Chapter 9: Hydrocarbons

Exercises — Exercises

Q1 How do you account for the formation of ethane during chlorination of methane?

SOLUTION

Chlorination of methane proceeds by a free radical chain mechanism with three stages: initiation, propagation, and termination.

Initiation: Cl-Cl bond undergoes homolysis in the presence of UV light to form two chlorine free radicals.
Cl_2 --(hv)--> 2 Cl·

Propagation: Cl· abstracts a hydrogen from CH_4 to form a methyl free radical (CH_3·).
CH_4 + Cl· -> CH_3· + HCl
CH_3· + Cl_2 -> CH_3Cl + Cl·

Termination: Two methyl free radicals combine with each other in one of the chain-terminating steps.
CH_3· + CH_3· -> CH_3-CH_3 (ethane)

This coupling of two methyl radicals is a termination step that consumes the radicals and produces ethane as a by-product. Although ethane is formed in small amounts, it is an inevitable product of the termination stage of the free radical mechanism.

Answer: Ethane forms in the termination step of the free radical chain mechanism: two methyl radicals (CH_3·) combine to give CH_3-CH_3.

Q2 Write IUPAC names of the following compounds: (a) $CH_3CH=C(CH_3)_2$ (b) $CH_2=CH-C\equiv C-CH_3$ (c) $CH_2=CH-CH=CH_2$ (buta-1,3-diene bond-line structure) (d) benzene ring bearing a $-CH_2-CH_2-CH=CH_2$ substituent (e) benzene ring with $-CH_3$ and -OH on adjacent (ortho) carbons (f) $CH_3(CH_2)_4CH[CH_2CH(CH_3)_2](CH_2)_3CH_3$ (g) $CH_3-CH=CH-CH_2-CH=CH-CH(C_2H_5)-CH_2-CH=CH_2$

SOLUTION

(a) $CH_3CH=C(CH_3)_2$:
Longest chain through the double bond: $C_1H_3-C_2H=C_3(CH_3)-C_4H_3$ = 4 carbons (but-2-ene).
Methyl substituent on C_3; lower locant for double bond from C_1 end.
Name: 2-methylbut-2-ene

(b) $CH_2=CH-C\equiv C-CH_3$:
5-carbon chain; double bond at C_1-C_2, triple bond at C_3-C_4.
Numbering from the end giving lower locants: $C_1H_2=C_2H-C_3\equiv C_4-C_5H_3$ -> locants 1,3.
Name: pent-1-en-3-yne

(c) $CH_2=CH-CH=CH_2$ (the bond-line structure is a 4-carbon chain with two double bonds):
Parent chain = 4 carbons (buta-); double bonds between C_1-C_2 and C_3-C_4.
Name: buta-1,3-diene

(d) Benzene ring with $-CH_2-CH_2-CH=CH_2$ substituent:
Parent = benzene; substituent = but-3-en-1-yl ($-CH_2CH_2CH=CH_2$, a 4-carbon chain with the double bond at C_3 counting from the ring).
Name: (but-3-en-1-yl)benzene (but-3-enylbenzene)

(e) Benzene ring with $-CH_3$ and -OH on adjacent carbons:
Parent = phenol (benzene + OH). The OH-bearing carbon is C_1; the methyl on the adjacent carbon is at C_2 (ortho).
Name: 2-methylphenol (o-cresol)

(f) $CH_3(CH_2)_4-CH[-CH_2CH(CH_3)_2]-(CH_2)_3CH_3$:
Main chain: 10 carbons (decane) with the branch at C_5 from the shorter end.
Branch: $-CH_2-CH(CH_3)_2$ = 2-methylpropyl group.
Name: 5-(2-methylpropyl)decane

(g) $CH_3-CH=CH-CH_2-CH=CH-CH(C_2H_5)-CH_2-CH=CH_2$:
10-carbon chain with an ethyl branch and three double bonds.

Number from the $CH=CH_2$ end (right) to get lower locants: double bonds at C_1, C_5, C_8; ethyl branch at C_4.
Name: 4-ethyldeca-1,5,8-triene

Answer: (a) 2-methylbut-2-ene (b) pent-1-en-3-yne (c) buta-1,3-diene (d) (but-3-en-1-yl)benzene (e) 2-methylphenol (o-cresol) (f) 5-(2-methylpropyl)decane (g) 4-ethyldeca-1,5,8-triene

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Q3 For the following compounds, write structural formulas and IUPAC names for all possible isomers having the number of double or triple bond as indicated: (a) C_4H_8 (one double bond) (b) C_5H_8 (one triple bond)

SOLUTION

(a) C_4H_8 with one double bond (alkene isomers):

1. But-1-ene: $CH_2=CH-CH_2-CH_3$
2. But-2-ene: $CH_3-CH=CH-CH_3$ (exists as cis and trans geometrical isomers)
3. 2-methylpropene: $CH_2=C(CH_3)-CH_3$

These are all the possible open-chain structural isomers of C_4H_8 with one C=C double bond.

(b) C_5H_8 with one triple bond (alkyne isomers):
Degree of unsaturation of C_5H_8 = (2×5+2-8)/2 = 2; one triple bond accounts for both units, so no rings or double bonds.

1. Pent-1-yne: $CH\equiv C-CH_2-CH_2-CH_3$
2. Pent-2-yne: $CH_3-C\equiv C-CH_2-CH_3$
3. 3-methylbut-1-yne: $CH\equiv C-CH(CH_3)-CH_3$

Answer: C_4H_8 (one double bond): but-1-ene, but-2-ene, 2-methylpropene. C_5H_8 (one triple bond): pent-1-yne, pent-2-yne, 3-methylbut-1-yne.

Q4 Write IUPAC names of the products obtained by the ozonolysis of the following compounds: (i) Pent-2-ene (ii) 3,4-Dimethylhept-3-ene (iii) 2-Ethylbut-1-ene (iv) 1-Phenylbut-1-ene

SOLUTION

Ozonolysis (O_3/Zn-H_2O) cleaves C=C double bond; each carbon of the double bond becomes a carbonyl group (aldehyde if it bore one H, ketone if it bore no H).

(i) Pent-2-ene: CH_3-CH=CH-CH_2-CH_3
Cleavage at C_2=C_3: CH_3CHO + CH_3CH_2CHO
Products: ethanal (CH_3CHO) + propanal (CH_3CH_2CHO)

(ii) 3,4-Dimethylhept-3-ene: CH_3CH_2-C(CH_3)=C(CH_3)-$CH_2CH_2CH_3$
Cleavage at C_3=C_4: CH_3CH_2-CO-CH_3 + CH_3-CO-$CH_2CH_2CH_3$
Products: butan-2-one ($CH_3CH_2COCH_3$) + pentan-2-one ($CH_3COCH_2CH_2CH_3$)

(iii) 2-Ethylbut-1-ene: CH_2=C(CH_2CH_3)-CH_2CH_3
Cleavage at C_1=C_2: HCHO + $(CH_3CH_2)CO(CH_2CH_3)$
Products: methanal (HCHO, formaldehyde) + pentan-3-one (CH_3CH_2-CO-CH_2CH_3)

(iv) 1-Phenylbut-1-ene: C_6H_5-CH=CH-CH_2CH_3
Cleavage at C_1=C_2: C_6H_5-CHO + CH_3CH_2-CHO
Products: benzaldehyde (C_6H_5CHO) + propanal (CH_3CH_2CHO)

Answer: (i) ethanal + propanal (ii) butan-2-one + pentan-2-one (iii) methanal + pentan-3-one (iv) benzaldehyde + propanal

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Q5 An alkene 'A' on ozonolysis gives a mixture of ethanal and pentan-3-one. Write structure and IUPAC name of 'A'.

SOLUTION

Ozonolysis cleaves C=C; each fragment becomes a carbonyl compound.

Ethanal (CH_3CHO) comes from the fragment: CH_3-CH= (the left portion of A).
Pentan-3-one (CH_3CH_2-CO-CH_2CH_3) comes from the fragment: =C(CH_2CH_3)$_2$ (a carbon bearing two ethyl groups).

Joining these fragments at the double bond:
A: CH_3-CH=C(CH_2CH_3)$_2$

IUPAC name: Longest chain through the double bond starting from the end with lower locant.
Chain: C_1H_3-C_2H=C_3-C_4H_2-C_5H_3 with -C_2H_5 substituent on C_3 = pent-2-ene backbone with 3-ethyl group.
Name: 3-ethylpent-2-ene

Answer: Alkene A: CH_3-CH=C(CH_2CH_3)$_2$, IUPAC name: 3-ethylpent-2-ene

Q6 An alkene A contains three C-C sigma bonds, eight C-H bonds and one C=C pi bond. 'A' on ozonolysis gives two moles of an aldehyde of molar mass 44 u. Write IUPAC name of 'A'.

SOLUTION

Step 1: Determine molecular formula of A from bond count.
Alkene with 3 C-C sigma bonds: CH_3-CH=CH-CH_3 (but-2-ene) has C-C sigma bonds: C_1-C_2, C_2-C_3(sigma part of double bond), C_3-C_4 = 3 sigma C-C bonds ✓
C-H bonds in but-2-ene (CH_3-CH=CH-CH_3): 3+1+1+3 = 8 ✓
C=C pi bonds = 1 ✓

Step 2: Confirm by ozonolysis.
Molar mass of aldehyde = 44 u; ethanal (CH_3CHO) = 12+3+12+1+16 = 44 u ✓
Ozonolysis of but-2-ene (CH_3-CH=CH-CH_3): gives CH_3CHO + CH_3CHO (2 moles ethanal, MM=44) ✓

Alkene A is but-2-ene: CH_3-CH=CH-CH_3
IUPAC name: but-2-ene

Answer: Alkene A is but-2-ene (CH_3-CH=CH-CH_3). Molar mass of ethanal (44 u) and 3 C-C sigma, 8 C-H, 1 C=C pi bonds confirm this identity.

Q7 Propanal and pentan-3-one are the ozonolysis products of an alkene. What is the structural formula of the alkene?

SOLUTION

Ozonolysis cleaves the C=C bond. Reconstruct alkene by joining the two carbonyl fragments at their carbonyl carbons with a double bond.

Propanal: CH_3CH_2-CHO -> carbonyl carbon of propanal bears one H -> left portion of alkene = CH_3CH_2-CH=
Pentan-3-one: CH_3CH_2-CO-CH_2CH_3 -> carbonyl carbon of pentan-3-one bears no H -> right portion = =C(CH_2CH_3)$_2$

Alkene: CH_3CH_2-CH=C(CH_2CH_3)$_2$

Verification: ozonolysis of CH_3CH_2-CH=C(CH_2CH_3)$_2$ -> CH_3CH_2-CHO (propanal) + (CH_3CH_2)$_2$C=O (pentan-3-one) ✓

IUPAC name: 3-ethylpent-2-ene

Answer: Structural formula: CH_3CH_2-CH=C(CH_2CH_3)$_2$ (IUPAC: 3-ethylpent-2-ene)

Q8 Write chemical equations for combustion reaction of the following hydrocarbons: (i) Butane (ii) Pentene (iii) Hexyne (iv) Toluene

SOLUTION

Complete combustion of a hydrocarbon CxHy: $C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + (y/2)H_2O$

(i) Butane (C_4H_{10}):
$C_4H_{10} + 13/2\ O_2 \rightarrow 4CO_2 + 5H_2O$
O balance: 13 needed (4×2 + 5×1); from 13/2 O_2 = 13 ✓

(ii) Pentene (C_5H_{10}):
$C_5H_{10} + 15/2\ O_2 \rightarrow 5CO_2 + 5H_2O$
O balance: 10+5 = 15; from 15/2 O_2 ✓

(iii) Hexyne (C_6H_{10}):
$C_6H_{10} + 17/2\ O_2 \rightarrow 6CO_2 + 5H_2O$
O balance: 12+5 = 17; from 17/2 O_2 ✓

(iv) Toluene (C_7H_8):
$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$
O balance: 14+4 = 18; from 9 O_2 ✓

Answer: (i) $C_4H_{10} + 13/2\ O_2 \rightarrow 4CO_2 + 5H_2O$ (ii) $C_5H_{10} + 15/2\ O_2 \rightarrow 5CO_2 + 5H_2O$ (iii) $C_6H_{10} + 17/2\ O_2 \rightarrow 6CO_2 + 5H_2O$ (iv) $C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$

Q9 Draw the cis and trans structures of hex-2-ene. Which isomer will have higher b.p. and why?

SOLUTION

Hex-2-ene: CH_3-CH=CH-CH_2-CH_2-CH_3 (double bond between C_2 and C_3).

cis-Hex-2-ene: Both CH_3 (C_1) and n-propyl (C_4-C_5-C_6) groups are on the SAME side of the double bond.
Structure: CH_3 and $CH_2CH_2CH_3$ on same side of C_2=C_3.

trans-Hex-2-ene: The two groups are on OPPOSITE sides of the double bond.
Structure: CH_3 and $CH_2CH_2CH_3$ on opposite sides of C_2=C_3.

Boiling point comparison:
cis isomer has a non-zero dipole moment (bond dipoles do not cancel); it also has a less symmetrical shape, leading to stronger van der Waals interactions and slightly larger contact surface.

trans isomer is more symmetrical, dipole moments of C-C bonds across the double bond cancel partially.

The cis isomer (cis-hex-2-ene) has a higher boiling point than the trans isomer because its unsymmetrical shape results in greater surface contact area and stronger intermolecular van der Waals forces.

Answer: cis-hex-2-ene has higher b.p. than trans-hex-2-ene due to greater polarity and larger surface contact area giving stronger van der Waals forces.

Q10 Why is benzene extraordinarily stable though it contains three double bonds?

SOLUTION

Benzene appears to have three C=C double bonds, but it is actually a resonance hybrid of two equivalent Kekulé structures. Its exceptional stability arises from:

1. Resonance (delocalisation): The six pi electrons are delocalised uniformly over all six carbon atoms forming a continuous pi electron cloud above and below the ring plane. This delocalisation lowers the energy of the molecule (resonance energy of benzene ≈ 150 kJ mol^{-1}).

2. Bond equivalence: All six C-C bonds are equal in length (139 pm, between single-bond 154 pm and double-bond 134 pm), confirming the delocalised structure rather than alternating single and double bonds.

3. Hückel aromaticity: Benzene satisfies the (4n+2) pi electron rule with n=1 (6 pi electrons), making it aromatic and conferring exceptional thermodynamic stability.

Because of this delocalisation, benzene prefers electrophilic substitution (which preserves aromaticity) over addition reactions (which would destroy aromaticity).

Answer: Benzene is extraordinarily stable due to delocalisation of six pi electrons over the entire ring (resonance energy ≈ 150 kJ mol^{-1}) and compliance with Hückel's (4n+2) rule with n=1 (6 pi electrons).

Q11 What are the necessary conditions for any system to be aromatic?

SOLUTION

A compound is aromatic if it satisfies ALL of the following conditions (Hückel's criteria):

1. Cyclic structure: The molecule must be a cyclic (ring) compound.

2. Planarity: The ring must be planar so that p-orbitals on all ring atoms can overlap continuously.

3. Complete conjugation: Every atom in the ring must have an unhybridised p-orbital (sp^2 or sp hybridised); the system must be fully conjugated with no sp^3 carbon interrupting the pi system.

4. Hückel's rule (4n+2 pi electrons): The ring must contain (4n+2) pi electrons, where n = 0, 1, 2, 3, ...
Examples: benzene 6 pi (n=1), naphthalene 10 pi (n=2), azulene 10 pi (n=2).

Answer: A system is aromatic if it is (i) cyclic, (ii) planar, (iii) completely conjugated (all ring atoms sp^2/sp hybridised), and (iv) contains (4n+2) pi electrons (Hückel's rule).

Q12 Explain why the following systems are not aromatic: (i) Cyclobutadiene (ii) A ring compound with an sp^3 carbon (CH_2 group in the ring) (iii) A bicyclic non-planar system

SOLUTION

(i) Cyclobutadiene (4-membered ring with 2 double bonds, 4 pi electrons):
Cyclobutadiene has 4 pi electrons. Applying Hückel's rule: 4n+2 requires n = 0 (2e), 1 (6e), 2 (10e), etc. The number 4 fits 4n with n=1, NOT 4n+2. Systems with 4n pi electrons are antiaromatic (less stable than an open-chain analogue). Hence cyclobutadiene is not aromatic.

(ii) Compound with a CH_2 ($-CH_2^-$) group in the ring:
The CH_2 group in the ring has an sp^3-hybridised carbon. An sp^3 carbon has no available p-orbital for overlap with the pi system. This breaks the conjugation around the ring; the pi electrons cannot be uniformly delocalised. Hence the system is not fully conjugated and violates the planarity/conjugation condition for aromaticity.

(iii) Non-planar or bicyclic system:
For aromaticity, the ring must be planar so that the p-orbitals on all ring atoms align for continuous sideways overlap. In a non-planar system, the p-orbitals are not parallel and effective pi-electron delocalisation is impossible. The system may also lack proper orbital overlap due to steric constraints. Hence it is not aromatic.

Answer: (i) Cyclobutadiene: 4 pi electrons (4n, antiaromatic, not 4n+2). (ii) sp^3 CH_2 in ring: breaks conjugation (no available p-orbital). (iii) Non-planar system: p-orbitals cannot overlap continuously.

Q13 How will you convert benzene into (i) p-nitrobromobenzene (ii) m-nitrochlorobenzene (iii) p-nitrotoluene (iv) acetophenone?

SOLUTION

(i) p-Nitrobromobenzene:
Step 1: Benzene + Br_2 (anhydrous $FeBr_3$ or $AlCl_3$) -> bromobenzene
Step 2: Bromobenzene + HNO_3/H_2SO_4 (conc.) -> p-nitrobromobenzene
Bromine is an o/p director; nitration occurs preferentially at para position (major product, separated from ortho). This sequence ensures the final NO_2 is directed para to Br.

(ii) m-Nitrochlorobenzene:
For meta orientation, introduce a meta-director first (NO_2).
Step 1: Benzene + HNO_3/H_2SO_4 -> nitrobenzene
Step 2: Nitrobenzene + Cl_2 (anhydrous $AlCl_3$) -> m-nitrochlorobenzene
NO_2 is a meta director; Cl_2 is directed to the meta position. ✓

(iii) p-Nitrotoluene:
CH_3 is an o/p director, so introduce it first.
Step 1: Benzene + CH_3Cl (anhydrous $AlCl_3$, Friedel-Crafts alkylation) -> toluene
Step 2: Toluene + HNO_3/H_2SO_4 -> p-nitrotoluene (major) + o-nitrotoluene (minor); separate para product.

(iv) Acetophenone (C_6H_5-CO-CH_3, phenyl methyl ketone):
Friedel-Crafts acylation:
Benzene + CH_3COCl (anhydrous $AlCl_3$) -> C_6H_5-CO-CH_3 (acetophenone) + HCl

Answer: (i) Benzene -> $Br_2/AlCl_3$ -> bromobenzene -> HNO_3/H_2SO_4 -> p-nitrobromobenzene. (ii) Benzene -> HNO_3/H_2SO_4 -> nitrobenzene -> $Cl_2/AlCl_3$ -> m-nitrochlorobenzene. (iii) Benzene -> $CH_3Cl/AlCl_3$ -> toluene -> HNO_3/H_2SO_4 -> p-nitrotoluene. (iv) Benzene -> $CH_3COCl/AlCl_3$ -> acetophenone.

Q14 In the alkane $H_3C\text{-}CH_2\text{-}C(CH_3)_2\text{-}CH_2\text{-}CH(CH_3)_2$, identify primary, secondary, tertiary and quaternary carbon atoms and give the number of H atoms bonded to each one.

SOLUTION

Label carbons as C_1 through C_7 (main chain) with substituents:

Structure: $H_3C(C_1)$ - $CH_2(C_2)$ - $C(CH_3)_2(C_3)$ - $CH_2(C_4)$ - $CH(CH_3)(C_5)$ - $CH_3(C_6)$ with one more CH_3 on C_5

Breakdown:
C_1 (H_3C^-): bonded to only C_2 -> primary carbon; H atoms = 3
C_2 ($-CH_2^-$): bonded to C_1 and C_3 -> secondary carbon; H atoms = 2
C_3 ($-C(CH_3)^{2-}$): bonded to C_2, two CH_3 groups, and C_4 -> quaternary carbon (no H); H atoms = 0
Two CH_3 groups on C_3: each bonded to C_3 only -> primary carbons; H atoms = 3 each
C_4 ($-CH_2^-$): bonded to C_3 and C_5 -> secondary carbon; H atoms = 2
C_5 ($-CH^-$): bonded to C_4 and two CH_3 groups -> tertiary carbon; H atoms = 1
Two CH_3 groups on C_5: each bonded to C_5 only -> primary carbons; H atoms = 3 each

Answer: C_1 = primary (3H); C_2 = secondary (2H); C_3 = quaternary (0H); CH_3 groups on C_3 = primary (3H each); C_4 = secondary (2H); C_5 = tertiary (1H); CH_3 groups on C_5 = primary (3H each).

Q15 What effect does branching of an alkane chain have on its boiling point?

SOLUTION

Branching decreases the boiling point of an alkane.

Reason:
As the degree of branching increases, the alkane molecule becomes more compact and more spherical in shape. A spherical molecule has a smaller surface area compared to a linear (unbranched) molecule of the same molecular formula.

Boiling point depends on intermolecular van der Waals forces, which in turn depend on surface area (and molecular mass). A smaller surface area means less contact between adjacent molecules, weaker van der Waals forces, and therefore a lower boiling point.

Example: n-pentane (b.p. 309.1 K) > isopentane/2-methylbutane (b.p. 301.0 K) > neopentane/2,2-dimethylpropane (b.p. 282.6 K). The most branched isomer (neopentane) has the lowest b.p.

Answer: Branching decreases boiling point: the more branched the alkane, the more spherical and compact the molecule, the smaller its surface area, the weaker the van der Waals forces, and the lower the boiling point.

Q16 Addition of HBr to propene yields 2-bromopropane, while in the presence of benzoyl peroxide, the same reaction yields 1-bromopropane. Explain and give mechanism.

SOLUTION

Without peroxide (Markovnikov addition):
H^+ (electrophile from HBr) adds to C_1 (less substituted carbon) of propene CH_3-CH=CH_2, forming a more stable secondary carbocation (CH_3-CH^+-CH_3) at C_2.
Br^- then attacks C_2 -> 2-bromopropane (CH_3-CHBr-CH_3) as major product.
This follows Markovnikov's rule: H adds to C with more H atoms.

Mechanism without peroxide (ionic):
Step 1: H^+ + CH_3-CH=CH_2 -> CH_3-CH^+-CH_3 (2° carbocation, more stable) [major]
Step 2: CH_3-CH^+-CH_3 + Br^- -> CH_3-CHBr-CH_3 (2-bromopropane)

With benzoyl peroxide (anti-Markovnikov / Kharash effect):
Peroxide initiates a FREE RADICAL chain mechanism. Bromine radical (Br·) is the species that adds to the double bond, not H^+.
Br· adds to C_1 (less sterically hindered) generating a more stable SECONDARY free radical at C_2.
Then H· is abstracted from HBr, giving 1-bromopropane at C_1.

Mechanism with peroxide (free radical):
Initiation: $(C_6H_5CO)_2O_2$ -> 2 $C_6H_5CO\cdot$ -> $C_6H_5\cdot$ + CO_2 (then $C_6H_5\cdot$ + HBr -> C_6H_6 + Br·)
Propagation Step 1: Br· + CH_3-CH=CH_2 -> CH_3-CH·-CH_2Br (2° radical, more stable) [major]
Propagation Step 2: CH_3-CH·-CH_2Br + HBr -> CH_3-CH_2-CH_2Br + Br·
Product: 1-bromopropane (anti-Markovnikov addition)

Note: Peroxide effect is observed only with HBr, NOT with HCl or HI.

Answer: Without peroxide: Markovnikov addition (via secondary carbocation) -> 2-bromopropane. With benzoyl peroxide: free radical addition (Br· adds to C_1 forming more stable 2° radical) -> 1-bromopropane (anti-Markovnikov).

Q17 Write down the products of ozonolysis of 1,2-dimethylbenzene (o-xylene). How does the result support Kekulé structure for benzene?

SOLUTION

1,2-Dimethylbenzene (o-xylene) has two CH_3 groups on adjacent (1,2) carbons of the benzene ring.

Kekulé structure I of o-xylene (double bond between C_1-C_2, i.e., between the two CH_3-bearing carbons):
Ozonolysis cleaves C_1=C_2 bond -> gives CH_3CO-$COCH_3$ fragment (a diketone, glyoxal disubstituted).
Cleavage of remaining double bonds (C_3=C_4 and C_5=C_6) -> gives -CHO groups.
Overall products: methylglyoxal (CH_3-CO-CHO) [x_2] + glyoxal (OHC-CHO) [x_1]

Kekulé structure II of o-xylene (single bond between C_1-C_2, double bonds at C_2=C_3 and C_6=C_1):
Ozonolysis at C_2=C_3 -> CH_3CHO (from C_2-CH_3 side) and CHO fragment
Cleavage at remaining double bonds gives: glyoxal (OHC-CHO) and methylglyoxal (CH_3-CO-CHO)
Overall products are the same: methylglyoxal and glyoxal.

Support for Kekulé structure:
Both Kekulé structures of o-xylene (I and II) give IDENTICAL ozonolysis products (methylglyoxal and glyoxal). This is possible only if the two structures are rapidly interconverting resonance forms that together describe a single symmetric molecule — supporting the Kekulé resonance model for benzene.

Answer: Ozonolysis of o-xylene gives glyoxal (OHC-CHO) and methylglyoxal (CH_3-CO-CHO). Both Kekulé structures give the same products, supporting the concept that benzene is a resonance hybrid of the two Kekulé structures.

Q18 Arrange benzene, n-hexane and ethyne in decreasing order of acidic behaviour. Also give reason for this behaviour.

SOLUTION

Acidic character of a C-H bond depends on the s-character of the carbon atom involved: greater s-character -> greater electronegativity of carbon -> electrons held closer to C -> C-H bond more polar -> easier to release H^+ -> stronger acid.

s-characters of hybridised carbons:
sp (alkyne, ethyne): 50% s-character
sp^2 (aromatic, benzene): 33.3% s-character
sp^3 (alkane, n-hexane): 25% s-character

Decreasing order of acidity:
Ethyne (HC≡CH, sp carbon) > Benzene (C_6H_6, sp^2 carbon) > n-Hexane (C_6H_{14}, sp^3 carbon)

pKa values (approximate): ethyne ≈ 25, benzene ≈ 43, hexane ≈ 50 — confirming ethyne is the strongest acid of the three.

Answer: Decreasing acidity: Ethyne > Benzene > n-Hexane. Reason: s-character of C is sp (50%) > sp^2 (33%) > sp^3 (25%); higher s-character = more electronegative C = more acidic C-H.

Q19 Why does benzene undergo electrophilic substitution reactions easily and nucleophilic substitutions with difficulty?

SOLUTION

Benzene has a continuous pi electron cloud (6 delocalised electrons) above and below the ring plane. This makes the ring electron-rich.

Electrophilic substitution is easy because:
Electrophiles (E^+, electron-seeking species) are attracted to the electron-rich pi cloud of benzene. The pi electrons of the ring attack the electrophile, forming a sigma complex (arenium ion), and the aromaticity is restored when a proton is lost. The driving force is the re-establishment of the stable aromatic system.

Nucleophilic substitution is difficult because:
Nucleophiles (Nu^-, electron-rich species) are repelled by the electron-rich pi cloud of benzene. For a nucleophile to attack benzene, it must overcome the repulsion of the high electron density, requiring very harsh conditions. Additionally, loss of

the leaving group would require generating a carbanion intermediate, which is extremely unfavourable.

Hence benzene strongly prefers electrophilic substitution over nucleophilic substitution under normal conditions.

Answer: Benzene has a high electron density (pi cloud) that attracts electrophiles but repels nucleophiles. Electrophilic substitution preserves aromaticity (strong thermodynamic driving force); nucleophilic attack on the electron-rich ring is energetically unfavourable.

Q20 How would you convert the following compounds into benzene? (i) Ethyne (ii) Ethene (iii) Hexane

SOLUTION

(i) Ethyne to benzene:
Cyclic trimerisation of ethyne: 3 HC≡CH --(red-hot iron tube / V_2O_5, 873 K)--> C_6H_6 (benzene)
Three molecules of ethyne undergo cyclic polymerisation to form benzene.

(ii) Ethene to benzene:
Step 1: Dehydrogenate ethene to ethyne.
3 CH_2=CH_2 --(dehydrogenation, catalyst, high temp)--> 3 HC≡CH + 3 H_2
Step 2: Cyclic trimerisation of ethyne as in (i) -> benzene.
Overall: 3 CH_2=CH_2 -> C_6H_6 + 3 H_2

(iii) Hexane to benzene:
Dehydrocyclisation (catalytic reforming) of n-hexane:
n-C_6H_{14} --(Pt or Cr_2O_3/Al_2O_3, 773 K, high pressure)--> C_6H_6 + 4 H_2
n-Hexane loses four molecules of H_2 and cyclises to form benzene.

Answer: (i) 3 HC≡CH --(873 K, Fe/V_2O_5)--> C_6H_6 (cyclic trimerisation). (ii) 3 CH_2=CH_2 -> 3 HC≡CH -> C_6H_6. (iii) n-C_6H_{14} --(Pt, 773 K)--> C_6H_6 + 4 H_2 (dehydrocyclisation).

Q21 Write structures of all the alkenes which on hydrogenation give 2-methylbutane.

SOLUTION

2-Methylbutane: $(CH_3)_2CH\text{-}CH_2\text{-}CH_3$ (C_5H_{12}, i-pentane)

Any C_5H_{10} alkene that on addition of H_2 yields 2-methylbutane must have the same carbon skeleton (with the branch at C_2) and differ only in the position of the double bond.

Possible alkenes:

1. 2-Methylbut-1-ene: $CH_2=C(CH_3)\text{-}CH_2\text{-}CH_3$
   -> H_2 -> $CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}CH_3$ = 2-methylbutane ✓
2. 2-Methylbut-2-ene: $CH_3\text{-}C(CH_3)=CH\text{-}CH_3$
   -> H_2 -> $CH_3\text{-}CH(CH_3)\text{-}CH_2\text{-}CH_3$ = 2-methylbutane ✓
3. 3-Methylbut-1-ene: $CH_2=CH\text{-}CH(CH_3)\text{-}CH_3$
   -> H_2 -> $CH_3\text{-}CH_2\text{-}CH(CH_3)\text{-}CH_3$ = 2-methylbutane ✓

Answer: Three alkenes: (1) 2-methylbut-1-ene [$CH_2=C(CH_3)\text{-}CH_2\text{-}CH_3$], (2) 2-methylbut-2-ene [$CH_3\text{-}C(CH_3)=CH\text{-}CH_3$], (3) 3-methylbut-1-ene [$CH_2=CH\text{-}CH(CH_3)\text{-}CH_3$].

Q22 Arrange the following set of compounds in order of their decreasing relative reactivity with an electrophile E^+: (a) Chlorobenzene, 2,4-dinitrochlorobenzene, p-nitrochlorobenzene (b) Toluene, p-nitrotoluene, p-dinitrobenzene

SOLUTION

Reactivity with an electrophile E^+ decreases as the electron density on the ring decreases. Electron-withdrawing groups (deactivators like NO_2) decrease reactivity; electron-donating groups (activators like CH_3) increase reactivity.

(a) Chlorobenzene, 2,4-dinitrochlorobenzene, p-nitrochlorobenzene:
Cl is a weakly deactivating substituent (o/p director but inductive -I effect).
NO_2 is a strongly deactivating substituent (-M effect, pulls electron density out of ring).
Chlorobenzene: only one weakly deactivating Cl -> most reactive.
p-Nitrochlorobenzene: one Cl + one NO_2 -> moderately deactivated.
2,4-Dinitrochlorobenzene: one Cl + two NO_2 groups -> most strongly deactivated, least reactive.

Decreasing reactivity: Chlorobenzene > p-nitrochlorobenzene > 2,4-dinitrochlorobenzene

(b) Toluene, p-nitrotoluene, p-dinitrobenzene:
Toluene: CH_3 is an activating (electron-donating) group -> most reactive.
p-Nitrotoluene: CH_3 (activating) + NO_2 (deactivating) -> less reactive than toluene.
p-Dinitrobenzene: two strongly deactivating NO_2 groups -> least reactive.
Decreasing reactivity: Toluene > p-nitrotoluene > p-dinitrobenzene

Answer: (a) Chlorobenzene > p-nitrochlorobenzene > 2,4-dinitrochlorobenzene. (b) Toluene > p-nitrotoluene > p-dinitrobenzene.

Q23 Out of benzene, m-dinitrobenzene and toluene which will undergo nitration most easily and why?

SOLUTION

Nitration is an electrophilic substitution reaction. The ease of nitration depends on the electron density of the benzene ring.

Toluene: The CH_3 (methyl) group is an electron-donating group (EDG) through hyperconjugation and inductive effect. It increases the electron density of the ring (especially at ortho and para positions), making it more reactive towards electrophilic substitution.

Benzene: No substituent; intermediate reactivity.

m-Dinitrobenzene: Two NO_2 groups are strongly electron-withdrawing groups (EWG) through -M effect, which greatly decreases the electron density of the ring, making electrophilic attack very difficult.

Order of ease of nitration: Toluene > Benzene > m-Dinitrobenzene

Toluene undergoes nitration most easily because the CH_3 group activates the ring by donating electron density.

Answer: Toluene undergoes nitration most easily. CH_3 is an electron-donating group that activates the ring. m-Dinitrobenzene (two deactivating NO_2 groups) undergoes nitration least easily.

Q24 Suggest the name of a Lewis acid other than anhydrous aluminium chloride which can be used during ethylation of benzene.

SOLUTION

Friedel-Crafts ethylation of benzene: $C_6H_6 + C_2H_5Cl$ --(Lewis acid)--> $C_6H_5\text{-}C_2H_5 + HCl$

The Lewis acid generates the carbocation electrophile (C_2H^{5+}) from the alkyl halide by accepting the halide.

Lewis acids that can serve this purpose (other than $AlCl_3$):
1. Anhydrous ferric chloride ($FeCl_3$) — commonly used
2. Boron trifluoride (BF_3)
3. Stannic chloride ($SnCl_4$)
4. Zinc chloride ($ZnCl_2$)

Any of these anhydrous Lewis acids can catalyse Friedel-Crafts alkylation.

Answer: Anhydrous $FeCl_3$ (ferric chloride), BF_3 (boron trifluoride), $SnCl_4$ (stannic chloride), or $ZnCl_2$ (zinc chloride) can be used as Lewis acid catalysts for ethylation of benzene.

Q25 Why is Wurtz reaction not preferred for the preparation of alkanes containing odd number of carbon atoms? Illustrate your answer by taking one example.

SOLUTION

Wurtz reaction: 2 RX + 2 Na -> R-R + 2 NaX
When the same alkyl halide is used, it gives a symmetric alkane with even number of carbons (double the chain length of the starting halide).

For an alkane with an ODD number of carbons, we need to use TWO DIFFERENT alkyl halides (R_1X and R_2X).
However, the reaction cannot be controlled to give only $R_1\text{-}R_2$:
Three coupling products form:
(a) $R_1\text{-}R_1$ (from $R_1X + R_1X$)
(b) $R_1\text{-}R_2$ (desired product)
(c) $R_2\text{-}R_2$ (from $R_2X + R_2X$)

Example: Preparation of propane (C_3, odd) from CH_3Br and C_2H_5Br:
$CH_3Br + Na + C_2H_5Br$ -> $CH_3\text{-}C_2H_5$ (propane) + $CH_3\text{-}CH_3$ (ethane) + $C_2H_5\text{-}C_2H_5$ (butane) + 2 NaBr

A mixture of ethane, propane, and butane is obtained; propane cannot be isolated in pure form in good yield.

Therefore, Wurtz reaction is not preferred for odd-carbon alkanes because it inevitably yields a mixture of three different alkanes and the desired product cannot be obtained in a satisfactory yield.

Answer: Wurtz reaction with two different halides gives three products (R_1-R_1, R_1-R_2, R_2-R_2) in a statistical mixture. For odd-carbon alkanes (requiring two different halides), the desired alkane cannot be isolated in good yield. Example: CH_3Br + C_2H_5Br -> mixture of ethane, propane, and butane.