPr -> propene + B_2H_6 then H_2O_2 -> 1-PrOH; (xiv) iPrOH + I_2/NaOH -> CHI_3; (xv) PhCl -> p-$ClPhNO_2$ + NaOH(aq, high T) -> p-nitrophenol; (xvi) 2-BrPr -> propene + HBr/peroxide -> 1-BrPr; (xvii) 2 EtCl + 2Na -> butane (Wurtz); (xviii) Benzene -> PhBr -> PhMgBr + PhBr -> biphenyl; (xix) tBuBr + KOH(alc) -> isobutylene + HBr/peroxide -> isobutyl bromide; (xx) $PhNH_2$ + $CHCl_3$ + KOH(alc) -> PhNC (carbylamine)

Q20 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

SOLUTION

Aqueous KOH — nucleophilic substitution (SN_2) dominates:

In aqueous medium, water is present in large excess. OH^- (from KOH) acts primarily as a NUCLEOPHILE.

In the polar aqueous environment, ionic species are stabilised by solvation; the transition state for SN_2 (nucleophilic attack) is readily stabilised.

OH^- attacks the back side of the C-Cl bond (SN_2) → substitution:

R-Cl + OH^-(aq) -> R-OH + Cl^-

Product: alcohol.

Alcoholic KOH — elimination (E_2) dominates:

In alcoholic medium (e.g., ethanol as solvent), the concentration of water is negligible.

The OH^- ion (and ethoxide $C_2H_5O^-$ from the solvent) acts primarily as a BASE rather than a nucleophile in the relatively non-polar, less ionising medium.

The base abstracts a beta-H (hydrogen on the carbon adjacent to C-Cl), and Cl^- leaves simultaneously (E_2 mechanism):

R-CH_2-CH(Cl)-R' + OH^-(alc) -> R-CH=CH-R' + Cl^- + H_2O

Product: alkene (the more substituted alkene is major — Zaitsev's rule).

In summary: the choice of solvent and conditions controls whether OH^- acts as nucleophile (aqueous → substitution) or base (alcoholic → elimination).

Answer: With aqueous KOH: water as solvent makes OH^- a nucleophile; SN_2 substitution at C-X gives alcohol. With alcoholic KOH: in the less polar, non-ionising alcoholic medium, OH^- acts as a base; E_2 elimination of beta-H and Cl^- gives alkene (major product, Zaitsev's rule applies).

Q21 Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

SOLUTION

Deduction of structure (a):
(a) = primary C_4H_9Br. There are two primary C_4H_9Br isomers:
(A) 1-Bromobutane ($CH_3CH_2CH_2CH_2Br$)
(B) 1-Bromo-2-methylpropane [$(CH_3)_2CHCH_2Br$, isobutyl bromide]

Clue: (a) + Na gives C_8H_{18} DIFFERENT from n-octane (which n-BuBr + Na gives via Wurtz).
1-Bromobutane + 2Na → n-octane (C_8H_{18}). So (a) ≠ 1-bromobutane.
∴ (a) = 1-Bromo-2-methylpropane [$(CH_3)_2CHCH_2Br$].

Verification:
(a) + alcoholic KOH → (b):
$(CH_3)_2CHCH_2Br + KOH(alc) \rightarrow (CH_3)_2C=CH_2 + KBr + H_2O$
(b) = 2-methylpropene (isobutylene) ✓

(b) + HBr → (c):
$(CH_3)_2C=CH_2 + HBr \rightarrow (CH_3)_3CBr$ (Markovnikov addition)
(c) = 2-Bromo-2-methylpropane (tert-butyl bromide)
(c) is an isomer of (a) [both C_4H_9Br] ✓

(a) + Na → (d):
$2(CH_3)_2CHCH_2Br + 2Na \text{ (dry ether)} \rightarrow (CH_3)_2CHCH_2CH_2CH(CH_3)_2 + 2NaBr$
(d) = 2,5-dimethylhexane [C_8H_{18}, branched — different from n-octane] ✓

Summary of reactions:
Reaction 1: $(CH_3)_2CHCH_2Br + KOH(alc) \rightarrow (CH_3)_2C=CH_2 + KBr + H_2O$

Reaction 2: $(CH_3)_2C=CH_2 + HBr \rightarrow (CH_3)_3CBr$

Reaction 3: $2(CH_3)_2CHCH_2Br + 2Na \rightarrow (CH_3)_2CHCH_2CH_2CH(CH_3)_2 + 2NaBr$

Answer: (a) = $(CH_3)_2CHCH_2Br$ (1-bromo-2-methylpropane / isobutyl bromide). Reactions: (1) $(CH_3)_2CHCH_2Br + KOH(alc) \rightarrow (CH_3)_2C=CH_2$ [b] + KBr + H_2O; (2) $(CH_3)_2C=CH_2 + HBr \rightarrow (CH_3)_3CBr$ [c, 2-bromo-2-methylpropane]; (3) $2(CH_3)_2CHCH_2Br + 2Na \rightarrow (CH_3)_2CHCH_2CH_2CH(CH_3)_2$ [d, 2,5-dimethylhexane] + 2NaBr

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Q22 What happens when

(i) n-butyl chloride is treated with alcoholic KOH,

(ii) bromobenzene is treated with Mg in the presence of dry ether,

(iii) chlorobenzene is subjected to hydrolysis,

(iv) ethyl chloride is treated with aqueous KOH,

(v) methyl bromide is treated with sodium in the presence of dry ether,

(vi) methyl chloride is treated with KCN?

SOLUTION

(i) n-Butyl chloride + alcoholic KOH:

Alcoholic KOH causes E_2 elimination (dehydrohalogenation). H from C_2 and Cl from C_1 are eliminated.

$CH_3CH_2CH_2CH_2Cl + KOH(alc) \rightarrow CH_3CH_2CH=CH_2 + KCl + H_2O$

Product: but-1-ene

(ii) Bromobenzene + Mg in dry ether:

Formation of a Grignard reagent (aryl Grignard).

$C_6H_5Br + Mg$ (dry ether) $\rightarrow C_6H_5MgBr$

Product: phenylmagnesium bromide (Grignard reagent)

(iii) Chlorobenzene subjected to hydrolysis:

Aryl halides are very resistant to nucleophilic substitution under ordinary conditions because:

- Cl lone pairs conjugate with the ring (partial C-Cl double bond character) → C-Cl bond is stronger and shorter
- The sp^2 carbon does not permit easy back-side attack (SN_2 geometry unfavourable)
- SN_1 ionisation to aryl cation is very high energy

Hydrolysis requires very high temperature and pressure:

$C_6H_5Cl + NaOH(aq)$ --300°C, 300 atm--> $C_6H_5ONa + NaCl$

Acidification: $C_6H_5ONa + HCl \rightarrow C_6H_5OH + NaCl$
Product: phenol (Dow process)

(iv) Ethyl chloride + aqueous KOH:
Primary halide + NaOH/KOH (aqueous) → SN_2 substitution.
$CH_3CH_2Cl + KOH(aq) \rightarrow CH_3CH_2OH + KCl$
Product: ethanol

(v) Methyl bromide + Na in dry ether:
Wurtz reaction: coupling of two methyl groups.
$2CH_3Br + 2Na$ (dry ether) $\rightarrow CH_3\text{-}CH_3 + 2NaBr$
Product: ethane

(vi) Methyl chloride + KCN:
SN_2 reaction; CN^- attacks via the carbon (harder nucleophile in SN_2).
$CH_3Cl + KCN \rightarrow CH_3CN + KCl$
Product: acetonitrile (methyl cyanide / ethanenitrile)

Answer: (i) $CH_3CH_2CH_2CH_2Cl + KOH(alc) \rightarrow$ but-1-ene + KCl + H_2O (E_2 elimination); (ii) C_6H_5Br + Mg/dry ether $\rightarrow C_6H_5MgBr$ (phenylmagnesium bromide; Grignard reagent); (iii) $C_6H_5Cl + NaOH(aq, 300°C/300\ atm) \rightarrow C_6H_5ONa \rightarrow H^+ \rightarrow$ phenol (very harsh conditions needed; aryl halides are unreactive to normal hydrolysis); (iv) $CH_3CH_2Cl + KOH(aq) \rightarrow CH_3CH_2OH + KCl$ (SN_2 → ethanol); (v) $2CH_3Br + 2Na$/dry ether $\rightarrow CH_3CH_3 + 2NaBr$ (Wurtz → ethane); (vi) $CH_3Cl + KCN \rightarrow CH_3CN + KCl$ (SN_2 → acetonitrile)