Chapter 9: Amines

Exercises — Exercises

Q1 Write IUPAC names of the following compounds and classify them into primary, secondary and tertiary amines: (i) $(CH_3)_2CHNH_2$ (ii) $CH_3(CH_2)_2NH_2$ (iii) $CH_3NHCH(CH_3)_2$ (iv) $(CH_3)_3CNH_2$ (v) $C_6H_5NHCH_3$ (vi) $(CH_3CH_2)_2NCH_3$ (vii) m-$BrC_6H_4NH_2$

SOLUTION

(i) $(CH_3)_2CHNH_2$ — Propan-2-amine (1°)
(ii) $CH_3(CH_2)_2NH_2$ — Propan-1-amine (1°)
(iii) $CH_3NHCH(CH_3)_2$ — N-Methylpropan-2-amine (2°)
(iv) $(CH_3)_3CNH_2$ — 2-Methylpropan-2-amine (1°)
(v) $C_6H_5NHCH_3$ — N-Methylaniline / N-methylbenzenamine (2°)
(vi) $(CH_3CH_2)_2NCH_3$ — N-Ethyl-N-methylethanamine (3°)
(vii) m-$BrC_6H_4NH_2$ — 3-Bromoaniline / 3-bromobenzenamine (1°)

Answer: (i) propan-2-amine, 1° (ii) propan-1-amine, 1° (iii) N-methylpropan-2-amine, 2° (iv) 2-methylpropan-2-amine, 1° (v) N-methylaniline, 2° (vi) N-ethyl-N-methylethanamine, 3° (vii) 3-bromoaniline, 1°

Q2 Give one chemical test to distinguish between the following pairs of compounds: (i) Methylamine and dimethylamine (ii) Secondary and tertiary amines (iii) Ethylamine and aniline (iv) Aniline and benzylamine (v) Aniline and N-methylaniline.

SOLUTION

(i) Methylamine (1°) and dimethylamine (2°): Carbylamine test. Methylamine (1°) + $CHCl_3$ + alc. KOH gives foul-smelling methyl isocyanide; dimethylamine (2°) gives no such smell.
(ii) 2° and 3° amines: Hinsberg's test with benzenesulphonyl chloride. A 2° amine gives an N,N-disubstituted sulphonamide insoluble in KOH; a 3° amine does not react.
(iii) Ethylamine and aniline: Add to bromine water. Aniline gives a white precipitate (2,4,6-tribromoaniline); ethylamine does not. (Also, aniline gives an orange azo dye in the diazotisation-coupling test; ethylamine evolves N_2.)
(iv) Aniline and benzylamine: Diazotisation. Aniline (aromatic 1° amine) with HNO_2

at 273-278 K gives a stable diazonium salt (dye test positive); benzylamine (aliphatic 1° amine) evolves N_2 gas with effervescence.

(v) Aniline (1°) and N-methylaniline (2°): Hinsberg's test — aniline gives a sulphonamide soluble in KOH (acidic N-H); N-methylaniline gives one insoluble in KOH.

Answer: (i) carbylamine test (ii) Hinsberg's test (iii) bromine water / dye test (iv) nitrous acid (stable diazonium vs N_2) (v) Hinsberg's test

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Q3 Account for the following: (i) pKb of aniline is more than that of methylamine. (ii) Ethylamine is soluble in water whereas aniline is not. (iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide. (iv) Although amino group is o- and p-directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of m-nitroaniline. (v) Aniline does not undergo Friedel-Crafts reaction. (vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines. (vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

SOLUTION

(i) In aniline the nitrogen lone pair is delocalised into the benzene ring by resonance, so it is less available for protonation — aniline is a weaker base, hence higher pKb. In methylamine the +I effect of $-CH_3$ raises electron density on N, making it a stronger base (lower pKb).

(ii) Ethylamine forms hydrogen bonds with water and its small size lets it dissolve; aniline has a large hydrophobic phenyl group that outweighs H-bonding, so it is only slightly soluble.

(iii) Methylamine is a base: $CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$. The OH^- produced precipitates Fe^{3+} as hydrated ferric oxide, $Fe(OH)_3$ ($2Fe^{3+} + 6OH^- \rightarrow 2Fe(OH)_3$).

(iv) In the strongly acidic nitrating mixture aniline is largely protonated to the anilinium ion ($-NH_3^+$), which is deactivating and meta-directing; this gives a substantial amount (~47%) of m-nitroaniline alongside the o-/p-products from unprotonated aniline.

(v) The nitrogen lone pair of aniline reacts with the Lewis acid $AlCl_3$ to form a salt; the resulting positively charged nitrogen is strongly deactivating, and aniline also forms a complex with $AlCl_3$, so Friedel-Crafts reaction does not occur.

(vi) The aryl diazonium ion is stabilised by dispersal (resonance) of the positive charge into the benzene ring, so it is stable near 273-278 K; the aliphatic

diazonium ion has no such stabilisation and decomposes at once, evolving N_2.

(vii) Gabriel phthalimide synthesis gives exclusively pure primary amines (the alkyl group is introduced once on the phthalimide nitrogen and then set free on hydrolysis), avoiding the mixture of 1°, 2°, 3° and quaternary products formed by ammonolysis.

Answer: (i) lone-pair resonance into the ring weakens aniline's basicity (ii) hydrophobic phenyl group lowers aniline's solubility (iii) OH^- from the base precipitates $Fe(OH)_3$ (iv) protonated anilinium ion is meta-directing (v) N lone pair complexes $AlCl_3$ / deactivates the ring (vi) resonance stabilisation of the aryl diazonium ion (vii) gives only pure 1° amines

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Q4 Arrange the following: (i) In decreasing order of the pKb values: $C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$. (ii) In increasing order of basic strength: $C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2. (iii) In increasing order of basic strength: (a) Aniline, p-nitroaniline and p-toluidine; (b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$. (iv) In decreasing order of basic strength in gas phase: $C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3. (v) In increasing order of boiling point: C_2H_5OH, $(CH_3)_2NH$, $C_2H_5NH_2$. (vi) In increasing order of solubility in water: $C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

SOLUTION

(i) Decreasing pKb (weakest base first): $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$.

(ii) Increasing basic strength: $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2 < (C_2H_5)_2NH$.

(iii)(a) Increasing basic strength: p-nitroaniline < aniline < p-toluidine (the $-NO_2$ group is electron-withdrawing, $-CH_3$ is electron-donating).

(iii)(b) Increasing basic strength: $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$ (in benzylamine the $-NH_2$ is not attached to the ring, so its lone pair is fully available).

(iv) In the gas phase only the +I (inductive) effect operates, so basicity increases with the number of alkyl groups: $(C_2H_5)_3N > (C_2H_5)_2NH > C_2H_5NH_2 > NH_3$.

(v) Increasing boiling point: $(CH_3)_2NH < C_2H_5NH_2 < C_2H_5OH$. O-H bonds hydrogen-bond more strongly than N-H, and a 1° amine H-bonds more than a 2° amine.

(vi) Increasing solubility in water: $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$.

Answer: (i) $C_6H_5NH_2$ > $C_6H_5NHCH_3$ > $C_2H_5NH_2$ > $(C_2H_5)_2NH$ (ii) $C_6H_5NH_2$ < $C_6H_5N(CH_3)_2$ < CH_3NH_2 < $(C_2H_5)_2NH$ (iii)(a) p-nitroaniline < aniline < p-toluidine; (b) $C_6H_5NH_2$ < $C_6H_5NHCH_3$ < $C_6H_5CH_2NH_2$ (iv) $(C_2H_5)_3N$ > $(C_2H_5)_2NH$ > $C_2H_5NH_2$ > NH_3 (v) $(CH_3)_2NH$ < $C_2H_5NH_2$ < C_2H_5OH (vi) $C_6H_5NH_2$ < $(C_2H_5)_2NH$ < $C_2H_5NH_2$

Q5 How will you convert: (i) Ethanoic acid into methanamine (ii) Hexanenitrile into 1-aminopentane (iii) Methanol to ethanoic acid (iv) Ethanamine into methanamine (v) Ethanoic acid into propanoic acid (vi) Methanamine into ethanamine (vii) Nitromethane into dimethylamine (viii) Propanoic acid into ethanoic acid?

SOLUTION

(i) CH_3COOH -> (NH_3, heat) CH_3CONH_2 -> (Br_2 + KOH, Hofmann bromamide) CH_3NH_2 (methanamine).

(ii) $CH_3(CH_2)_4CN$ -> (H_3O^+ hydrolysis) $CH_3(CH_2)_4COOH$ -> (NH_3, heat) $CH_3(CH_2)_4CONH_2$ -> (Br_2 + KOH, Hofmann) $CH_3(CH_2)_3CH_2NH_2$ = pentan-1-amine (1-aminopentane).

(iii) CH_3OH -> (HBr / red P) CH_3Br -> (alc. KCN) CH_3CN -> (H_3O^+ hydrolysis) CH_3COOH (ethanoic acid).

(iv) $C_2H_5NH_2$ -> (HNO_2) C_2H_5OH -> ([O]) CH_3COOH -> (NH_3, heat) CH_3CONH_2 -> (Br_2 + KOH, Hofmann) CH_3NH_2 (methanamine).

(v) CH_3COOH -> ($LiAlH_4$) C_2H_5OH -> (PBr_3) C_2H_5Br -> (alc. KCN) C_2H_5CN -> (H_3O^+ hydrolysis) C_2H_5COOH (propanoic acid).

(vi) CH_3NH_2 -> (HNO_2) CH_3OH -> (HBr) CH_3Br -> (alc. KCN) CH_3CN -> ($LiAlH_4$) $C_2H_5NH_2$ (ethanamine).

(vii) CH_3NO_2 -> (Sn/HCl reduction) CH_3NH_2; then CH_3NH_2 + CH_3I (controlled) -> $(CH_3)_2NH$ (dimethylamine) [remove excess by fractional distillation].

(viii) C_2H_5COOH -> (NH_3, heat) $C_2H_5CONH_2$ -> (Br_2 + KOH, Hofmann) $C_2H_5NH_2$ -> (HNO_2) C_2H_5OH -> ([O]) CH_3COOH (ethanoic acid).

Answer: (i)-(viii) achieved by ascending (nitrile route: -X/KCN then hydrolysis, adds 1 C) or descending (Hofmann bromamide on the amide, removes 1 C) the series, plus HNO_2 on 1° amines to give the alcohol

Q6 Describe a method for the identification of primary, secondary and tertiary amines. Also write chemical equations of the reactions involved.

SOLUTION

Hinsberg's test — treat the amine with benzenesulphonyl chloride ($C_6H_5SO_2Cl$) in the presence of aqueous KOH.

Primary amine: forms an N-alkyl benzenesulphonamide with an acidic N-H, which dissolves in KOH.

$C_6H_5SO_2Cl + H_2N\text{-}R \rightarrow C_6H_5SO_2NHR$ (soluble in KOH -> $C_6H_5SO_2NR^- K^+$).

Secondary amine: forms an N,N-dialkyl benzenesulphonamide with no N-H, insoluble in KOH.

$C_6H_5SO_2Cl + R_2NH \rightarrow C_6H_5SO_2NR_2$ (insoluble in KOH).

Tertiary amine: has no replaceable hydrogen on N, so it does not react with benzenesulphonyl chloride.

Answer: Hinsberg's test: 1° amine gives a KOH-soluble sulphonamide, 2° amine gives a KOH-insoluble sulphonamide, 3° amine does not react

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Q7 Write short notes on the following: (i) Carbylamine reaction (ii) Diazotisation (iii) Hofmann's bromamide reaction (iv) Coupling reaction (v) Ammonolysis (vi) Acetylation (vii) Gabriel phthalimide synthesis.

SOLUTION

(i) Carbylamine reaction: a primary amine heated with chloroform and alcoholic KOH gives a foul-smelling isocyanide (carbylamine). $R\text{-}NH_2 + CHCl_3 + 3KOH \rightarrow R\text{-}NC + 3KCl + 3H_2O$. (Test for 1° amines; 2° and 3° amines do not respond.)

(ii) Diazotisation: an aromatic primary amine treated with nitrous acid ($NaNO_2$ + HCl) at 273-278 K forms a diazonium salt. $C_6H_5NH_2 + NaNO_2 + 2HCl \rightarrow C_6H_5N_2{}^+Cl^- + NaCl + 2H_2O$.

(iii) Hofmann's bromamide reaction: an amide treated with Br_2 and aqueous KOH (or NaOH) gives a primary amine with one carbon fewer. $R\text{-}CONH_2 + Br_2 + 4KOH \rightarrow R\text{-}NH_2 + K_2CO_3 + 2KBr + 2H_2O$.

(iv) Coupling reaction: a diazonium salt reacts with an activated aromatic ring (phenol or aniline) to give an azo compound (dye), usually at the para position. $C_6H_5N_2{}^+Cl^- + C_6H_5OH \rightarrow p\text{-}HOC_6H_4\text{-}N{=}N\text{-}C_6H_5$ (orange dye) + HCl.

(v) Ammonolysis: an alkyl halide reacts with excess ammonia to replace the halogen by an $-NH_2$ group, giving a mixture of 1°, 2°, 3° amines and a quaternary ammonium salt. $R\text{-}X + NH_3 \rightarrow R\text{-}NH_2 + HX$ (then further alkylation).

(vi) Acetylation: replacement of an N-H hydrogen of an amine by an acetyl group using acetic anhydride or acetyl chloride. $C_6H_5NH_2$ + $(CH_3CO)_2O$ -> $C_6H_5NHCOCH_3$ (acetanilide) + CH_3COOH.
(vii) Gabriel phthalimide synthesis: phthalimide is converted to its potassium salt, alkylated with an alkyl halide, and the product hydrolysed to give a pure primary amine (used only for aliphatic amines).

Answer: (i) 1° amine + $CHCl_3$/alc.KOH -> isocyanide (ii) Ar-1° amine + HNO_2/273 K -> diazonium salt (iii) amide + Br_2/KOH -> 1° amine (one C less) (iv) diazonium + phenol/aniline -> azo dye (v) R-X + NH_3 -> amine mixture (vi) amine + $(CH_3CO)_2O$ -> N-acetyl amide (vii) phthalimide route to pure 1° amines

Q8 Accomplish the following conversions: (i) Nitrobenzene to benzoic acid (ii) Benzene to m-bromophenol (iii) Benzoic acid to aniline (iv) Aniline to 2,4,6-tribromofluorobenzene (v) Benzyl chloride to 2-phenylethanamine (vi) Chlorobenzene to p-chloroaniline (vii) Aniline to p-bromoaniline (viii) Benzamide to toluene (ix) Aniline to benzyl alcohol.

SOLUTION

(i) $C_6H_5NO_2$ -> (Sn/HCl) $C_6H_5NH_2$ -> ($NaNO_2$/HCl, 273 K) $C_6H_5N_2{}^+Cl^-$ -> (CuCN/KCN) C_6H_5CN -> (H_3O^+) C_6H_5COOH.
(ii) C_6H_6 -> (conc. HNO_3/H_2SO_4) $C_6H_5NO_2$ -> (Br_2/Fe) m-Br-C_6H_4-NO_2 -> (Sn/HCl) m-Br-C_6H_4-NH_2 -> ($NaNO_2$/HCl, 273 K then H_2O, warm) m-bromophenol.
(iii) C_6H_5COOH -> (NH_3, heat) $C_6H_5CONH_2$ -> (Br_2 + KOH, Hofmann) $C_6H_5NH_2$ (aniline).
(iv) $C_6H_5NH_2$ -> (Br_2 water) 2,4,6-tribromoaniline -> ($NaNO_2$/HCl, 273 K) 2,4,6-tribromobenzenediazonium chloride -> (HBF_4 then heat, Balz-Schiemann) 2,4,6-tribromofluorobenzene.
(v) $C_6H_5CH_2Cl$ -> (NaCN/alc.) $C_6H_5CH_2CN$ -> ($LiAlH_4$ / H_2-Ni) $C_6H_5CH_2CH_2NH_2$ (2-phenylethanamine).
(vi) C_6H_5Cl -> (conc. HNO_3/H_2SO_4) p-Cl-C_6H_4-NO_2 -> (Sn/HCl) p-Cl-C_6H_4-NH_2 (p-chloroaniline).
(vii) $C_6H_5NH_2$ -> (acetylation, $(CH_3CO)_2O$) acetanilide -> (Br_2/CH_3COOH) p-bromoacetanilide -> (hydrolysis, H_3O^+) p-bromoaniline. (Acetylation lowers the ring's reactivity so only the para product forms.)
(viii) $C_6H_5CONH_2$ -> (Br_2 + KOH, Hofmann) $C_6H_5NH_2$ -> ($NaNO_2$/HCl, 273 K) $C_6H_5N_2{}^+Cl^-$ -> (H_3PO_2 + H_2O) C_6H_6 -> (CH_3Cl, anhydrous $AlCl_3$, Friedel-Crafts)

$C_6H_5CH_3$ (toluene).

(ix) $C_6H_5NH_2$ -> ($NaNO_2$/HCl, 273 K) $C_6H_5N_2{}^+Cl^-$ -> (CuCN/KCN) C_6H_5CN -> (H_3O^+) C_6H_5COOH -> ($LiAlH_4$) $C_6H_5CH_2OH$ (benzyl alcohol).

Answer: Routes via diazonium salt (Sandmeyer/CuCN, hydrolysis, Balz-Schiemann) and Hofmann bromamide as shown; (viii) benzamide -> aniline -> benzene (via diazonium + H_3PO_2) -> toluene by Friedel-Crafts methylation

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Q9 Give the structures of A, B and C in the following reactions: (i) CH_3CH_2I -(NaCN)-> A -(OH^-, partial hydrolysis)-> B -(NaOH + Br_2)-> C (ii) $C_6H_5N_2Cl$ -(CuCN)-> A -(H_2O/H^+)-> B -(NH_3)-> C (iii) CH_3CH_2Br -(KCN)-> A -($LiAlH_4$)-> B -(HNO_2, 0 C)-> C (iv) $C_6H_5NO_2$ -(Fe/HCl)-> A -($NaNO_2$/HCl, 273 K)-> B -(H_2O/H^+)-> C (v) CH_3COOH -(NH_3)-> A -(NaOBr)-> B -($NaNO_2$/HCl)-> C (vi) $C_6H_5NO_2$ -(Fe/HCl)-> A -(HNO_2, 273 K)-> B -(C_2H_5OH)-> C

SOLUTION

(i) A = CH_3CH_2CN (propanenitrile); B = $CH_3CH_2CONH_2$ (propanamide); C = $CH_3CH_2NH_2$ (ethanamine, by Hofmann bromamide).

(ii) A = C_6H_5CN (benzonitrile); B = C_6H_5COOH (benzoic acid); C = $C_6H_5CONH_2$ (benzamide).

(iii) A = CH_3CH_2CN (propanenitrile); B = $CH_3CH_2CH_2NH_2$ (propan-1-amine); C = $CH_3CH_2CH_2OH$ (propan-1-ol).

(iv) A = $C_6H_5NH_2$ (aniline); B = $C_6H_5N_2{}^+Cl^-$ (benzenediazonium chloride); C = C_6H_5OH (phenol).

(v) A = CH_3CONH_2 (acetamide); B = CH_3NH_2 (methanamine, by Hofmann); C = CH_3OH (methanol).

(vi) A = $C_6H_5NH_2$ (aniline); B = $C_6H_5N_2{}^+Cl^-$ (benzenediazonium chloride); C = C_6H_6 (benzene).

Answer: (i) A=propanenitrile, B=propanamide, C=ethanamine (ii) A=benzonitrile, B=benzoic acid, C=benzamide (iii) A=propanenitrile, B=propan-1-amine, C=propan-1-ol (iv) A=aniline, B=benzenediazonium chloride, C=phenol (v) A=acetamide, B=methanamine, C=methanol (vi) A=aniline, B=benzenediazonium chloride, C=benzene

Q10 An aromatic compound 'A' on treatment with aqueous ammonia and heating forms compound 'B' which on heating with Br_2 and KOH forms a compound 'C' of molecular formula C_6H_7N. Write the structures and IUPAC names of compounds A, B and C.

SOLUTION

C (C_6H_7N) is aniline, $C_6H_5NH_2$, formed by Hofmann bromamide degradation (Br_2 + KOH), which converts an amide to an amine with one carbon fewer.

Therefore B is the amide benzamide, $C_6H_5CONH_2$ (7 carbons -> 6 carbon amine).

B (benzamide) is obtained from A by heating with aqueous ammonia, so A is benzoic acid, C_6H_5COOH: $C_6H_5COOH + NH_3 \rightarrow C_6H_5COONH_4 \xrightarrow{heat} C_6H_5CONH_2 + H_2O$.

Then $C_6H_5CONH_2 + Br_2 + 4KOH \rightarrow C_6H_5NH_2 + K_2CO_3 + 2KBr + 2H_2O$.

Answer: A = benzoic acid (C_6H_5COOH); B = benzamide ($C_6H_5CONH_2$); C = aniline ($C_6H_5NH_2$)

Q11 Complete the following reactions: (i) $C_6H_5NH_2 + CHCl_3$ + alc. KOH -> (ii) $C_6H_5N_2Cl + H_3PO_2 + H_2O$ -> (iii) $C_6H_5NH_2 + H_2SO_4$ (conc.) -> (iv) $C_6H_5N_2Cl + C_2H_5OH$ -> (v) $C_6H_5NH_2 + Br_2(aq)$ -> (vi) $C_6H_5NH_2 + (CH_3CO)_2O$ -> (vii) $C_6H_5N_2Cl$ -(i) HBF_4 (ii) $NaNO_2$/Cu, heat->

SOLUTION

(i) $C_6H_5NH_2 + CHCl_3 + 3KOH(alc.) \rightarrow C_6H_5NC$ (phenyl isocyanide) + 3KCl + $3H_2O$.

(ii) $C_6H_5N_2^+Cl^- + H_3PO_2 + H_2O \rightarrow C_6H_6$ (benzene) + $N_2 + H_3PO_3 + HCl$.

(iii) $C_6H_5NH_2 + H_2SO_4$ (conc.) -> $C_6H_5NH_3^+ HSO_4^-$ (anilinium hydrogensulphate); on heating at 453-473 K it gives sulphanilic acid (p-aminobenzenesulphonic acid).

(iv) $C_6H_5N_2^+Cl^- + C_2H_5OH \rightarrow C_6H_6$ (benzene) + $N_2 + CH_3CHO + HCl$.

(v) $C_6H_5NH_2 + 3Br_2(aq)$ -> 2,4,6-tribromoaniline (white precipitate) + 3HBr.

(vi) $C_6H_5NH_2 + (CH_3CO)_2O \rightarrow C_6H_5NHCOCH_3$ (acetanilide) + CH_3COOH.

(vii) $C_6H_5N_2^+Cl^- \xrightarrow{(HBF_4)} C_6H_5N_2^+BF_4^- \xrightarrow{(NaNO_2/Cu,\ heat)} C_6H_5NO_2$ (nitrobenzene) + $N_2 + NaBF_4$.

Answer: (i) phenyl isocyanide (ii) benzene (iii) sulphanilic acid (iv) benzene (+ N_2, CH_3CHO) (v) 2,4,6-tribromoaniline (vi) acetanilide (vii) nitrobenzene

Q12 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

SOLUTION

Gabriel synthesis needs the phthalimide anion to displace the halide of an alkyl halide by nucleophilic substitution (SN_2).

Aryl halides do not undergo nucleophilic substitution readily (the C-X bond has partial double-bond character and the ring resists SN_2/SN_1), so an N-aryl phthalimide cannot be formed.

Hence aromatic primary amines cannot be made by this route.

Answer: Aryl halides do not undergo nucleophilic substitution with the phthalimide anion, so N-aryl phthalimide (and hence the aromatic 1° amine) cannot form

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Q13 Write the reactions of (i) aromatic and (ii) aliphatic primary amines with nitrous acid.

SOLUTION

(i) Aromatic primary amine: with HNO_2 ($NaNO_2$ + HCl) at 273-278 K it gives a stable diazonium salt. $C_6H_5NH_2 + HNO_2 + HCl \rightarrow C_6H_5N_2^+Cl^- + 2H_2O$.

(ii) Aliphatic primary amine: with HNO_2 it gives an unstable diazonium salt that decomposes at once to an alcohol, evolving nitrogen gas. $R\text{-}NH_2 + HNO_2 \rightarrow R\text{-}OH + N_2 + H_2O$ (brisk effervescence of N_2).

Answer: (i) aromatic 1° amine + HNO_2 (273 K) -> stable aryldiazonium salt; (ii) aliphatic 1° amine + HNO_2 -> alcohol + N_2 (effervescence)

Q14 Give plausible explanation for each of the following: (i) Why are amines less acidic than alcohols of comparable molecular masses? (ii) Why do primary amines have higher boiling point than tertiary amines? (iii) Why are aliphatic amines stronger bases than aromatic amines?

SOLUTION

(i) Nitrogen is less electronegative than oxygen, so the N-H bond is less polar than the O-H bond and releases H^+ less readily; also the conjugate base RO^- is more stable than R_2N^-/RNH^- because oxygen accommodates the negative charge better. Hence amines are less acidic than alcohols.

(ii) A primary amine has two N-H bonds and forms extensive intermolecular

hydrogen bonding, whereas a tertiary amine has no N-H bond and cannot hydrogen-bond; so more energy is needed to boil the primary amine, giving it a higher boiling point.

(iii) In an aromatic amine the nitrogen lone pair is delocalised into the ring by resonance, making it less available for protonation; in an aliphatic amine the lone pair is fully available and the alkyl groups push electron density onto N (+I effect), so aliphatic amines are stronger bases.

Answer: (i) less polar N-H bond / less stable conjugate base than alcohols (ii) 1° amines H-bond (two N-H), 3° amines cannot (no N-H) (iii) aromatic lone pair delocalised into the ring vs fully available + alkyl +I in aliphatic amines